





February 2016 Ph.D Thesis

# Mechanical properties and morphology of styrene ionomers containing dimer acid derivatives and styrene ionomers possessing Na-sulfopropyl methacrylate units

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Mechanical properties and morphology of styrene ionomers containing dimer acid derivatives and styrene ionomers possessing Na-sulfopropyl methacrylate units

이량체 산 유도체를 포함한 스타이렌 아이오노머 및 Na-술포프로필 메타크릴레이트 단위를 포함한 스타이렌 아이오노머의 기계적 성질과 형태학

2016年2月25日

# 朝鮮大學校大學院

尖端部品素材工學科

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Mechanical properties and morphology of styrene ionomers containing dimer acid derivatives and styrene ionomers possessing Na-sulfopropyl methacrylate units

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#### ABSTRACT

이량체 산 유도체를 포함한 랜덤 아이오노머 및 Na-술포프로필 메타크릴레이트 단위를 포함한 아이오노머의

기계적 성질과 형태학

고광환

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아이오노머는 비극성 주사슬에 비교적 적은 양의 이온기 (<15 mol%)를 가지고 있는 고분자 물질을 말한다. 아이오노머의 물리적/기계적 성질은 주사슬의 종류, 이온 함량, 이온기의 종류, 첨가제의 사용 등 여러 변수에 의해 변한다고 알려져 있다. 본 연구에 서는 여러 변수 중에서 이온기/주사슬 사이의 거리, 다이머산 첨가 그리고 열처리가 아 이오노머의 물리적 성질에 어떤 영향을 미치는지에 대해 조사하였다. 이 논문은 총 다 섯 개의 장으로 구성되어 있다. 제 1장에서는 아이오노머의 특성과 아이오노머의 형태 학적인 모델들 그리고 아이오노머를 만드는 방법에 대해 간단히 기술하였다. 또한 아 이오노머의 특성을 연구하기 위해 사용되는 주요 기기들에 대한 원리와 설명을 담았 다. 제 2장은 먼저 아이오노머의 정의, 멀티플릿/클러스터, 아이오노머의 유리 전이에 대한 내용을 다루고 있으며, PE, PTFE 및 PS 등 다양한 아이오노머의 물리적 성질 등 에 대해 간단히 소개하고 있다. 이어서 아이오노머의 가소화, 블렌드를 설명하고 최근 에 주로 사용 및 연구되고 있는 아이오노머의 응용 분야를 총 13개 부분으로 나누어 자세히 기술하고 있다. 제 3장에서는 술포네이트 혹은 카복실레이트 음이온 작용기를 가지고 있는 스타이렌 아이오노머에 Na로 중화된 카복실레이트를 포함한 다이머산을 첨가했을 때 이 첨가제가 아이오노머의 기계적인 성질과 형태학에 어떤 영향을 끼치는 지에 대해 논하고 있다. 또한 이 결과들을 Na로 중화된 카복실레이트 작용기를 사슬 양 끝에 가지고 있는 저분자량 화합물을 첨가한 아이오노머에서 얻은 실험 결과들과 비교하였다. 제 4장에서는 새롭게 합성된 스타이렌 Na-술포프로필 메타크릴레이트 아

Collection @ chosun

이오노머의 Na-술포네이트 이온기가 아이오노머의 기계적 성질과 형태학에 어떠한 영 향을 미치는지에 대해 알아보았다. 이 결과를 스타이렌 메타크릴레이트와 스타이렌 술 포네이트 아이오노머를 이용하여 얻은 결과 값과 비교하여 이온기와 주사슬 사이의 거 리 효과 그리고 이온기의 종류 (술포네이트, 카복실레이트)의 효과를 비교 분석하여 아 이오노머의 화학 구조가 아이오노머의 기계적인 성질과 형태학에 어떤 영향을 끼치는 지에 대해 알아보았다. 제 5장에서는 황산 작용기가 벤젠 고리의 파라 위치에 붙어 있 는 폴리(스타이렌-co-스타이렌술폰산) 공중합체를 60 ℃에서 열처리 하면 고분자의 화 학 구조에 어떤 변화가 생기는지에 대해 다루고 있다. 열처리를 하면 공중합체 시료의 색이 흰색에서 황갈색으로 변화하는데 그 색 변화를 라디칼의 생성 및 사슬 구조 변화 와 연결하여 해석하였다. 라디칼 생성은 EMR 장치를 통해 확인하였고 고분자 사슬에 서의 탈 수소화는 NMR을 통해 알아내었다. 한편 황산기의 구조 변화 및 황산 작용기 의 수소 이동에 대해서는 FT-IR로 연구하였다. 제 5장의 마지막에 색 변화에 영향을 미치는 라디칼의 생성 및 사슬 구조 변화에 대한 메커니즘을 제시하였다.





Chapter 1 Introduction





This chapter consists of two parts. The first part is devoted to a short introduction to ionomers and a summary of some of the early findings in the ionomer research area (1.1). In addition, the main techniques used in this work are also discussed briefly. The structure of this thesis, including the descriptions of each chapter, is given in the last part of this chapter (1.2).

#### 1.1. Ionomers

#### 1.1.1. Definitions

Ion-containing polymers can be divided into two groups: Ionomers and polyelectrolytes. In general, the ionomers contain a relatively small amount of ionic groups (< ca. 15.0 mol% of ions). On the other hand, the polyelectrolytes have a much higher ion content. While this definition is still commonly accepted, under certain conditions the ionomers may have polyelectrolyte properties and vice versa. Thus, the ambiguity in the definitions the ionomers and polyelectrolytes is not clear. To prevent this, in 1990 Eisenberg and Rinaudo<sup>1</sup> proposed new definitions for these two ion-containing polymers. According to their definitions, ionomers are "polymers in which the bulk properties are governed by ionic interactions in discrete regions of the material (the ionic aggregates)", while polyelectrolytes are defined as "polymers in which solution properties in solvents of high dielectric constants are governed by electrostatic interactions over distances larger than typical molecular dimensions".

#### 1.1.2. General background

Relatively small amounts of the ionic groups attached to the chains of the non-ionic polymers may exert profound effects on the physical properties of material (i.e. melt





viscosity, electric conductivity, adhesion property, etc.). These effects have been attributed to aggregation of the ionic groups, known as "multiplet". Because of their unique properties, ionomers can be used as ionomer coating, packaging materials, golf ball inlayers, proton exchange membrane, self-healing materials, shape-memory materials, etc.<sup>2-5</sup> These multiplets act as cross-links make a region restricted mobility surrounding it, call cluster,<sup>6</sup> and increase the modulus and glass transition temperature ( $T_g$ ) of the polymer. In addition, the non-ionic polymers obtained one  $T_g$ , while the ionomer obtained two  $T_gs$  ( matrix  $T_g$  and cluster  $T_g$ ) (see detailed explain 1.2.4.3. EHM model).

Over past two decades, a large number of studies have dealt with the morphology and viscoelastic properties of a wide range of random ionomer.<sup>7-12</sup> There are several different methods used to study the morphology and mechanical properties of ionomers (e.g., scattering techniques,<sup>13-19</sup> spectroscopic techniques,<sup>20-31</sup> thermal analysis techniques,<sup>32-38</sup> microscopic techniques,<sup>39-46</sup> etc.). In the present work, dynamic mechanical analysis (DMA), small-angle X-ray scattering (SAXS), differential scanning calorimetry (DSC) were used. The next section will be discuss the techniques used in present work, because of these techniques are importance to understand the chemical structure-morphology-property relations of the ionomers.

#### 1.1.3. Main techniques used in this work

#### 1.1.3.1. Dynamic mechanical analysis

DMA is used to measure the dynamic mechanical properties of materials. When a sinusoidal stress is applied to an elastic material, the deformation (i.e., strain) occurs exactly in phase with the stress, while a viscous material will respond with the strain delayed 90° behind the applied stress. When the stress is applied to a viscoelastic material (a material with both elastic and viscous properties), the resulting strain will be delayed





behind the stress by some loss angle between  $0^{\circ}$  and  $90^{\circ}$ . At this point, the loss angle is dependent on the amount of internal dissipative motion occurring in the same frequency range as the applied stress.

A modulus equals to stress/strain, and the storage modulus, E', and loss modulus, E'', can be calculated as illustrated in Scheme 1-1.<sup>47</sup> The storage modulus (E') is the elastic component and related to the sample's ability to dissipate mechanical energy through molecular motion. The tangent of phase difference, or tan  $\delta$ , is another common parameter that provides information on the relationship between the elastic and inelastic components.



Scheme 1-1.

#### 1.1.3.2. Small-angle x-ray scattering

The technique of SAXS is used to study the structures (i.e. sizes and distances) of entities, the size of which is on the order of 10 Å or larger. Since, the distances between the entities are large in comparison to atomic dimensions, the material is considered as a continuum with an average electron density difference characteristic of the two phase





materials.<sup>48</sup> As a result, it can be considered that the scattering arises from the scattering objects, i.e., the entities with the higher electron density. These scattering objects are considered to be embedded in a phase of lower electron density.

The general principles of X-ray scattering are presented below.<sup>48</sup> Since X-ray beams interact with electrons, X-ray scattering is a technique sensitive to the difference in the electron densities of the materials. The amplitude (A) of the scattered X-ray is described as follows:

$$A(q) = \iiint \rho(r) e^{-iqr} dr$$

where  $\rho(r)$  is the average electron density, q is the scattering vector, and r indicates the location of an atom. The scattering vector q is the difference between the wave vectors of the incident beam and that of scattered beam. q is defined as:

$$q = 4\pi \mathrm{sin}\theta/\lambda$$

where  $\theta$  is half the scattering angle and  $\lambda$  is the X-ray wavelength. The scattering intensity is the product of the amplitude and its complex conjugate:

$$I(q) = |A(q)|^2 = A(q) \cdot A(q)^*$$

If the sample is composed of interacting particles, the scattering intensity can be related to the geometry of the particles and their spatial correlations. For identical, randomly oriented, centrosymmetric particles, the scattering intensity can be described as below:

$$I(q) = P(q) \bullet S(q)$$

where P(q) is the shape factor of the particles which is a function of the size and shape of the particles and S(q) is the structure factor of the assembly and is dependent on the spatial correlation between particles. In random ionomer systems, the SAXS profile shows only the peak due to the structure factor, since the size and the shape of the particles are





irregular. From the position of the peak maximum, one can get the  $q_{\text{max}}$  value. For very small angles,  $q_{\text{max}}$  is equal to  $2\pi/d_{\text{Bragg}}$  where  $d_{\text{Bragg}}$  is the Bragg spacing (=  $n\lambda/2\sin\theta$ , where  $\theta$  is X-ray diffraction angle, and n=1, 2, 3,...). In the present study, the X-ray source was synchrotron radiation (Phohang, Korea).

#### 1.1.3.3. Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) is a technique that can determine the glass transition temperature  $T_g$  of polymers by measuring the accompanying change in the heat capacity.<sup>49</sup> At this point, it is useful to give a very brief description of the glass transition, since its meaning is very important in this work. When a polymer is heated to high temperature, a polymer will soften at a certain temperature, well bellow its melting point; this softening is referred to as the glass transition.<sup>50</sup> At the  $T_g$ , dramatic changes in the local motion of polymer chains result in large changes in a physical property (e.g., density, specific hest, modulus, energy absorption, dielectric permeativity, etc.). The behavior of polymers at the  $T_g$  has been discussed in great detail elsewhere.<sup>50</sup>

In the DSC measurement, the sample and reference cells are placed in a controlled temperature environment. A temperature control circuit measures and controls the temperature of the two cells. Using the temperature circuit, it is possible to compare the temperature of the sample and reference cell, and apportion power to the heater in each cell, so that the temperatures remain equal. When the sample undergoes a glass transition, the power to the two heater is adjusted to maintain the same temperature in both cells. This power difference is related to the heat capacity of the sample. In the plot of the heat flow vs temperature, the  $T_g$  appears as a step. Two methods can be used to determine the  $T_g$  from DSC thermogram. In one method, the  $T_g$  is taken as the intersection point of the extrapolated baseline with the extrapolated line passing through the inflection, while in the





second method the  $T_{\rm g}$  is taken as the onset point of inflection.

#### 1.1.4. Synthesis

Carboxy containing ionomers are synthesized by the direct copolymerization of acrylic or methacrylic acid with vinyl monomers such as styrene, ethylene and similar monomers by free radical copolymerization. The resulting copolymer is obtained as the free acid, which can be neutralized with metal hydroxides, acetates and similar salts (Scheme 1-2)



Scheme 1-2

Sulfonated ionomers are synthesized by introducing ion groups (-SO<sub>3</sub>H) and ion groups neutralized by the salts (Scheme 1-2).



Scheme 1-3





#### 1.1.5. Morphological models

It is known that the physical and mechanical properties of the ionomers have been influenced significantly by the ionomer morphology. Thus, in this section, the ionomer morphology will be discussed briefly.

A number of studies have been conducted to demonstrate the ionomer morphology. Especially, the X-ray scattering studies in a low angle range have been performed extensively to explore the shape and structure of multiplets in the ionomer. In 1968, Wilson et al.<sup>51</sup> and Longworth and Vaughan<sup>52</sup> reported that an X-ray scattering peak was seen in a small-angle range, and proposed the this peak was due to the presence of ionic aggregates. Later on, the peak, a small-angle X-ray scattering (SAXS) ionomer peak, was interpreted as a owing to either intraparticle scattering from an ionic core and an ionic sub-shell (i.e. core-shell model) or interparticle scattering from ionic aggregates (i.e. Hard-Sphere model).

#### 1.1.5.1. Core-shell model

This is an intracluster model proposed by MacKnight and co-workers.<sup>53</sup> According to this model, a number of ion pairs (ca. 50 ion pairs) form a core (radius ca 8-10 Å) that id surrounded by a relatively thick (radius ca. 20 Å) shell of hydrocarbon material of low electron density, which, in turn, is surrounded by another shell of material having relatively low ion content. At this point, it should be noted that the electron density of the outermost shell is lower than that of the inner ionic core. In this model, the position of the SAXS peak was influenced by the distance between the center of the outermost shell and the center of ionic core.

#### 1.1.5.2. Hard-sphere model

In 1983, Yarusso and Cooper proposed hard-sphere model,<sup>54</sup> which assumes that the





multiplets have a liquid like order at a distance of closest approach, determined by the hydrocarbon layer attached to and surrounding each multiplet. This model postulated that the SAXS peaks were affected by the average distance from between the hard-sphere centers.

1.1.5.3. EHM model

However, the two types of models described above cannot explain the results obtained from mechanical study (i.e. two glass transition) and morphological study (i.e. the presence of SAXS peaks) at the same time. Thus, in 1990, Eisenberg, Hird and Moore proposed a multiplet/cluster model (so-called Eisenberg-Hird-Moore (EHM) model) for amorphous random ionomers.<sup>55</sup> According to the model, the ionic groups of the ionomer form an ionic aggregate due to the electrostatic interactions between ion-pairs and the phase separation by polarity difference between polymer chains and ion-pairs. The ionic aggregate, known as "multiplet", reduces the mobility of polymer chains surrounding it for the following reasons. Firstly, the multiplets act as physical cross-links that reduce the mobility of polymer chain segments emanating from the multiplets (anchoring effect). Secondly, the mobility of the chains are relatively restricted because of an increasing number of chain segment in the immediate vicinity of the multiplet (crowding effect). Finally, to the ionic groups form the multiplets, the polymer chain segments that possess an ion pair should be unfolded, which induces the tension, and, thus, the stiffness of polymer chain segment (tension effect).

The thickness of the restricted mobility region is known to indirectly correspond with the persistence length, (in the case of polystyrene, ca. 10 Å). Thus, the size of the restricted mobility region, including a multiplet is ca. 30 Å. When an ion content is low, the size of the reduced mobility regions of polymer chains is too small to show their own glass transition temperature ( $T_g$ ). However, as the ion content increases, the number of multiplets increases, and the regions of restricted mobility start overlapping. When the size of the region of restricted mobility exceed ca. 50 to 100 Å, the regions, call cluster, begin to





show independent phase behavior. Thus, the cluster regions show their own glass transition temperature, i.e., cluster  $T_g$ . As the ion content increases further, the volume fraction of cluster increases, while that of unclustered material, i.e., the matrix, decreases. At this point, it should be mentioned that even though the relative sizes of the unclustered and clustered regions change in opposite manners, both the cluster and matrix  $T_g$ s increase with increasing ion content.

It is also proposed that the size of the multiplets is affected by a number of factors. The factors include the steric hindrance of the polymer chain segments emanating from the multiplet, the size of ion pairs<sup>56,57</sup> the dielectric constant of polymers<sup>58,59</sup> the distance between an ionic group and a polymer backbone,<sup>60</sup> and an ion content.<sup>61</sup>

#### 1.2. Structure of This Thesis and Brief Explanation of Each Chapter

In the ionomer field, the morphology are also of very importance because the physical and mechanical properties of the ionomers can be changed by the ionomer morphology. Thus, the morphological study on the ionomer should be conducted simultaneously with the mechanical study to understand the chemical structure-morphology-property relations of the ionomers. Therefore, the present studies were targeted primarily at improving our understanding of ionomer system.

Following this Introduction, the first part of the thesis is a review article on ionomers (Chapter 2). Chapter 2 is an invited review article written for a Kirk-Othmer Encyclopedia of chemical technology and will published by John & Wiley Publishing Company in 2016. It gives an overall view of various ionomers and ionomer applications. The chapter was written last and includes the lastest views on the topic.

The second part deals with the effects of sodium salts of dimer acid (DA) compounds on





the mechanical properties and morphology of the PS-based ionomers, i.e. sulfonated polystyrene ionomer (SSNa) and poly(styrene-co-sodium methacrylate) (SMANa) ionomer (Chapter 3). The DA compounds were prepared from waste fatty acid cooking oils (vegetable and animal oils) as raw materials. To compare the results obtained from the DA-containing ionomers with those obtained from the ionomers containing only one type of sodium salt of aliphatic diacids, we also prepared PS-based ionomers containing varying amounts of sodium salt of aliphatic diacid, i.e. sodium hexadecanedioate.

In the styrene ionomers, having ionic groups placed at the ends of variable-length of side chains randomly attached directly to the para-position of the benzene ring, the distance between the ionic groups and the polymer backbone chain changed the mechanical properties and morphology of the ionomers systematically.<sup>62,63</sup> However, in the case of ionomers containing Na-sulfonate ionic groups, no systematic study was conducted to explore the effect of the distance between the ionic groups and polymer backbone chain. Thus, earlier the groups of Kim had carried out a preliminary work on new Na-neutralized polystyrene-based ionomers, namely poly(styrene-*co*-3-sulfopropyl methacrylate) (SSPMANa) ionomers to know the effect of the presence of alkyl ester side chain between the Na-sulfonate ionic groups and polymer backbone chain on the mechanical properties of the ionomers.<sup>64</sup> However, unfortunately, we found that the preliminary data were not sufficiently enough to understand the alkyl ester side chain effect. Therefore, we conducted a more thorough investigation on the mechanical properties and morphologies of the SSPMANa ionomers and compared the results with those obtained using two styrene-based ionomer, i.e. SSNa and SMANa ionomers (Chapter 4).

Chapter 5 describes the effect of sample annealing on the poly(styrene-co-styrenesulfonic acid) copolymer (PSSA). To prepare the dehydration annealed, the samples were prepared in two ways; one was untreated and the other was thermally treated at 60  $^{\circ}$ C for 24h. for dehydration. We found that, during annealing process, the color of the acid copolymer





changed from white to yellowish brown, which, we claimed, might be related to the bond break of H-OH to yield hydrogen atom and OH species, having one unpaired electron ( $\cdot$  OH). We discussed their mechanisms in detail in Chapter 5.





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Chapter 2 Ionomers





#### 2.1. Introduction

In mid-1950's, it was recognized that the introduction of jonic groups to non-jonic elastomers was one of effective ways for the modification of the properties of elastomer, giving many of the properties of vulcanized and filled systems to the polymers.<sup>1</sup> Eventually, in 1965 the word "ionomer" was first used by E. I. DuPont Company for the description of thermoplastic random polyethylene-based copolymers, having a small amount of methacrylic acid units, partly neutralized with Na<sup>+</sup> (Surlyn<sup>®</sup>).<sup>2</sup> Shortly afterward, the word ionomer was applied to thermoplastic copolymers that contain a small fraction (usually less than 15 mol%) of ionic groups covalently tethered as pendant groups to the polymer backbone of a relatively low dielectric constant. At this point, it should be mentioned that even though polyelectrolytes and glass-ionomer cements also contain ionic groups, we do not intent to discuss them here because they have much higher ion contents (> 80%) and also have been discussed elsewhere.<sup>3,4</sup> The chemical structures of some of random ionomers, i.e. poly(ethylene-co-methacrylate) (EMAA or PE or Surlyn<sup>®</sup>), sulfonated polytetrafluoroethylene (PTFE or perfluorosulfonate or Nafion<sup>®</sup>), poly(styrene-co-sodium styrenesulfonate) (Na-SPS), and poly(styrene-co-sodium methacrylate) (PSMANa) ionomers, are shown in Scheme 2-1.

The ionic groups of ionomers form aggregates, so-called multiplets<sup>5</sup> (Figure 2-1), in the matrix of relatively low polarity due to the difference in the physical characteristics of the polymer matrix and ionic groups and the electrostatic interactions between ionic groups. The unique properties and morphology of ionomers come from the presence of the multiplets. For instance, the glass transition temperature ( $T_g$ ), mechanical properties, transport properties, and viscosity of polymers can be enhanced by the ion aggregation of the ionomers. The  $T_g$  of some of inorganic polymers is a good example of the increase in the  $T_g$  of polymer. It is well known that the ionization of poly(phosphoric acid), (HPO<sub>3</sub>)<sub>x</sub> with monovalent Na<sup>+</sup> and divalent Ca<sup>2+</sup>, increases the  $T_g$  of the polymer from -10 °C to





280 °C and 520 °C, respectively.<sup>6</sup> The magnitude of the change in the  $T_g$  values (from – 10 to 520 °C) indicates the importance of ionic interactions on the  $T_g$  of polymers. Similar trends in the ionization effects on the  $T_g$  were found in silicates,<sup>7</sup> acrylates,<sup>8</sup> ionenes,<sup>9</sup> and ethyl acrylate–based ionomers.<sup>10</sup>

Partly neutralized PE (Surlyn or Na-EMAA) ionomer



PTFE (Nafion) ionomer





Scheme 2-1. Chemical structures of some of ionomers







Figure 2-1. Representative scheme of a multiplet and of the region of restricted mobility surrounding it in an Na-SPS ionomer.




Some of the storage modulus (E') and loss tangent curves of PSMANa ionomers are shown in Figure 2-2.11 It is seen that the presence of multiplets affects ionomer modulus significantly. For example, for the ionomers of intermediate ion contents, the modulus value changes as a function of temperature from the glassy modulus, to the glass transition of the ion-poor matrix phase  $(T_{g,m})$ , to the descending "ionic" plateau, to the glass transition of the ion-rich cluster phase  $(T_{g,c})$ , to the descending rubbery plateau, and to sample flow. This suggests that the ionomer shows two glass transitions and the ionic plateau, which are not found in non-ionic polymers. At a certain temperature, one sees the increase in the modulus value with increasing ion content. For example, at 200 °C, the modulus of nonionic polystyrene is  $\sim 10^{5.6}$  Pa, the typical rubbery modulus of non-ionic polymer, that of the ionomer containing 5 mol% of ionic groups is  $\sim 10^{6.3}$  Pa, and that of the ionomer containing 11 mol% of ions is  $\sim 10^{7.7}$  Pa. It is also seen that the position of descending ionic plateau shifts to high positions with increasing ion content, and the modulus drops related with the glass transition move also to higher temperatures. In the case of the loss tangent curves, there are two peaks for the ionomer of intermediate ion contents. The positions of the loss tangent peak at low and high temperatures represent the  $T_{g,m}$  and  $T_{g,c}$ of the ionomer, respectively, and the relative sizes of the peaks are related to the relative amounts of the matrix and cluster regions of the ionomer. This implies further that the ionomer resembles either an immiscible blend or a block copolymer, to some extent. It is seen that the loss tangent peaks shift to higher temperatures with increasing ion content. In addition, the size of the  $T_{g,m}$  peak decreases, while that of the  $T_{g,c}$  peak increases, as the ion content increases, suggesting that, with increasing ion content, the nature of the ionomer changes from a matrix-dominant material to a cluster-dominant material. Various ionomers based on polytetrafluoroethylene (PTFE) show excellent thermal and mechanical stability, which makes the ionomers useful in proton exchange membrane (PEM) fuel-cells as proton conductors.







Figure 2-2. Storage moduli (E') and loss tangents, measured at 1 Hz, as a function of temperature for PSMANa ionomers with ion contents (mol%) marked near each plot (some of data were obtained from reference 11).





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For the ionomers to be highly conductive, the aggregates of ion pairs of ionomer or acid groups of acidic form copolymer must be hydrated to form percolative ionic or acid domains containing water. A number of models have been proposed to describe the morphology of the fully hydrated PTFE ionomers, which include parallel cylindrical water nano-channels,<sup>12</sup> a network of interconnected nanoscale spherical water clusters,<sup>13,14</sup> bicontinuous network of ionic clusters embedded in a matrix of fluorocarbon chains.<sup>15</sup> a ribbon-like structure of polymer separated by water molecules,<sup>16</sup> a locally flat, layered structure of water domains,<sup>17,18</sup> and a random channel-type interconnected network.<sup>19</sup> For example, according to the model of parallel cylindrical water nano-channels, the sulfonic acid groups of Nafion form channels (~2.4 nm diameter) with water molecules, and the water channels act as passages for the water molecules, protons, and small ions to pass through. On the other hand, the hydrophobic polymer matrix provides good mechanical properties, and the crystalline regions ( $\sim 25 \text{ nm}^2$  cross-section) of the Nafion act as physical cross-links.<sup>12</sup> Computational modelling work on the structure and proton transport of PTFE ionomer membrane also shows a nano-scale phase-separated morphology, in which the ionic side chains and counter-ions with water molecules are segregated from the hydrophobic fluorocarbon backbone to form aqueous clusters or channels.<sup>20</sup> The small-angle X-ray scattering (SAXS) studies on the hydrated Nafion suggest that the polymer chains aggregate to form elongated polymer chain bundles, which are covered with the salt solution.<sup>16,21</sup> Other sulfonated ionomer membranes, other than PTFE ionomer membranes, have also shown similar results, which include, for example, poly(arylene ether sulfone) membranes,<sup>22</sup> methyl methacrylate-based ionomer,<sup>23</sup> and styrene-based ionomer.<sup>24</sup> At this point, it should be mentioned that a number of ion-containing polymers have been developed as alternative polymer systems for proton exchange membrane (PEM), also termed "polymer electrolyte membrane" (PEM), and the review article on this topic is also available; thus, interested readers are referred to it.<sup>25</sup>



It is also known that ion aggregation enhances the melt viscosity of bulk ionomers drastically. For example, when the Na–carboxylate ionic groups are introduced to the paraposition of 3 % of benzene ring of styrene units, the melt viscosity of polystyrene homopolymer (PS) at 220 °C increases from  $4 \times 10^3$  poise to  $7 \times 10^5$  poise.<sup>26</sup> In addition, when the carboxylate ionic groups are replaced with sulfonate ionic groups, the melt viscosity increases further to  $9 \times 10^8$  poise, i.e. an increase of over 5 orders of magnitude. As expected, the melt viscosity of the ionomer is related directly to the ion content of the ionomer. In the case of the zero–shear rate viscosity of the Na–SPS ionomers, it increases from  $10^{7.7}$  Pa·S for PS, to  $10^{8.2}$  Pa·S for 0.11 mol % ionomer, and further to  $10^{10.0}$  Pa·S for 1.71 mol% ionomer.<sup>27</sup>

The above examples indicate that the ion aggregation is the key element in controlling the properties and morphology of ionomers. Thus, in this overview we start with a brief discussion of a multiplet/cluster model and morphology of ionomers, followed by the glass transition temperatures of ionomers. Then, we will devote a separate section to the mechanical properties of various ionomers. Subsequently, we will move on to a discussion of plasticization of ionomers using polar, non-polar or amphiphilic plasticizers and, then, to ionomer blends. Finally, a brief discussion of applications will be presented as the conclusions of this overview.

### 2.2. Multiplets and Clusters

In 1968, Wilson et al. reported that PE-based ionomers exhibited an "ionomer" peak in a small angle region of the X-ray scattering profile.<sup>28</sup> It is believed that the multiplets, having usually a relatively high electron density, act as scattering centers. Thus, under a certain condition, some ionomers show the small-angle X-ray scattering (SAXS) ionomer peak (Figure 2-3). However, the interpretation of the ionomer peak is not always straightforward,







Figure 2-3. Small-angle X-ray scattering profile as a function of q for polystyrene (PS) and poly(styrene-co-lithium styrenesulfonate) (Li-SPS) ionomer containing 6.0 mol% of ions.





and, thus, different models, e.g. Hard-sphere model<sup>29</sup> and Core-shell model<sup>30</sup>, have been proposed to interpret the SAXS ionomer peak.

It should also be mentioned that the ionomer morphologies were also investigated by other techniques, including transmission electron microscopy (TEM),<sup>31-35</sup> scanning transmission electron microscopy (STEM),<sup>36-38</sup> and combination of X-ray scattering and STEM imaging methods.<sup>39-41</sup> It is worth noting that different sample preparation methods<sup>42</sup> and morphology measurement techniques<sup>34,38</sup> also changed the morphological pictures of the ionomers. For example, a TEM image of sulfonated polystyrene ionomers showed spherical aggregates, but an STEM image, in some cases, exhibited vesicular aggregates.<sup>38</sup> It was also found that the morphology of tailored poly(dimethyl siloxane) (PDMS) ionomers was also altered significantly by a sample preparation method.<sup>43</sup> The PSMACu films cast either at room temperature or at much higher temperature showed a typical SAXS ionomer peak and STEM images of uniform-sized spherical ionic aggregates. On the other hand, the precipitated ionomer did not exhibit an SAXS ionomer peak, but its STEM images showed various sizes and shapes of separated Cu-rich regions. However, the annealing of the precipitated material made the ionomer morphology identical with that prepared by solvent casting.<sup>42</sup> Sometimes, ionomers showed ionic aggregates in STEM images but no SAXS ionomer peak,<sup>41,43</sup> or vice versa.<sup>39</sup> In addition to the TEM and STEM methods, a smallangle neutron scattering (SANS) technique was also utilized to study the inter-phase morphology of ionomers as well as chain conformation.<sup>14,44-52</sup> It should also be mentioned that an X-ray absorption spectroscopy technique was employed to determine the structure around the neutralizing cations in multiplets and/or the ratio of isolated/aggregated ions.<sup>53-60</sup> Electron spin resonance (ESR)<sup>61-63</sup> and nuclear magnetic resonance (NMR)<sup>64-67</sup> techniques were also used to study the fraction of ion pairs in the multiplets. It should be mentioned that the NMR technique was also applied to investigated the structure and dynamics of ionic multiplets.<sup>68</sup>



An atomic force microscope (AFM) method was utilized to explore the surface and nearsurface morphology of the ionic domains in various ionomers.<sup>69,70</sup> Since a review article on the ionomer morphology is present, interested readers are referred to it.<sup>71</sup>

According to a multiplet/cluster model proposed by Eisenberg et al. to interpret both the morphology and dynamic mechanical data of random ionomers,<sup>72</sup> the ionic groups of the ionomer reside inside of a multiplet while the polymer chain segments are outside of the multiplet. As expected, this model accepts the hard-sphere model<sup>29,73</sup> to interpret the SAXS peak. It is also proposed that the size of the multiplets is affected by a number of factors such as the steric hindrance of the polymer chain segments emanating from the multiplet, the size of ion pairs,<sup>10,74</sup> the dielectric constant of polymers,<sup>6,75</sup> the distance between an ionic group and a polymer backbone,<sup>76</sup> and an ion content.<sup>76,77</sup> That is, the bulkiness and stiffness of polymer backbone chains naturally lead to the formation of smaller multiplets. When one considers the size of ion pair, at first, one can expect that the size of the multiplet will be proportional to the size of the ion pair. However, at the same time, one should also think that the interactions between the ion pairs are inversely proportional to the size of the ion pair. These two aspects influence the multiplet size in opposite directions. The polymer matrix of high dielectric constant would solvate the ion pairs, and, thus, no multiplet can be formed. If the ionic groups were placed at the end of flexible alkyl side chain, attached to the polymer chain backbone, the ionic groups would experience less steric hindrance when they formed multiplets, and, thus, the average size of the ionic aggregates should be larger.

Now, let us think about the polymer chain segments surrounding the multiplets. In amorphous ionomers, the multiplets act as physical cross-links. The mobility of the polymer chains emanating from the multiplet will be restricted, with the restriction degree decreasing as the distance between the polymer chain segments and the multiplet increases.<sup>78,79</sup> First of all, the polymer chains in the immediate vicinity of the multiplets





would be less mobile because they are anchored to the multiplets, compared to the polymer chains far from the multiplet. Secondly, bridging between neighboring multiplets by polymer chains would put the polymer chains under tension that makes the polymer chains restricted in their mobility. Thirdly, the crowding of polymer chains in the immediate vicinity of the multiplets also decreases the mobility of polymer chains.<sup>80</sup> These three factors indicate that the chains in the vicinity of the multiplets of the ionomer do not move as easily as the chains of non-ionic polymers. The restricted mobility of polymer chains have been recognized by a number of studies using NMR, dynamic mechanical techniques, and other methods.<sup>78,79,81-85</sup> The thickness of the layer of restricted mobility region surrounding the multiplet is of the order of the persistence length of polymer chain (e.g. ca. 1 nm for polystyrene), and, thus, the size of the reduced mobility region including the multiplet is of the order of 3 nm or less (Figure 1), which is too small to show its own glass transition. However, as the ion content increases, the restricted mobility regions start overlapping, and eventually the sizes of the overlapping regions become large enough to show a second  $T_{\rm g}$  at a temperature much higher than that of a normal  $T_{\rm g}$  of a corresponding non-ionic polymer.<sup>72</sup> Now, these large regions are called "clusters". As the ion content increases further, the clustered regions become dominant and even continuous.

In the case of block ionomers in bulk, multiple morphologies have been proposed.<sup>86-88</sup> On one hand, the block ionomers in solution show equilibrium, near–equilibrium, and non–equilibrium morphologies, including spheres, rods, bi–continuous rods, bilayers, lamellae, vesicles, inverse bi–continuous rods, large compound micelles, aggregate of spheres, large rod–shaped compound micelles, large compound vesicles, and many others.<sup>87</sup> On the other hand, the blends of oppositely charged block ionomers formed either core–shell type of supramolecular assembly<sup>88</sup> or amphiphilic polyion complex vesicular structures,<sup>89</sup> depending on the solvating of non–ionic blocks.



### 2.3. Glass Transition Temperatures

In Figure 2-2, it is seen that polystyrene (PS) homopolymer and the PSMANa ionomer containing 16 mol% of ions exhibit only one loss tangent peak at ca. 120 °C and at ca. 320 °C, respectively. Since the loss tangent peak for the PS at 120 °C represents a glass transition, the loss tangent peak of 16 mol% ionomer is indeed due to a glass transition. As mentioned before, the ionomers of intermediate ion contents show two loss tangent peaks, and the positions of the peaks as a function of ion content for the PSMANa system are shown in Figure 2-4 along with those obtained from Na–SPS ionomers.<sup>11,90,91</sup> It is clear that there are two groups of lines, i.e.  $T_{g,m}s$  and  $T_{g,c}s$ . Several other investigations have been performed to bear on the duality of the glass transitions in polystyrene ionomers by using a differential scanning calorimeter (DSC),<sup>11,91–96</sup> and by measuring the specific volume of ionomers as a function of temperature.<sup>97</sup>

#### 2.3.1. Glass transition of matrix regions

In the case of Na-EMAA ionomers, the loss tangent peak was observed at ca. 0 °C,<sup>98</sup> which was due to a  $\beta$  relaxation of polymer chains in the amorphous branched polyethylene phase, from which most of the ions had been depleted. It was also found that the peak position shifted to lower temperatures with the increasing degree of neutralization. In other study, the  $T_{g,m}$  of the poly(ethylene-*co*-Na acrylate) ionomers was found to increase with increasing ion content.<sup>99</sup>

In the case of the PSMANa ionomers, the  $T_{g,m}$  increased slowly with increasing ion content.<sup>11,100</sup> According to the multiplet/cluster model, the reason for the increase in the  $T_{g,m}$  is that isolated multiplets and the surfaces of clusters act as cross-links, and thus the  $T_{g,m}$  naturally increases with increasing ion content.<sup>72</sup>







Figure 2-4. Glass transition temperatures of matrix and clustered regions vs. ion content for Na-SPS and PSMANa ionomers (some of data were obtain from reference 11).





At this point, it should be noted that the  $T_{g,m}$  does not always increase with ion content. When poly(styrene-*co*-styrenesulfonic acid) copolymers are quaternized with various amines, in which at least one of the substituents on the nitrogen is an alkyl chain, the  $T_{g,m}$ decreases with increasing ion content if the alkyl chain is long enough.<sup>67</sup> As expected, in that system the long alkyl chain acts as an internal plasticizer.

2.3.2. Glass transition of cluster regions

Regarding the  $T_{g,c}$ , the most extensively investigated system is the PSMANa ionomers.<sup>11</sup> At low ion contents, the  $T_{g,c}$  increases almost in parallel with the  $T_{g,m}$ , but only along the temperatures ca. 60 °C higher than the latter (Figure 4). However, with increasing ion content further, the  $T_{g,c}$  increases more rapidly so that for the ionomer containing 16 mol% of ions the difference between the two  $T_{g}s$  ( $\Delta T_{g}$ ) becomes ca. 110 °C. It is also found that the type of ionic groups changes the  $\Delta T_{g}$ . For example, the cluster  $T_{g}$  of the Na–SPS ionomers is much higher than that of the PSMANa ionomers.<sup>90,91,101,102</sup> In the case of the Na–SPS ionomer containing 3.5 mol% of ions, the  $\Delta T_{g}$  is ca. 115 °C, but for the 11 mol% ionomer it increases to ca. 130 °C. This large difference in  $\Delta T_{g}$  is due to the fact that the interactions between Na–sulfonate ion pairs are much stronger than those of Na– carboxylate ion pairs owing to the difference in the three–dimensional arrangement of the cations and anions.<sup>102</sup>

In terms of the  $T_{g,c}$ , one very interesting system is the poly(styrene-*co*-*N*-methyl-4vinylpyridinium iodide) ionomers.<sup>74,103</sup> Whereas the  $T_{g,m}$  increases with increasing ion content in exactly the same way as it does for other polystyrene-based ionomers, the  $T_{g,c}$ is not detected dynamic mechanically. This implies that this system behaves like unclustered ionomer. The reason for the absence of  $T_{g,c}$  in vinylpyridinium ionomers is that the sizes of the *N*-methyl vinylpyridinium cation and iodide anion are too large to make strong ionic interactions. In addition, the  $T_{g,m}$  of the polymer matrix is too high for those ionic groups to form a sufficient amount of multiplets. Therefore, no proper clustering is





allowed. Above the  $T_{g,m}$ , only the chain entanglement is operative to control the ionomer properties. However, when the ionomer is plasticized, which lowers the  $T_{g,m}$  of the polymer, clustering becomes activated,<sup>74</sup> and thus, two loss tangent peaks can now be observed.

Even though the mechanism of the matrix glass transition is the same as that of non-ionic polymer, those of the cluster glass transition involve both ion-hopping and the relaxation of polymer chains in the clustered regions. The ion-hopping mechanism (the hopping of ion pairs with sufficient thermal energy between multiplets) was proposed to occur at and above the  $T_{g.c.}^{90,104}$  According to this mechanism, the glass transition can only be encountered when the ion pairs can move out of the multiplets at a fast rate. Furthermore, the activation energies for the ion-hopping in the PSMANa system are generally higher than those in the Na-SPS system despite the opposite trend in the strength of ionic interaction.<sup>11,90</sup> This indicates that the strength of the ionic interaction influences the  $T_{g.c}$  but is not directly related with the activation energies for ion-hopping.<sup>11</sup>

### 2.4. Physical Properties of Various Ionomers

## 2.4.1. Polyethylene-based ionomers

Since their appearance in 1965, polyethylene (PE)-based ionomers have been studied extensively.<sup>2,28,98,105-125</sup> The PE ionomers are semi-crystalline ionomers and are well known for their flexibility, transparence, toughness, and melt processibility. The rate of stress relaxation was found to be very slow, but the sharp glass transition region was not observed.<sup>103</sup> The shapes of the stress relaxation curves were different from those for amorphous styrene ionomers, but were very similar to those of some amorphous ionomers of very high ion content or highly crystalline non-ionic polymers.<sup>103</sup> When the superposition of the individual curves was carried out, it was found that the shift factors





were not the WLF type, and that the master curves could not be constructed since more than one mechanism might be involved in the relaxation of the polymer chains.<sup>103</sup>

In the plots of decrement against temperature, four peaks were observed.<sup>98</sup> The first peak  $(\gamma)$  at ca. –120 °C was assigned to the crankshaft motion of short hydrocarbon segments in the amorphous phase. The second peak ( $\beta$ ) (–20–0 °C) was ascribed to a relaxation in the amorphous branched PE phase having no ionic group in it. In the case of the third peak ( $\beta$ ') (0–50 °C), it was assigned to the micro–Brownian motion of polymer chains, occurring in the amorphous polymer having hydrogen bonds. The forth peak ( $\alpha$ ) at high temperatures (> 50 °C) was attributed to the micro–Brownian motions of the relatively large segments of polymer backbone. This peak was also assumed to reflect the dissociation of the ionic aggregates. At a relatively high degree of neutralization, an additional  $\alpha$ ' relaxation peak was observed at ca. 50 °C,<sup>115</sup> which might be due to the melting of small 'secondary' PE crystallites that formed slowly after the formation of primary crystallites.<sup>110,111,120</sup> However, since the peak position was independent of frequency, it was also proposed that this endothermic feature might be attributed to an order–disorder transition of ionic clusters.<sup>113,115,117,118</sup>

The stiffness of alkaline and alkaline earth metal-neutralized EMAA ionomers showed a maximum at ca. 33 % neutralization, but no maximum was found up to 60 % neutralization for transition metal-neutralized ionomers.<sup>113</sup> For example, in the case of the Na-neutralized ionomers (MAA content = 5.4 mol%) aged for 2 months, the stiffness (bending modulus) values were ca. 82, 169, 277, 256, and 245 MPa for the ionomers of 0, 20, 40, 60, and 80 % neutralization, respectively. In the case of the Zn-neutralized ionomers, the stiffness values were 124, 183, 255, and 298 MPa for the ionomers of 20, 40, 60, and 80 % neutralization, respectively. It was also found that the degree of the crystalline order of the ionic crystallites affected the stiffness and yield stress of the ionomers strongly, and the strength of the interactions between ion pairs influenced the





tensile strength and elongation at break of the ionomers.<sup>114</sup>

Two relaxations below the melting temperature of crystalline regions were also seen, similar to the double relaxation behavior of amorphous ionomers.<sup>124,125</sup> In addition, the ionomer behaved dynamic mechanically like a material consisting of four distinct entities; primary crystalline regions, secondary crystalline regions, ion depleted regions, and ion-rich regions. As expected, above the melting temperature of the primary crystalline regions, the ionomer showed flow behavior, and below that temperature the ionomer acted as a composite material containing two different regions, i.e. the rigid primary crystalline regions and flexible amorphous regions, having ionic aggregates in them.<sup>125</sup> Upon decreasing temperature to room temperature, the secondary crystalline regions and ion-rich regions formed a cocontinuous hard phase in the amorphous phase. This resulted in the high moduli of the amorphous phase and hard phase. When the temperature decreased further, the ion-depleted regions started devitrifying. At this point, it should be mentioned that the ion-depleted regions did not form a continuous phase and, thus, did not change the modulus of the ionomer significantly. When the temperature increased above the melting temperature of the secondary crystalline regions, the continuity of the hard phase was no longer operative, leading to a strong decrease in modulus. As expected, the thermal treatment of ionomers could change the size of secondary crystalline regions.

To reduce the melt viscosity of ionomers partly neutralized with  $Zn^{2+}$ , long alkyl chain carboxylic acid molecules of low molecular weight (MW) were incorporated into the ionomers.<sup>120</sup> In some cases, the blended ionomers formed new coordination structures between  $Zn^{2+}$  and carboxylic acid, resulting in a homogeneous material. This type of materials exhibited a strong decrease in storage and loss moduli, compared to the Znionomer without long alkyl chain carboxylic acid molecules, and the modulus decreased more significantly than what we expected from both a plasticizing effect and a partial neutralization effect.





When the degree of neutralization of EMAA copolymer (MAA content = 5.4 mol%) was as low as 20 %, the dynamic shear study showed that the super-master curve could be obtained for the acidic copolymer and its ionomer form,<sup>122</sup> suggesting that the bonding between ionic groups only increased chain friction in the linear region. In addition, it was also observed that the ionic bonding did not affect the damping behavior of the acidic copolymer and partly neutralized ionomers, but the damping property of the Zn-ionomer was much weaker than those of acidic copolymer and Na-ionomer.

It was observed that the complex viscosity, storage modulus, and loss modulus of EMAA ionomers increased dramatically with decreasing precursor melt index.<sup>126</sup> The rheological properties were also enhanced, to a lesser extent, by increasing neutralization level. It was also reported that the modulus and yield strength of the ionomer increased with increasing neutralization level up to 40 %, and then remained more or less constant or even slightly decreased upon further neutralization.<sup>127</sup>

As expected, the EMAA ionomers showed complex morphology and very different mechanical properties, compared with its acidic form copolymers.<sup>128,129</sup> Both polyethylene crystal plasticity and incomplete mechanical relaxation of the amorphous ion-rich phase contributed to the yield stress of the ionomers. The restricted mobility regions surrounding the multiplets interrupted the chain relaxation, except at extremely low strain rates, which increased the yield stress of the ionomers. In addition, as polyethylene crystalline regions formed after quenching from the melt, these secondary crystalline regions covered the gaps between the locally-vitrified amorphous regions, which increased the yield stress.

Impact fracture behavior of Na–EMAA ionomer (15 wt% MAA) was also studied.<sup>118</sup> Ductile fracture was shown in both high speed tensile impact and very low speed tensile. When the ordered structure surrounding the multiplets was disrupted, the secondary melting point of the ionomer was disappeared. In the case of Zn–ionomers, similar behavior was observed when the neutralization level was < 60 %. However, 80 % neutralized ionomer





exhibited brittle failure in high-speed tensile impact and the secondary melting point. In the case of a large deformation hysteresis study on Na- or Zn-neutralized ethylene methacrylic acid butyl acrylate (EMAABA) ionomers, two major hysteresis mechanisms were proposed: a characteristic viscoelastic mechanism was operative at all strains and a microstructural evolution/breakdown mechanism incurred during large strains.<sup>130</sup> It was also observed that the ionomers were significantly stiffer, stronger and more dissipative, compared to the neat material, keeping the same level of recovery. Thus, it was suggested that the neutralization affected the stiffness and dissipation of the material with retaining resilience, providing mechanical performance properties attractive for abrasion, impact and puncture resistant applications.

## 2.4.2. Polytetrafluoroethylene-based ionomers

Polytetrafluoroethylene (PTFE) ionomers are semi-crystalline ionomers with wide applications, such as chlor-alkali cell,<sup>131</sup> batteries,<sup>132</sup> electrolyzers,<sup>133</sup> fuel cells,<sup>134</sup> and artificial muscles.<sup>135</sup> The excellent chemical and thermal stability and selective ion transport behavior of PTFE ionomers are due to the chemical structure of PTFE, i.e. perfluoroether side chains terminated with sulfonic acid groups in its tetrafluoroethylene backbone chain.<sup>136</sup> In the late 1960s, E. I. DuPont Company developed a perfluorosulfonate ionomer, Nafion<sup>®</sup>.<sup>137</sup> Since then, various perfluoro ionomers have been developed by other companies, e.g. Flemion<sup>®</sup> (Asahi Glass Company), Aciplex<sup>®</sup> (Asahi Chemical Company), PFSA ionomer (Dow Chemical),<sup>138</sup> Hyflon<sup>®</sup> (Solvay Solexis), and PFSA ionomer (3M Company).<sup>139</sup> At this point, it is useful to know that a review on the understanding of Nafion is present, and interested readers are referred to the original article.<sup>139</sup>

In the case of perfluorosulfonate ionomers, the backbone chains induced semi-crystallinity, while the side chains containing the sulfonate parts resulted in phase-separation from the PTFE matrix into micro-domains (i.e. ionic aggregates).<sup>140</sup> Thus, the length of the ionizable side chain strongly influenced both the crystallization and ion aggregation of PTFE





ionomer.<sup>52,141</sup> In the case of Nafion, the crystallinity degree was also affected by the equivalent weight of the ionomers.<sup>13,142</sup> The nano-sized phase-separated ionic aggregates,<sup>12,143</sup> specifically their shape, order, spatial distribution and connectivity, determined the supramolecular structure and functions of the ionomers used as ionic conductors.<sup>144,145</sup>

A number of morphological investigations on Nafion by using SAXS or SANS techniques were focused on the characterization of the complex, nano-sized phase-separated ionic domains of the materials.<sup>13,14,16,17,21,51,140,141,146-159</sup> There were two scattering peaks in the plot of scatting intensity versus scattering vector (*q*); one peak at low *q* was for the presence of a crystalline phase, and the other peak at high *q* was for the ionic aggregates. A number of morphological models used to interpret the ionomer peak of Nafion have been proposed. For example, the models are cluster-network model,<sup>143,145</sup> lamellar model,<sup>148,151</sup> rod -like model,<sup>51,152</sup> and fringed-micelle model,<sup>154</sup> and many more.

The properties of perfluorosulfonate ionomers have also been studied extensively.<sup>160-165</sup> In the case of a K-neutralized ionomer, time-temperature superposition was not applicable below ca. 180 °C, but above that temperature it became operative again.<sup>120</sup> In the plots of the 10 second modulus values vs. temperature of the K-neutralized ionomer, the two drops in the modulus were not observed, which was probably due to the crystallinity and the different morphology, compared to amorphous ionomers.<sup>161</sup> There were three loss tangent peaks for the completely neutralized Cs-ionomer;<sup>160</sup> the  $\alpha$  peak at 110 °C was ascribed to the glass transition in ionic cluster regions and shifted to higher temperatures with the increasing degree of neutralization,<sup>162</sup> the  $\beta$  peak at ca. 20 °C was due to the glass transition in the matrix regions, and the  $\gamma$  peak at ca. -20 °C was due to the local motions of CF<sub>2</sub> groups of the polymer main chains in non-crystalline regions. It was found that the 10 sec modulus curve of the amorphous Nafion was essentially parallel to that of the crystalline Nafion, but only shifted to ca. 40 °C lower than that of the crystalline





Nafion.<sup>164,166</sup> In the case of the perfluorocarboxylate ionomers, an additional  $\beta$ ' peak was also seen between temperatures for the  $\beta$  and  $\gamma$  relaxations and assigned to the local motions of the polar side groups.<sup>166</sup>

At this point, it should be mentioned that Nafion is usually used in a condition of high temperature (i.e. over 80 °C) and relative humidity (50-100 %) for extended periods of time.<sup>167-172</sup> It is known that the elastic modulus decreased but the creep strain increased with temperature.<sup>168,172</sup> These two findings were useful to interpret the rupture of the membrane, which was occurred at a lower draw ratio during cold drawing than during high -temperature stretching.<sup>173</sup> It was observed that the maximum of E' as a function of humidity was moved to higher humidity with increasing temperature. In addition, the glass transition of the ionic regions was moved to higher temperatures with increasing water activity. Therefore, it was proposed that at low temperatures, in general, water acted as plasticizer. On the other hand, at elevated temperatures, water made the membrane stiff by stabilizing the network of hydrophilic clusters. At very low humidity levels, there was a moderate increase in the mechanical strength of the membrane, which was due to the formation of hydrates and hydrogen bridge bonds between neighboring sulfonic acid groups.<sup>174</sup> It was found that the elastic modulus of the Nafion decreased significantly with increasing amount of water absorbed by Nafion.<sup>175-177</sup> In addition, the low degree of hydration by Nafion increased the stress relaxation rate,<sup>160</sup> but the high level of hydration decreased the stress relaxation rate.<sup>172</sup> As expected, the addition of a large amount of water weakened the interactions between ionic groups.<sup>162</sup> On the other hand, a small amount of water stiffened the ionomer.171,172

The hydration and transport properties of Nafion were studied in terms of water uptake,<sup>178-184</sup> diffusion of water,<sup>185,186</sup> swelling behavior,<sup>183,187</sup> and proton conductivity.<sup>188</sup> Various techniques, such as FT-IR,<sup>189-193</sup> TEM,<sup>194,195</sup> light scattering,<sup>196-200</sup> X-ray and neutron scattering,<sup>13,14,16,201-204</sup> dielectric spectroscopy,<sup>205</sup> and NMR have been used to investigate the





hydration and transport properties.<sup>206-209</sup> The simulation was also applied to understand the hydration and transport behavior of Nafion;<sup>210,211</sup> both continuum modeling for macroscopic. thermodynamic descriptions.<sup>212–214</sup> and atomistic modelling for hydration associated nanoscopic polymer dynamics<sup>12,158</sup> were used to explain the hydration and transport behavior.<sup>215,216</sup> Self-diffusion of water in the oriented structure of stretched Nafion membrane was measured to study the correlations between the stress-induced order and the transport properties of the membrane.<sup>156,173,217,218</sup> It was reported that the wetting interactions in thin Nafion film interfaces affected the internal morphology of ionomers strongly and modified the transport properties of the Nafion film.<sup>204</sup> The ionic and hydrophilic channels in thin films cast onto hydrophobic substrates were parallel-oriented, which made the slow absorption of water from humidified environments. However, those in films cast onto SiO<sub>2</sub> were oriented isotropically, which enhanced water sorption and swelling of the polymer. Since the review article on the water-mediated transport in ion-containing polymers is present,<sup>219</sup> interested readers are referred to the article. At this point, it should be mentioned that although Nafion has excellent properties, its high cost and relatively poor durability are obstacles for its use in PEFCs. Especially, the crucial factors, such as the formation of cracks and pinholes, and the oxidative degradation, limit the durability and lifetime of Nafion in a fuel cell.<sup>165,220</sup> Thus. Nafion replacements have been attempted in two ways: the preparation of new polymers that have covalently attached acidic/ionic groups<sup>25</sup> and the preparation of polymer blends or polymer composites.<sup>221-223</sup>

# 2.4.3. Polystyrene ionomers

In the case of PSMANa ionomers, the 6 mol% of ions is a threshold value for the continuity of either matrix regions or clustered regions.<sup>11</sup> Below 6 mol%, the matrix regions are a dominant and continuous phase. Above 6 mol%, the cluster regions are a dominant and continuous phase. Thus, above 6 mol% of ions, two types of relaxations of the ionomer chains in either matrix or clustered regions are applicable. Therefore, the



application of time-temperature superposition in the plots of stress vs. strain of the ionomer of high ion contents is failed.<sup>100</sup>

The dynamic mechanical properties, i.e. storage modulus and loss tangent, of PSMANa ionomers as a function of temperature are seen in Figure 2. In the plot of modulus vs. temperature, the ionomers of intermediate ion content showed three plateaus. The plateau at a highest position is definitely related with glassy modulus, the middle plateau, the "ionic" plateau, resides in the range from ca.  $10^{6.5}$  Pa to  $10^{8.5}$  Pa, depending on the ion content, and the plateau at a lowest position of ca.  $10^{5.6}$  Pa is associated with rubbery modulus. It is clear that the heights of the glassy plateaus and rubbery plateaus do not change significantly with ion content, but the that of ionic plateaus increases with ion content. At this point, it should be mentioned that the modulus of a polymer can be increased by the addition of filler, and, thus, the ionomers can be considered as filled materials by assuming that the clusters acted as filler particles in the temperature range between the two  $T_gs$  of the ionomers. In addition, it has been known that the percolation concept is also applicable to explain the continuity of the cluster regions of the ionomers.<sup>11</sup>

The storage modulus curves for the Na–SPS and PSMANa ionomers containing ca. 7 mol% of ions are shown in Figure 2-5. The "ionic plateau" of the Na–SPS ionomer extends to higher temperatures, but its position is lower, compared to that of PSMANa ionomer. The extended ionic plateau is due to the larger difference between the matrix and cluster  $T_{\rm g}$ s of the Na–SPS ionomer. Since the interactions between the Na–sulfonate ion pairs are stronger than those between Na–methacrylate ion pairs, the cluster  $T_{\rm g}$ , related to ion–hopping mechanism (one of cluster  $T_{\rm g}$  mechanisms), is higher for the Na–SPS ionomer. Thus, the ionic plateau of the sulfonate ionomer persists to higher temperatures. Furthermore, the ionic groups of the sulfonated ionomer are located at the *para* position of the benzene ring, while those of the methacrylate ionomer are directly attached to the main chain.<sup>90</sup>







Figure 2-5. Storage modulus curves for the Na-SPS and PSMANa ionomers containing ca. 7 mol% of ions.





Therefore, the ion pairs of the Na–SPS ionomer can form larger multiplets because the distance between the ion pair and the main chain is longer, leading to less steric hindrance for the ion pairs to form multiplets. It is natural that the larger size of the multiplets results in the formation of fewer multiplets. If the thickness of the restricted mobility layer surrounding multiplets were the same in the two ionomers, the total size of restricted mobility regions would be smaller for the Na–SPS ionomer. At this point, it should also be noted that, the strength of the ionic interactions also affects the multiplet size. If the strength of the ionic interactions were stronger, the number of ion pairs per multiplet should be increased, which naturally enlarged the multiplet size.<sup>90</sup>

When the dynamic mechanical properties of poly(styrene-co-sodium acrylate) (PSANa) ionomers were compared to those of PSMANa, having a methyl group attached to the  $\alpha$ carbon of the acrylate unit, it was found that the PSANa ionomer exhibited a lower cluster  $T_{\rm g}$  and a lower and shorter ionic plateau in comparison with the PSMANa ionomer.<sup>224</sup> This difference is due to the contact surface area occupied by two polymer chains emanating from the multiplet of the PSMANa ionomer was larger because of the presence of the methyl group on the  $\alpha$ -carbon of the acrylate unit, compared to that of the PSANa ionomer. The presence of two methyl groups attached to both the  $\alpha$ - and  $\beta$ -carbons of the acrylate unit induced the high energy barrier for the bond rotation, which resulted in the formation of only a few small-sized ionic aggregates.<sup>225</sup> In the case of polystyrene-based ionomers possessing both methacrylate (MA) and styrenesulfonate (SS) units in each polymer chain (PSMA-SSNa), the ionic moduli of the ionomers depended directly on the total ion content.<sup>226</sup> When the mechanical properties of PSMA-SSNa, PSMANa, and Na-SPS ionomers were compared to each other, it was seen that the ionic modulus was highest for the PSMANa ionomer and lowest for the PSMA-SSNa ionomer. The matrix  $T_{gs}$ of the three ionomer systems were similar to each other, but the cluster  $T_{\rm g}$  of PSMA-SSNa ionomer was higher than that of Na-SPS ionomer at low SS contents and closer to each other at high SS contents. In addition, the SAXS results indicated that the multiplet size



decreased in the following order, PSMA-SSNa > Na-SPS > PSMANa. This implied that at the same ion content, the fraction of cluster regions was smallest for PSMA-SSNa ionomer in comparison with those of Na-SPS or PSMANa ionomers.

According to some of rheological studies on styrene-based ionomers, it was found that the ionomers showed linear rheological behavior only for a limited range of low strain (rates).<sup>27,227,228</sup> However, the polymer processing has usually been carried out under nonlinear stress and strain operation conditions; these operation conditions naturally affect the multiplet formation of the ionomers. Thus, the understanding of the relationship between nonlinear rheological behavior and morphological changes is very important for the actual manufacturing processes of the ionomers. The linear viscoelastic behavior of very lightly sulfonated SPS ionomers was investigated.<sup>27</sup> The interactions between ion pairs made the terminal flow region of the ionomers of modulus-frequency master curves move to lower frequencies. In addition, at very low sulfonation levels as low as 0.11 mol%, there was a new low-frequency relaxation, not observed in the non-ionic PS, which was due to the presence of an ion-rich phase. As expected, the change of the cation type from sodium to ammonium weakened the strength of the interactions between the ion pairs, which affected the viscoelasticity of the ionomer significantly. The rheological study of the alkaline metal salts of oligomeric sulfonated polystyrene (SPS) (MW = ca. 4000 (far below the entanglement MW of non-ionic PS)) revealed that there was the separation of an ionrich phase, and, thus the time-temperature superposition was not applicable even for the 2.5 mol% ionomer.<sup>227</sup> It was also found that the ionic interactions increased the terminal relaxation time of the ionomer melt by seven orders of magnitude, compared to the unentangled PS. In addition, there was a critical shear rate for shear-thickening or shearthinning behavior of the ionomers. The shear-thickening might be due to the enhancement of the interchain association of the polymer chains when the polymer chains were deformed under shear. On the other hand, the shear-thinning took place when the shear rate was 1-2orders of magnitude higher than the chain relaxation rate. Linear viscoelastic properties of





oligomeric SPS ionomer melts were found to be similar to well-entangled non-ionic PS melts.<sup>228</sup> A shear rubbery modulus was comparable to that of high MW PS. As expected, time-temperature superposition was not applicable for the SPS ionomer because of two types of relaxations for the cluster  $T_{\rm g}$ . In addition, it was found that, with increasing extensional strain rate, the modulus of the ionomer increased, and a maximum in the stress, causing the destruction of multiplets, occurred at a relatively low Hencky strain that was not affected by a strain rate. Furthermore, the structural changes in the multiplets by the large deformation flows affected the viscosity and elasticity of the ionomers.<sup>229</sup> Large strains or strain rates disrupted the multiplet formation and induced pseudoplastic behavior, and the melt elasticity by large deformation flows decreased strongly. There were three regions of the flow curve of the ionomers: a Newtonian-like viscosity region at low shear rates, a power-law shear thinning region above a certain shear rate at which the destruction of multiplets occurred, and a second Newtonian region at sufficiently high shear rates. Shear flows did not induce stress overshoot behavior once the ionomer flew, and the stress growth became rapid even at low shear rates. It was also found that with increasing ion content, the flow curve shifted to higher shear rates. In general, the high elasticity of the ionomers was due to the presence of multiplets, which was different from the presence of chain entanglements.

Since it is not possible to describe all the ionomer families in this article, we will just name a few more extensively studied ionomers here; block ionomers,<sup>86,87,230-253</sup> telechelic ionomers,<sup>254-276</sup> star ionomers,<sup>277-289</sup> polyurethane ionomers,<sup>290-301</sup> ionenes,<sup>302-314</sup> zwitterionomers,<sup>95,315-323</sup> ethyl acrylate ionomers,<sup>10,94,324-328</sup> methyl methacrylate ionomers,<sup>23,327,329-331</sup> and liquid crystalline ionomers.<sup>332-348</sup>

### 2.5. Plasticization

Since ionomers have the ion-rich regions and the hydrocarbon-rich regions, each region of the ionomer separately or both regions of the ionomers can be plasticized by using





plasticizers of high or low polarity or amphiphilic plasticizer, respectively. One of early studies on this dual plasticization was conducted by Lundberg and Markowski who found that a polar additive could plasticize the ion-rich regions of Na-SPS ionomer.<sup>349</sup> Generally. in the case of polar plasticizers, they reside in the multiplets and weaken the interactions between ionic groups, which, thus, induces fast ion-hopping. As a result, the  $T_{g,c}$ , melt viscosity, and terminal relaxation time of the ionomer decrease significantly [Figure 2-6-(a)].<sup>171,349-355</sup> In the case of non-polar plasticizers, they embed themselves evenly in the hydrocarbon-rich regions (both matrix and cluster regions) [Figure 2-6-(b)]. Consequently, the plasticizers increase the free volume in the material, and thus decrease both  $T_{g,m}$  and  $T_{\rm g,c}$  significantly.<sup>352,354,356,357</sup> In the case of amphiphilic plasticizers, e.g. surfactants, the ionic head groups of the plasticizers reside in the multiplets with the ionic groups of the ionomers and the hydrocarbon tails of the plasticizer reside in the restricted mobility regions of the ionomer [Figure 2-6-(c)].<sup>358,359</sup> Therefore, the addition of the plasticizer makes the polymer chains in the immediate vicinity of the multiplets more mobile, decreasing  $T_{g,c}$ . At this point, it should be noted that some of the surfactant molecules can form crystalline regions, when the alkyl chains are long enough to form phase-separated crystalline regions; as a result, the ionic modulus increases when the crystalline regions act as filler.359 In addition, if the types of the ionic groups of the surfactant and ionomer were different, the surfactant, again, would become phase-separated and act usually as filler. On the other hand, if the multiplets contained two different types of ion pairs, the interactions between ion pairs would become weaker, and, thus, the surfactant might behave like multiplet plasticizer. This indicates that amphiphilic additives can act either as plasticizer or filler or both, depending on the chemical structure of the amphiphiles, the types of ionic groups, the valency of cations, the type of ionomers, and the melting point of the phaseseparated surfactant domains, if there are any.<sup>360-366</sup>





Figure 2-6. Schematic drawing of the possible plasticization of ionomers using (a) polar plasticizer, (b) non-polar plasticizer, and (c) amphiphilic plasticizer.





A styrene oligomer, one end of which contained Cs and Ba neutralized *p*-carboxylate unit, can be used as plasticizer for the ionic domains of *p*-carboxylated polystyrene.<sup>367</sup> In this case, short styrene chains can reside in the restricted mobility regions surrounding the multiplet, resulting in a reduced clustering.

The alkyl ammonium ions can also behave like multiplet plasticizer. When PTFE ionomers are neutralized with various alkyl ammonium ions, the large-sized ions can plasticize the ionomer effectively, thus decreasing the relaxation temperatures.<sup>153</sup> As expected, the acid groups of under-neutralized ionomer can also act as multiplet plasticizer, decreasing the melt viscosity<sup>368</sup> or  $T_{g,c}$  of the ionomers.<sup>369,370</sup>

It is useful to mention the role of inorganic salts in the ionomers. It was found that with increasing inorganic salt contents, the ionic modulus of the PS ionomer increased,<sup>371</sup> In addition, the ionomer containing a large amount of inorganic salts showed x-ray diffraction peak, indicating that the inorganic salts in the ionomers acted as filler particles.<sup>371</sup> It was also observed that the inorganic salts did not change the  $T_{g,m}$  of the ionomers but reduced the  $T_{g,c}$ . This implies that some of the inorganic salts resided in the multiplet with the ionic groups of the ionomers, enlarging the contact surface area of the ionic groups of the ionomer.

At this point, it should be mentioned that when the amount of liquid plasticizer, usually solvent, are very large, the ionomer naturally becomes dissolved in the solvent to make ionomer solution. However, even though the solution properties of ionomers are of great importance, the discussion on the topic is omitted; readers who are interested in this topic can look up other review articles.<sup>372-375</sup>

2.6. Ionomer Blends





Polymer blends are polymeric materials, in which at least two different types of polymers are mixed together to create materials that have new and/or different physical properties, compared to those of virgin polymers. At this point, it should be mentioned that, on the basis of the thermodynamics of mixing, the mixing entropy of polymers is positive but very small because of the high MWs of the polymers. Thus, even a very small positive enthalpy change for the mixing of two polymers causes an immiscible blend. Therefore, it is not easy to obtain miscible polymer blends. However, if there were specific interactions between the pairs of polymers that were mixed together, the change in mixing enthalpy would decrease, sometimes even to negative values. Then, the miscibility enhancement of polymer blend can be achieved by the introduction of functional groups to polymer pairs. The interactions between functional groups range from ionic interactions to hydrogen bonding<sup>376,377</sup> to dipole–dipole interactions to the formations of donor–acceptor complexes or charge transfer complexes.<sup>378</sup> Since early 1980s, the introduction of ionic groups to nonionic polymers has been used extensively as a tool for the polymer miscibility enhancement. Typical examples of this type of miscibility improvement are the formation of homogeneous polyelectrolyte complexes with either polyanions or polycations.<sup>379-383</sup> As expected, a number of papers on the ionomer blends have been reported, and the reviews on the subject are also available.<sup>384-387</sup>

As shown in Figure 2-7, one can find various types of interactions between the ionic groups of ionomer blends. For example, a copolymer containing sulfonic acid neutralized with a large cation, such as an alkyl ammonium ion can be mixed with a copolymer having pendent pyridinium ions with a large anion, such as iodide.<sup>108,388,389</sup> This type of ionomer blend shows simple ion-ion interactions [Figure 2-7-(a)]. When a polymer containing a pyridine group is blended with a polymer having a sulfonic acid group, proton transfer takes place from the sulfonic acid to the vinylpyridine, resulting in a cationic pyridinium polymer chain and an anionic sulfonate polymer chain.<sup>390</sup>







Figure 2-7. Various ionic interactions for miscibility enhancement. (a) ion-ion, (b) H-bond assisted ion-ion, (c) complementary ion pair-ion pair, (d) identical ion pair-ion pair, (e) ion-dipole, and (f) ion-coordination.





This type of ionomer blend exhibits proton transfer–assisted ion–ion interactions [Figure 2-7-(b)]. Ion pair–ion pair interactions can also be possible in some of ionomer blends.<sup>389,391,392</sup> The example is a system in which a sodium carboxylate ion pair of one ionomer chain interacts with a quaternary ammonium halide<sup>392</sup> [Figure 2-7-(c)] or the same sodium carboxylate ion pair of the other ionomer<sup>391</sup> [Figure 2-7-(d)]. In the case of alkali and alkaline earth metal cations, the cations can interact with poly(ethylene oxide) PEO, through ion–dipole interactions [Figure 2-7-(e)].<sup>360,393-397</sup>

Ion-coordination with the presence of transition metal ions can also be used for the ionomer blends.<sup>398-400</sup> An example is seen in a poly(ethyl acrylate-co-4-vinylpyridine) copolymer mixed with a Zn-SPS ionomer [Figure 2-7-(f)].<sup>400</sup>

As expected, if the ionic interactions between two copolymers were strong, and the blend would be naturally more miscible as the ion contents of the two polymers increase. However, at this point, it should be mentioned that at high ion contents, the melt viscosities of the ionomer blends are too high for the ionomer blends to be processable. In addition, in the case of ionomer blends using ion pair-ion pair interactions (i.e. Nacarboxylate and Na-sulfonate ion pairs), sometimes each ionomer would form its own phase-separated regions, thus, leading to immiscible or only partly miscible blends.<sup>401,402</sup> The above results indicate that the ion contents and the types of ionic interactions should also be considered for the specific applications of ionomer blends. In addition, if the repulsion between the ionic and non-ionic species of the ionomer chain were stronger than that between the components of the ionomer and other polymer, the ionomer/polymer blends could be miscible, to some extent.403-407 Ionomers can also be utilized to decrease the interfacial tension between two different polymers and increase interfacial adhesion, which improves the mechanical properties of the blends.<sup>408-414</sup> Using ionic interactions, one can make rod-like macromolecules well-dispersed in the polymer matrix. For example, ionic interactions can be utilized for mixing relatively rigid rod-like liquid crystalline polymers





with flexible coiled matrix polymers.<sup>415-417</sup> In addition, when a rod-like polymer, such as sulfonated poly(*p*-phenylene) with varying lengths of alkyl side chains, is mixed with the matrix polymers, such as poly(ethyl acrylate-*co*-4-vinylpyridine) or poly(styrene-*co*-4-vinylpyridine), the acid-base reactions take place between the polymer pairs, which creates the proton transfer-assisted ion-ion interactions [Figure 2-7-(b)]; thus, the rod-like macromolecules acting as effective filler are dispersed in the matrix polymer to form ionomeric nanocomposites.<sup>418</sup> The mechanical properties of the nanocomposites are enhanced drastically, which were influenced by the MW of rigid-rod polymer (i.e. the aspect ratio of the filler), the types of the ionic interactions, and the volume fraction of the rod-like polymer in the blend. The outstanding mechanical properties, compared to those of conventional fiber-reinforced polymer composites, are probably due to ionic interactions.

Ionically modified rigid rod-like poly(*p*-phenylene terephthalamide) (PPTA) neutralized with  $K^+$  could be added to PEO<sup>419</sup> or poly(propylene oxide) (PPrO)<sup>420</sup> to prepare molecular composites. The tensile strength, stiffness and resistance to stress relaxation of the composites increased strongly.<sup>419,420</sup> It was also found that even though the amount of the ionic PPTA in the blends was relatively small, the increasing amount of the ionomer led to the increase in the  $T_g$  and decomposition temperature<sup>343</sup> of the PPrO-based composite.<sup>420</sup> The above results were due to a good dispersion of the rigid ionic PPTA and the presence of ion-dipole interactions between the ionic groups of the ionic PPTA and the dipolar units of the PEO or PPrO matrix. It was also found that the divalent Ca<sup>2+</sup> increased the strength and rigidity of the PPrO composite more strongly, compared to the monovalent K<sup>+</sup>.<sup>420</sup> PPTA containing propane sulfonate groups was also blended with poly(4-vinylpyridine) (4VP).<sup>421</sup> Ionic interactions between the two polymers increased the effective entanglement strand density. The deformation mode of the 4VP changed from pure crazing mode for pure polymer to combined crazing and shear deformation mode for the polymer containing 15

wt% of the K-ionomer. When the ionomer was neutralized with  $Ca^{2+}$ , pure shear deformation mode had already been observed for the polymer containing only 5 wt% of the Ca-ionomer.

When the blends of ionic naphthalene thermotropic polymer (NTP) and poly(ethylene terephthalate) (PET) were prepared by melt blending, the blends having ion-dipole interactions between the ionic groups of the ionic NTP and the dipolar units of the PET were found to be homogeneous at low wt% of ionic NTP but inhomogeneous at high wt% of ionic NTP.<sup>422</sup> Both the stiffness and strength of the blends were increased for all the blend samples, compared to those of the PET. Very strongly enhanced ductility and toughness were observed during a necking process in these blends. Thus, it was suggested that the ionic NTP chains acted as a reinforcing agent in the homogeneous blends as well as a nucleating agent to increase the crystallinity and as a good stress transfer agent. Surlyn can be used to make a nano-composite system with poly(ethylene vinyl alcohol) (EVOH) and organically modified nano-clays like montmorillonite to develop flexible gas barrier materials.<sup>423</sup> It was found that the permeabilities of oxygen gas and water vapor through the composite film decreased by two orders of magnitude, compared to that of Surlyn. In addition, it was also observed that the encapsulation using these ionomer blend composites increased the device lifetime by more than an order of magnitude.

Acrylonitrile–styrene–acrylic (ASA) terpolymer was blended with Na–EMAA ionomers to develop a weather–resistant ASA, having good heat sealing and adhesion properties.<sup>424</sup> It was observed that the tensile strength and modulus of the ASA were reduced by up to 45% with increasing amount of Na–ionomer up to 50 wt%. In addition, the thermal stability of ASA increased upon the incorporation of the ionomer. For example,  $T_{d-50\%}$  increased from ca. 400 °C for pure ASA to ca. 430 °C for ASA/ionomer (50/50 wt%/wt%) blend. It was also found that the ionomer content determined the structures of the ionomer chains of either "mushroom" or "brush" type, which affected the dynamic rheological and





mechanical, and creep properties of the materials.<sup>425</sup> Furthermore, in all the blend systems, there was no crossover between G' and G'' relaxation, and the Rouse type relaxation was applicable to interpret the chain relaxation.

The fast vulcanization and higher cross-linking degree of the ethylene/*n*-butyl acrylate/glycidyl methacrylate (EBA-GMA) terpolymer blended with Zn-polylactide (PLA)<sup>367</sup> were achieved by the addition of Zn-EMAA ionomer.<sup>426</sup> In that blend, the zinc cations acted as *in situ* catalysts for crosslinking of the EBA-GMA elastomer and also enhanced the reactive compatibilization of PLA/elastomer at their interface, which induced the excellent impact strength of PLA.

Ionomers could also be used to enhance the crystallization of non-ionic polymers. For example, ethylene-based ionomers<sup>427,428</sup> and styrene-acrylate ionomers<sup>429</sup> were applied as nucleating additives for the crystallization enhancement of PET. In addition, it was found that ethylene-acrylate was more effective than ethylene-methacrylate to increase the crystallization rate of the PET, which was due to their different nucleation mechanisms.<sup>427</sup> In the acrylate ionomer case, they initiated heterogeneous nucleation that accelerated the crystallization of PET. On the other hand, the methacrylate ionomers, dissolved in molten PET, reacted with PET to create ionic chain ends forming ionic clusters that acted as the nucleation sites. Furthermore, the nucleation efficiency of the ionomers was found to depend on the valency of the cations, which naturally influenced the formation of multiplets as well as ion-hopping of the ionomers.<sup>428</sup>

At this point, it should be mentioned that the polymer blends between some of the functional polymers showed various interactions between the polymers at the same time. For example, blends of SPS ionomers with polyamides such as  $poly(\epsilon$ -caprolactam), PA6, were partially miscible due to hydrogen bonding, ion-dipole interaction, or metal complexation between the sulfonated ionic groups and the amide groups.<sup>395,396,430-440</sup>





# 2.7. Applications of Ionomers

Ionomers are currently used in various places, and this section is devoted to the brief description of some of the interesting applications. Up to June 2015, almost 57,000 articles related to ionomers, including 16,200 patents, were found using SciFinder<sup>®</sup>. Regarding detailed information about the applications of ionomers, extended abstracts,<sup>441</sup> book chapters<sup>442-452</sup> and review articles<sup>221,453-466</sup> deal with, sometimes in part, the ionomer applications; interested readers are referred to the original articles.

## 2.7.1. Superpermselective membrans

Proton exchange membrane fuel cells (PEMFCs) are an alternative power source for portable and stationary applications due to their high power density and conversion efficiency.<sup>467</sup> As mentioned before, perfluorosulfonic acid (PFSA) copolymers such as Nafion are widely used as PEMs because of their excellent chemical and mechanical stabilities and high proton conductivity. However, there are several drawbacks of the PFSAs such as high fuel permeabilities, high cost, difficult synthesis, and low  $T_g^{25,468}$  Thus, to overcome these drawbacks, sulfonated aromatic polymers such as sulfonated poly(arylene ether)s<sup>469-476</sup> and sulfonated polyimides<sup>477-480</sup> were prepared. They showed excellent thermal stabilities and low fuel permeabilities, but also exhibited relatively low proton conductivity because of the presence of rigid hydrocarbon polymer chains that made the formation of ionic channels difficult.<sup>481</sup> As a result, another copolymers, such as block copolymers,<sup>482-489</sup> pendant or comb-shaped copolymers.<sup>31,467,480,490-493</sup> and highly sulfonated copolymers<sup>494-498</sup> have been prepared to improve proton conductivity. In the case of the sulfonated block copolymers having well-defined morphologies, each block component can show its own properties.<sup>497</sup> Thus, one could design block components to make them suitable for desired applications.<sup>483</sup> At this point, it should be mentioned that sulfonated polymers are degradable when exposed to severe operation conditions.<sup>499</sup> Thus, the thermal treatment of the sulfonated polymer membranes, which reduces water uptake but produces well-ordered morphology,





can be applicable to gain required membrane properties for proton conduction applications.<sup>470,500-502</sup>

One of the most important applications of this ionomer family is their use as a membrane for super permselectivity because they allow water transport and the diffusion of cations at a fast rate.<sup>262,466</sup> Since PTFE has high dimensional and thermal stability, the perfluorinated ionomers find extensive applications in the chlor–alkali industry, where the ionomer membranes are used to separate the cathode and anode compartments for the electrolysis of sodium chloride to produce chlorine and sodium hydroxide, with a lower electricity consumption. At this point, it should be mentioned that there are thousands of articles dealing with ionomer membranes; interested readers are referred to the relevant articles.

### 2.7.2. Ionomer plastics

Ionomers are used as bulk plastic materials extensively.<sup>262,503</sup> Golf ball covers, bowling pin covers, side molding strips, bumper guards, and shoe parts are good examples.<sup>504-509</sup> In this case, the moldability and toughness are required properties for the ionomer plastics. Especially, for golf ball covers, the ion aggregation is a crucial and spectacular factor that controls the mechanical properties. The toughness of the ionomers allows the ionomer covered ball to have strong cut resistant so that an off-center swing does not damage the ball significantly. In addition, since this ionomer is easily moldable, injection molding can be used to manufacture the golf balls, which reduces the unit cost of production.<sup>510,511</sup> Furthermore, the low rebound problem and cold crack problem encountered in Zn-ionomer and Na-ionomer, respectively, can be solved effectively by blending both Zn- and Na-ionomers.<sup>512</sup> Therefore, since early 1970's, golf balls with ethylene ionomer covers have been sold widely in the world market.

## 2.7.3. Ionomeric elastomers

The mechanical properties of ionic elastomers, such as carboxylated nitrile rubber (XNBR),





were mainly controlled by ionic aggregates formed during the crosslinking of the elastomers with ZnO<sup>513</sup> and Zn salts.<sup>514</sup> These ionic aggregates induced micro-phase separation, and the ionic elastomer exhibited an additional relaxation on a high-temperature side in dynamic mechanical study.<sup>513</sup> It was found that all Zn-containing compounds (ZnO, Zn-Allayered double hydroxide, and ZnCl<sub>2</sub>) reacted with the carboxylic groups of XNBR,<sup>1</sup> but the dynamic mechanical properties of the XNBR changed with the type of cross-linking agent. Zn compounds. This was attributed to the different coordination numbers in the ionic cross-links or clusters. It was also observed that only ZnO induced the formation of a Znenriched second phase, showing a certain kind of lamellar structure of the ionic phase inside the rubber. Thus, the XNBR exhibited the high-temperature relaxation of polymer chains. At this point, it should be mentioned that different metal oxides or peroxide, such as  $CaO_{2}^{515}$   $ZnO_{2}^{516}$  MnO<sub>2</sub><sup>517</sup> and  $CuSO_{4}^{518}$  could be used to prepare XNBR ionic elastomers. Sulfonated poly(ethylene–octene) or poly(ethylene–butene) elastomeric ionomers neutralized with Zn acetate were prepared as ionic elastomers.<sup>519</sup> It was found that the ionization of the base elastomers significantly improved the tensile stress and storage modulus at low temperatures, compared to those of the corresponding pristine elastomer and acidic copolymer. In addition, sulfonated poly(ethylene-butene) exhibited better thermomechanical properties, compared to sulfonated poly(ethylene-octene). The grafting of acrylic acid (AA) onto poly(ethylene-octene) or poly(ethylene-butene), and the neutralization of the acid groups with Zn acetate also created new ionic elastomers.<sup>520</sup> Again, it was observed that multiplets acted as secondary cross-links and improved the mechanical and thermal properties of the polymer significantly, compared to the corresponding virgin polymer and acidic elastomers. That is, the tensile strength and modulus increased upon the grafting of AA and increased further by neutralization. In addition, as expected, the tensile strength and modulus increased with increasing degree of crystallinity. The Zn-EPDM can be used as self-vulcanizing rubber. The multiplets in these ionomers, acting as physical cross-links, make it unnecessary to vulcanize the polymer. Ionomers, including the Zn-EPDM ionomers, can be used as roofing materials.<sup>104,521-526</sup> Since the ionomer is physically cross-linked,




creep is unavoidable, to some extent; however, the problem caused by rupture can be prevented. This type of ionic elastomers has advantages in the sealing of sheets by thermal treatment and in the reprocessing of ionomers by simply heating and molding them. Finally, there is a review of ionic thermoplastic elastomers based on ionic elastomers, block ionomers, and ionomer blends,<sup>453</sup> and thus, interested readers are referred to the review.

## 2.7.4. Compatibilizer

The mechanical properties of incompatible polymer blends can be enhanced by means of compatibilization, which decreases the interfacial tension but increases the adhesion between the two polymer phases.<sup>527</sup> The compatibilization is usually obtained by promoting chemical reactions between the blend components<sup>528</sup> or by adding compatibilizer to the two polymers. The Zn salt of lightly sulfonated polystyrene ionomer (Zn-SPS) was used as physical compatibilizer for the blends of a wholly aromatic liquid crystalline polyester (LCP) with nylon 66 (PA66) or bisphenol-A polycarbonate (PC).<sup>529</sup> Zn-SPS and PA66 were miscible due to strong intermolecular interactions between the sulfonate and amide groups. On the other hand, the Zn-SPS was miscible with the PC and LCP because of intramolecular repulsive interactions of the PC and LCP along the ionomer molecules. It was found that by the addition of Zn-SPS to LCP/PA66 and LCP/PC blends, the size of dispersed phase decreased but the adhesion between the phases was improved. The blends containing Zn-SPS showed much higher tensile modulus and tensile stress at break than the blends without Zn-SPS. Thermotropic liquid crystalline ionomer (LCI) can also be used as compatibilizer that promotes intermolecular interactions (i.e. ion-dipole association) and enhances the interfacial adhesion between the two phases of the blend. For example, the addition of LCI to the blends of poly(butylene terephthalate)/polypropylene (PP) improved the miscibility of the blends.<sup>530</sup> This was due to the sufficient partitioning of the ionomer into each phase, which improved the interphase adhesion. It was also observed that the addition of LCI increased the ultimate tensile strength and the ultimate elongation of the



blends.

EMAA ionomers neutralized with Zn. Na. and Li can also be utilized as compatibilizer for various polymer blends, such as polyamide 6/low-density polyethylene (LDPE),<sup>531</sup> highdensity polyethylene (HDPE)/PET,<sup>532</sup> HDPE/hydrotalcite nanocomposites,<sup>533</sup> PP/EVOH,<sup>534-538</sup> PP/poly(amino ether),<sup>524,527</sup> poly(lactic acid) with EBA-GMA terpolymer.<sup>539-542</sup> For example, it was found that the shear viscosity of the PA6/LDPE blend increased by the addition of EMAA ionomers of varying degree of neutralization.<sup>543</sup> This was presumably due to the formation of graft copolymer by the reaction of the primary amine with the free acid groups of partly neutralized MAA ionomers. The increasing neutralization degree of the ionomers induced the increase of the shear and elongational viscosity properties of the blend. In the case of the blend of high contents of PA of PA, Zn-ionomer resulted in the highest shear and elongational viscosities. On the other hand, for the blend of low contents, Li-ionomer yielded the highest viscosities. In addition, it was also observed that the type of neutralizing agent exhibited some differences in the mechanical properties, dispersed phase size, and thermomechanical properties of the blends. However, the differences were not related to the neutralization degree or the amount of ionomer. This might be due to the inconsistency in the viscosity of the blends.<sup>531</sup> In the case of Zn-EMAA-compatibilized PP/EVOH blends, the initiation energy release rates ( $G_{IC}$ ) for the blends with EVOH content lower than 30 wt% were slightly lower or similar to that of neat PP.<sup>538</sup> This might be due to the premature failure induced by the critical-sized flaws generated by the debonding of second phase particles. On the other hand, the blends with 40 wt% EVOH exhibited higher G<sub>IC</sub> values than the neat PP, which was due to the increasing number of EVOH particles, responsible for energy-absorption mechanisms. However, it was also confirmed that the effect of the addition of ionomer on the impact fracture properties of the blends was not observed. For the ternary blend of PA66/PS/PP, two compatibilizers, i.e. Surlyn for PA66 and styrene-b-ethylene-co-butylene-b-styrene (SEBS) for PS were used, and there was no gross interference between the two compatibilization systems.<sup>544</sup> In this





system, there were three findings to be concerned: (1) an association of the PS with the PA66 in the compatibilized blends (partial wetting), (2) the formation of larger particles when both compatibilizers were added to the binary blends, and (3) the smaller amount of each compatibilizer needed when both of them were present.

2.7.5. Ionomeric nanocomposites

An organically modified clay mineral montmorillonite (MMT) can be melt-blended with ionomers to make nanocomposites. In this case, the exfoliation of the organoclay into the polymer matrix generates high aspect ratio particles that enhance the physical properties of the composites. Ionomeric nanocomposites showing the good exfoliation of the organoclay were prepared by using a number of ionomers, such as ionomers based on polyethylene,<sup>545-</sup> <sup>548</sup> polypropylene, <sup>549</sup> poly(ethylene terephthalate), <sup>550–556</sup> and poly(butylene terephthalate). <sup>557</sup> Naturally, it is expected that various factors of an ionomer, such as MW, acid content, type of neutralizing ions, and degree of neutralization, can affect the exfoliation of the organoclay. For instance, nanocomposites were prepared by blending the Na-EMAA ionomers and a series of organoclays that were obtained by an ion exchange reaction of Na-MMT with various amine surfactants.<sup>558</sup> The exfoliation level and stiffness of the composites increased by a number of factors, including higher number of alkyl tails of the amine, longer alkyl tails, and an excess amount of the amine surfactant. Organoclavcontaining nanocomposites prepared from the Na- and Zn-EMAA ionomers showed much better exfoliation and significant reinforcement, compared to the nanocomposites prepared from Li-ionomer. The organoclay exfoliation in the Li-ionomer was found to be lower level, suggesting the irreversible exchange of quaternary ammonium ions of the organoclay for the small-sized Li ions of the ionomer.<sup>559</sup> It was observed that the nanocomposite films prepared from Na-ionomer exhibited greater enhancements of mechanical and barrier properties, compared to similar films prepared from nanocomposites based on LDPE. Needless to say, this was due to the greater degree of organoclay exfoliation in the



ionomer, compared to LDPE. The addition of a small amount of MMT to the ionomer increased the tensile modulus of the films without reducing tear strength, puncture resistance or film extensibility and decreased the gas permeability and moisture transmission rate.<sup>560</sup> The increasing degree of neutralization of Na-EMAA ionomer increased the degree of organoclay exfoliation progressively and decreased the particle length and thickness, but increased the particle aspect ratio and particle density.<sup>561</sup> The enhanced exfoliation of the clay led to the higher levels of reinforcement and the reduced elongation at break of the nanocomposites. The relative moduli of the nanocomposites as a function of neutralization level did not quantitatively agree well with the calculated values using Halpin-Tsai equation, which was due to the incomplete orientation of the clay platelets, in part. The highly exfoliated nanocomposites by a simple extrusion process can be obtained by mixing of Na sulfonated poly(butylene terephthalate) (PBT) and organically modified MMT.<sup>557</sup> It was found that at least 1.0 mol% of  $-SO_3Na^+$  groups was needed to obtain the reasonable exfoliation of  $R_4 N^+$ -MMT. It was also observed that the exfoliation degree was not strongly related with the sulfonate content, and the Young's moduli and high-temperature storage moduli increased with increasing-SO<sub>3</sub> Na<sup>+</sup> content.

The effect of anionic clay, layered double hydroxide (LDHs), particles on the thermomechanical properties of partly-neutralized Na-EMAA ionomer was investigated.<sup>548</sup> The thermal and dynamic mechanical responses of EMAA were strongly modified by the LDH particles, which increased the storage modulus and decreased the loss factor values, and shifted the alpha relaxation of the composites to higher temperatures. In addition, organically-modified LDH particles effectively increased thermal stability and reinforced the EMAA ionomer matrix.

## 2.7.6. Drilling fluids

SPS and sulfo-EPDM ionomers can be applied as drilling fluids.<sup>562-565</sup> The ionomer in this application improves the suspension property of various agents. It should be noted that





during the drilling operation, the drilling fluids are exposed to very harsh conditions at high temperatures. Thus, the ionomers should keep the drilling products as well as elements necessary to assist the drilling under the severe conditions. In addition, the use of ionomers helps to extend the applicable temperature of drilling fluids to much higher temperatures than non-ionic polymers.

#### 2.7.7. Ionomer coatings

Ionomers have been used as coating layers.<sup>566-575</sup> For example, ionomeric coatings for agricultural fertilizers change release behavior.<sup>566,567</sup> In more detail, the volatile polar solvent plasticizes multiplets, lowering the solution viscosity, which, in turn, allows the easy spraying of ionomer solutions on the surface of fertilizer particles. As the polar solvent evaporates very rapidly at relatively high temperatures, the ionomer yields a strong film with uniform thickness and high melt strength. Thus, various release patterns of the fertilizer can be achieved, depending on the size of the fertilizer particles and film thickness. When the fertilizers are exposed to water, the water molecules diffuse through the coating layer, and dissolve the fertilizer particles inside the coating layer. This causes a sharp increase in the osmotic pressure of water inside the coating layer. As the amount of water increases further, and the pressure on the coating layer increases to a point, where cracks on the coating layer occur, then the fertilizer solution is released through the cracks. Because of the variation in the thickness of the coating layers, the release of the fertilizer solution occurs in a relatively long period of time. Thus, ionomeric-coating technique on the fertilizer particles allows that the appropriate amount of fertilizers can be released on the time when they are most needed. The same idea can also be applied to pesticide.<sup>569</sup>

2.7.8. Ionic polymer-metal composites

Some of organic polymers can change their shape and/or size by electrical, chemical, or magnetic stimuli. Among the stimuli, the electrical stimulation is one of the most promising





methods to generate elastic deformation in ionic polymers. Ionic polymer-metal composites (IPMCs) are very feasible electro-active polymers that resemble the biological muscles, for their large bending deformation under low electric voltage; thus, they can be utilized as dynamic sensors, robotic actuators and artificial muscles.<sup>576-578</sup> Generally, the IPMC has a sandwich type structure, consisting of a base membrane (usually Nafion membrane) and two thin metallic electrodes on both sides of the membrane.<sup>579–584</sup> Under a low electric potential, the hydrated cations can move to the oppositely charged electrode, i.e. cathode, which leads to a volume difference between both sides of the electrodes. As a result, a bending deformation of membrane towards the anode takes place.<sup>585</sup> As the base membrane materials for the IPMC applications, usually perfluorinated polymers are used because of their excellent mechanical strengths, chemical stability and high proton conductivity. However, as mentioned before, the drawbacks of perfluorinated polymers, such as a short operation time, a low generative blocking force, high cost, and less environment friendliness, urge researchers to find alternative materials that can be prepared easily, cheap, high-performing, and environmentally more acceptable.<sup>586-598</sup> The IPMC materials have numerous industrial and biomedical applications.<sup>578</sup> The industrial applications include mechanical grippers, various types of actuators, metering valves, diaphragm pumps, exoskeletal human joint power augmentation, micro-electromechanical systems, contractile and slithering configurations, electromechanical relay switches, musical instruments, and many others. The examples of biomedical devices are artificial ventricular or cardiac-assist muscles, peristaltic pumps, artificial smooth muscle actuators, artificial ocular muscles, correction of refractive errors of the human eyes and bionic eyes and vision, and many more. At this point, it should be mentioned that recent reviews have surveyed the progress in the development and understanding of actuator and their application, 599,600 and thus, interested readers are referred to the original articles.

2.7.9. Biomaterials



The multiplets can serve as nano-carriers for the delivery of drugs, genes, and imaging agents.<sup>601-605</sup> The nanomedicine field in diagnosis and treatment of devastating human diseases is expanding lately, and novel nanomaterials including block ionomer complexes have found their potential to improve the diagnosis and therapy of neurodegenerative disorders such as Alzheimer's and Parkinson's diseases, and stroke.<sup>602</sup> For example, poly(ethylene oxide)-b-poly(methacrylic acid) neutralized with divalent cations (e.g.  $Ca^{2+}$ ) can be used as templates for the synthesis of biodegradable ionic cross-linked micelles. Intramicellar cross-linking is one of methods that enhance the stability of polymeric micelles against dilution, ionic strength, temperature and shear forces. Recently, polymer micelles with cross-linked ionic cores were introduced.<sup>606-609</sup> The ionic cross-linked coacervate core of the micelles can impart gel-like behavior to the nanostructures and may allow the encapsulation of the pharmaceutical agents with high loading capacity. The biodegradation of cross-linked micelles under intracellular redox conditions can release incorporated drugs and remove empty carriers after drug release. Thus, these biodegradable cross-linked micelles based on the ionomers can be used as nano-carriers for the drug delivery.604

Biocompatible and biodegradable ionomers e.g. phosphoryl choline (PC) ionomer have been developed for the applications in the adsorption of proteins and the adhesion of cells.<sup>610</sup> It was found that the addition of PCs made the surface of films more hydrophilic. Since the *in vivo* acceptance of biomaterials is determined by their ability to withstand protein adsorption, the PC ionomer can be used in *in vivo* applications, in which the adsorption of proteins is a crucial part.<sup>611</sup> Recently, it was found that polyurethane-based ionomers were blood compatible and, thus, used as foams for the treatment of wound.<sup>611,612</sup> *In vitro* cellular interactions of polyester-based ionomers, e.g. poly(butylene succinate)-based ionomers containing Na sulfoisophthalate, were also studied.<sup>613</sup> It was found that the unique topological and hydrophilic nature of the surfaces of the ionomers affected cellular interactions. It should also be mentioned that the electrostatic layer-by-layer self-assembly





of Nafion in alternation with Fe<sup>3+</sup> ions made highly stable and biocompatible hollow capsules, which allowed controlled permeability of low MW species.<sup>614,615</sup> These ionomer hollow capsules showed hydrolytic stability over a wide range of pH and at high temperature. Thus, they are useful for applications, such as drug delivery and biosensors, for which the controlled diffusion of small molecules, biocompatibility and stability are very important factors. PTFE-based ionomers are not only a very useful candidate for membrane applications, but also highly suitable for biomedical applications that require biocompatibility. Recently, an acid-labile polyphosphoramidate was prepared by using organo based-catalyzed ring-open polymerization, and the phosphoramidate was converted to polyphosphoester ionomers.<sup>616</sup> It was observed that the resulting polyphosphoester acidic polymer and polyphosphoester Na salt form exhibited excellent thermal stability, and showed low cytotoxicities toward HeLa cells and RAW 264.7 mouse macrophage cells.

## 2.7.10. Self-healing smart materials

Self-healing polymers can repair themselves without the detection or repair by manual intervention when they are damaged. In the case of brittle plastics, the failure of the materials usually comes together with the formation and propagation of crack. However, if the sizes of the cracks were very small and the propagation of the cracks were prevented, the lifetime of the material could be extended significantly. At this point, it should be mentioned that for the self-healing process, there must be a balance between elasticity that is in charge of the material's shape memory and viscosity that is related with the diffusion of polymeric materials across the cracks [Figure 2-8]. The self-healing behavior of ionomers has recently attracted great attention because the very effective self-healing results can be obtained when the crack of the ionomer is caused by a high energy impact. Thus, the self-healable ionomers have become potential candidates for military and aerospace applications to enhance the durability of devices that are used in high impact and other extreme conditions.







Figure 2-8. Microscopic images of the scratch on the surface of Na-SPS ionomers (a) before and (b) after thermal treatment at 180  $^{\circ}$ C for 20 min.





In the case of ionomers, there are possibly two factors associated with the self-healing process. The first factor is the melting and hardening of the damaged part. The heat generated by a high energy impact makes the melting of the damaged part of the ionomer possible. Subsequently, the hardening of the ionomer takes place when the temperature decreases right after the impact; this suggests that this type of healing process is almost instantaneous even though, at this stage, the ion aggregation in the vicinity of the cracks remains disordered, and, thus, the ionomer lacks its strength.

However, during the further cooling process, ion pairs, disaggregated by the impact, hop slowly along with chain movement to re-form the ionic aggregates, healing the material.<sup>617-619</sup> The second factor associated with the self-healing of the ionomer is the strong interactions between the ion pairs in the multiplets, which make the multiplets remain intact even though the ion pairs become disordered in the melt state. Even at this stage, the ionomer can show elastic properties, at least to some extent. In addition, the polymer chains can move back to the positions to recover the damage. The ion-hopping process is also potentially useful for energy dissipation or damage resistance. Upon impact, the ion-hopping process dissipates the impact energy, initiating self-healing on extremely short time scales, and prevent failure.<sup>620</sup>

Some of the studies on the self-healing behavior of ionomers were focused on the ionomers after ballistic impacts.<sup>618,619,621-626</sup> It was observed that a high-energy transfer damage event that created heat in the polymer was needed for the EMAA ionomer to heal.<sup>621</sup> Then, the heat made the films viscoelastic melt and the repair of the damage possible. It was also found that the healing process of the ionomer was effectively maintained even at -30 °C with a significant healed strength. Two-stage theory on the healing of the ionomer was also proposed: Once the temperature of the ionomer increased upon a high-energy transfer damage, the polymer chains moved to elastically close the hole (i.e. sealing) in the first stage of healing and then bound together to gain "adhesive





strength" (i.e. chain inter–diffusion) in the second stage. It was also observed that the ion content was not important for the self–healing response.<sup>622</sup> The effect of the addition of aliphatic di– and tri–carboxylic acids and their salt or amide forms on the autonomous damage initiated self–healing behavior of a partially neutralized PEMA ionomer was investigated.<sup>624</sup> It was found that the acid form additives decreased the elastic properties of the ionomer but increased elastomeric behavior, which enhanced elastic self–healing. On the other hand, the sodium salt and amide forms exhibited the opposite trend, increasing elastic properties, decreasing elastomeric behavior, increasing ionic cluster strength, and reducing elastic healing. Thus, it was concluded that the decreasing  $T_g$  by plasticization and the increasing dynamic behavior of the multiplets improved the healing behavior of the ionomers. Finally, The molecular dynamics simulations with a coarse–grained representation of the repeating units were carried out to understand the self–healing mechanism of ionomers.<sup>627</sup> There are some of review articles on self–healing polymers,<sup>628,629</sup> and, thus, interested readers are referred to the reviews.

#### 2.7.11. Shape-memory ionomers

Shape memory polymers (SMPs) are an important class of stimuli-responsive materials that can be deformed and subsequently keep a temporary shape unless they are exposed to a relevant external stimulus that makes the polymers recover to their original shape.<sup>629</sup> The external stimuli include heat,<sup>630,631</sup> light,<sup>632</sup> electric<sup>633,634</sup> or moisture<sup>635,636</sup> or the presence of specific ions.<sup>637</sup> In the case of the SMPs made of ionomers, the metal salt of sulfonated PEEK (M-SPEEK) ionomer and the composites of the M-SPEEK ionomers and a fatty acid salt (Na-oleate) were prepared as high switching temperature SMPs.<sup>638</sup> It was found that the shape memory behavior of the ionomer composite was better than that of neat M-SPEEK ionomers. Ionic aggregates acted as a permanent physically cross-linked network, while strong dipolar interactions between the ionomer and a dispersed phase of crystalline Na-oleate led to the formation of the temporary network. Above the melting temperature





 $(T_{\rm m})$  of Na-oleate, the ionomer composite formed a temporary shape that was fixed by deforming the material and then cooling under stress to below  $T_{\rm m}$ . On the other hand, the permanent shape recovery of the material could be achieved by increasing temperature above  $T_{\rm m}$ . Triple shape memory cycle behavior was also observed for the ionomer compounds using the  $T_g$  of the ionomer and the  $T_m$  of the Na-oleate as two separate switching temperatures. Zn-sulfonated EPDM ionomer composites were also used as ionic SMP by the introduction of various fatty acids (salts) (e.g. decanoic acid, lauric acid, myristic acid, Mg-stearate, Zn-oleate, and Zn-stearate) into sulfonated EPDM.<sup>639</sup> The merit found in this type of SMP was that a series of ionic SMPs with varying critical temperatures ( $T_c$ ) could be easily prepared by simply choosing fatty acids (salts), having different melting temperatures. Again, the ionomer provided strong intermolecular interactions between the fatty acid crystalline regions and the polymer, which formed relatively strong physical cross-links below  $T_{\rm c}$  and allowed the shape recovery of the material above T<sub>c</sub>.<sup>640</sup> Shape memory behavior of a partially neutralized Zn-EMAA ionomer was also investigated.<sup>641</sup> Again, the multiplets and crystallinity of the ionomer provided permanent cross-links and temporary network, respectively. Since the ionomer had relatively broad melting temperatures (60–100 °C), a switching temperature,  $T_c$ , anywhere within the melting temperatures showed multiple shape memory behavior.

An ionic SMP was also developed by introducing cetyltrimethylammonium bromide ( $C_{16}TAB$ ) into poly(acrylic acid-*co*-methyl methacrylate) (PAA-*co*-MMA).<sup>642</sup> In this complex system, the surfactant  $C_{16}TAB$  molecules provided the thermo-reversible phase, linked to the matrix via ionic interactions, and the crystalline phase among the long alkyl chains of the  $C_{16}TAB$  acted as the physical cross-links.

Nafion also showed its shape memory behavior when it was programmed and patterned with micrometer- and nanometer-scale surface textures using an imprinting process in a nanometerscale. Highly ordered and well-defined micrometer- and nanometer-scal surface





textures formed the permanent shape memory. When damaged by mechanical rubbing and radiation exposures, the permanent shapes of the ionomers were recovered upon a thermal treatment near their  $T_{\rm g}$ s. The recovery level reached above 90% of the original shape.<sup>643</sup>

2.7.12. Catalysis or catalytic supports

Ionomers could act as catalysts for organic synthesis.<sup>644-663</sup> For examples, perfluorosulfonic acid copolymers can be used as superacid catalysts in various reactions.<sup>644-646</sup> In addition, the multiplets can behave like nano-reactors, implying a wide range of potential applications in this area. The active ions in the multiplets can serve as catalysts.<sup>448</sup> Now, the cations in the multiplets can also be reduced, and converted to metallic particles that can also be catalysts.<sup>649-663</sup> Recently, the polyion complex<sup>664 664</sup> can incorporate charged macromolecules of synthetic polymers and biological materials into the micelles.<sup>665-667</sup> The cores of the micelles act as nano-sized reservoirs for these charged compounds, controlling properties such as stability, reactivity, and solubility. If the PICs contained enzymes in the core, they could also be useful as enzymatic nano-reactors for diagnostics and therapeutics.<sup>668-670</sup>

#### 2.7.13. Anti-static materials

The static charge built on the molded parts becomes serious problems when sensitive electronic devices and interference with circuit are operating. Thus, to solve the problems, low MW anti-static agents, usually surfactants, are added to the polymer during the molding process. However, for the strong anti-static effect, the materials should be kept under relatively high humidity. In addition, the low MW additives can also be removed by rubbing, washing, and drying, which makes the anti-static effect disappear. Thus, the hydrophilic or conducting polymers can be utilized to obtain anti-static effect. When Na-EMAA ionomers were blended with poly(ether ester amide) (PEEA), it was found that the anti-static performance was improved significantly.<sup>671</sup> In addition, it was also observed that





the enhancement of the anti-static properties was not related with the types of the neutralizing cations.<sup>672</sup> Interfacial segregation of PEEA to domains of Li-, Na-EMAA ionomers and EMAA acidic copolymer was observed at the center of the molded samples. Those ionomers and acidic copolymer domains were partially or completely covered by PEEA. Near-surface morphology observations showed the alignment of elongated PEEA domains parallel to the molded surface, with both the encapsulation and bridging of ionomer domains.





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# Chapter 3

Tangible plasticization/filler effects of sodium salts of dimer acids on the mechanical properties of styrene ionomers





#### 3.1. Introduction

Ionomers are polymeric materials containing a relatively small amount of ionic groups (< 15 mol %) embedded in a polymer matrix of low dielectric constant.<sup>1</sup> The presence of the ionic groups in the polymer matrix generally causes ion aggregation. The ionic aggregates (so-called multiplets) induce the restriction of the mobility of the polymer chains emanating from the multiplet and in the vicinity of the multiplets.<sup>2</sup> When the concentration of ionic groups of an ionomer is very low, the number of the multiplets is relatively small so that the restricted mobility regions of the polymer chains do not overlap, and the ionomer shows only the glass transition  $(T_g)$  of non-ionic polymer matrix (i.e. matrix  $T_g$ ). On the other hand, with increasing ion content, the number of the multiplets increases, and the restricted mobility regions start overlapping. When the size of the restricted mobility regions becomes large enough to have their own  $T_g$  (i.e. cluster  $T_g$ ), the regions are called clustered regions. At this stage, the ionomer shows two  $T_{g}s$ ; the matrix  $T_{g}$  is seen at low temperatures, and the cluster Tg occurs at high temperatures. In addition, the ionomer exhibits an "ionic" plateau in the plots of log (storage modulus) vs. temperature, which is shown in the temperature range between the matrix and cluster  $T_{gs}$ .<sup>3,4</sup> The height and width of ionic plateau are mainly related with the amounts of clustered regions and the strength of interactions between ionic groups in the multiplets, respectively.<sup>1</sup>

Only a few studies have been performed on the effects of the aliphatic dicarboxylic acid salts on the properties of amorphous polystyrene (PS)-based random ionomers.<sup>5,6</sup> It was suggested that the di-functional organic salts became phase-separated and actedmainly as filler particles in poly(styrene-*co*-sodium methacrylate) (PSMANa) ionomers.<sup>5</sup> It was also found that when a large amount of sodium hexadecanedioate was added to the poly(styrene-*co*-sodium styrenesulfonate) (PSSNa) ionomer, the organic salt acted both as a reinforcing filler and as preferential plasticizer for the clustered region of PSSNa ionomers.<sup>6</sup>





of the additives was responsible for the increasing ionic modulus.

These days, the environmental regulations on industrial consumption have been tightened up, and there is an urgent need for qualified teacher the development of new eco-friendly materials. Thus, natural products (e.g. vegetable oil), non-toxic and environmental-friendly products, have gained much attention in regard to the development of "green chemicals". Recently, we have conducted a research on the preparation and modification of bio-based monomers. In course of the research, various "dimer acids" (DA), e.g. monocyclic, bicyclic, acyclic DA (Scheme 3-1), have been prepared from waste fatty acid cooking oils (vegetable and animal oils) as raw materials; the detailed compositions of the dimer acids are not known at present, but it is known that the reaction condition could control the compositions. From our previous studies,<sup>5,6</sup> we have known that the DA obtained from the waste cooking oil, being eco-friendly additives, can also be utilized as filler/plasticizer for the PS-based ionomers. Thus, in this study, we attempted to investigate the effects of the addition of sodium salts of DA compounds to the PS-based ionomers on the mechanical properties and morphology of the ionomers.







Scheme 3-1. Chemical structures of dimer acids obtained from waste fatty acid vegetable oils



### 3.2. Experimental Section

#### 3.2.1. Sample preparation

The preparation method of DA using the fatty acids of soybean oil, modified from the work by Paschke et al.<sup>7</sup> and Wheeler and White,<sup>8</sup> is described briefly below: Fatty acid, catalyst, hypophosphoric acid and deionized water were placed in a high-pressure stainless-steel reactor that was equipped with a mechanical stirrer and a cooling water line equipped with a temperature controller. The reactor was sealed and purged with N<sub>2</sub> gas four times to remove  $O_2$ , and then  $N_2$  gas was released. The reactor was heated to 250 °C. and kept at that temperature for 6 hr. When the reaction was complete, the products were taken out from the reactor, and the hypophosphoric acid was added to the products for the neutralization, which was then stirred at 80 °C for 1 hr. Subsequently, diatom earth was added to the products: The solution was stirred sufficiently and, then, filtered. Finally, the dimer acids were separated from the monomer fatty acids by using a distillation process at 270 °C. To prepare the ionomers, polystyrene (PS) homopolymer (MW = ca. 300,000) and poly(styrene-co-methacrylic acid) PSMAA copolymer (MW = ca. 300,000) containing 7.0 mol% of methacrylic acid units were synthesized by the method described elsewhere.<sup>4</sup> Poly(styrene-co-styrenesulfonic acid) copolymer was prepared by the sulfonation of the PS using the method reported by Makowski et al.<sup>9</sup>; the content of the styrenesulfonic acid units was 7.7 mol%. To prepare the ionomer samples containing varying amounts of DA, the DA and copolymers were dissolved in a benzene/methanol (9/1, v/v) mixture, and the acid groups of the DA and copolymers were fully neutralized with methanolic NaOH solution. Then, the samples were freeze-dried and dried further in a vacuum oven at ca. 150 °C for 24 h. For the dynamic mechanical property measurements, the samples were compression-molded when the mold temperatures reached ca. 190 and 230  $^\circ$ C for the methacrylate and sulfonated ionomers, respectively, at a pressure of ca. 25 MPa. The molded samples were annealed under a vacuum at 150  $^\circ$ C for 12 h. The sample denotation used in the present work is PSSNa-x and PSMANa-x, where PSSNa and PSMANa are Na-neutralized sulfonated polystyrene and poly(styrene-co-sodium methacrylate) ionomers, respectively, and x indicates the weight % of Na-neutralized DA.





To compare the results obtained from the DA-containing ionomers with those obtained from the ionomers containing only one type of sodium salt of aliphatic diacids, we also prepared PSSNa and PSMANa ionomers containing varying amounts of sodium salt of aliphatic diacid, i.e. sodium hexadecanedioate (HD). An ASPECT 1000 Fourier transform infrared spectrometer (Bruker AXS, Madison, WI) was used to check the neutralization of PSSNa-x ionomers. The samples were pelletized with KBr and scanned 64 times, and the scanning range was from 4000 to 400 cm<sup>-1</sup>. It was found that in the wavenumber range of 900-1300 cm<sup>-1</sup> the IR spectrum of pure PSSNa ionomer was similar to those obtained by other researchers<sup>10-19</sup> and was also similar to those of DA-containing ionomers (spectra are not shown here), indicating that the ionomers were fully neutralized. At this point, it should be mentioned that the PSMANa and PSSNa ionomers are known to be thermally stable well above 300 °C,<sup>20</sup> but the thermal stability of Na-neutralized DA is not known yet. Thus, a TA instrument 2050 thermogravimetric analyzer (TGA) was utilized to study the thermal stability of the Na-neutralized DA in the ionomers. The experiments were carried out as a function of temperature, over the range of 50–500  $^{\circ}$ C, at a heating rate of 10  $^{\circ}$ C/min under nitrogen and at a N2 flow rate of 30 mL/min. For a thermal property study, a TA DSC 2010 differential scanning calorimeter (TA Instruments, USA) was used. The samples were scanned using the DSC from 30  $^{\circ}$ C to 300  $^{\circ}$ C, with a heating rate of 10  $^{\circ}$ C/min.

#### 3.2.2. Dynamic mechanical analysis

The storage modulus (*E'*) and loss tangent (tan  $\delta$ ) of each sample were measured as a function of temperature using a TA Instruments Q 800 dynamic mechanical analyzer in a dual cantilever-bending mode. The samples were heated at a heating rate of 1 °C/min. The detailed data analysis was performed using the data obtained at 1 Hz. When deconvolutions on the loss tangent data were necessary, we performed the curve deconvolutions using PeakFit program (Jandel). The best fits were achieved by assuming an exponential background and fitting the matrix and cluster peaks with Gaussian Area peaks.



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## 3.2.2. Small angle x-ray scattering

The small angle X-ray scattering (SAXS) experiments were conducted at Station 3C of Pohang Light Source (PLS) synchrotron radiation source (Pohang, Korea). The sample-to-detector distance was 1 m, which allowed SAXS data to be obtained in the q (scattering vector) ranging from ca. 0.2 to 4.2 nm<sup>-1</sup>, where  $q = 4\pi \sin\theta/\lambda$ ;  $\theta$  is half the scattering angle, and  $\lambda$  is the X-ray wave length ( $\lambda = 0.1608$  nm).





#### 3.3. Results and Discussion

Figure 3-1 shows the weight loss of PSMANa-0 and PSSNa-x ionomers as a function of temperature. At this point, it should be mentioned that we chose only one ionomer system that contains Na-neutralized DA, i.e. PSSNa-x ionomers, because the purpose of this TGA study was to investigate the thermal stability of the Na-neutralized DA, not those of the ionomers. The PSMANa-0 and PSSNa-0 ionomers are shown to be thermally stable well above 300 °C.<sup>20</sup> The temperatures of 2% and 5% weight loss for the PSSNa-0 ionomer are ca. 320 and 370 °C, respectively, while those for the PSSNa-6.1 ionomer are ca. 270 and 370 °C. On the other hand, the temperatures of 2% and 5% weight loss for the PSSNa-41.5 ionomer are ca. 260 and 310 °C, respectively. Thus, in the present work, the mold temperatures of 190 and 230 °C for the methacrylate and sulfonate ionomers are suitable for the sample preparation and for the measurement of dynamic mechanical properties of these ionomers, since residence times are short.

The loss tangents of PSSNa and PSMANa ionomers containing varying amounts of DA are shown in Figure 3-2 as a function of temperature. First of all, as expected, two loss tangent peaks are seen in the Figure; the matrix peak at low temperatures and the cluster peak at high temperatures. The presence of well-developed two loss tangent peaks indicates that these ionomers are well clustered ionomers.<sup>1</sup> Secondly, it is observed that the positions of the matrix and cluster peaks of the PSSNa ionomers shift to lower temperatures with increasing amounts of DA. In addition, the intensity of the matrix peak decreases gradually with increasing DA amounts, but that of the cluster peak seems to increase slightly. In the case of PSMANa ionomers, only the cluster peak position shifts to lower temperatures, but the matrix peak position seems to remain constant. The intensities of the matrix and cluster peaks of the PSSNa ionomers. In the case of the loss tangent and storage modulus curves of the PSSNa and PSMANa







Figure 3-1. TGA thermograms of PSMANa-0, PSSNa-0, PSSNa-6.5, and PSSNa-41.5 ionomers.







Figure 3-2. Loss tangents of the PSSNa and PSMANa ionomers containing varying amounts of DA as a function of temperature, measured at 1 Hz.





ionomers containing HD, even though we obtained them by using the samples that we prepared in the present work, we do not show them here because similar results had already been shown elsewhere.<sup>5,6</sup> We only use the  $T_{g}$ s and ionic moduli of HD-containing ionomers to compare them with those of the ionomers containing DA.

Figure 3-3 shows, as a function of the amounts of DA or HD, the  $T_{gs}$  of the PSSNa and PSMANa ionomers obtained from the positions of the loss tangents peaks.

The data can be fitted to linear functions and the intercepts and slopes of the fitted lines for the  $T_{gs}$  of PSSNa and PSMANa ionomers containing either DA or HD are listed in Table 3-1.

Table 3-1. The intercepts and slopes of the lines fitted to the  $T_{gs}$  of PSSNa and PSMANa ionomers containing either DA or HD

Ionomers	cluster $T_{\rm g}$		matrix T <sub>g</sub>	
	intercept (°C)	slope (°C/wt%)	intercept ( $^{\circ}$ C)	slope (°C/wt%)
PSSNa-DA	237	-1.2	124	-1.0
PSMANa-DA	209	-0.5	125	0
PSSNa-HD	245	-0.3	126	-0.2
PSMANa-HD	213	-0.4	127	0

The matrix and cluster  $T_{gs}$  of the PSSNa ionomers decrease in similar rates with increasing amounts of DA. This suggests that the DA might act as plasticizer, at least to some extent, in the PSSNa ionomer. In addition, the decreasing rates of  $T_{gs}$  (i.e., ca. 1 °C/wt%) imply that the DA might be very effective plasticizer, which is one of very important factors for polymer processing. In the case of PSMANa ionomer, the cluster  $T_{g}$  also







Figure 3-3. Matrix and cluster  $T_{g}s$  of PSSNa and PSMANa ionomers containing DA (left) or HD (right) obtained from the loss tangent peak positions (at 1 Hz) as a function of wt% of DA or HD.





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decreases but slowly. On the other hand, the matrix  $T_{\rm g}$  seems to remain constant at 125  $^{\circ}$ C. The results mentioned above imply that the roles of DA in the PSSNA and PSMANa ionomers are not the same; the DA in the PSMANa ionomers might be have like plasticizer only for the cluster regions. In the cases of the ionomers containing HD, the decreasing rates of the matrix and cluster  $T_{gs}$  are lower than those of the PS ionomers containing DA. These results clearly indicate that the effect of the presence of the DA on the  $T_{gs}$  of PSSNa ionomers is stronger than that of the HD. The storage moduli of the PSSNa and PSMANa ionomers containing varying amounts of DA are shown in Figure 3-4 as a function of temperature. In the case of PSSNa-0 ionomer, it is seen that the modulus curve changes from a glassy modulus, a sharp modulus drop due to the glass transition of matrix regions, a relatively long and horizontal "ionic" plateau (the segment of the modulus curve between the matrix and cluster  $T_{\rm g}$ s), a second modulus drop due to the glass transition of the cluster regions, a slight downward slope related to a rubbery modulus and the last modulus drop related to sample flow. It is observed that, with increasing amounts of DA, the slopes of the modulus curve for the matrix  $T_g$  and cluster  $T_g$  become less steep. This indicates that, with increasing amounts of DA, the glass transitions take place in a relatively wider temperature range. The onset points of the modulus drops for the matrix and cluster T<sub>g</sub>s of the PSSNa ionomer shift to lower temperatures with increasing DA contents. It is also observed that the slope of ionic plateau becomes slightly steeper with increasing DA amounts. In the case of the PSMANa ionomers, it is seen that the changes of modulus curves with the amounts of DA are different from those found in the PSSNa ionomers. Especially, with increasing amounts of DA, the onset points of the modulus drop for the matrix glass transition of the PSMANa ionomers seems to remain at similar positions. The slope of ionic plateau of the PSMANa ionomers becomes also steeper with increasing amounts of DA.



The presence of ionic plateau is the unique characteristics of PS-based ionomers. Thus, it is useful to analyze the ionic plateau in more detail to gain an insight into the roles of DA in the ionomers. Before we start to discuss the ionic plateau of the ionomer containing DA, let us review the ionic plateaus of pure PSSNa and PSMANa ionomers. Since some of amorphous ionomers show the ionic plateau between the matrix and cluster  $T_{g}s$ , it can be thought that the cluster regions including multiplets act as cross-links as well as reinforcing filler particles.<sup>3,21-24</sup> If the multiplets remained intact in the temperature range between the matrix and cluster  $T_{gs}$ , the ionomer would show a modulus plateau (i.e. ionic plateau), higher than the rubbery plateau, due to the filler effect of the clusters. The height and width of ionic plateau are related to the degree of clustering and the strength of the interactions between the ion pairs in the multiplets, respectively.<sup>1,3,20</sup> As can be seen in Figure 3-4, the ionic plateau of the PSSNa ionomer is lower but wider than that of the PSMANa ionomer of the same ion content. This is due to the differences in the position of ionic groups and the strength of interactions between the ion pairs in the multiplets. Firstly, the sulfonate anionic group of the PSSNa ionomer and the carboxylate anionic group of the PSMANa ionomer are attached to the *para* position of the benzene ring of a styrene unit and the main chain of the ionomer, respectively. Thus, the distance between the anionic group and the main chain is longer for the PSSNa ionomer, compared to the PSMANa ionomer. This implies that the ion pairs of the PSSNa ionomer can form larger multiplets, compared to the PSMANa ionomer,<sup>3</sup> because of less steric hindrance. Secondly, the interactions between the Na-sulfonate ion pairs are stronger than those between the Na-carboxylate ion pairs.<sup>3,25</sup> This leads to more ion pairs per multiplet of the PSSNa ionomer, compared to those of PSMANa ionomer of the same ion content. At this point, it should be mentioned that the ion-hopping is related to the strength of interactions between ion pairs in the multiplets and is one of the cluster glass transition mechanisms:<sup>3,4,26-33</sup> When the ion-hopping occurs, the storage modulus of the ionomer starts decreasing. Naturally, the more ion pairs per multiplet and the stronger interactions between ion pairs in the multiplets of the PSSNa ionomer make the ion-hopping occur at higher temperatures







Figure 3-4. Storage moduli of the PSSNa and PSMANa ionomers containing varying amounts of DA as a function of temperature, measured at 1 Hz.





(i.e. higher cluster  $T_g$ ), compared to the PSMANa ionomer. This higher cluster  $T_g$  causes a wider ionic plateau for the PSSNa ionomer. Now, let us talk about the height of ionic plateau in the modulus-temperature plots, which, again, is not directly related with the cluster  $T_{\rm g}$  that is mainly related with the strength of interactions between ion pairs. It is known that with increasing ion contents, the ionic plateau shifts to higher positions,<sup>4</sup> indicating that the ionic plateau position is associated with the degree of clustering. Since the PSSNa ionomer has more ion pairs per multiplet than the PSMANa ionomer, there must be fewer multiplets for the PSSNa ionomer, at the same ion content. If the thickness of reduced mobility regions surrounding the multiplets were constant, the size of the restricted mobility regions would be smaller for the ionomer having fewer multiplets. Thus, at the same ion content, the degree of clustering (i.e. the size of reduced mobility regions) of the PSSNa ionomer is lower than that of the PSMANa ionomer. As a result, the ionic plateau of the PSSNa ionomer is lower than that of the PSMANa ionomer, even though the cluster  $T_g$  of the PSSNa ionomer is higher than that of the PSMANa ionomer.<sup>3</sup> One should keep these aspects in mind when one interprets the modulus data of polystyrene ionomers.

To evaluate the position of ionic plateau, we obtained the ionic moduli ( $E'_{ionic}$ ) of the ionomers. The ionic modulus is a modulus at the point of a minimum slope in the ionic plateau region. Figure 3-5 shows the ionic moduli of the PSSNa and PSMANa ionomers containing various amounts of DA as a function of wt% of DA. This Figure also includes the ionic moduli of styrene ionomers containing HD. It is seen that, with increasing DA amounts, the log  $E'_{ionic}$  (Pa) of the PSSNa seems to remain constant at 7.0 ± 0.008, but that of the PSMANa ionomers containing HD also increase not linearly but rather quadratically, with increasing HD amounts. It is clear that the increasing rates of log  $E'_{ionic}$  of the ionomers containing HD are higher than those of the PSSNa-HD or







Figure 3-5. Ionic moduli of the PSSNa and PSMANa ionomers containing varying amounts of DA or HD as a function of wt% of DA or HD, measured at 1 Hz.





PSMANa-DA or PSMANa-HD ionomers might be due to the fact that the DA or HD in the ionomer might act as filler particles (the endothermic DSC peak for the  $T_m$  of Na-neutralized HD and DA is seen at 222 and 228 °C, respectively). In addition, the filler effect of the HD in the PSMANa ionomer is stronger than that of DA in the PSSNa and PSMANa ionomers on the increasing ionic moduli of the ionomers.

Shown in Figure 3-6 are the SAXS profiles of PSSNa and PSMANa ionomers containing varying amounts of either DA or HD. First of all, small-angle upturn is seen for all the ionomers. This upturn might be due to the compositional heterogeneity or the large-scale density fluctuations of scattering centers of the ionomers.<sup>34-40</sup> In the case of PSSNa ionomer, a well-developed SAXS peak is seen at q (scattering vector) = ca. 1.5 nm<sup>-1</sup>, and the peak position shifts to slightly higher q (indicating that the Bragg distance between scattering centers becomes slightly shorter) and the peak intensity increases, with increasing DA amounts. In addition, the width of the SAXS peak becomes narrower with increasing DA amounts. This implies that the DA molecules in the PSSNa ionomer act as plasticizer, which makes the  $T_{es}$  of the matrix and cluster regions of the PSSNa ionomer lower, to some extent. This makes the formation of multiplets at relatively regular distances easier, which leads to the appearance of a narrower SAXS peak at higher q values. In the case of PSMANa ionomer, there is no well developed SAXS peak in the q range of  $0.5 - 4 \text{ nm}^{-1}$ . However, upon the addition of DA, a peak is seen at  $q = ca. 2.0 \text{ nm}^{-1}$ , and the peak intensity increases progressively with increasing DA amounts, without changing the peak position and width, suggesting that the DA acts as plasticizer. In addition, a shoulder is seen at q = ca. 1.2 nm<sup>-1</sup> upon the addition of DA and becomes more visible with increasing DA amounts. This suggests that the shoulder is related to the formation of phase-separated DA molecules. In the case of PSSNa-HD ionomers, the SAXS peak at q =ca. 1.5  $nm^{-1}$ , shifts to slightly higher q, but its intensity decreases strongly, with increasing HD contents. In addition, a new peak is seen at  $q = ca. 3.0 \text{ nm}^{-1}$ , and the peak intensity

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Figure 3-6. SAXS profiles of PSSNa and PSMANa ionomers containing varying amounts of DA or HD.





increases noticeably as the HD content increases. For the PSMANa, usually showing a very weak shoulder at q = ca. 3.0 nm<sup>-1</sup>, a new peak is also seen at the same position, with increasing its intensity, as the HD content increases. The above results imply that the appearance of the peak at q = ca. 3.0 nm<sup>-1</sup> is related with the presence of phase-separated HD that acts as filler particles and increases ionic modulus.

The IR spectra of Na-neutralized dimer acid (DA), PSSNa and PSMANa ionomers in the wavenumber range of 900–2000 cm<sup>-1</sup> are seen in Figure 3-7. We assigned IR bands with reference to others' interpretation.<sup>42,42</sup> In the case of PSSNa ionomers, the intensity of IR bands at ca. 1740 cm<sup>-1</sup> increases with increasing DA contents, but the intensities of the rest of IR bands decrease systematically. At this point, it should be noted that the IR band at ca. 1680 cm<sup>-1</sup> decreases drastically for the PSSNa-41.5 ionomer; we do not have clear explanation for this finding, yet. For the PSMANa ionomers, the IR spectra do not show any new IR band upon the addition of DA compound. Only the relatively intensities of the IR bands decrease with increasing DA contents. This different trend in IR band intensities also supports the idea that the roles of DA in PSMANa and PSSNa ionomers are not the same.

The DSC thermograms of Na-neutralized DA itself, PSSNa and PSMANa ionomers are shown in Figure 3-8. It is seen that the DA shows a broad endothermic peak at 228  $^{\circ}$ C, which is related to the melting of crystalized dimer acid compounds. For the PSSNa ionomers, only the glass transitions of the matrix regions of the ionomers are seen at ca. 120  $^{\circ}$ C. In the case of the PSMANa ionomers of low DA contents, they also exhibit only the matrix glass transition. In addition to the matrix glass transition, PSMANa-24.0 and PSMANa-41.5 ionomers show a small shoulder at ca. 245  $^{\circ}$ C and a small, broad endothermic peak at ca. 240  $^{\circ}$ C, respectively. This endothermic peak is probably related to the phase-separated Na-neutralized DA. These DSC results are in agreement with the findings in DMA results discussed earlier.







Figure 3-7. IR spectra of DA, PSSNa and PSMANa ionomers containing varying amounts of DA.







Figure 3-8. DSC thermograms of DA, PSSNa and PSMANa ionomers containing varying amounts of DA.





Now, let us talk about the roles of DA molecules in the PSSNa and PSMANa ionomers in more detail. The fact that the matrix and cluster  $T_{gs}$  of PSSNa ionomers decrease significantly in a similar way with increasing DA amounts suggests that the DA molecules may reside in both the matrix and cluster regions of PSSNa ionomer relatively evenly and act as effective plasticizer for both the matrix and cluster regions, which lowers the matrix and cluster  $T_{es}$ . Naturally, some of Na-carboxylate ion pairs of the DA may participate in the formation of multiplets with Na-sulfonate ion pairs of the PSSNa ionomer. If this were the case, the interactions between ion pairs in the multiplets might become weaker due to the heterogeneous compositions of ion pairs in the multiplets, at least to some extent. Thus, the ion-hopping would occur at relatively lower temperatures, leading to a lower cluster  $T_{g}$ . In the case of ionic modulus, since the DA molecules in the PSSNa act mainly as plasticizer, the ionic modulus would not be expected to change; this is what we observed here. According to the dynamic mechanical data of the PSMANa ionomer containing DA, the presence of the DA does not change the matrix  $T_{gs}$ , but it decreases the cluster  $T_{g}$ , and it increases the ionic modulus strongly. This is due to the phase-separation of DA molecules. It should be recalled that the DA molecules in the present work are mixtures that consist of monocyclic, bicyclic and acyclic compounds, but the HD molecules have linear alkyl chains having Na-carboxylate ion pairs at both ends of the chain. Since aliphatic dicarboxylate can form the filler particles more easily, the filler effect of HD would be stronger than that of DA.5,6 In addition, as expected, the plasticization effect of DA is more profound than that of HD because of the nature of DA, i.e. mixture of various dimer acids.




#### 3.4. Conclusions

The DA molecules resided in the hydrocarbon matrix and cluster regions of PSSNa ionomers, and acted mainly as plasticizer to decrease the matrix and cluster  $T_{gS}$  without changing the ionic modulus. In the case of PSMANa ionomer, the monocyclic and bicyclic DA molecules in the PSMANa ionomer also acted as plasticizer, but the acyclic DA molecules were phase-separated to form filler particles that increased the ionic modulus of the PSMANa ionomer. The above findings suggested that the monocyclic and bicyclic DA molecules could be used as very effective plasticizer.





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### Chapter 4

# Detailed interpretation of the dynamic mechanical and morphological data of poly(styrene-co-sodium sulfopropyl methacrylate) ionomers





#### 4.1. Introduction

Polymers having a small amount of ionic groups attached directly to a relatively less or non-polar polymer chains are called ionomers. The interactions between the ionic groups lead to the formation of small ionic aggregates, so-called "multiplets", and the multiplets reduce the mobility of the polymer chains surrounding them.<sup>1</sup> At very low ion content, the number of multiplets is too small for the multiplets to affect the properties of polymer. Thus, the ionomer shows only one glass transition  $(T_g)$ , i.e. matrix  $T_g$ . As the ion content increases, the number and size of the multiplets increase, and, eventually, the restricted mobility regions surrounding the multiplets start overlapping and forming contiguous regions, called "clusters".<sup>1</sup> The mobility of the polymer chains in the clustered regions becomes so restricted that the clustered regions behave no longer as part of a matrix phase. This leads to the appearance of a separated glass transition for the clustered regions at higher temperatures (i.e. the cluster  $T_{\rm g}$ ), compared to the matrix  $T_{\rm g}$ .<sup>1</sup> In this state, the ionomer acts as a bi-phasic material. At a sufficiently high ion content, the restricted mobility regions become a predominant phase, and, thus, the ionomer behaves again like a mono-phasic material (i.e. a clustered material), exhibiting only one  $T_g$  (i.e. cluster  $T_g$ ). Due to the presence of the ionic groups, the ionomers show significantly different mechanical properties and morphologies in comparison with their non-ionic counter parts.<sup>2-4</sup> For example, some of the ionomers exhibit a cluster  $T_{\rm g}$ , a plateau-like feature (so-called ionic plateau) in log (storage modulus) vs. temperature plots placed between the matrix and cluster Tgs, an X-ray scattering peak in a small angle range, a high melt viscosity, and a high relaxation time for polymer chains.<sup>2-4</sup> Using the ionic interactions in the ionomers, the polymer scientists can have a wide variety of options to tailor the properties of the polymers. The options include, for instance, the type, position and content of the ionic groups, the type of the backbone chains, and the type of counter ions.<sup>4</sup> Thus, even very recently, the research on the mechanical properties, morphology, physical properties, and application of various ionomers has been carried out extensively by a number of research

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groups.5-16

In the case of the styrene-based ionomers, Gauthier and Eisenberg<sup>17</sup> and Moore et al.<sup>18</sup> reported that, in the styrene ionomers that have ionic groups placed at the ends of variable-length of side chains randomly attached directly to the para-position of the benzene ring, the distance between the ionic groups and the polymer backbone chain changed the mechanical properties and morphology of the ionomers systematically. In addition, Hird and Eisenberg demonstrated that the type of anionic groups affected the mechanical properties of styrene-based ionomers (i.e. the sulfonated polystyrene, SSNa, where the ionic groups are attached to the polymer backbone chain through a benzene ring and poly(styrene-co-Na methacrylate), SMANa, where the ionic groups are attached directly to polymer backbone chain)<sup>19</sup>; their findings will be discussed briefly in a Discussion section. The above results naturally suggest that one can control the mechanical properties of ionomers by changing the type of ionic groups or the distance between the ionic groups and the polymer backbone chain. However, in the case of ionomers containing Na-sulfonate ionic groups, no systematic study has been conducted to explore the effect of the distance between the ionic groups and polymer backbone chain. Thus, earlier we had carried out a preliminary work on new polystyrene-based ionomers, namely Na-neutralized poly(styrene-co-3-sulfopropy) methacrylate) (SSPMANa) ionomers to know the effect of the presence of alkyl ester side chain between the Na-sulfonate ionic groups and polymer backbone chain on the mechanical properties of the ionomers.<sup>20</sup> The chemical structures of SSPMANa, SSNa, and SMANa ionomers are shown in Scheme 4-1. We observed that the matrix  $T_{\rm g}$  and ionic modulus increased with increasing ion content, but the cluster  $T_{\rm g}$  did not change strongly. However, we found that the preliminary data were not sufficiently enough to understand the alkyl ester side chain effect. Therefore, we conducted a more thorough investigation on the mechanical properties and morphologies of the SSPMANa ionomers and compared the results with those obtained using two styrene-based ionomers, i.e. SSNa and SMANa ionomers.







Scheme 4-1. Chemical structures of SSPMANa, SSNa, and SMANa ionomers

Thus, the mechanical properties of the data SSPMANa ionomer was reinterpreted in a new perspective and implement additional morphological studies. We will skip the polymer synthesis and sample preparation for detailed description here, and immediately proceed to interpret the data.





#### 4.2. Experimental Section

#### 4.2.1. Small angle x-ray scattering

For the small-angle X-ray scattering (SAXS) experiments, the ionomer samples were also compression-molded; the sample dimensions were ca. 0.5 mm (t) × 10 (d) mm. At this point, it should be mentioned that to compare the morphology of the SSPMANa ionomers to those of the SSNa and SMANa ionomers, we also prepared the SSNa and SMANa ionomer specimens for the SAXS experiments. The SAXS experiments were conducted at Station 3C of Pohang Light Source (PLS) synchrotron radiation source (Pohang, Korea). The generated beam energy was 10.0 keV (at 3.0 GeV operation modes). The position-sensitive two-dimensional Rayonix MAR 165 detector was used, and the sample-to-detector distance was 1.0 m. The SAXS intensity was obtained as a function of scattering vector q, where  $q = 4\pi \sin\theta/\lambda$ ,  $\theta$  is half the scattering angle, and  $\lambda$  is the X-ray wavelength. The SAXS data were plotted as relative intensity vs. q after the correction for background.





#### 4.3. Results

Figure 4-1 shows the log (storage modulus) (log *E'*) plots as a function of temperature for some of poly(styrene-*co*-3-sodium sulfopropyl methacrylate) SSPMANa ionomers of varying ion contents. With increasing temperature, the modulus plots go through various states, i.e. from a glassy region, to a matrix glass transition, to an ionic plateau, to a cluster glass transition, to a rubbery plateau, and to a flow region. The glassy moduli of the SSPMANa ionomers are found to be similar for all the samples irrespective of the ion contents, similar to those of the SMANa ionomers.<sup>21</sup> However, with increasing ion content, the temperature range for the glassy state is extended to higher temperature, and, thus, the position of the modulus drop related with the matrix glass transition shifts to higher temperatures. The presence of ionic plateau is a characteristic of the styrene-based ionomers, emerged from the formation of ionic clusters.<sup>1,4,19,21-23</sup> It is clear that the height of the ionic plateau increases with increasing ion content. Above the cluster glass transition, there is no significant difference in the modulus plot for the high ion content ionomers, i.e. 7.0 and 11.7 mol% ionomers.

In Figure 4-2, the loss tangents of the SSPMANa ionomers are plotted as a function of temperature. It is observed that the position of the matrix loss tangent peak shifts from ~120 °C to ~150 °C with increasing ion content. On the other hand, except for the 1.8 mol% ionomer, the position of the cluster loss tangent peak shifts to slowly from ~235 °C to ~228 °C. In addition, with increasing ion content, the height of the matrix loss tangent peak decreases, but the opposite trend is true for that of the cluster loss tangent peak. It is known that the position of the ionic plateau is related with the degree of clustering, i.e. the relative amount of the ionomers to analyze the ionic plateau quantitatively. The ionic modulus ( $E'_{ionic}$ ) is the modulus value at the point of the minimum slope of the ionic plateau of log E' vs. temperature plots. Shown in Figure 4-3 are the  $E'_{ionic}$  plots as a







Figure 4-1. Representative storage modulus (E') plots as a function of temperature for the SSPMANa ionomers, measured at 1 Hz.







Figure 4-2. Representative loss tangent plots as a function of temperature for the SSPMANa ionomers, measured at 1 Hz.







Figure 4-3. Ionic moduli of the SSPMANa, SSNa, and SMANa ionomers as a function of ion content, measured at 1 Hz. First-order polynomial fits are also shown.





function of ion content of the SSPMANa, SMANa, and SSNa ionomers. Some of the data for the SMANa and SSNa ionomers were obtained from our previous work.<sup>24</sup>

As reported before, the log  $E'_{ionic}$  values of the SMANa and SSNa ionomers increase linearly with increasing ion content. The data can be fitted to first-order polynomials as follows:

For the SSNa ionomers

 $\log E'_{\text{ionic}}$  (Pa) = 6.0 + 0.14 × (ion content)

and for the SMANa ionomers

 $\log E'_{\text{ionic}}$  (Pa) = 6.0 + 0.19 × (ion content)

In the case of the SSPMANa ionomers, above  $\sim 3 \mod \%$  of ion content, the log  $E'_{ionic}$  values can also be fitted to a first-order polynomial as follows:

 $\log E'_{ionic}$  (Pa) = 6.4 + 0.080 × (ion content)

It is clear that the increasing rate of log  $E'_{ionic}$  as a function of ion content is lowest for the SSPMANa ionomers and highest for SMANa ionomers. In addition, on comparing the ionic modulus of the SSPMANa ionomer with those of the SMANa and SSNa ionomers of similar ion contents, it is seen that, above ~6 mol% of ions, the ionic modulus of the SSPMANa ionomers is lower than those of the SSNa and SMANa ionomers.





From the positions of loss tangent peaks, one can obtain the matrix and cluster glass transition temperatures of the ionomers,  $T_{g,m}$  and  $T_{g,c}$ , respectively. The  $T_{g,m}$  and  $T_{g,c}$  of the SSPMANa, SMANa, and SSNa ionomers are shown in Figure 4-4 as a function of ion content; again, some of the  $T_g$  data of the SMANa and SSNa ionomers were obtained from reference 26. It is observed that the  $T_{g,m}$ s of the three ionomer systems are similar to each other at the same ion content and increases somewhat linearly with increasing ion content. The data can be fitted to a first-order polynomial as follows:

 $T_{g,m}$  (°C) = 116 + 3.0 × (ion content)

This indicates that the  $T_{g,m}$  is almost independent of the type of ionic groups (i.e.  $-COO^-$  Na<sup>+</sup> or  $-SO_3^-$  Na<sup>+</sup>)<sup>22,23</sup> and the distance between the ionic groups and the polymer backbone chain studied in this work. In the case of the  $T_{g,c}$ , the SSNa and SMANa ionomers show similar rates of increasing  $T_{g,c}$  as a function of ion content as follows:

For the SSNa ionomers

 $T_{g,c}$  (°C) = 227 + 4.7 × (ion content)

and for the SMANa ionomers

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 $T_{g,c}$  (°C) = 178 + 4.8 × (ion content)

However, the  $T_{g,c}$ s of the SSPMANa ionomers, except for the  $T_{g,c}$  of 1.8 mol% ionomer, seem to remain constant at  $T_{g,c}$  (°C) = 229 ± 1. In addition, below ~11 mol% of ions, the  $T_{g,c}$  of SSPMANa ionomers is higher than that of SMANa ionomers, but lower than that of the SSNa ionomers.





Figure 4-4. Matrix and cluster  $T_{gs}$  of the SSPMANa, SSNa, and SMANa ionomers as a function of ion content, measured at 1 Hz. First-order polynomial fits are also shown.





The apparent activation energies ( $E_as$ ) for the glass transitions of the ionomers can be calculated using Arrhenius plots of log frequency vs. inverse temperature (confidence limits  $< \pm 30$  kJ/mol). Figure 4-5 shows the plots of the  $E_as$  for the glass transitions of the matrix and cluster regions of the SSPMANa, SMANa and SSNa ionomers as a function of ion content. Some of the  $E_as$  for the SSNa and SMANa ionomer were obtained from elsewhere.<sup>19,21,25</sup>

It is seen that the  $E_{a}s$  for the matrix  $T_{g}$  and cluster  $T_{g}$  do not change significantly with ion content; the  $E_{a}s$  for the matrix  $T_{g} = 500 \pm 51$  kJ/mol and the  $E_{a}s$  for the cluster  $T_{g} =$  $206 \pm 34$  kJ/mol. In addition, the  $E_{a}s$  are not significantly influenced by the types of the ionomers. The above findings indicate that their glass transition mechanisms are not much different from each other. As mentioned before, the relatively large  $E_{a}$  values for the cluster  $T_{g}$  suggest that the cluster peak is related with a true glass transition that is mainly attributed to the ion-hopping mechanism.<sup>15,21,23</sup>

Shown in Figure 4-6 are the SAXS profiles of the SSPMANa, SSNa, and SMANa ionomers. A well-developed SAXS peak is seen for 3.8 mol% SSPMANa ionomer at  $q = ~1.6 \text{ nm}^{-1}$ . It is also observed that the peak intensity increases progressively with increasing ion content, and the peak position shifts to slightly higher q. In the case of the SSNa ionomers, unlike 3.8 mol% SSPMANa ionomer, 3.0 mol% SSNa ionomer does not show a well-developed SAXS peak, which might be due to low ion content. However, as the ion content increases, a well-developed SAXS peak starts to appear, the peak intensity increases, and the peak position shifts to higher q. In the case of the SMANa ionomers, the ionomers of low and middle ion contents do not show an SAXS peak, which might be due to smaller-sized multiplets having a relatively low electron density; only 10.1 mol% SMANa ionomer shows a very weak SAXS peak at  $q = ~2.8 \text{ nm}^{-1}$ .







Figure 4-5. Apparent activation energies for the glass transitions of the SSPMANa, SMANa, and SSNa ionomers as a function of ion content.







Figure 4-6. SAXS profiles of the SSPMANa, SSNa, and SMANa ionomers.





Now, one can calculate the Bragg distances ( $D_{Bragg}$ ) between scattering centers (i.e. multiplets in this study) using the q value of SAXS peak maximum ( $q_{max}$ ). Figure 4-7 shows the  $D_{Bragg}$  values of the SSPMANa, SSNa, and SMANa ionomers as a function of ion content. It is clear that the  $D_{Bragg}$  value of the SSPMANa ionomer is slightly lower than that of the SSNa ionomer at the same ion content. In addition, the  $D_{Bragg}$  value of the SSPMANa ionomer decreases only slightly from ~4.0 nm to ~3.8 nm with increasing ion content from 3.8 mol% to 11.2 mol%. In the case of the SSNa ionomers, the  $D_{Bragg}$  decreases in a regular manner from ~4.6 nm to ~3.4 nm with increasing ion content from 5.9 mol% to 11.1 mol%. Lastly, the  $D_{Bragg}$  of 10.1 mol% SMANa ionomer is ~2.2 nm. At this point, it should be recalled that the number of multiplets in the material is inversely proportional to the SAXS  $q_{max}$  value.<sup>1</sup> Thus, the above results suggest that the number of multiplets might be largest for the SMANa ionomers and smallest for the SSNa ionomers at the same ion content.







Figure 4-7. Bragg distances of the SSPMANa, SSNa, and SMANa ionomers, calculated from  $q_{\text{max}}$ .





#### 4.4. Discussion

It would be useful to recall the reason for the lower  $T_{g,c}$  but higher E'<sub>ionic</sub> of the SMANa ionomer, compared to the higher T<sub>g,c</sub> but lower E'ionic of the SSNa ionomer.<sup>4,19</sup> It is known that the interactions between Na-carboxylate ion pairs in the multiplet of the SMANa ionomer are relatively weaker than those between Na-sulfonate ion pairs in the multiplet of the SSNa ionomer.<sup>19,26</sup> In addition, the distance between the ion pair and polymer backbone chain is shorter for the SMANa ionomer than that for the SSNa ionomer. This means that when the ion pairs form multiplets, the polymer chains of the SMANa ionomer experience more steric hindrance than those of the SSNa ionomer. This leads to the formation of small-sized multiplets for the SMANa ionomer, compared to relatively large-sized multiplets for the SSNa ionomer (see Figure. 4-8-(a) and (b)). Now, let us think of the number of multiplets. In the case of the SMANa ionomer, because of the small-sized multiplets, the ionomer has a relatively larger number of multiplets, compared to the SSNa ionomer (see Figure. 4-8-(a) and (b)). If one assumed that the amount of clustered regions is directly related to the number of multiplets, one would know that the SMANa ionomer has a larger amount of clustered regions than the SSNa ionomer at the same ion content. Since the height of the ionic modulus is mainly associated with the amount of clustered regions,<sup>1,19,21-23</sup> the ionic modulus of the SMANa ionomer is higher than that of the SSNa ionomer. At this point, it is worth recalling that the  $T_{g,c}$  is associated with both the degree of clustering and the strength of interactions between ion pairs in the multiplets, which is, in turn, related to ion-hopping.<sup>1,19,21,27-34</sup> Thus, the  $T_{g,c}$  is naturally affected by the type of an ion pair and the distance of an ion pair from a polymer backbone chain, the bulkiness and flexibility of the chain segment containing the ion pair, and so on.<sup>4</sup> Thus, it is reasonable that the  $T_{gc}$  of the SMANa ionomer is lower than that of the SSNa ionomer because of the relatively weaker interactions between the ion pairs in the multiplets of the SMANa ionomer.4,19





Figure 4-8. Schematic representation of the morphologies of (a) SMANa, (b) SSNa, and (c) SSPMANa ionomers.





It is time to discuss the relationship between the chemical structures and mechanical properties of the SSNa and SSPMANa ionomers. The type of pendent ionic groups of the two ionomers, i.e.  $-SO_3^-$  Na<sup>+</sup>, is identical, but the distance between the ion pair and polymer backbone chain is longer for the SSPMANa ionomer than that for the SSNa ionomer. Thus, the size of the multiplets of the SSPMANa ionomer should be somewhat larger than that of the SSNa ionomer at the same ion content due to less steric hindrance for the multiplet formation (see Figure. 4-8-(b) and (c)). Since the SSPMANa ionomers have flexible side chains, consisting of propyl chain (-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-) and ester group (-COO), at the end of which the anionic group is located, the SSPMANa ionomers can form multiplets more easily, compared to the SSNa ionomers. This leads to the formation of a sufficient number of relatively large-sized multiplets even at low ion contents. Thus, even the 3.8 mol% ionomer exhibits a strong SAXS peak. At this point, it should be noted that the multiplets of the SSPMANa ionomer are, then, covered by a layer containing flexible alkyl ester side chain units that are, in turn, attached directly to the polymer backbone chains. With increasing ion content, more multiplets form at their prevalent distances and the size of multiplets (i.e. the number of ion pairs per multiplet) increases, as well, and the multiplets covered by a thick layer of flexible chains are dispersed throughout the matrix relatively evenly because of the relative easiness in the multiplet formation process. Thus, we suggest that, with increasing ion content, the number of the multiplets that are well dispersed in the matrix phase increases (Figure. 4-8-(f)). However, this agglomeration process of the multiplets is somewhat different from those of the SSNa and SMANa ionomers. In the latter two ionomer systems, the ionic groups form the multiplets in the vicinity of pre-existing multiplets, leading to the agglomeration of the multiplets (see Figure. 4-8-(d) and (e)). Thus, as the ion content increases, the restricted mobility regions including the multiplets grow outward and increase in the sizes. In the present work, the type of the pendent ion pairs is the same for both the SSPMANa and SSNa ionomers; the strength of the interactions between the ion pairs in the multiplet

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should be the same. However, the  $T_{g,c}s$  of the two ionomer systems are not the same. This indicates that the flexibility of the side chain segment attached to the polymer backbone chain of the SSPMANa ionomer may be responsible for this difference in the  $T_{g,c}s$ . As mentioned above, for the SSNa ionomers, the increasing ion content results in the increase in both the size and amount of clustered regions; thus, the  $T_{g,c}$  increases rapidly with increasing ion content. On the other hand, for the SSPMANa ionomers that have the evenly distributed multiplets throughout the matrix phase, the  $T_{g,c}$  might be dependent mainly on the strength of the interactions between ion pairs in the multiplet, but weakly on the degree of clustering because the size of the clustered regions does not increase like those of the SSNa ionomers (see Figure. 4-8-(e) and (f)).

Here, we would like to summarize the above findings. It has already been seen in Figure 4-6 and Figure 4-7 that with increasing ion content, the SAXS peak intensity of the SSPMANa ionomer increased somewhat in a regular manner, and the  $D_{\text{Bragg}}$  decreased very slowly. Thus, we suggested that, with increasing ion content, the SSPMANa ionomer had more multiplets at their prevalent distances throughout the polymer matrix; as a result, the intensity of SAXS peak increased and the peak shifted to a slightly higher q. Consequently, the number, probably not the size, of the clustered regions increased, causing the increase and decrease in the sizes of the cluster and matrix loss tangent peaks, respectively, which was indeed what we observed in Figure 4-2. The minor change in the cluster  $T_{gs}$  of the SSPMANa ionomers above 3 mol% of ions is puzzling. At this point, we do not have any clear explanation for this finding. However, in the present study, the multiplets of the SSPMANa ionomer are thought to be covered by the relatively thick layer of flexible side chains. This type of multiplets is different from those of the SSNa and SMANa ionomers. In the SSNa and SMANa systems, the multiplets are directly contacted with the polystyrene chains of restricted mobility (Figure. 4-8-(a) and (b)). Thus, the hopping of ion pairs between multiplets is also hindered by the enlarged restricted mobility regions surrounding the multiplets. Therefore, the ion pairs cannot hop from one multiplet





to another until most of the polymer chains in the restricted mobility regions have enough energy to overcome the interactions between ion pairs in the multiplet and to move together with the ion-hopping. As a result, the on-set temperature of ion-hopping is directly proportional to the size of the clustered regions, i.e. ion content. In the case of the SSPMANa ionomer, however, the imminent vicinity of the multiplet is occupied by the flexible side chains and the multiplets are thought to be dispersed in the polymer matrix more or less evenly. If this were the case, with increasing ion content, the amount of clustered regions would increase mainly by growing the number of clustered regions not by the overlapping of the restricted mobility regions. Thus, the  $T_{g,c}$  would not increase strongly with increasing ion content, which is indeed what we observed here.

In this section, we would like to interpret the mechanical properties of the ionomers by considering the clusters as filler since the multiplets with restricted mobility regions are thought to be dispersed in the polymer matrix relatively evenly. It is known that the ionic modulus increases as the volume fraction of clusters increases, and that the matrix or cluster loss tangent peak areas can be regarded as a measure of the volume fraction of the matrix or cluster regions of the ionomer.<sup>21,22,35</sup> The areas under the matrix  $(A_m)$  and cluster peaks (A<sub>c</sub>), and the total area ( $\Sigma A$ ) are shown in Figure 4-9. It is observed that the  $\Sigma A$ values are similar to each other, and the average of the  $\Sigma A$  for the ionomers is measured to be 49  $\pm$  1 °C. It is seen that the  $A_c$  increases but the  $A_m$  decreases, rapidly and subsequently slowly. Above  $\sim 10 \text{ mol}\%$  of ions, the areas change only slightly with ion content. The data for the  $A_m$  and  $A_c$  as a function of ion content can be fitted with second-order polynomials and are useful to demonstrate the smooth transition from the dominance of the matrix peak to that of the cluster peak. At this point, it should be mentioned that the intersection of  $A_m$  and  $A_c$  occurs at ~6.5 mol% for the SSPMANa ionomer. On the other hand, for the SMANa ionomer, it happens at ~4 mol%.<sup>21</sup> In addition, at ~12 mol% of ions, the  $A_c/\Sigma A$  of the SSPMANa ionomer is ~0.63, but that of

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Figure 4-9. Areas under loss tangent peaks and the sum of the areas as a function of ion content, measured at 1 Hz.





the SMANa ionomer is ~0.95.<sup>21</sup> These two aspects indicate that the SMANa ionomer is a much more clustered material than the SSPMANa ionomer. Again, this is due to the different processes in the multiplet formation and clustering.

Firstly, the multiplets of the ionomers can be regarded as physical crosslinks, and, thus, the ionic modulus can be related to a crosslinking effect by the formation of multiplets using the following equation.<sup>36</sup>

$$G = \rho RT/M_{\rm c}$$

Here, G is the shear storage modulus at the inflection point of the ionic plateau,  $\rho$  is the ionomer density, R is the gas constant, T is the absolute temperature (in the present work it is ~448 K), and  $M_c$  is the average molecular weight between crosslinks. At this point, it should be mentioned that, to calculate the modulus, we also obtained the ionomer densities of the SSPMANa ionomers as follows:

$$\rho$$
 (g/mL) = 0.996 + 0.0273 × (ion content) - 0.00115 × (ion content)<sup>2</sup>

In Figure 4-10-(a), it is shown that in the ion content range of 2-7 mol%, the equation is valid reasonably well. This indicates that, in that ion content range, the multiplets act as effective crosslinks. Above ~7 mol%, the ionic modulus is seen to be higher than the calculated value. This implies that the multiplets as well as the restricted mobility regions now behave like effective crosslinks.

It is known that the Guth equation can be used to relate the Young's modulus of the material with the amount of filler of a spherical form, which is applicable up to  $\sim$ 30 vol % of filler. The Guth equation is as follows:

$$E^* = E \times (1 + 2.5 \times V_{\rm f} + 14.1 \times V_{\rm f}^2)$$





Figure 4-10. (a) Log E'<sub>ionic</sub> vs. ion content. Dashed line for the calculated storage modulus using a rubber elasticity concept. (b) Log E'<sub>ionic</sub> vs. volume fraction of clustered regions obtained from the fraction of cluster loss tangent peak area against total area. The dotted line and dashed line represent the Guth equation and the regular system by Halpin-Tsai (H-T), respectively.





Here,  $E^*$ , E, and  $V_f$  are the Young's modulus of the filled and unfilled systems, and the volume fraction of filler, respectively. In this work, we take the  $E'_{\text{ionic}}$  as  $E^*$  and the rubbery modulus of polystyrene as E, and the volume fraction of clusters as  $V_f$ . In Figure 4-10-(b), it is seen that in the  $V_f$  range of 0–0.55, the data seem to be in good agreement with the Guth equation. Above ~55 vol % of clustered material, the experimental value increases dramatically and shows deviations from the calculated value. At this point, it should be mentioned that for the SMANa ionomers, the Guth equation was applicable only in the range of low volume fraction for the successful application of the Guth equation also implies that the SSPMANa ionomers are less clustered materials than the SMANa ionomers.

At this point, it is useful to discuss the so-called regular system, in which rigid spherical particles are dispersed in the elastomeric matrix. In this case, the modulus of the material can be calculated using the Halpin-Tsai equation.<sup>37</sup>

$$(M / M_1) = (1 + AB\varphi_2) / (1 - B\varphi_2)$$

and

$$B = (M_2 / M_1 - 1) / (M_2 / M_1 + A)$$

Here, M is the modulus of the material and the subscripts 1 and 2 refer to the continuous phase and the dispersed phase, respectively. We consider the rubbery and glassy moduli of polystyrene, i.e.  $E' = 10^{6.1}$  Pa and  $E' = 10^{8.9}$  Pa, as  $M_1$  and  $M_2$ , respectively. The constant A, influenced by the morphology of the material, is generally given by

$$A = (7 - 5v_1) / (8 - 10v_1)$$



Here,  $v_1$  is Poisson's ratio for the matrix. We take the Poisson's ratio of natural rubber at room temperature as that of polystyrene in the rubbery state, i.e.  $0.50^{36}$ , which makes A =1.5. The result of the calculation is shown in Figure 10-(b). Even though the fit is not perfectly satisfactory, it can be suggested that in the range of low volume fraction of clusters, the cluster regions seem to be dispersed as more or less spherical particles in the matrix phase, at least to some extent. At this point, it should be mentioned that the constant A is related with the dimensions and geometries of the filler particles.<sup>39</sup> For instance, the A increases with increasing number of spheres per aggregate. Thus, we tried to fit the data with a single value of A; the better result ( $r^2 = 0.9608$ ) is shown in Figure. 4-10-(b), using A = 5.1. It is seen that even though it is not the best fit, it is better than the fit, using A = 1.5. In addition, when we ignore one or two data of higher fraction of  $A_c$  (> 0.60), we can obtain even a better result, using A = 4.3 (r<sup>2</sup>= 0.9922) or 4.0 (r<sup>2</sup>= 0.9948), respectively. As mentioned before, when the reinforcing filler consists of isolated spherical particles (e.g., multiplets with their surrounding regions of restricted mobility), the constant A is expected to be  $\sim 1.5$ . However, the A values obtained from the better fits (i.e. 5.1, 4.3, and 4.0) are much higher than that. This means that the clusters acting as filler are, most likely, in the form of irregular aggregates, and the shape of the clustered regions may not be spherical, and the number of multiplets per cluster increases. At this point, it should also be mentioned that for the SMANa ionomers, the better fit was obtained by using A = 6.6 that is larger than the A values for the SSPMANa ionomers. This suggests again that the clusters of the SMANa ionomers are more irregular in their size and shape and contain more multiplets than those of the SSPMANa ionomers, which is indeed what we observed in the present work.





#### 4.5. Conclusions

We synthesized new polystyrene-based ionomers, SSPMANa, and studied their mechanical properties and morphology. On increasing ion content, the E'ionic increased slowly, and the rate of increasing E'ionic was lower than those of the SSNa and SMANa ionomers. The matrix  $T_g$  of the SSPMANa ionomer increased as much as those of the SSNa and SMANa ionomers. On the other hand, above  $\sim 3 \text{ mol}\%$  of ions, the cluster  $T_g$  of the SSPMANa ionomer did not change significantly, which was different from those of the SSNa and SMANa ionomers. In addition, even 3.8 mol% SSPMANa ionomer showed a welldeveloped SAXS peak, and the intensity of SAXS peak increased progressively with increasing ion content; the SAXS peak shifted to slightly higher angles. Thus, we suggested that the ionic groups of the SSPMANa ionomer formed multiplets more easily at their prevalent distances because of the very flexible side chains, compared to those of the SSNa ionomer. As a result, a large number of multiplets formed even at low ion content. This, in turn, led to the well-developed SAXS peak for the ionomers of low ion contents. From the cluster  $T_{gs}$  and the SAXS peak positions, we speculated that the multiplets of the SSPMANa ionomers were surrounded by a thick layer containing flexible side chains, making the multiplets isolated from the polymer backbone chains in the clustered regions, and the multiplets were well-dispersed in the polymer matrix more or less evenly. Thus, the cluster  $T_g$  of SSPMANa ionomer was mainly affected by the ion-hopping temperature, not by the size of the regions of restricted mobility. It was found that the multiplets acted as effective crosslinks in the ion content range of 2-7 mol%. In addition, the Guth equation was applicable for the ionomers containing < 55 vol% of clustered regions. This indicated that, the clusters of the ionomers of low ion contents acted as filler. The modification of A value of the Halpin-Tsai equation suggested that the ionomer behaved like a regular system and the clustered regions were irregular in their size and shape, and the SSPMANa ionomers were less clustered than the SMANa ionomers.



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## Chapter 5

# Effects of low-temperature dehydration on poly(styrene-co-styrenesulfonic acid) membrane




#### 5.1. Introduction

Proton conductivity is an essential mechanism for fuel cell.<sup>1</sup> In the case of polymer electrolyte materials, the proton  $(H^+)$  exists as  $[SO_3^- H^+]$  ionic pairs. Here, the anionic  $SO_3^-$  moiety is covalently bonded to a main chain of polymers, while cationic  $H^+$  is associated with hydrogen bond networks between H<sub>2</sub>O molecules. Therefore, such proton  $(H^{+})$  can move via the hydrogen bond networks. This is why the H<sup>+</sup> conductivity is very sensitive to the molecular state of  $SO^{-}$  ions, as well as to the nature of the hydrogen bond networks. Zundel and Eigen cations are representative of hydrogen bond networks that include H<sup>+</sup>, and thus many researchers have focused on their investigations into molecular structural behaviors as a function of hydration level.<sup>2-7</sup> However, as a counter anionic partner, there have been few studies on the variation of the molecular state of  $SO_3^{-1}$  ions. In fact, the role of  $SO_3^{-}$  is expected to be critical at very low levels of hydration because the Zundel and Eigen cations would be broken. Also,  $[SO_3^{-} \cdots H^+]$  ionic pairs can experience a reverse dissociation process as the hydration level decrease. Therefore, in order to understanding for the role of  $SO_3^-$  more precisely, it is necessary to extend our study to the variation of the molecular state of  $SO_3^-$  at the dehydration limit. It is well known that poly(styrene-co-styrenesulfonic acid) (PSSA) had been used as a prototype polymer electrolytes for fuel cell in the early development of spaceship.<sup>8</sup> Here,  $[SO_3^{-}...H^+]$  ionic pairs can be controlled by introducing the sulfonic acid groups in the polystyrene skeleton polymers. The H<sup>+</sup> ion content and the hydrogen bond networks can be manipulated by adjusting the hydration level. Because of these advantages, we chose PSSA as a model system for exploring a variation of  $SO_3^-$  ions at the dehydration limit.





#### 5.2. Experimental Section

#### 5.2.1. Sample preparation

Polystyrene (MW = ca. 580,000, MWD = ca. 1.6) was prepared via radical polymerization with benzoyl peroxide as the initiator. For homogeneous sulfonation, the modified method of Makowski et al. was used to produce PSSA.<sup>9</sup> To determine the acid content, the copolymer was dissolved in a benzene/methanol (9/1 v/v) mixture to make a 5% (w/v) solution. The solution was titrated with standard methanolic NaOH to the phenolphthalein end point; the acid content was 3.2 mol %. The as-prepared PSSA was a white powder in an ambient environment. In order to obtain PSSA without hydration, we divided the as-prepared PSSA into two portions. One portion was left as-is and the other was thermally treated for dehydration at 60  $^{\circ}$ C in a vacuum oven for 24 h.

#### 5.2.2. Differential scanning calorimetry

Thermal analysis of the polymer samples was carried out using differential scanning calorimetry (DSC) (TA Instrument, USA). Before measuring the polymer samples, the DSC was calibrated with indium. Each sample (1~10 mg) was firstly loaded into an aluminum pan, heated to 300  $^{\circ}$ C, and then immediately cooled down to 10  $^{\circ}$ C at a heating rate of 10  $^{\circ}$ C/min during a purge of dry nitrogen. These thermal cycles were used to check whether or not there was thermal hysteresis.

#### 5.2.3. Infrared spectroscopy

Fourier transform infrared (FT-IR) spectroscopy was performed over a frequency range of  $4000 - 600 \text{ cm}^{-1}$  using a NICOLET 6700 FT-IR spectrometer (Thermo Scientific, USA). Every IR signal was drawn from the average of 64 scans. To prepare thin film specimens





for FT-IR spectroscopy, respective dimethyl formamide (DMF) solutions containing as-prepared sample (10 mg/mL) with/without thermal treatment was cast onto a polytetrafluoroethylene (PTFE) mold and dried in an ambient condition for 24 h and dried further in a vacuum oven at room temperature for 24 h.

5.2.4. Solid state nuclear magnetic resonance

<sup>13</sup>C cross-polarized magic angle spinning nuclear magnetic resonance (CP-MAS NMR) and <sup>1</sup>H MAS NMR was carried out for each sample at room temperature using Unity Inova 500 NMR (Bruker Co., Germany). For the <sup>13</sup>C CP-MAS NMR, 4  $\mu$ s and 5  $\mu$ s of  $\pi/2$ pulses were used for <sup>13</sup>C and <sup>1</sup>H nuclei, respectively at a spinning rate of 15 kHz. A contact time of 1 ms was used for cross polarization between the <sup>13</sup>C and <sup>1</sup>H nuclei. For the <sup>1</sup>H MAS NMR, a  $\pi/2$  pulse of 5  $\mu$ s was used at spinning rate of 15 kHz. Every spectrum was obtained from the average of fast Fourier transforming of free induction decay of 50 scans.

#### 5.2.5. Electron magnetic resonance

The X-band electron magnetic resonance spectra were recorded at room temperature using JES-FA200 spectrometer (Jeol, Japan). The static magnetic field was swept from 3150 G to 3350 G. The amplitude of AC magnetic modulation was 5 G at 100 kHz. The microwave power was 1 mW and the amplifier gain was  $5 \times 10^2$ . Each sample was sealed in a quartz tube (diameter = 3 mm) under a pressure of  $5 \times 10^{-5}$  torr.





#### 5.3. Results and Discussion

Figure 5-1 presents DSC thermograms obtained from the as-prepared poly(styrene-co-styrenesulfonic acid) copolymers (as-PSSA) dehvdratedand the poly(styrene-co-styrenesulfonic acid) copolymers (dhyd-PSSA), respectively. For the case of as-PSSA, the first heating run shows two thermal transitions; one is the broad concave endothermic peak in the temperature range from 25  $\degree$  to 100  $\degree$  centered around 80  $\degree$ ; the other is a stepwise transition at 115  $^{\circ}$ C. Interestingly, this combination of thermal transitions is only observed at the first heating run for as-PSSA. In the subsequent cooling run, the as-PSSA shows only a stepwise glass transition at 115 °C, with no trace of thermal transition at 80  $^{\circ}$ C, which means that the thermal transition of the as-PSSA copolymer is irreversible for thermal cyclization. Therefore, the former can be identified to be due to a dehydration of water molecules involved in the as-PSSA, and the latter stepwise transition to a glass transition. On the other hand, dhyd-PSSA exhibits only a glass transition for thermal cyclization, indicating that the dehydration mechanism is efficiently completed even at 60  $^{\circ}C$ .

Except for these differences in DSC thermograms during thermal cyclization, there was an unexpected but clear shift of color from white for the as-PSSA to yellow-brown for the dhyd-PSSA is revealed as shown in Figure 5-2. Physically, such a color shift could be cause by selective absorption of blue, which is the complementary color of the yellowish brown, from visible light. In the current case, the molecular group capable of absorbing blue is the benzene ring. However, either carbon-carbon (C=C) or carbon-oxygen double bond (C=O) are possible if they can be formed during low-temperature dehydration. Finally, there are  $SO_3$ · radicals, which have been known to absorb specific wavelengths of light.<sup>10</sup> Thus, we examined radical species using EMR.





Figure 5-1. DSC thermograms obtained for the as- and dhyd-PSSA. The dashed-vertical line indicates the glass transition temperature  $(T_g)$ .









Figure 5-2. Color shift from white for the (a) as-PSSA to yellowish brown for the (b) dhyd-PSSA.





Figure 5-3 shows EMR results at room temperature. The as-PSSA copolymer is EMR silent; However, the dhyd-PSSA copolymer has an EMR peak of g = 2.0031, where g is a spectroscopic splitting factor that equals  $hv/\mu_BH_{res}$  (h = Planck constant, v = microwave frequency,  $\mu_B =$  Bohr magneton,  $H_{res} =$  resonant magnetic field). As pointed out in our previous study, the peak is attributed to the presence of SO<sub>3</sub>· radicals.<sup>11</sup> Because double integration of EMR spectrum has been known to be proportional to the spin number, one can quantify the absolute spin number under a spectrum by obtaining an additional EMR signal from a standard sample with a known a absolute spin number under the same conditions. For our case, double integration of the EMR spectrum for dhyd-PSSA (13 mg) gave  $1.64 \times 10^{11}$  spins when 210 µg ( $5.24 \times 10^{12}$  spins) of CuSO<sub>4</sub>·5H<sub>2</sub>O was used as the standard sample. This means that sub-ppm SO<sub>3</sub>· radicals are generated by the low-temperature dehydration because  $2.35 \times 10^{18}$  units of sulfonic acid are calculated to be included in 13 mg of dehyd-PSSA (3.2 mol%). When referring to Nafion membranes, this type of SO<sub>3</sub>· radical can be generated by an attack of intermediate hydrogen (H·) or hydroxyl radical (HO SO<sub>3</sub>·) to SO<sub>3</sub>H.

Accordingly, we carefully performed FT-IR spectroscopy to demonstrate the existence of –  $SO_3H$ . The experimental results are shown in Figure 5-4, and the main assignments for the as- and dhyd-PSSA are listed in Table 5-1. Dhyd-PSSA clearly shows various bands for  $SO_3H$ : 1172 cm<sup>-1</sup> (symmetric stretching vibration of S=O), 1101 cm<sup>-1</sup> (in-plane skeleton vibration of benzene ring with  $SO_3H$  substitutes), and 891 cm<sup>-1</sup> (S-O stretching vibration of  $SO_3H$ ). On the other hand, as-PSSA does not show any FT-IR bands described above. Instead, as-PSSA reveals FT-IR characteristics caused by the presence of H<sub>2</sub>O, and  $SO_3^-$ : 3485 cm<sup>-1</sup> (OH stretching vibration of hydrated H<sub>2</sub>O), 1248 cm<sup>-1</sup> (antisymmetric stretching vibration of  $-SO_3^-$ ), 1127 cm<sup>-1</sup> (in-plane skeleton vibration of benzene ring with  $SO_3^-$  substitutes), and 1004 cm<sup>-1</sup> (in-plane C-H bending of benzene ring with  $-SO_3^-$  substitutes). These results mean that the  $SO_3H$  group appears in dhyd-PSSA after the disappearance of the [ $-SO_3^- \cdots H^+$ ] ionic pair.







Figure 5-3. Electron magnetic resonance signals obtained for the as- and dhyd-PSSA copolymers.







Figure 5-4. Room-temperature FT-IR spectra of as- and dhyd-PSSA. Note that the FT-IR spectrum of polystyrene is displayed, together with those of as- and dhyd-PSSA, in order to visualize the vibration bands from the polystyrene skeleton.





	as-PSSA	dhyd-PSSA	
Assignments	$(cm^{-1})$	$(cm^{-1})$	
OH stretching vibration of hydrated H <sub>2</sub> O	3400 (b)*		
CH <sub>2</sub> stretching	2900-2950	2900-2950	
Polystyrene stretching bands	2800-3100	2800-3100	
C-C in-plane stretching of ring	1600	1600	
S-O <sub>2</sub> stretching in SO <sub>3</sub> H	1415 (w) <sup>*</sup>	1415 (s) <sup>*</sup>	
SO3 <sup>-</sup> stretching vibration, antisymmetric	1248		
S=O stretching vibration, symmetric	-	1172	
In-plane skeleton vibration of benzene ring with $SO_3^-$ substituents	1127	_	
In-plane skeleton vibration of benzene ring with $\mathrm{SO}_3\mathrm{H}$ substituents	_	1101	
In-plane C-H bending of benzene ring with $SO_3^-$ substituents	1004 (vw) <sup>*</sup>	-	
S-O stretching vibration	891 (sh)*	891 (sh)*	
C-H out-of-plane vibration for para position	834	834	
=CH <sub>2</sub> bending vibration	-	811	
C-H out-of-plane bending	756	756	
Phenyl out-of-plane bending	697	697	

# Table 5-1. Characteristic infrared spectral data of PSSA<sup>4,12-14</sup>

\*sh = shoulder, s = strong, b = broad, vw = very weak, w = weak



Therefore, one can say that the presence of  $SO_3$  radicals is caused by caused by an attack of intermediate H· or HO· on SO<sub>3</sub>H groups; at the same time, the possibility that such intermediate radicals are capable of attacking another chemical group in PSSA cannot be excluded. For this, the most plausible scenario is that either H· or HO· attack the tertiary hydrogen at the  $\alpha$ -carbon of PSSA and thus induce a proton abstraction reaction, leading to a C=C bond. Interestingly, close inspection of the FT-IR spectrum of dhyd-PSSA shows an additional band at 811 cm<sup>-1</sup>, which is known to be one of the FT-IR bands from a substituted C=C group. Furthermore, the proton abstraction was detected as a lacking <sup>1</sup>H nuclei in <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy as described below.

Figure 5-5 displays <sup>1</sup>H NMR MAS spectra obtained for as- and dhyd-PSSA at a spinning rate 50 kHz. As a whole, three different <sup>1</sup>H MAS peaks were obtained at the chemical shift of 1.4, 3.6 and 6.5 ppm, respectively. Since CH<sub>2</sub>, CH, phenyl ring and hydrated water molecules are major <sup>1</sup>H sources from the PSSA copolymer, 1.4, 3.6 and 6.5 ppm can be assigned to CH<sub>2</sub>, CH and phenyl rings, respectively. It should be mentioned here that the NMR peaks from  $[H^{+}(H_2O)_m]$ , where m is the number of water molecules in hydrogen-bonded networks<sup>15-19</sup> are considered to overlap with the peak at  $\delta = 6.5$  ppm.<sup>15,20</sup> One can immediately know that the <sup>1</sup>H intensity at 6.5 ppm is drastically diminished at dhyd-PSSA when the absorption maxima of  $\delta = 1.4$  ppm are kept at the same amplitude, indicating the disappearance of  $[H^{+}(H_2O)_m]$  protons for dhvd-PSSA.<sup>17</sup> Simultaneously, the decrease at  $\delta = 3.6$  ppm for the CH group is manifested as well. The Lorentzian function fitting to  $\delta = 3.6$  ppm reveals that the <sup>1</sup>H MAS intensity for dhyd-PSSA (olive dotted line in Figure 5) is 5% less than that for as-PSSA (red solid line in Figure 5). This suggests the possibility that 5% of the proton atoms can be abstracted at the CH group ( $\alpha$ -carbon) of dhyd-PSSA by attacking intermediate H. or HO. radical species, as mentioned the above. In contrast, the <sup>13</sup>C CP-MAS NMR spectrum of as-PSSA (not shown here) is exactly the same as that of dhvd-PSSA when each spectrum is normalized by the mass.<sup>21</sup> The <sup>13</sup>C CP-MAS NMR spectrum showed no change in the carbon skeletons after dehydration





Figure 5-5. Solid-state <sup>1</sup>H MAS nuclear magnetic resonance signals obtained for as- and dhyd-PSSA. The chemical structure at right-up side is the molecular structure of PSSA. The arabic numerals on both the molecular structure and the NMR spectra represent the <sup>1</sup>H MAS chemical shifts expected for different chemical sites in PSSA. The olive dotted line and the red solid line indicate Lorentzian functions fitted to  $\delta = 3.6$  ppm signals from as- and dhyde-PSSA, respectively.



of the as-PSSA copolymer. The SSNMR studies thus show a disappearance of  $[H_+(H_2O)_m]$ , as well as partial abstraction of the tertiary H at the  $\alpha$ -carbon in dhyd-PSSA.

To conclude, to explain the presence of SO<sub>3</sub> · radicals and C=C bonds within dhyd-PSSA, one should consider that intermediate H · or HO · radical species can be generated in the process of low-temperature dehydration of as-PSSA. Such intermediate H · or HO · radicals can attack the SO<sub>3</sub>H moiety as well as the tertiary proton at the  $\alpha$ -carbon of PSSA, as shown in Figure 5-6. As is well known, the SO<sub>3</sub> · radical can absorb light in the wavelength range from 210 nm to 320 nm.<sup>10</sup> The substituted C=C bond can also absorb light with a 200 nm wavelength to obtain the excited state of the  $\pi_z$ -orbital ( $\pi$ - $\pi$ \* transition). Here, it is worth recalling that poly(p-phenylene vinylene) (PPV) with light absorption in a similar wavelength range was yellowish brown.<sup>22-24</sup> Thus, it is thought that light absorption by the SO<sub>3</sub> · radical and the substituted C=C bond induce a color shift in the present system.

#### 5.4. Conclusions

PSSA has been widely used as a proton exchange membrane material for fuel cells, and its thermal degradation is a hot issue. According to previously reported results, the degradation can be caused by either very high temperatures or radicals.<sup>25</sup> With very high temperatures, fuel cells based on PSSA membranes cannot be operated above 60  $^{\circ}$ C. With radicals, two different degradation mechanisms have been suggested so far; one is the degradation of hydrogen at the α-carbon of PSSA<sup>26</sup> and the other is oxidative decomposition due to oxidative radicals in the cathode reaction.<sup>27,28</sup> More recently, the simultaneous loss of an aromatic ring and SO<sub>3</sub> · groups has also been suggested as a degradation mechanism of PSSA membranes.<sup>29</sup> In any case, the formation of intermediate and reactive radicals plays a major role in the degradation of the polymers. However, our experimental results show that all degradation mechanisms mentioned above can be triggered by dehydration, even below 60  $^{\circ}$ C. In a further study, we plan to study the low-temperature dehydration effect of Nafion membranes as well.







Figure 5-6. Schematic of the varying molecular structure of PSSA by low-temperature dehydration.





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# APPENDIXES





# List of My Publications

- "Effects of molecular weights of sulfonated polystyrene ionomers on the formation of stable colloidal particles in THF/water (1/99) mixture" Jeong-A Yu, Kwang-Hwan Ko and Joon-Seop Kim Journal of Nanoscience and Nanotechnology 2008, 8(10), 5450-5453.
- 2) "Formation of the colloidal particles of sulfonated polystyrene ionomers neutralized with either Na(I) or Ba(II) in THF/water (1/99) mixture" Kwang-Hwan Ko, Jeong-A Yu, and Joon-Seop Kim *Journal of Nanoscience and Nanotechnology* 2008, *8(10)*, 5459–563.
- 3) "Randomly sulfonated liquid crystalline polymers containing Triad mesogen of butylene terephthalate" Ju-Myung Song, Kwang-Hwan Ko, Yu-Sung Choi, Jae-Kon Choi, Byung-Wook Jo, and Joon-Seop Kim Molecelar Crystals & Liquid Crystals 2009, 511, 255-264.
- "Dynamic mechanical properties of polystyrene ionomers containing both carboxylate and sulfonate anionic groups" Ju-Myung Song, Kwang-Hwan Ko, Joon-Seop Kim, Kwanwoo Shin Journal of Polymer Science Part B: Polymer Physics 2012, 50(16), 1181-1187.
- "Dynamic mechanical properties and morphology of polystyrene-co styrenesulfonic acid copolymers neutralized with aliphatic diamines"
   Mohammad Luqman, Kwang-Hwan Ko, Joon-Seop Kim, Kwanwoo Shin Journal of Applied Polymer Science 2013, 128(3), 1764-1770.
- 6) "Tangible plasticization/filler effects of sodium salts of dimer acids obtained from waste natural oil on the mechanical properties of styrene ionomers" Kwang-Hwan Ko, Hye Ryeon Park, Joon-Seop Kim, Young-Wun Kim *Journal of Applied Polymer Science* 2013, 129(5), 2443-2450.
- 7) "Effect of the number of methyl groups on the ionic repeat unit of poly(styrene-co-acrylate) ionomers on their mechanical properties and morphology" Jae-Jin Park, Kwang-Hwan Ko, Ju-Myung Song, Joon-Seop Kim *Polymer* 2013, *54*, 3914-3920.
- 8) "Effects of the addition of dimer acid alkyl esters on the properties of ethyl cellulose"
   Sangjun Lee, Kwang-Hwan Ko, Jihoon Shin, Nam-Kyun Kim, Young-Wun Kim, Joon-Seop Kim
   Carbohydrate Polymers 2015, 121, 284-294.

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# 감사의 글

지금의 제가 있기까지 관심과 격려로 저에게 큰 힘이 되어주신 모든 분들께 감사의 마음을 전합니다.

먼저 이 논문이 완성되기까지 항상 성실함과 노력하는 자세로 진정한 학자의 모습을 보여 주시며 따뜻한 격려와 충고로 지도해 주신 김준섭 교수님께 진심으로 감사의 마 음을 전합니다. 그리고 부족한 논문을 심사해 주신 최재곤 교수님, 김영운 박사님, 이 창훈 교수님, 김호중 교수님께 감사의 마음을 전합니다. 또한, 대학원 생활동안 지도해 주신 유지강 교수님, 홍진후 교수님, 조훈 교수님, 김현경 교수님 그리고 많은 조언과 격려를 해주신 유정아 교수님께도 감사 드립니다. 함께 기초실험실에서 생활하며 많은 도움을 준 주명, 재진 선배, 후배 혜련, 은희, 인섭, 어려운 일이 있을 때 함께 고민해 준 친구 영민과 함께 생활한 대학원 선·후배님들께 깊은 감사의 마음을 전합니다. 또 한 오랜 시간동안 어려움과 기쁨을 함께 해준 인성, 성훈, 기상, 경현, 재록에게 이 글 을 통해 고마움을 전합니다.

항상 관심과 사랑으로 격려를 보내주신 장인어른과 장모님께도 감사드리며 처갓집 식 구들 선일 형님, 연준 형님, 선옥 처형에게 고마움을 전합니다.

마지막으로 아낌없는 사랑과 정성으로 뒷받침해주신 아버지와 어머니 그리고 동생 광 청과 힘든 상황에서 두 아들을 잘 키워주고 잘 내조해준 사랑하는 와이프 미옥과 두 아들 건과 겸이 사랑하는 가족 모두에게 이 논문을 바치며 깊은 감사와 존경 그리고 사랑의 마음을 전합니다.

> 2015년 12월 고광환

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# Effects of Molecular Weights of Sulfonated Polystyrene Ionomers on the Formation of Stable Colloidal Particles in Tetrahydrofuran/Water (1/99) Mixture

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The effects of the molecular weights (MWs) of sulfonated polystyrene copolymers on the colloidal particle sizes and the size distributions were investigated. It was found that the size of colloidal particle of acid copolymer of relatively low MW, being largest in comparison with higher MW sample, decreased strongly and then remained constant at ca. 11 nm upon dilution. These findings implied that at relatively high concentrations the colloids aggregated together due to the interactions between particles having relatively non-polar surface and that the colloids might contain more than one polymer chain. In the cases of copolymers of high MWs, the colloid sizes did not change much with the solution concentration, but the particle size of the higher MW copolymer, the longer polymer chain, and the larger colloid. The size of the ionomeric colloids was found to increase slightly upon dilution, which was due to the repulsion of ionic groups on the surface. As expected, the size of the particles of the ionomers showed a similar trend found in the acid samples.

Keywords: Ionomer, Ionization, Colloids, Aggregates, Molecular Weight.

## 1. INTRODUCTION

Ionomer are polymers having ionic groups along the relatively non-polar polymer backbone chains.<sup>1</sup> In consideration of the hydrophilicity and the relative amounts, and the types of the ionic groups of the ionomers, one can expect that the ionomers either can or cannot be dissolved in aqueous solution. Because of its hydrophobicity of the polymer main chain, the dissolution of the ionomer in water results in the formation of nanometer sized colloidal particles when the ionomer solution shows a homogeneous phase. At this point, it should be noted that the ionomer in a solvent of low polarity, the ionic groups of the ionomer form aggregates.<sup>2,3</sup> This is due to electrostatic interactions between fixed ions attached to the polymer backbone chain directly or as pendent ionic groups and counter-ions that are excluded from the non-polar polymer matrix and solvent.<sup>4</sup> In the case of sulfonated polystyrene in THF system, at low concentrations, the reduced viscosity of the ionomer solutions was found to be lower than that of the non-ionic polymer, indicating that the size of particles (i.e., coils) of the ionomer is smaller than that of the non-ionic polymer.<sup>5</sup> Thus, it was suggested that the shrinkage of the polymer coils was due to the intramolecular interactions. When the concentration of the ionomer solution increased, the reduced viscosity of the ionomer solution increased drastically, and the ionomer formed a gel at very high concentrations, which was thought to be the result of the dominant intermolecular interactions.

As expected, when the ion contents are low, styrenebased ionomers are not well dissolved in water because the non-ionic, non-polar polymer backbone segments are hydrophobic. Thus, only a few studies on the styrene ionomer in aqueous solution have been reported.<sup>6–14</sup> Using a TEM (transmission electron microscopy) method, Liu et al. found that the water-induced self-assembly of an acid form random copolymer of poly(styrene-*co*-methacrylic acid) (PSMAA) showed a bowl-shaped structure.<sup>11</sup> In the SEM (scanning electron microscopy) study on the morphology of the PSMAA copolymer, it was found that the acid copolymer formed spherical particles, with the average size of ca. 160 nm, and that the sizes did not change by the acid content.<sup>13</sup> However, the neutralization of the acid groups with NaOH induced the formation of

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network-like feature consisting of much smaller particles (<50 nm). With increasing degree of neutralization, the boundary of formed networks became vague. According to the work by the group of Wu, Na-sulfonated polystyrene (NaSPS) ionomers (molecular weight (MW) of polymer = ca. 300,000) formed stable nano-sized colloidal particles, possibly consisting of one polymer chain, in water.<sup>6–9</sup> The average diameter of the nano-particles was in the range of 5-12 nm, and the particle sizes depended on the degree of sulfonation, the concentration of the stock solution, and the mixing order.<sup>6</sup> However, the effects of MW of the polymer on the formation of colloidal particles of the acid form copolymers and their ionomer forms have not been explored. Thus, in the present work, we attempted to study the MW effects using a light scattering technique. The results obtained in the present work might be very useful for the researchers working on the ionomer solution.

#### 2. EXPERIMENTAL DETAILS

#### 2.1. Sample Preparation

Polystyrene samples of different molecular weights were prepared by bulk free-radical polymerization using benzoyl peroxide as the initiator. The MWs of the samples were determined using a Varian 5010 size exclusion chromatograph with THF as the solvent. For homogeneous sulfonation, the modified method of Makowski et al. was used to obtain the poly(styrene-co-styrenesulfonic acid) (PSSA) samples.<sup>15</sup> To determine the acid contents, the samples were dissolved in a benzene/methanol (9/1 v/v)mixture to make a 5% (w/v) solution, and titrated with standard methanolic NaOH to the phenolphthalein end point. The MWs, the acid contents, and sample notations are given in Table I. For the neutralization of the acid groups, a predetermined quantity of methanolic NaOH solution was added to a 5% (w/v) acid copolymer solution in a benzene/methanol (9/1 v/v) mixture. The solutions were freeze-dried and then dried further under a vacuum at 130 °C for 24 h.

For particle size analysis, the acid from samples and ionomers were dissolved in a mixture of tetrahydrofuran (THF)/water (9/1 v/v) to make the ionomer stock solutions of  $2.0 \times 10^{-2}$  g/mL. To obtain ionomer dispersions in the solutions of various concentrations, the ionomer stock solution was diluted with water and THF to make the

**Table I.** Notation, ion contents and molecular weights of poly(styreneco-styrenesulfonic acid) and their Na-neutralized ionomer forms.

Sample notation		Acid (or ion)	м	М	M /	
Acid form	Ionomer form	content (mol%)	(g/mol)	(g/mol)	$M_{w'}$ $M_{n}$	
PSSA-37k	NaSPS-37k	3.5	55,000	37,000	1.5	
PSSA-104k	NaSPS-104k	4.0	158,000	104,000	1.5	
PSSA-273k	Na-SPS-273k	3.5	447,000	273,000	1.6	

ratio of the mixed solvents of THF/water to be 1/99 (v/v) under ultrasonication. Before the measurement of the particle sizes, the solutions were filtered using a polytetrafluoroethylene (PTFE) filter of 0.45  $\mu$ m pore size.

#### 2.2. Dynamic Light Scattering Measurements

For the particle size analysis, a Melvern Zetasizer Nano-S instrument with a 633 nm He-Ne "red" laser (4.0 mW) was employed. The scattered intensity was registered using an avalanche photodiode detector at room temperature.

### 3. RESULTS AND DISCUSSION

Shown in Figure 1 are the dynamic light scattering (DLS) data of the PSSA-37k copolymer containing 3.5 mol% of acid groups in the solution of various concentrations as a function of the diameter of the particles. It is seen that the position of the peak maximum is located at ca. 22 nm in diameter for the  $2.0 \times 10^{-4}$  g/mL sample, and that it shifts to smaller diameters with decreasing solution concentration, i.e., the maxima of the peak are located at ca. 13 and 11 nm for  $1.0 \times 10^{-4}$  and  $5.0 \times 10^{-5}$  g/mL samples, respectively. This indicates that the size of the colloidal particles decreases with decreasing solution concentration.

From the analysis of the DLS data, one could obtain the average diameter of the particles and the width of the main peak at its half height. The diameter of the colloids and the peak width at half height of the acid form samples as a function of the solution concentration are shown in Figure 2. The diameter of the PSSA-37k copolymer is found to decreases strongly with decreasing solution concentration from  $2.0 \times 10^{-4}$  g/mL to  $5.0 \times 10^{-5}$  g/mL



**Fig. 1.** Typical dynamic light scattering diagrams of the stable colloidal particles of PSSA-37k acid copolymer in THF/water (1/99 v/v) mixture as a function of the size of particles.

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Fig. 2. Diameters of the colloidal particles of acid copolymers of different MWs in THF/water (1/99 v/v) mixture as a function of solution concentration.

and then remains relatively constant upon further dilution to  $1.0 \times 10^{-5}$  g/mL. In the case of the higher molecular weight copolymers, the sizes of the colloidal particles do not change strongly with the solution concentration: The average size of the particles are  $8.2 \pm 0.5$  nm and  $9.7 \pm 0.5$  nm for PSSA-104k and PSSA-273k, respectively. It should be noted that, however, at comparable solution concentrations the size of the particle for the PSSA-273k is relatively larger than that for the PSSA-104k. The width of the peak at its half height shows a similar trend. From these findings, one could speculate that when the molecular weight of the acid form copolymer is relatively low (e.g., PSSA-37k) and the concentration of the polymer solution is relatively high (e.g.,  $2.0 \times 10^{-4}$  g/mL), the polymer chains form colloidal particles that aggregate together through the interactions between the relatively non-polar surfaces of the colloids via van der Waals forces. According to the thermodynamic aspect, one can expect that when the concentration of the polymer solution decreases, the colloidal particles dissociate themselves from the large aggregates, which might be what we observed here. If this were the case, the size of the dissociated particles would not be changed significantly upon further dilution. At this point, it should also be mentioned that if the MW of the copolymer were low and the colloidal particle had a critical size to be stable in aqueous solution owing to the thermodynamic aspects (e.g., balance between the enthalpy and entropy of particle formation in solution), it could be thought that the colloid could contain more than one polymer chain. If this speculation were applicable here, the size of the particle of low MW polymer might be slightly larger than that of high MW polymer, which might contain only one polymer chain. When the molecular weight of the copolymer is relatively high and larger than the critical mass to make a stable colloid, the polymer chains

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form stable colloids but not larger aggregates. It should be noted that in the cases of the copolymers of PSSA-273k and PSSA-104k the average size of the colloidal particles increases slightly with increasing MWs of the copolymers at comparable solution concentrations. This could be understood; the higher MW copolymer has a longer chain, which naturally leads to the formation of a larger colloidal particle.

In the case of the sodium-neutralized ionomers, the diameters of the colloidal particles as a function of solution concentration are shown in Figure 3. Unlike the acid copolymer samples, the average sizes of particles for the three ionomers of different MWs seem to increase slightly with decreasing solution concentration. It is also observed that the NaSPS-37k ionomer in the solution concentration of  $2.0 \times 10^{-4}$  g/mL does not form large aggregates of colloidal particles. From this finding it can be speculated that the neutralization of the acid groups of the copolymers makes the nature of the copolymer more hydrophilic, and then this strong hydrophilicity of the ionomer, not the low polarity of polystyrene moieties, starts to control the behavior of the colloids in an aqueous solution. Thus, the ionomers do not show aggregation behavior but exhibit polyelectrolyte behavior. The slow increase in the diameter of the particles on dilution can also be understood. Upon the dilution, the cations of the ionomers separate from sulfonate anions that reside on the surface of the colloidal particles. Thus, the dilution results in more repulsion between the anions on the colloid surface, which, in turn, induces the expanding of the colloid surface and the slight enlargement of the colloid size. In Figure 3, it is also seen that the average particle size at the same solution concentration is largest for the NaSPS-37k, lowest for the NaSPS-104k, and in the middle for the NaSPS-273k. This finding is similar to the results obtained from acid samples. As expected, the peak width shows a similar trend.



Fig. 3. Diameters of the colloidal particles of Na-neutralized sulfonated polystyrene (NaSPS) ionomers of different MWs in THF/water (1/99 v/v) mixture as a function of solution concentration.

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## 4. CONCLUSION

In the present work, the colloidal particle sizes and the size distributions of the sulfonated polystyrene of three different MWs were determined. It was found that the size of colloidal particle of PSSA-37k copolymer decreased drastically with decreasing solution concentration and then remained more or less constant at ca. 11 nm. This suggested that at relatively high concentrations the colloids aggregated together due to the interactions between particles having relatively non-polar surface. Upon dilution, the particles dissociated from the large aggregate. However, in the cases of PSSA-273k and PSSA-104k copolymers, the size of the particles did not change much with the solution concentration, with the average size of the particles of the PSSA-273k being slightly larger than that of the PSSA-104k at the same solution concentration. This indicated that the higher MW copolymer had longer polymer chains, and, thus, the colloidal particle would be larger, compared to the lower MW copolymer case. The size of the PSSA-37k was found to be largest: this implied that, since the length of the polymer chain was relatively short, the colloidal particle might contain more than one polymer chain. In the case of the ionomers, the size of the particles increased slightly upon dilution, indicating that the system showed polyelectrolyte behavior. As expected from the results obtained from the acid copolymers, the average size of the particles of the ionomers in aqueous solution was in the order of NaSPS-37k > NaSPS-273k > NaSPS-104k at the same solution concentration.

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# Formation of the Colloidal Particles of Sulfonated Polystyrene lonomers Neutralized with Either Na(I) or Ba(II) in THF/Water (1/99) Mixture

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The sizes of colloidal particles in THF/water (1/99 v/v) of the sulfonated polystyrene copolymers containing 2.1, 5.1 and 9.4 mol% of either acidic or ionic repeat units were determined using a dynamic light scattering technique. It was observed that for the acid copolymer containing 2.1 mol% of acidic units the size of the particle and size distribution decreased significantly as the solution concentration decreased from  $2.0 \times 10^{-4}$  to  $5.0 \times 10^{-6}$  g/mL. However, when the content of acidic units increased to 5.1 and 9.4 mol%, the size of the particles and size distribution increased slightly with decreasing solution concentrations. It was also found that the neutralization of the acid group with Na(I) induced the slow increase in the diameter of colloidal particles of the ionomers with decreasing solution concentration, and that the size of the colloids decreased with increasing ion contents. Thus, it was suggested that the former and latter findings could be understood using the polyelectrolyte effect and charge density concepts, respectively. For the ionomers neutralized with Ba(II), it was found that the size of the colloids were not easily separated by the ultrasonication. Thus, it was speculated that the Ba(II) cations placed inside the aggregates of hydrophobic environment acted as the links between colloidal particles.

Keywords: Ionomer, Ionization, Colloids, Aggregates, Cation, Size.

## **1. INTRODUCTION**

Ion-containing polymers can be classified into two families: polyelectrolytes and ionomers. The former has ionic groups usually in every single repeat unit, but the latter has a relatively small amount of ionic groups along nonpolar polymer backbone chains. When one considers the hydrophilicity of the ionic groups and the relative amounts of the ionic groups in the polyelectrolytes and ionomers, one can expect that the polyelectrolytes can be dissolved in water easily but the ionomers cannot. This limited solubility of the ionomers in water leads to the formation of nano- and micrometer sized colloidal particles. It was found that the solvent of high polarity makes the ionomer behave like polyelectrolyte, which is due to the repulsive interaction between pendant ionic groups attached to the polymer main chains.<sup>1–6</sup> In the case of the solvent of low polarity, however, the ionic groups of the ionomer form

aggregates, which is due to electrostatic attractive interaction between fixed ions and counter-ions that are excluded from the non-polar polymer matrix and solvent.<sup>7</sup>

When one dissolves a di-block ionomer, i.e., a block copolymer containing a non-ionic block and an ionic block, one can find that the di-block ionomer shows multiple morphology, depending on the solvent, block length, the ratio of two block lengths, and so on.<sup>8,9</sup> This makes the block ionomers a very interesting ionomer family that can find their applications in possible encapsulation materials, drug delivery agents, and nano-reactors. At this point, it should be mentioned that the block ionomers, having relatively monodispersive molecular weight, resemble surfactants, to a certain extent. Therefore, extensive studies on this system have been carried out by a number of research groups. The difference in the surfactant and the block ionomer is that the number of ionic units of the surfactant is usually only one, but the lengths of the ionic and non-ionic blocks can be changed as we need.

Commercially available ionomers are random ionomers, have polydispersive molecular weights, and the position

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of the ionic groups along the chains is random. As expected, the random structures cause the complication in the interpretation of the morphology of random ionomers in solution. In the case of polystyrene ionomers, the styrene ionomer is not dissolved easily in water for the non-ionic non-polar polymer backbone segments are hydrophobic. Therefore, only a few studies on the styrene ionomer in aqueous solution have been reported.<sup>10-18</sup> In the case of poly(styrene-co-methacrylate) ionomers, Liu et al. observed a bowl-shaped morphology in the waterinduced self-assembly of an acid form random copolymer of poly(styrene-co-methacrylic acid).<sup>15</sup> Park et al. investigated the aggregation behavior of poly(styreneran-methacrylic acid) (PSMAA) copolymers in water using a SEM technique.<sup>16</sup> It was found that the unneutralized copolymer formed spherical particles, with the average size of ca. 160 nm, and that the sizes did not altered by the acid content. The neutralization of the acid groups with NaOH caused the formation of network-like feature consisting of much smaller particles (<50 nm), compared to those of the acid copolymers. As the ionization level increased, the boundary of formed networks became unclear, indicating the transition of spherical-to-tubular structures. The group of Wu reported that Na-sulfonated polystyrene (PSSNa) ionomers formed nano-size colloidal particles in water.<sup>10-13</sup> It was found that the average diameter of the nano-particles was in the range of 5-12 nm, and that the sulfonation level, the concentration of the stock solution, and the mixing order changed the particle sizes.<sup>10</sup> However, the formation of colloidal particles of the acid form copolymers and the effect of the neutralization of the acid copolymer with Ba(II) on the colloidal particle sizes, compared to the Na(I)-neutralized ionomers, have not been explored. Thus, in the present work, we attempted to study the effects mentioned above using a light scattering technique.

### 2. EXPERIMENTAL DETAILS

#### 2.1. Sample Preparation

Polystyrene ( $M_w = ca. 580,000$  and polydispersity index = ca. 1.6) was prepared by bulk free-radical polymerization using benzoyl peroxide as the initiator. For homogeneous sulfonation, the modified method of Makowski et al. was used to obtain the poly(styrene-*co*-styrenesulfonic acid) samples.<sup>19</sup> To determine the acid content, the samples were dissolved in a benzene/methanol (9/1 v/v) mixture to make a 5% (w/v) solution, and titrated with standard methanolic NaOH to the phenolphthalein end point; the acid contents were found to be 2.1, 5.1 and 9.4 mol%. For neutralization of the acid groups, a predetermined quantity of methanolic base solution in a benzene/methanol (9/1 v/v) mixture. The bases used to neutralize the acid groups were NaOH and Ba(OH)<sub>2</sub>. The solutions were freeze-dried and then

dried further under a vacuum at 130 °C for 24 h. To make ionomer solutions, firstly, the ionomers were dissolved in a mixture of tetrahydrofuran (THF)/water (9/1 v/v): the concentration of the ionomer stock solutions was  $2.0 \times$  $10^{-2}$  g/mL. To obtain ionomer dispersions in the solutions of various concentrations, the ionomer stock solution was diluted with water and THF to make the ratio of the mixed solvents of THF/water (1/99 v/v) under ultrasonication. Before the measurement of the particle sizes, the solutions were filtered using a polytetrafluoroethylene (PTFE) filter of 0.45  $\mu$ m pore size. At this point, it should be mentioned that the filtration of the Ba-ionomer solutions was not easy, indicating that the neutralization of the acid groups with divalent cation caused the formation of large aggregates in solution, and that the sizes of these aggregated particles were too large to pass through the pore of the filter. Thus, we prepared the Ba-ionomer solution without filtration.

#### 2.2. Dynamic Light Scattering Measurements

For the particle size analysis, a Melvern Zetasizer Nano-S instrument with a 633 nm He-Ne "red" laser (4.0 mW) was employed. The scattered intensity was registered using an avalanche photodiode detector at room temperature.

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### 3. RESULTS AND DISCUSSION

As suggested by Li et al.,<sup>10</sup> the sulfonated polystyrene in water is thought to form stable colloidal particles. Figure 1 shows the dynamic light scattering diagram of the acid form copolymer containing 2.1 mol% of acid groups in the solution of various concentrations as a function of the



**Fig. 1.** Typical dynamic light scattering diagram of the stable colloidal particles of acid copolymer in THF/water (1/99 v/v) mixture as a function of size of the particles.

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diameter of the particles in solution. It is seen that the position of the peak maximum is located at *ca*. 17 nm in diameter for the  $2.0 \times 10^{-4}$  g/mL sample, and that it shifts to smaller diameters with decreasing solution concentration, i.e., the positions of the peak show at *ca*. 13 and 12 nm for  $5.0 \times 10^{-5}$  and  $1.0 \times 10^{-5}$  g/mL samples, respectively. It is also seen that for the solution of highest concentration, the peak is relatively broad and shows a shoulder-like feature at *ca*. 9 nm. This indicates that in the solution of highest concentration, the colloidal particles formed have a relatively broad size distribution.

From the diagram, one can obtain the average diameter of the particles and the width of the main peak at its half height. The peak broadening might be partly due to the polydispersity of the molecular weight of the starting material, i.e., polystyrene. Figure 2 shows the diameter of the particles and the peak width at half height of the acid form samples as a function of the solution concentration. It is clear that the diameter of the 2.1 mol% acid sample decreases with decreasing solution concentration. It is also seen that the width of the peak at half height decreases drastically with decreasing solution concentration. From these results, one could suggest that when the solution concentration is relatively high but the amount of the hydrophilic acid groups is not enough to show an effective hydrophilicity of the colloidal surface, the colloidal particles would form aggregates with another particles through the interactions between relatively non-polar colloidal particles. If this is the case, one should see both single colloids and their aggregates, leading naturally to the broad distribution of the particle sizes. Upon the dilution of the polymer solution, the aggregated colloidal particles become separated due to the thermodynamic factor, i.e., increasing entropy. Once the particles are separated, and, then, the average size of the particles and the size

distribution do not change much with dilution. In the cases of the copolymers containing 5.1 and 9.4 mol% of acid groups, however, the particle sizes and the size distribution are found to increase slightly with decreasing solution concentration. This indicates that once the amount of the acid groups is enough for the colloidal particles to show the characteristics of hydrophilic surface, the relatively stable colloidal particles are formed and the average size of the particles increases upon the dilution. At this point, it should be mentioned that some of the acid groups are ionized to give  $-COO^-$  H<sup>+</sup> ion pairs. This implies that the surface of the colloids becomes ionized, to a small extent. If this is the case, the dilution induces the wide separation between ionized species, leading to more repulsion between anionic groups attached directly to the surface of the colloids; i.e., showing a polyelectrolyte effect. This, in turn, results in the enlargement of the colloidal particles; this might be what we observed here. At 9.4 mol%, the amount of the acid groups and ionized groups might be enough to make stable colloidal particles and show a stronger polyelectrolyte effect, compared to 5.1 mol% copolymer. Thus, the size of the particles is larger than that of the 5.1 mol% copolymer at a comparable solution concentration and increases slightly with the dilution process. At very diluted solution, all the copolymers show very similar diameters.

In Figure 3, it is seen that the diameter of the colloidal particles of the Na-ionomers, which is in the range of the diameters reported by Li et al.,<sup>10</sup> increases upon dilution, except for 2.1 mol% ionomer in  $2 \times 10^{-4}$  g/mL. It is also seen that the average size of the ionomers is biggest for the 2.1 mol% ionomer and lowest for the 9.4 mol% ionomer; accordingly, the size distribution shows a similar trend. In the case of the 2.1 mol% ionomer in  $2 \times 10^{-4}$  g/mL,



Fig. 2. Diameters of the colloidal particles of acid copolymers in THF/water (1/99 v/v) mixture as a function of solution concentration.



Fig. 3. Diameters of the colloidal particles of Na(I)-neutralized ionomers in THF/water (1/99 v/v) mixture as a function of solution concentration.

the diameter of the colloidal particles decreases upon dilution. Again, this might be due to the separation of single particles from the aggregation of colloidal particles. The increase in the average diameter by the dilution can be understood. As mentioned above, the dilution process induces the wider separation of cations, i.e., Na(I), from anions, i.e., carboxylates, attached to the polymer chains and residing on the surface of the colloidal particles. Thus, the dilution results in more repulsion between anions, i.e., a stronger polyelectrolyte effect; thus, the average size of the colloids increases. It should also be noted that the average size of the particle decreases slightly with ion contents, which is different from the findings in the acid samples. As the ion content increases, the hydrophilicity of the surface of the colloids enhances. If there were a critical amount of ions on the colloid surface, i.e., a critical charge density, to form a stable particle and the ion contents were higher than that content, the size of the colloid should decrease with increasing ion content of the ionomer. In that way, the ionomer particles can have a similar amount of the ions on the surface, i.e., maintain a similar charge density. In the case of the acid samples, the degree of ionization of the carboxylic acids in water is too low for the acid copolymers to be considered "common" ionomers. Thus, the concept of the critical charge density is not applicable to the acid copolymers.

For the Ba(II)-neutralized ionomers, the diameters and peak widths are shown in Figure 4. First of all, it should be mentioned that in the bulk Ba-ionomers the Ba(II) cations needs two carboxylate anions to form ionic aggregates. When the ionomers are dissolved in water, the ionomer chains rearrange themselves to form particles consisting of the non-polar polystyrene chains inside and the ionic

△ 9.4 mol% 90 Diameter (nm) 60 30 0 1e-5 1e-4

Fig. 4. Diameters of the colloidal particles of Ba(II)-neutralized ionomers in THF/water (1/99 v/v) mixture as a function of solution concentration.

gram, it is seen that some samples show more than one peak, which indicates the formation of aggregates of the particles in various sizes. In addition, this implies that the ultrasonication could not make the complete separation of the aggregated colloidal particles linked with Ba(II). In Figure 4, the data obtained from the major peak are also present as filled symbols. It is seen that the trend of the data for the major peaks is similar to that found in Na-ionomers, i.e., the decreasing and slight increasing diameters for the 2.1 mol% ionomers and the ionomers of higher ion contents, respectively. It is also seen that some of the data show that the average diameters as a function of solution concentration of the ionomer particles of various ion contents are placed in the range of 8 to 16 nm, which is similar to that of the Na-ionomers. This implies that the size of the colloidal particle of the Ba-ionomer in a mixed solvent of THF/water is indeed similar to that of the Na-ionomer, and the particles reside in the solution both singly and in aggregated forms. From this result, we could speculate that some of Ba(II) cations acting as links between colloidal particles reside inside the large aggregate of colloids. In other words, the links, i.e., Ba(II) and two carboxylate anions, are surrounded by the hydrophobic polystyrene colloids. If this is the case, water molecules cannot penetrate into the colloids aggregates, and, thus, the links remain intact, and, thus, the size of the colloids depends on external factors, such as the sample preparation methods.

groups on the particle surface. In the light scattering dia-

#### 4. CONCLUSION

The size of the particle and the size distribution were found to increase slowly with decreasing solution concentration for the 5.1 and 9.4 mol% acid copolymers, which was due to the relatively weak polyelectrolyte effect. On the other hand, the particle size and size distribution decreased significantly for the 2.1 mol% acid copolymer. This might due simply to the separation of the aggregated colloidal particles. In the case of Na-ionomers, the diameter of colloidal particles increased slightly with decreasing solution concentration, and the size of the colloids at comparable solution concentrations decreased with increasing ion contents. The increase in diameter was probably due to the polyelectrolyte effect, and the decrease in diameter could be interpreted using a charge density concept. For the Ba-ionomers, both the single colloidal particles and the aggregates of the single particles were found in the solution. In addition, the size of the single particle was similar to that of the Na-ionomer, which suggested that the Ba(II) cations were placed inside the aggregates and acted as the links between colloidal particles.

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## Randomly Sulfonated Liquid Crystalline Polymers Containing Triad Mesogen of Butylene Terephthalate

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A thermotropic liquid crystalline polymer (LCP) containing a terephthaloyl bis(4-oxybenzoyl) (Triad) rigid moiety and a butylene terephthalate flexible unit was solution-polymerized and was subsequently partly sulfonated. It was found that the introduction of sulfonic acid groups to the LCP did not change the position of the DSC peak for the nematic-to-isotropic transition of the LCP ( $T_{n.i}$ ). However, the sulfonation induced a peak related to the melting of crystalline phase of the Triad domains ( $T_{m(T)}$ ). When the acid groups of the sulfonated LCP were neutralized with NaOH, the  $T_{n.i}$  DSC peak shifted to lower temperatures with a strong decrease in its size, but the  $T_{m(T)}$  DSC peak did not change its position strongly. Furthermore, a new peak for the melting of crystalline phase of the butylenes domains ( $T_{m(BT)}$ ) appeared at much lower temperatures. The above results suggested that the sulfonation introduced ionic characters to the TLCP polymer successfully; as expected, it changed the liquid crystalline characters of the TLCP significantly.

Keywords: ionomer; liquid crystalline; mesogen; nematic

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### **1. INTRODUCTION**

Ionomers are polymers that contain a relatively small amount of ionic groups along the relatively non-polar polymer backbone chains [1,2]. In comparison with non-ionic polymers, the ionomers show improved mechanical and physical properties; e.g., high melt viscosity, enhanced dimensional stability, and conductivity. These enhanced properties are caused by the formation of ionic aggregates, i.e., multiplets, in the matrix phase of low dielectric constants. According to the Eisenberg-Hird-Moore (EHM) model for random amorphous ionomers, the multiplets reduce the mobility of chains surrounding them [3]. The size of the single reduced mobility region surrounding the multiplet is assumed to be in the range of ca. 2–3 nm [3]. In addition, the size of the multiplet and restricted mobility region is one of the key factors controlling the physical properties of the ionomers [1,2].

In general, liquid crystalline polymers have either rod-like structures or spherulitic molecular structures and are classified as materials that have the properties of both liquid crystals and polymers, and, thus, exhibit both mesophase characteristic of liquid crystals and many of the useful properties of polymers [4]. The major problem found in common non-ionic liquid crystalline polymers is, however, their very weak interactions between the polymer chains, leading to poor transverse properties of the oriented, extruded polymer samples and weak shear and compressive strengths. This is due to the high stiffness of polymer chains, which results in only few chain entanglements. From these non-ionic liquid crystalline systems, we anticipate only weak disperse forces between the polymer chains. One can find the solution to solve this problem by the introduction of functional groups to the polymer chains to generate specific interactions between the polymer chains. Among the specific interactions, an ionic interaction is the most effective interaction because it is strongest among secondary interactions. Therefore, the synthesis and characterization of liquid crystalline ionomers have been studied extensively [5–16].

The liquid crystalline copolymer containing terephthaloyl bis(4-oxybenzoate) (Triad) mesogen with a butylene terephthalate flexible segment was synthesized by the Group of Lenz [17,18]. This Triad LCP is known as a thermotropic liquid crystalline polymer that shows its liquid crystalline transitions in the temperature range of ca. 250–290°C. In the present work, we prepared new liquid crystalline ionomer system via the synthesis of non-ionic liquid crystalline polymer based on a triad mesogen with a butylene terephthalate flexible segment and the subsequent conversion of this polymer to ionic LCP via sulfonation (see Scheme 1).





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SCHEME 1 Synthetic route for the preparation of ionic LCP.

## 2. EXPERIMENTAL

## 2.1. Materials

Liquid crystalline polyester (LCP) containing Triad units was prepared using the method reported elsewhere [18]. For homogeneous sulfonation, the method developed by Makowski et al. was used to obtain the sulfonated LCP (SLCP) sample [19]. For the readers' convenience, only a short procedure is given below. The LCP was dissolved in a mixture of 1-chloronaphthalene/1,2-dichloroethane, and different amounts of acetyl sulfate were added slowly to the polymer solution to obtain desired degrees of sulfonation. The reaction temperature was kept at 60°C, and the reaction time was 1 h. The samples were recovered by precipitation into hot water, filtered and washed several times with water and subsequently with ethanol. The filtered samples were then dried under a vacuum at 100°C for 1 day. The chemical structure of the acid form of LCP polymer is shown in Scheme 1. To determine the acid contents of the SLCP polymers, the samples were dissolved in a benzene/methanol (9/1/v/v) mixture to make a 5% (w/v) solution, and titrated with standard methanolic NaOH to the phenolphthalein end point. The acid contents were found to be 0.279, 0.345, and  $0.457 \,\mathrm{mmol/g}$ . For the neutralization of the acid groups of the SLCPs, the predetermined amount of NaOH was added to the polymer in a benzene/methanol mixture. The sodium-neutralized samples (Na-SLCPs) were freeze-dried and dried further under a vacuum at 130°C for 1 day.

## 2.2. Thermal Property Measurements

For the measurements of the thermal properties of the LCP, SLCPs and Na-SLCP samples, TA differential scanning calorimeter DSC 3000 and Thermogravimetric Analyser TGA 2050 (New Castle, DE) were used. The DSC was calibrated with indium. The sample cell containing ca. 8 mg of a sample was stored under a nitrogen atmosphere.







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The samples were scanned from  $30^{\circ}$ C to  $300^{\circ}$ C to span the transition temperatures of the samples, and the heating rate was  $20^{\circ}$ C/min. The DSC data were obtained from the second scan. In the case of the TGA study, the heating rate was  $20^{\circ}$ C/min, and the samples were heated to  $600^{\circ}$ C.

# 2.3. X-Ray Diffraction and Polarized Light Microscopy

The x-ray diffraction (XRD) patterns of the samples were recorded using a PANalytical x-ray diffractometer X'pert PRO MPD (Almelo, the Netherlands). The Cu radiation ( $\lambda = 0.1542$  nm) was utilized, and the power of the x-ray generator was 40 kV and 30 mA. The scanning speed and the sampling width were 1°/min and 0.05°, respectively. For the morphological study, a Carl Zeiss AG's cross polarized-light microscope (Oberkochen, Germany) equipped with Linkam Scientific Instruments THMS 600 hot stage (Surrey, United Kingdom) was utilized.

# 3. RESULTS AND DISCUSSION

Figure 1 shows DSC thermograms of the non-ionic LCP, SLCPs and Na-SLCPs. In the case of the LCP, an endothermic peak starts to appear at ca. 275°C, and the peak maximum locates at ca. 290°C that is a so-called isotropic temperature for a phase transition from a nematic liquid crystalline phase to an isotropic liquid,  $T_{n-i}$ ; the texture type of liquid crystalline phases will be discussed later. This result is in good accordance with the results reported by the group of Lenz [18]. As expected, the exothermic peak was also detected at ca. 270°C, when



FIGURE 1 DSC thermograms for LCP, SLCP, and Na-SLCP polymers.



the sample in an isotropic liquid form was cooled down to room temperature. The second heating showed the endothermic peak, again, at the same temperature, i.e., ca. 290°C (not shown here).

In the case of the SLCP polymers, the endothermic peak for the nematic-to-isotropic transition is seen at similar temperatures in comparison with to the peak of the LCP. In addition, a weak endothermic peak is shown at ca. 250°C, which is due to the transition of a crystalline phase of the Triad domains to a nematic phase of the polymer  $(T_{m(T)})$  [18]. These transition temperatures are listed in Table 1. The positions of the two peaks seem to change only slightly with increasing degree of sulfonation, and the size of the peak at ca. 290°C decreases a little. The presence of the two peaks for the SLCP, instead of only one peak for the LCP, implies that the introduction of the sulfonic acid groups to the LCP results in hydrogen bonding between polymer chains, which, in turn, leads to the formation of the liquid crystalline domains of Triad segments, to some more extent. At the same time, the introduction of the acid groups induces irregularity in a chemical structure of the polymer chain segments, which decreases the degree of the crystallinity of polymers, as a whole. Thus, the size of the  $T_{\rm m(T)}$  peak becomes more noticeable, and the  $T_{\rm n-i}$  peak at ca. 290°C, related to the amount of crystalline domains, decreases in its size slightly with increasing degrees of sulfonation.

For the Na-SLCP ionomer system, two peaks related with  $T_{n-i}$  and  $T_{m(T)}$  are also observed. In addition to the two peaks, however, a third peak at ca. 165°C is also seen, which is due to the melting of the crystalline domains of butylene terephthalate (BT) moieties [18].

Samples	Contents of functional groups (mmol/g)	$T_{ m m(BT)}$ (°C)	$\Delta H \ (J/g)$	$T_{ m m(T)}$ (°C)	$\Delta H \ (J/g)$	$T_{ ext{n-i}}$ (°C)	$\Delta H \ (J/g)$
LCP	0	_	_	_	_	288.7	18.19
SLCP-2	0.279	_	_	247.0	0.17	285.3	16.70
SLCP-3	0.345	_	_	248.9	1.12	289.1	15.89
SLCP-4	0.457	_	_	249.3	1.62	287.6	11.60
Na-SLCP-2	0.279	166.4	3.59	251.2	2.82	276.7	8.09
Na-SLCP-3	0.345	165.9	3.63	249.2	2.60	274.3	7.21
Na-SLCP-4	0.457	165.6	3.85	251.5	4.10	266.9	4.43

**TABLE 1** Contents of the Functional Groups, Melting Temperatures of the Crystalline Regions of BT Units  $(T_{m(BT)}s)$  and Triad Units  $(T_{m(T)}s)$ , and the Temperatures for Nematic-to-isotropic Transitions  $(T_{n-i}s)$ , Obtained from DSC Thermograms



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It is seen that the position of the  $T_{n-i}$  peak shifts to low temperatures significantly and that upon neutralization it moves to lower temperatures slowly as the ion content increases; in addition, the size of the peak becomes smaller. However, the position of the  $T_{m(T)}$  peak seems to be unchanged at ca. 250°C. At this point, it should be mentioned that the presence of the three peaks for the Na-SLCP ionomers indicates that the neutralization results in the formation of the crystalline domains of BT moieties, to some extent, in addition to the crystalline domains of Triad moieties,. This can be understood. In the case of SLCPs, only the H-bonding between polymer chains leads to the formation of crystalline domains containing Triad moieties. However, the BT units, rather flexible sequences, do not form crystalline domains easily. Once the acid groups are neutralized with NaOH, the interactions between the ionic groups of polymer chains would make polymer chains close together. Then, the polymer chains have more chance to form crystalline domains containing BT units. At this point, it should be mentioned that ionic interactions between polymer chains reduce the mobility of chains significantly. Thus, it is not easy for the polymer chains to form a nematic phase in the temperature range for the LC behavior. As a result, the position of the  $T_{n-i}$  peak shifts to lower temperatures strongly, and the size of the  $T_{n-i}$  peak decreases with increasing ion contents.

Shown in Figure 2 are the photomicrographs with crossed polarizers of the LCP, SLCPs, and Na-SLCPs, taken at the temperature where the polymers showed typical liquid crystalline textures. In the case of the LCP, showing a typical nematic liquid crystalline texture (see Fig. 2(a)), it shows a birefringence at ca.  $250^{\circ}$ C, and flow behavior at ca. 275°C, and becomes an isotropic liquid at ca. 320°C. In the cases of SLCP polymers, also giving rise to a nematic liquid crystalline texture (see Figs. 2(b), (c) and (d)), the polymers show a birefringence at ca. 240°C and flow behavior at ca. 265°C, and become an isotropic liquid at ca. 310°C. In comparison with Figures 2(b) and (d), it is seen that the increasing amounts of acid groups in the SLCPs reduce slightly the size of the regions that show liquid crystalline behavior. In the cases of Na-SLPCs, at ca. 160°C the ionomers give rise to a nematic liquid crystalline texture (see Figures 2(e), (f) and (g)) and flow behavior at ca. 225°C, and the ionomers became an isotropic liquid at ca. 280°C. Figures 2(e), (f) and (g) show that the size of the liquid crystalline phases of Na-SLCP ionomers decreases strongly upon neutralization. These slight and strong decreases in the size of the liquid crystalline phases of the SLCP and Na-SLCP polymers, respectively, found in photomicrographs are in good accordance with the relative sizes of the DSC  $T_{n-i}$  peaks of the corresponding polymers.



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(g)

**FIGURE 2** Photomicrographs with crossed polarizers of (a) LCP, (b) SLCP-2, (c) SLCP-3, (d) SLCP-4, (e) Na-SLCP-2, (f) Na-SLCP-3, and (g) Na-SLCP-4 polymers.

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Shown in Figure 3 are the x-ray diffraction (XRD) patterns of the LCP, SLCP, and Na-SLCP polymers. It is seen that the LCP polymer shows XRD peaks at  $2\theta = 18^{\circ}$ ,  $23^{\circ}$ , and  $27^{\circ}$ . Generally, it is known that nematic liquid crystalline materials show XRD peaks mainly in the angle  $(2\theta)$  range  $17^{\circ}$ - $30^{\circ}$ . Thus, the XRD results of the LCP in the present study support that the LCP has, indeed, a nematic liquid crystalline phase. In the case of the SLCPs, the XRD peaks in their positions and sizes are very similar to those of the LCP. In the case of Na-SLCP ionomer, however, even though the positions of the peaks are the same, the sizes of the peaks are relatively smaller than those of the LCP and SLCPs. At this point, it should be mentioned that the same positions of the XRD peaks imply that the structures of the polymer chains in the crystalline domains are identical. The decreasing size of XRD peak, however, indicates that the amount of the liquid crystalline domains decreases. Again, the trend in the XRD peak sizes is in good accordance with those found in both the DSC results and the photomicrographs, as mentioned above. This implies that the introduction of the acid group to the LCP and the neutralization affect the liquid crystalline behavior of the polymer slightly and strongly, respectively.

Figure 4 shows the weight loss of the samples studied here as a function of temperature. The temperatures of 5% weight loss  $(T_{d-5\%})$  are listed in Table 2 that also includes the temperatures at which the maximum loss rate occurred  $(T_{d-max})$ , and the weight percentages of the sample residue at 550°C. First of all, the  $T_{d-5\%}$  of the SLCPs decreases with increasing acid contents. This might be due to the fact



FIGURE 3 XRD patterns of LCP, SLCP-4, and Na-SLCP-4 polymers.

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## Randomly Sulfonated Liquid Crystalline Polymers



FIGURE 4 TGA results of LCP, SLCP, and Na-SLCP polymers.

that the presence of sulfonic acid groups in polystyrene is known to initiate thermal decomposition above 200°C [20]. Thus, in the present work, the decreasing  $T_{d-5\%}$  of SLCPs with increasing acid contents can be understood. In the case of Na-SLCP ionomers, they start to decompose at lower temperatures than the LCP and SLCPs and the  $T_{d-5\%}$  decreased drastically from ca. 382°C for the LCP to 318°C for Na-SLCP-2 and then increased to ca. 335°C for Na-SLCP-4 with increasing ion contents. At this point, we do not have any clear explanation for this finding. However, it is worth recalling that once the acid groups are neutralized with NaOH, the amounts of liquid crystal-line domains decrease significantly. The  $T_{d-max}$ s of all the samples remain more or less constant at  $419 \pm 2.5$ °C. These thermal degradation results along with the DSC and XRD results suggest that the

Samples	$T_{ m d -5\%}(^\circ{ m C})$	$T_{ ext{d-max}}\left(^{\circ} ext{C} ight)$	Residue at 550°C (%)
LCP	381.6	421.8	24.6
SLCP-2	381.8	420.5	14.7
SLCP-3	371.4	420.0	15.1
SLCP-4	362.4	415.1	15.5
Na-SLCP-2	317.8	419.3	15.9
Na-SLCP-3	321.6	419.2	17.5
Na-SLCP-4	334.6	415.1	18.5

**TABLE 2** Thermogravimetric Analysis of the LCP Polymer, SLCPCopolymers and Na-LCP Ionomers





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 $T_{d-5\%}$  is related with the amount of crystalline domains as a whole, and the  $T_{d-max}$ s is dependent mainly on the chemical structure of the LCP polymer backbone chains.

## 4. CONCLUSIONS

This study showed that the sulfonation of the LCP copolymer gave ionic characters to the LCP polymer successfully. At the same time, the ionization of the LCP changed the liquid crystalline character of the TLCP significantly; i.e., the formation of crystalline regions containing either Triad units or BT units and the disruption of the LC phase as a whole.

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## Dynamic Mechanical Properties of Polystyrene lonomers Containing Both Carboxylate and Sulfonate Anionic Groups

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**ABSTRACT:** Polystyrene-based ionomers possessing sodium methacrylate (MA) and sodium styrenesulfonate (SS) units in each polymer chain [poly(styrene-*co*-methacrylate-*co*-styrenesulfonate) (PSMA-SS)] were synthesized. The dynamic mechanical properties of PSMA-SS ionomers were studied and compared with those of styrene ionomers containing only MA (PSMA ionomer) or SS (PSS ionomer) units. It was observed that the ionic moduli of PSMA-SS ionomers depended directly on the total ion content and that the ionic modulus was highest for the PSMA ionomer and lowest for the PSMA-SS ionomer. The matrix  $T_{g}$ s of the three ionomer systems were found to be similar

**INTRODUCTION** Ionomers are polymers containing a small amount of ionic groups along the polymer chains of a relatively low dielectric constant. Since their first appearance in the market in 1965 under the trade name "Surlyn," the ionomers have been studied widely because they show unique physical properties caused by the interactions between the ionic groups.<sup>1–3</sup> One can find, using SciFinder, that ionomers can serve in a wide variety of applications; some of the examples include ionomer coating, drilling fluids, ionic elastomers, catalytic supports, ionomer plastics, superpermselective membranes for fuel and chlor-alkali cells, electroactive membranes, membranes for energy storage, self-healing smart materials, and nanoparticles for delivery of drugs, genes, and imaging agents.

The ionic groups of the ionomer form ionic aggregates, socalled multiplets, because of the electrostatic interactions between ionic groups and the difference in polarities of polymer hydrocarbon matrix and ionic groups. According to the EHM (multiplet/cluster) model for amorphous random ionomers, the multiplets reduce the mobility of polymer chain segments in the vicinity of the multiplets.<sup>4</sup> When the ion concentration of an ionomer is very low, the number of to each other; the cluster  $T_g$  of PSMA-SS ionomer was higher than that of PSS ionomer at low SS contents but became closer to each other at high SS contents. In addition, the small-angle X-ray scattering study revealed that the multiplet size might be in the following order: PSMA-SS > PSS > PSMA. This implied that at the same ion content, the fractions of cluster regions were smallest for PSMA-SS ionomer in comparison with those of PSS or PSMA ionomers. © 2012 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 50: 1181–1187, 2012

KEYWORDS: glass transition; ionomers; mechanical properties

multiplets is so small that the regions of reduced mobility cannot overlap, and the ionomer shows only the glass transition ( $T_g$ ) of nonionic polymer matrix, that is, matrix  $T_g$ . With increasing ion content, however, the number of the multiplets increases, and, thus, the regions of the reduced mobility start overlapping. When the size of the regions of the reduced mobility become large enough to have their own  $T_g$ (i.e., cluster  $T_g$ ), the regions are called clusters. At this stage, the ionomer shows two  $T_gs$ ; the one at low temperatures for the matrix  $T_g$ , and the other at high temperatures for the cluster  $T_g$ . In addition, the ionomer exhibits an "ionic" plateau in the plots of log(storage modulus) versus temperature, which is related, in part, with the degree of clustering and is shown in the temperature range between the matrix and cluster  $T_gs$ .<sup>3,4</sup>

It is well known that the size, charge, position, and type of anionic groups attached to the polymer chain affect the cluster  $T_{\rm g}$  of ionomers significantly.<sup>3</sup> So far, however, most of the studies on the bulk properties of ionomers have dealt with ionomers containing only one type of anionic groups, for example, either sulfonate or carboxylate ionic groups, and the mechanical properties of the ionomers containing two

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different types of anionic groups have remained widely unexplored. Among a few studies on the mechanical properties of ionomers having sulfonate and carboxylate ionic groups, one study on model polyurethane ionomers containing both sulfonate and carboxylate ionic groups was done by Visser and Cooper.<sup>5</sup> The authors found that the stress and strain at break changed as predicted on the basis of the acid strength of the ionomers. On the other hand, they also observed that in a very low strain range, the stress values of the ionomers containing the mixed anionic groups were higher than those of the ionomers containing only one type of ionic group. Thus, they suggested that the combination of two different anionic groups led to the formation of more closely packed aggregates.

Recently, our group has broadened research area to the development of polymeric materials that can be used as materials for biotechnology. As heparin, one of the natural polymers and a sulfated glycosaminoglycan, has been widely used as an injectable anticoagulant and can form an anticoagulant surface in various medical devices (e.g., test tubes), we attempted to synthesize copolymers that have both sulfonic acid and carboxylic acid groups, that is, sodium-neutralized poly(styrene-co-methacrylate-co-styrenesulfonate) (PSMA-SS) ionomers and found that the copolymers showed interesting results in cell growth studies. To process them, one should know about their mechanical properties as a function of temperature. Thus, in this work, we investigated their dynamic mechanical properties. Subsequently, their mechanical properties were compared with those of poly(styrene-co-Na methacrylate) (PSMA) and Na-neutralized sulfonated polystyrene (PSS) ionomers and their blend (PSMA + PSS). In addition, in this article, the morphology of the PSMA-SS ionomers was discussed briefly. At this point, it should be mentioned that it surely makes more sense to prepare ionomers that have carboxylic acid and sulfonic acid groups in equivalent positions, that is, the para-position of benzene ring of styrene unit. However, the carboxylation of polystyrene usually requires multistep reactions that are not desirable in mass production. Thus, in this work, we used relatively simple methods to introduce two different types of ionic groups to polystyrene, that is, the copolymerization of styrene and methacrylic acid first and the sulfonation of poly(styrene-co-methacrylic acid) (PSMAA) copolymers next.

## **EXPERIMENTAL**

## **Preparation of Ionomers**

PSMAA random copolymers were prepared by free radical polymerization of purified styrene and methacrylic acid monomers in bulk at 60 °C.<sup>6</sup> To determine the acid contents, the acid form of samples were dissolved in a mixture of benzene/methanol (9/1 v/v) and were titrated with standard NaOH methanolic solution to the phenolphthalein end point. The acid contents were found to be about 0.8, 2.1, and 3.1 mol % equivalent to ion-exchange capacity (IEC) of 0.08, 0.20, and 0.30 mmol/g, respectively. To prepare poly (styrene-*co*-methacrylic acid-*co*-styrenesulfonic acid) (PSMAA-SSA) copolymer samples, a modified sulfonation method of



SCHEME 1 Chemical structure of PSMA-SS ionomer.

Makowski et al. was used.<sup>7</sup> An ASPECT 1000 Fourier transform infrared spectrometer (Bruker AXS, Madison, WI) with 2 cm<sup>-1</sup> resolution was used to verify the success of the sulfonation. The PSMAA-SSA samples were pelletized with KBr and scanned 64 times, and the scanning range was from 4000 to 400  $\text{cm}^{-1}$ . It was found that with increasing sulfonation degree, the PSMAA-SSA copolymers showed the increasing intensities of IR bands at 1220 cm<sup>-1</sup> for antisymmetric stretching vibrations of  $-SO_3^-$  ions, at 1180 cm<sup>-1</sup> for symmetric stretching vibrations of S=0 double bonds, and at 1120 and 1010  $\text{cm}^{-1}$  for in-plane skeleton vibration of the para-substituted benzene ring,<sup>8</sup> indicating that the sulfonation was successful (the IR spectra are not shown here). To determine the total acid contents of PSMAA-SSA copolymers, we used a titration method. Assuming that methacrylic acid units remained intact by the sulfonation, the mol % of styrenesulfonic acid units was calculated from the titration results; they were in the range of 0.8-11 mol %, equivalent to IEC of 0.08-0.95 mmol/g. To neutralize the acid groups of the PSMAA-SSA copolymers, the copolymers were dissolved in a mixture of benzene/methanol (9/1 v/v), and a predetermined amount of methanolic NaOH was added to the polymer solutions to give sodium-neutralized PSMA-SS ionomers (Scheme 1).

The solutions were freeze dried and, subsequently, dried further under a vacuum at about 170 °C for 24 h. For the dynamic mechanical experiments, the ionomers were compression molded at about 200–250 °C, depending on the ion contents, under a pressure of about 25 MPa. The samples were annealed under a vacuum at about 170 °C for 24 h. To compare the dynamic mechanical properties of these ionomers with those of other polystyrene-based ionomers that have only one type of anionic group, we also prepared PSS ionomers and measured their mechanical properties. In the case of the dynamic mechanical data of PSMA ionomers, we obtained them from Ref. 6. For simplicity, in this article, we use the sample notations of PSMA(y)-SS(z), PSS(z), and PSMA(y) for sodium-neutralized PSMA-SS, poly(styrene-costyrenesulfonate), and poly(styrene-co-methacrylate) ionomers, respectively, where y and z are the mole percentage of sodium methacrylate (MA) and sodium styrenesulfonate (SS) units, respectively.

#### **Dynamic Mechanical Analysis**

A Q-800 dynamic mechanical analyzer (TA Instruments, New Castle, DE) was used to study the dynamic mechanical properties of ionomers. The experiments were carried out in a dual cantilever bending mode at five different frequencies: 0.3, 1, 3, 10, and 30 Hz. Storage moduli (E') and loss





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tangents (tan  $\delta$ ) were obtained as a function of temperature at a heating rate of 1 °C/min. The detailed data analysis was performed only on 1 Hz data. Deconvolutions on the loss tangent data were performed using a PeakFit (Systat Software) program. The best fits were achieved assuming an exponential background and fitting the matrix and cluster peaks with Gaussian area peaks.

## **Small-Angle X-ray Scattering Experiments**

The small-angle X-ray scattering (SAXS) experiments were conducted at Station 4C1 of Pohang Light Source synchrotron radiation source (Pohang, Korea). The generated critical beam energy was 5.5 keV (at 2.5 GeV operation modes). The position-sensitive two-dimensional CCD X-ray detector was used. The sample-to-detector distance was 1000 mm. The SAXS intensity was obtained as a function of scattering vector q, where  $q = 4\pi \sin \theta/\lambda$ ,  $\theta$  is half the scattering angle and  $\lambda$  is the X-ray wavelength. The SAXS data were plotted as relative intensity versus q after the correction for background.

## **RESULTS AND DISCUSSION**

Before starting this section, it will be useful to review very briefly the differences in the mechanical properties of PSMA and PSS ionomers for the better understanding of the effects of the position and type of anionic groups on the mechanical properties of PS ionomers. At this point, let us discuss about "ionic plateau." It can be thought that the multiplets act as crosslinks as well as reinforcing filler particles effectively, which increases the ionomer modulus. If the ion pairs remained intact in the multiplets even above the matrix  $T_{g}$ , the ionomer would show a well-defined "ionic" plateau in the modulus-temperature curve above the matrix  $T_{g}$ , that is, the ionic plateau is the segment of the modulus curve between the matrix and cluster  $T_{gs}$  and is horizontal or shows a slight downward slope. The height and width of ionic plateau are related to the degree of clustering and the strength of the interactions between ion pairs in the multiplet to some extent. For example, one can find that the ionic plateau of the PSS ionomer is wider but lower than that of the PSMA ionomer of the same ion content.9,10 To understand this finding, two aspects should be considered. First, the sulfonate group of the PSS ionomer is located on the para position of the benzene ring of a styrene unit, whereas the carboxylate group of the PSMA ionomer is directly attached to the main chain of the ionomer. Thus, the distance between the ionic group and the main chain of the PSS ionomer is longer than that of the PSMA ionomer. Therefore, the ion pairs of the PSS ionomer experience less steric hindrance when they form multiplets when compared with those of the PSMA ionomer.9 This leads to the larger size of the multiplets of the PSS ionomer when compared with that of the PSMA ionomer. The second aspect to be considered is the strength of interactions between ion pairs. The interactions between the Na-sulfonate ion pairs of the PSS ionomer are stronger than those between the Na-carboxylate ion pairs of the PSMA ionomer.<sup>3,9,11</sup> Thus, the ion hopping, that is, one of the cluster glass transition mechanisms, related to the strength of interactions between ion pairs occurs at higher





**FIGURE 1** Storage modulus and loss tangent values of PSMA(2.1)-SS ionomers as a function of temperature, measured at 1 Hz.

temperatures for the PSS ionomer when compared with the PSMA ionomer. Of course, the number of ion pairs per multiplet of the PSS ionomer is larger than that of the PSMA ionomer of the same ion content. These two aspects led to higher cluster Tg and wider ionic plateau for the PSS ionomer when compared with the PSMA ionomer. Now, let us assume the position of ionic plateau, which is related with the degree of clustering.<sup>3,6</sup> The stronger interactions between ion pairs and larger multiplets naturally led to more ion pairs per multiplet but fewer multiplets for the PSS ionomer when compared with the PSMA ionomer of the same ion content. If the thickness of reduced mobility regions surrounding the multiplets did not change as the type of anionic groups of the ionomers changed, the amount of reduced mobility regions should increase with the number of the multiplets. Therefore, at the same ion content, the degree of clustering (i.e., the size of reduced mobility regions) of the PSS ionomer is lower than that of the PSMA because of the fewer numbers of multiplets. As a result, the ionic plateau of the PSS ionomer is lower than that of the PSMA ionomer. One should keep these aspects in mind when one interprets the dynamic mechanical property data.

The log(storage modulus) and loss tangent values of PSMA(2.1)-SS ionomers containing varying amounts of SS units as a function of temperature are shown in Figure 1. With increasing temperature, the modulus curve exhibits a glassy modulus, a matrix glass transition, an "ionic" plateau, a cluster glass transition, a rubbery plateau, and flow.<sup>3,6</sup> It is clear that on sulfonation, the ionic plateau becomes wider. This indicates that the introduction of Na-sulfonate ion pairs shifts the cluster glass transition to higher temperatures because the interaction between Na-sulfonate ion pairs is stronger than that between Na-carboxylate



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**FIGURE 2** Storage modulus and loss tangent values of (a) PSMA, PSS and PSMA-SS ionomers, and PSMA + PSS blend and (b) PSMA, PSS, and PSMA-SS ionomers containing about 5–6 mol % of ionic units as a function of temperature, measured at 1 Hz.

ion pairs. In addition, the ionic plateau shifts to higher positions progressively with increasing degree of sulfonation, as expected. In the case of a matrix loss tangent peak, it shifts gradually from about 135 to 145 °C with increasing degree of sulfonation, which is due to the increase in ion content. On sulfonation, the cluster loss tangent peak moves drastically from about 190 °C for PSMA(2.1) ionomer to about 250 °C for PSMA(2.1)-SS(0.8) ionomer, and then the peak shifts slowly to higher temperatures with increasing degree of sulfonation. As mentioned above, the drastic increase of cluster  $T_{\rm g}$  is due to the introduction of Na-sulfonate ion pairs. The PSMA(0.8)-SS and PSMA(3.1)-SS ionomers also show similar trends (data are not shown here).

Now, one question arises: Are the mechanical properties of PSMA(2.1)-SS(3.9) ionomer similar to those of a blend of PSMA(2.1) and PSS(3.9) ionomers? Figure 2(a) shows the storage modulus and loss tangent data of PSMA ionomer containing 2.1 mol % of MA units [i.e., PSMA(2.1)], PSS ionomer containing 3.2 mol % of ions [i.e., PSS(3.2)], and their blend [50:50 wt:wt; i.e., PSMA(2.1) + PSS(3.2)].

This figure also includes the mechanical data of PSMA(2.1)-SS(3.9) ionomer. It is seen that the ionic plateau of the PSMA(2.1)-SS(3.9) ionomer is wider than that of the PSMA(2.1) ionomer but narrower than that of the PSS(3.2) ionomer. However, the modulus drops for the cluster glass transition of the PSMA-SS and PSS ionomers occur at about 240 °C. In the case of the PSMA(2.1) + PSS(3.2) blend, it shows two ionic plateaus. This indicates that the ionomer blend exhibits three glass transitions. Now, let us look at loss tangent peaks. Two well-developed peaks are seen for the PSMA(2.1), PSS(3.2), and PSMA(2.1)-SS(3.9) ionomers. The

matrix peaks are located at about 140 °C; however, the cluster peaks are shown at about 190 °C for PSMA and at about 250 °C for PSS and PSMA-SS ionomers. However, the PSMA(2.1) + PSS(3.2) ionomer blend shows three peaks; the first peak at about 135 °C, the second peak at about 185 °C, and the third peak at about 245 °C. The first peak is due to the matrix  $T_{g}$ . On the other hand, the positions of the second and third peaks are similar to those of the cluster peak for the PSMA and PSS ionomers, respectively. Thus, the second peak is probably due to the glass transition of the regions containing carboxylate-rich multiplets, and the third peak is due to the glass transition of the regions containing sulfonate-rich multiplets.<sup>12</sup> This suggests heterogeneity in the compositions of the multiplets of the PSMA + PSS ionomer blend at least to some extent. The above finding implies that the PSMA-SS ionomer behaves like a homogeneous ionomer system; however, the PSMA + PSS ionomer blend is a partially phase-separated system.

Now, another question arises: Are the mechanical properties of PSMA(2.1)-SS(3.9) ionomer different from those of the PSMA and PSS ionomers having similar amounts of ionic repeat units in total? The storage modulus and loss tangent values of the PSMA(2.1)-SS(3.9), PSS(5.2), and PSMA(5.5) ionomers are shown in Figure 2(b). At this point, it should be noted that the changing ionomers from PSS to PSMA to PSMA-SS ionomers means that the total content of ionic repeat units increases from 5.2 mol % (for PSS ionomer) to 5.5 mol % (for PSMA ionomer) to 6.0 mol % (for PSMA-SS ionomer). This increasing ion content causes the shift of the modulus drop related with the matrix glass transition to higher temperatures progressively. It is also observed that the center of the cluster peak of the PSMA is located at about 210  $\,^\circ\text{C}$  , but those of the PSS and PSMA-SS ionomers appear at about 260 °C. This implies that the dynamic mechanical properties of the PSMA-SS ionomers are not much different from those of the PSS ionomers. This is understood because the amount of SS units in PSMA-SS ionomer is only slightly higher than that of PSS ionomer, that is, 3.9 vs. 5.2 mol %.

As one of the characteristic features of polystyrene-based ionomers is the presence of ionic plateau in the plots of log(storage modulus) versus temperature, we have analyzed the ionic plateaus of the ionomers in more detail. Specifically, we have evaluated the ionic modulus  $(E'_{ionic})$  of the ionomers. The ionic modulus is a modulus at the point of a minimum slope in the ionic plateau region. In the case of PSS ionomers, it is observed that the modulus value of the ionic plateaus increases slightly and then decreases again with increasing temperature. Thus, we have chosen the modulus value at the slope of zero as the ionic modulus of the PSS ionomers. Figure 3(a) shows the ionic moduli of PSMA-SS ionomers as a function of degree of sulfonation, that is, SS content. This figure also includes the  $E'_{\text{ionic}}$  values of PSS ionomers. It is clear that the  $E'_{ionic}$  values of the PSMA-SS and PSS ionomers increase with increase in SS content; needless to mention, this is due to the increasing amount of cluster regions in the ionomer. As expected, the  $E'_{\text{ionic}}$  of PSMA(0.8)-SS





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FIGURE 3 lonic moduli of (a) PSS (solid line) and PSMA-SS (dotted line) ionomers as a function of SS content and (b) PSS (solid line), PSMA-SS (dotted line), and PSMA (dash line) ionomers as a function of total content of ionic repeat units, measured at 1 Hz.

ionomer, the MA content of which is very low, is not much different from that of the PSS ionomers.

It is also seen that the increase of MA content in PSMA-SS ionomers gives a higher initial  $E'_{ionic}$  value but lowers the rate of increasing log  $E'_{\text{ionic}}$ s. Figure 3(b) shows the log  $E'_{\text{ionic}}$ values of the PSMA-SS ionomers as a function of total content of ionic repeat units. It also includes the log  $E'_{ionic}$  values of the PSMA and PSS ionomers. Interestingly, the log  $E'_{ionic}$ values of the PSMA-SS ionomers seem to fall onto a single curve. This indicates that the total ion content, not the SS content alone, can explain the increase in the  $\textit{E}_{\rm ionic}^{\prime}$  values of PSMA-SS ionomers more effectively. In the same figure, it is also seen that above 3 mol % of ion content, the  $E^{\prime}_{\rm ionic}$  value of the PSMA ionomer is the highest, that of the PSS ionomer is middle, and that of the PSMA-SS ionomer is the lowest at a given ion content. The reason for the higher  $E'_{\text{ionic}}$  value of the PSMA ionomer, when compared with that of the PSS ionomer, has already been discussed earlier; however, the lowest ionic modulus of the PSMA-SS ionomer is puzzling. Now, it should be stressed that the lowest ionic modulus indicates that at the same ion content, the degree of clustering of the PSMA-SS ionomer is the lowest among the three ionomer systems. In other words, if all the ionic groups of the three ionomers participate in the multiplet formation, the average size of the multiplets of the PSMA-SS ionomer might be largest, and, thus, the number of multiplets might be smallest when compared with those of the PSMA and PSS ionomers of the same ion content. This will be again discussed later along with SAXS data.

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The  $T_{\rm g}$ s of the ionomers were determined from the positions of the centers of deconvoluted loss tangents peaks. Figure 4(a) shows the matrix and cluster  $T_{gs}$  of PSMA-SS ionomers as a function of SS content. This figure also includes the  $T_{gs}$ of PSS and PSMA ionomers as a function of either SS content or MA content, respectively. It is seen that the matrix and cluster T<sub>g</sub>s of the PSMA-SS, PSMA, and PSS ionomers increase with increase in ion content. Again, this is due to the increasing amount of the cluster regions. In the figure, it is observed that the matrix and cluster  $T_{g}$ s of the PSMA-SS ionomers are somewhat higher than those of the PSS ionomers when they are plotted as a function of SS content. However, the difference in the cluster  $T_{gs}$  of PSMA-SS and PSS ionomers becomes smaller as the SS content increases, and finally, two cluster  $T_{gs}$  of the ionomers containing about 11 mol % of SS units become very similar to each other.

It should be mentioned that at a cluster glass transition, ion hopping is operative,  $^{6,9,13-19}$  which is directly related with the strength of interactions between ion pairs. If the size of the multiplets of the PSMA-SS ionomer is larger, due to the presence of more ion pairs per multiplet, than those of the PSS and PSMA ionomers, the ion pairs in the multiplet of the PSMA-SS ionomer will experience difficulty in hopping. In addition, as suggested by Visser and Cooper,<sup>5</sup> there might be more densely packed ionic aggregates in the PSMA-SS ionomers when compared with those in the PSS and PSMA ionomers. These two aspects may explain the highest cluster  $T_g$  of PSMA-SS ionomer. Now, as the SS content increases, the multiplets start containing more Na-sulfonate ion pairs per multiplet, and eventually, the relative amount of the Na-sulfonate ion pairs per multiplet will be close to that of the PSS ionomer. Then, the PSMA-SS ionomer behaves like the PSS ionomer; this might be what we observed for the PSMA(3.1)-SS(11) ionomer in Figure 4(a).

The matrix and cluster  $T_{gs}$  of the ionomers as a function of total ion content are shown in Figure 4(b). Interestingly, the



**FIGURE 4** Glass transition temperatures of PSMA-SS (dotted line), PSS (solid line), and PSMA (dash line) ionomers as functions of (a) SS (or MA) content and (b) total ion content, measured at 1 Hz.





**FIGURE 5** SAXS profiles of PSMA, PSS, and PSMA-SS ionomers.

matrix  $T_{\rm g}$ s of the PSMA-SS ionomers are very similar to those of the PSMA and PSS ionomers. The rates of the elevating matrix  $T_{\rm g}$  are also similar to each other, that is, in the range of 3-4 °C × (total ion content in mol %) that is in good accord with the results reported elsewhere.<sup>3</sup> This is not surprising because the matrix  $T_{\rm g}$  is affected strongly, not by the types of ionic groups, but by the content of ionic units.<sup>3,9,18</sup> In this figure, it is also seen that the rate of the elevating cluster  $T_{\rm g}$  increases from about 2 °C × (total ion content in mol %) for the PSMA-SS ionomer to about 5–6 °C × (ion content in mol %) for the PSS and PSMA ionomers. This will be discussed in the next section.

The SAXS profiles for the PSMA(2.1) and PSS(4.4) ionomers and PSMA(2.1)-SS ionomers containing 0.8 and 3.2 mol % of SS units are shown in Figure 5.

Before we start discussing the SAXS profiles of the present ionomers, it would be useful to review very briefly some of the findings in the SAXS studies on PSMA and PSS ionomers. It is worth recalling that Cs-neutralized PSMA ionomer of high ion content (e.g., ca. 11 mol % of ions) shows a weak SAXS peak at  $q = \sim 2.8 \text{ nm}^{-1} (d_{\text{Bragg}} = \sim 2.2 \text{ nm}).^{20}$  In the case of PSS ionomers, it is known that a well-developed SAXS peak is seen at about 1.7 nm<sup>-1</sup>  $(d_{\text{Bragg}} = \sim 3.7 \text{ nm}).^{21-27}$ In the current work, it is clear that the PSMA(2.1) ionomer shows only a small-angle upturn, without showing a profound SAXS peak. This is due to the relatively low ion content and the relatively low electron density of the multiplets. The PSMA(2.1)-SS(0.8) ionomer still does not show a SAXS peak, except for the more developed small-angle upturn. However, the PSMA(2.1)-SS(3.2) ionomer exhibits an SAXS peak centered at  $q_{\rm max} = \sim 1.7 \ {\rm nm}^{-1}$ , where the SPS(4.4) ionomer also shows a well-developed SAXS peak. This implies that the sulfonation induces the formation of multiplets, consisting of a sufficient amount of Na-sulfonate

ion pairs, at their preferred distance that is similar to that of the PSS ionomer. Thus, it can be speculated that when the neutralizing agents are added to the acid form of PSMAA-SSA copolymers, Na-sulfonate ionic groups, whose interaction is stronger than that between Na-carboxylate ionic groups, form ionic aggregates with another Na-sulfonate ion pairs at their preferred distance. The Na-carboxylate ion pairs also take part in the formation of ionic aggregates that have already contained Na-sulfonate ion pairs. This implies that the size of multiplets of the PSMA-SS ionomers might be slightly larger than that of the PSS ionomers of the same SS content because the multiplets contain additional Na-carboxylate ion pairs. This explains the lowest  $E'_{ionic}$  value of PSMA-SS ionomer. Now, let us discuss the lower rate of increasing cluster  $T_{\rm g}$  of PSMA-SS ionomers. Once the ionomer chain contains both Na-sulfonate and Na-carboxylate ion pairs, the multiplet formation is strongly governed by the Na-sulfonate ion pairs, leading to higher cluster  $T_{g}$ . On the other hand, the Na-carboxylate ion pairs in the multiplet now act as multiplet plasticizer, resulting in the relatively easy ion hopping.<sup>28,29</sup> This lowers the cluster  $T_{\rm g}$  of PSMA-SS ionomer to some extent. This results in the low rate of increasing cluster  $T_{\rm g}$  of the PSMA-SS ionomers.

## CONCLUSIONS

In this study, we provided a new method to change the mechanical properties of ionomers by introducing Na-sulfonate ion pairs into an ionomer that had Na-carboxylate ion pairs. It was observed that the ionic plateau of PSMA-SS ionomer was wider than that of PSMA ionomer, and the drops of ionic plateaus of PSMA-SS and PSS ionomers occurred at similar temperatures. In addition, the ionic modulus values of the PSMA-SS ionomers fell on one curve when they were plotted against total ion content, indicating that the degree of clustering was affected by the total ion content more effectively. It was also found that the matrix  $T_{gs}$  of the PSMA-SS, PSMA, and PSS ionomers depended mainly on the ion content, not the type of ionic groups. On the other hand, it was observed that the type of anionic groups significantly affected the cluster  $T_{\sigma}$  of the ionomers, as expected. The SAXS profile of PSMA-SS ionomer suggested that the multiplets formed at their preferred distance was similar to that of the PSS ionomer. Thus, it was proposed that Na-sulfonate ionic groups formed the multiplets, and, then, the Na-carboxylate ion pair would reside in the multiplets with Na-sulfonate ionic groups to make larger and/ or more densely packed multiplets. These Na-carboxylate ion pairs then lowered the cluster  $T_{\rm g}$  of PSMA-SS ionomer, to some extent, by acting as multiplet plasticizer.

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## Dynamic Mechanical Properties of Polystyrene-co-Styrenesulfonic Acid Copolymers Neutralized with Aliphatic Diamines

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**ABSTRACT:** In this article, we reported the effects of the addition of various aliphatic diamines (ADAs) on the dynamic mechanical properties of poly(styrene-*co*-styrenesulfonic acid) copolymers. It was found that the ionic modulus decreased with increasing chain length of ADAs but increased for the ADA12-containing ionomers. Upon the neutralization of the copolymers with ADAs, a minor change in the size and position of the matrix loss tangent peak was observed. However, the position of the cluster loss tangent peaks shifted to lower temperatures, and the shift rate depended on the chain length of ADAs. Thus, it was suggested that the ADAs acted mainly as preferential plasticizer for the cluster regions. In addition, the effect of the amount of ADA on the difference between the matrix and cluster temperatures of the ionomers was strongest than that of the type of ADA or ion content. The X-ray peak of ADA12 suggested that the ADA12 acted both as plasticizer and as filler. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 1764–1770, 2013

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## INTRODUCTION

Ionomers have a small amount of ionic groups along relatively nonpolar polymer chains.<sup>1-4</sup> Because of the attractive electrostatic interactions between the ion pairs of the ionomer and the high degree of incompatibility between the ionic groups and the relatively nonpolar hydrocarbon polymer matrix, the ionic groups tend to aggregate themselves. These ionic aggregates, called "multiplets,"5 lead to the reduction of the mobility of the polymer chain segments surrounding them.<sup>6</sup> At very low ion contents, only a small amount of multiplets exists. At this stage, the ionomers show behavior that is similar to that of a nonionic polymer, that is, only one glass transition  $(T_g)$  for nonionic amorphous matrix regions. With increasing ion contents, the number and size of the multiplets increase, and, hence, the restricted mobility regions surrounding the multiplets start overlapping, making large continuous regions.<sup>6</sup> When the restricted mobility regions exceed about 10 nm in their size, they exhibit their own  $T_g$  at higher temperatures than that for the nonionic matrix regions. At this point, the restricted mobility regions along with the multiplets are termed "clusters," and the ionomer behaves like a biphasic material, showing two  $T_gs$ , that is, matrix and cluster  $T_gs$ .<sup>6</sup> It should be mentioned that at the cluster  $T_g$ , in addition to the relaxation of polymer chains in the restricted mobility regions, the hopping of ionic groups from one multiplet to another also becomes operative.<sup>7</sup>

It is well known that the mechanical properties and morphology of ionomer systems are influenced by various factors such as ion contents, type of counter-ions, type and position of ionic groups attached to polymer chains, and type of backbone chains.<sup>3,6</sup> For example, Weiss et al. investigated the mechanical and rheological properties of sulfonated polystyrene (SPS) ionomers neutralized with mono-, di-, and trisubstituted alkyl amines.<sup>8</sup> The authors demonstrated that the properties of the ionomers were affected by the chain lengths of the alkyl amines and the number of the substituents. Later, Smith and Eisenberg investigated the effects of neutralization of SPS ionomers with either flexible or rigid monofunctional amines on the mechanical properties of the ionomers.<sup>9</sup> They found that the flexible aliphatic monofunctional amines (AMAs) acted as plasticizer and, thus, decreased the  $T_g$  of the ionomers, proportional to the

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number of carbon atoms of amines  $(C_n)$ . Fan and Bazuin studied the mechanical properties of SPS ionomer neutralized with 1,6-hexamethylene diamine.<sup>10</sup> They found that this ionomer also behaved like SPS ionomers neutralized with metal ions. A number of other groups have also studied the various properties of the ionomers containing amine derivatives.<sup>11–31</sup>

Although the effects of the organic diamines on the properties of crystalline ethylene-based ionomers had been studied, little attempts have been made to explore the effects of aliphatic diamines (ADAs), having one amine group at both ends of the alkyl chain, on the dynamic mechanical properties of the amorphous polystyrene (PS)-based ionomers.<sup>10,18,19</sup> In addition, very recently we studied the effects of aliphatic dicarboxylate (DCA) salts, having varying length of alkyl chains, on the mechanical properties of PS-based ionomers<sup>32</sup>; in this case, the DCAs are additives, not neutralizing agents. We found that the DCA salts acted mainly as filler. The above two facts lead us to the study on the effects of the neutralizing agent ADAs on the properties of PS-based ionomers. Thus, in the present work, SPS ionomers containing four ADAs were prepared: the length of alkyl chain of ADAs varies from C<sub>2</sub> (ethylene) to C<sub>12</sub> (dodecamethylene). The copolymers of low, medium, and high acid contents were also prepared to explore the effects of the ion contents on the mechanical properties of the ionomers containing ADAs. This study will make us to gain an insight of the effects of small ionizable organic molecules on the properties of amorphous ionomers.

## **EXPERIMENTAL**

## **Polymer Synthesis**

Polystyrene (PS) homopolymer (MW = ca. 500,000) was synthesized by the free radical polymerization of purified styrene at  $60^{\circ}$ C using benzoyl peroxide as the initiator. The sulfonation method reported by Makowski et al. was used to prepare poly (styrene-*co*-styrenesulfonic acid) SPS random copolymers.<sup>33</sup> The contents of acidic repeat units of the copolymers were 4.1, 7.3, and 11.5 mol %.

## Sample Preparation

As suggested by Smith and Eisenberg in their AMA-neutralized SPS ionomers,9 to neutralize the acid groups of the copolymers with ADAs, the copolymer and the ADAs were dissolved in a benzene/methanol (9/1, v/v) mixture to make a 5% (w/v) solution. The ratio of the moles of the acid groups of the copolymers to those of the amine groups of the ADAs was kept at 1/1. The copolymer solutions were freeze-dried and dried further under a vacuum at about 130°C for 24 h. The Fourier transform infrared results indicated that ADA-SPS ionomers are fully neutralized like the Na-SPS ionomer. We also prepared SPS ionomers neutralized with NaOH to compare the mechanical data of the ADA-neutralized SPS ionomers with those of the Naneutralized SPS ionomers. The sample notation used for these samples is x-ADAy or x-Na, where "x" indicates the mol % of the ionic repeat units of the SPS ionomers neutralized with either ADAs or sodium, and "y" is the number of the carbon atoms  $(C_n)$  of a particular ADA molecule; i.e., 2 for 1,2-ethylene diamine (m.p. =  $8.5^{\circ}$ C),<sup>34</sup> 6 for 1,6-hexamethylene diamine (m.p. =  $42^{\circ}$ C),<sup>34</sup> 10 for 1,10-decamethylene diamine (m.p. =  $59-61^{\circ}C$ ,<sup>34</sup> and 12 for 1,12-dodecamethylene diamine (m.p. =

 $67-69^{\circ}$ C).<sup>34</sup> For the dynamic mechanical property measurements, the samples were compression molded at about  $150-250^{\circ}$ C and at a pressure of about 25 MPa. All the molded samples with approximate dimensions of  $2.5 \times 7.0 \times 30.0 \text{ mm}^3$  were transparent and annealed under a vacuum at  $130-150^{\circ}$ C for 24 h. For the small-angle X-ray scattering (SAXS) measurements, the samples were compression-molded at about  $150-250^{\circ}$ C. A pressure of about 25 MPa was applied for 5 min, and then slowly released, and the mold was allowed to cool to below the matrix  $T_g$ . The dimensions of the molded samples were about 0.5 mm (thickness)  $\times$  10 mm (diameter).

## Dynamic Mechanical Analysis

To measure the dynamic mechanical properties of the ionomers, a Q-800 dynamic mechanical analyzer (DMA) (TA Instruments, DE) was used. The dual cantilever bending mode at frequencies of 0.3, 1, 3, 10, and 30 Hz was utilized, but the detailed data analysis was performed only on 1 Hz data. The heating rate was  $1^{\circ}$ C min<sup>-1</sup>. For each sample, the storage moduli (*E'*) and loss tangents were obtained as a function of temperature.

## X-ray Experiments

The small angle X-ray scattering (SAXS) experiments were conducted at Station 4C1 of Pohang Light Source (PLS) synchrotron radiation source (Pohang, Korea). The sample-to-detector distance was 400 mm, which allowed SAXS data to be obtained in the *q* (scattering vector) ranging from about 0.2 to 4.2 nm<sup>-1</sup>, where  $q = 4\pi \sin\theta/\lambda$ ;  $\theta$  is half the scattering angle, and  $\lambda$  is the X-ray wavelength ( $\lambda = 0.1608$  nm). A PANalytical X' pert PRO MPD X-ray diffractometer was used to obtain the X-ray diffraction (XRD) patterns.

## **RESULTS AND DISCUSSION**

Figure 1 shows the storage moduli (E') as a function of temperature for the SPS ionomers containing either 4.1 or 11.5 mol % of ionic repeat units, neutralized with either NaOH or ADAs. With increasing temperature, the ionomers show a plateau for glassy moduli, a steep slope for a matrix  $T_g$ , a narrow ionic plateau, a gentle slope for a cluster  $T_g$ , and a descending plateaulike feature for rubbery moduli and sample flow. The width of ionic plateau (i.e., the moduli between the matrix and cluster  $T_{cs}$ ) extends to about 260°C for the 4.1-Na ionomer. However, it becomes narrower for the 4.1-ADA ionomers and extends only to about 170-200°C, depending on the chain length of ADAs. At this point, it should be mentioned that the width of the ionic plateau is treated as a symbol of the strength of the interactions between the ion pairs in the multiplets; the narrower the ionic plateau is, the weaker the interactions between the ion pairs are.<sup>3,7,35</sup> This is due to the fact that the electrostatic force  $F_{el}$ between the charges is inversely proportional to the square of the distance (x) between two charges: i.e.,  $F_{\rm el} \propto q_a q_d x^2$ , where  $q_a$ and  $q_c$  are the anion and cation charges, respectively.<sup>36</sup> Thus, if the size of cation is smaller, the distance between two charges is shorter and the cluster  $T_{g}$ , at which ion-hopping occurs and is related to the  $F_{el}$ , becomes higher. Because the size of Na<sup>+</sup> is smaller than that of quaternary ammonium cation (e.g., the ionic radius of Na<sup>+</sup> is 0.95 Å, but that of NH<sub>4</sub><sup>+</sup> is 1.43 Å),<sup>37</sup> the ionic plateau is wider for the Na ionomer, compared to the ADA





**Figure 1.** Storage moduli of SPS ionomers neutralized with either Na or ADAs as a function of temperature (1 Hz data). The ion contents of ionomers are (a) 4.1 mol % and (b) 11.5 mol %. For clarity, arrows indicate the ionic moduli of 11.5-ADA6, ADA10, and ADA12 ionomers.

ionomer, at a particular ion content; this will be discussed later in connection with cluster  $T_{g}$ .

It is worth mentioning that the height of the ionic plateau in the plots of E' vs. temperature generally reflects the amount of the clustered regions (i.e., the degree of clustering).<sup>3,6,35</sup> The height of ionic plateau of 4.1-ADA ionomers is lower, compared to that of 4.1-Na ionomer, and decreases further as the chain length of the ADAs increases. However, the ionic plateau of 4.1-ADA12 ionomer moves to higher moduli in comparison with that of 4.1-ADA10 ionomer. The ionic plateau of 11.5-Na ionomer is higher than that of 4.1-Na ionomer and the ionic plateau also shifts to lower modulus values upon the neutralization with ADAs, and moves further down to lower moduli with increasing chain length of ADAs. Again, the position of the ionic plateau of 11.5-ADA12 ionomer is higher than that of 11.5-ADA10 ionomer. It is also seen that the segment of the modulus curve for the cluster  $T_g$  becomes steeper and shifts to lower temperatures upon the neutralization with ADA and with increasing chain length of ADAs. The 7.3 mol % ionomers show a similar trend (not shown here).

Because the position of the ionic plateau is related with the degree of clustering, we tried to analyze it more quantitatively. The modulus values at the point of a minimum slope of the ionic plateau in log E' vs. temperature plots, so-called ionic modulus ( $E'_{ionic}$ ), are shown in Figure 2(a) as a function of the number of carbon atoms of ADAs. It is seen that the  $E'_{ionic}$  decreases smoothly with increasing chain length up to  $C_{10}$  (i.e., ADA10), and that the decreasing rate seems to increase with ion content. It is also shown that the  $E'_{ionic}$  values of the three ionomers neutralized with ADA12 are higher than those of the ionomers neutralized with ADA10. This implies that the role of ADA12 might be different from that of the rest of ADAs, at least to some extent. Figure 2(a) also includes the  $E'_{ionic}$  data of

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4.5-Na ionomers containing aliphatic dicarboxylates (DCAs) that act mainly as reinforcing filler,<sup>22</sup> the ion content of which is slightly higher than that of 4.1-ADA ionomers. It is seen that the E'<sub>ionic</sub> of 4.5-DCA ionomer increases initially and remains more or less constant as the chain length of DCA increases from  $C_6$  to  $C_{12}$ .<sup>32</sup> The difference in the trends of  $E'_{\text{ionic}}$  values 4.5-DCA and 4.1-ADA ionomers indicates that the roles of DCA and ADA in SPS ionomer are not the same. Interestingly, the  $E'_{ionic}$  value of 4.1-ADA12 is in the middle of those of 4.5-DCA12 and 4.1-ADA10 ionomers. This suggests that the ADA12 molecules might act as filler in part. At this point, it should be mentioned that the increasing chain length of ADAs results in the increase in the weight percentage (wt %) of ADA in the ADA-neutralized ionomers. Thus, in Figure 2(b) we plotted the  $E'_{\text{ionic}}$  data as a function of wt % of ADAs in the ionomers. It is seen that the  $E'_{\text{ionic}}$  values, except for that of ADA12, decrease regularly with increasing wt % of ADAs. Figure 2(c) shows the  $E'_{\text{ionic}}$  data as a function of the ion content of ionomers. It is clear that the  $E'_{ionic}$ s of ADA-neutralized ionomers increase with increasing ion content, similar to those of Na-neutralized PSbased ionomers.<sup>3,35</sup> This indicates that the diamines act also as neutralizing agents for the sulfonic acid groups effectively, to some extent.9,10,18,19 It is observed that at a certain ion content, the  $E'_{ionic}$  value is the highest for Na-ionomer and decreases with increasing chain length of ADAs, except for the ADA12. This means that the ADA2, ADA6, and ADA10 act as effective plasticizer to make the ionomer relatively softer at the temperatures where the ionomer show its ionic modulus, while the ADA12 behaves differently.

Shown in Figure 3 are the loss tangents as a function of temperature for the Na and ADA ionomers having either 4.1 or 11.5 mol % of ionic repeat units. It is clear that these ionomers represent biphasic behavior by showing two loss tangent peaks; one



**Figure 2.** Ionic moduli ( $E'_{\text{ionic}}$ ) of SPS ionomers neutralized with either Na or ADAs as functions of (a) number of carbon atoms of ADAs, (b) wt % of ADAs (the numbers near the symbols indicate the number of carbon atoms of the ADAs) and (c) ion contents of ionomers (1 Hz data). The ionic modulus values of DCA-containing SPS ionomers (ion content = 4.5 mol %) (data were obtained from Ref. 32) are also included in (a).





**Figure 3.** Loss tangents of (a) SPS ionomers neutralized with either Na or ADAs as a function of temperature (1 Hz data). The ion contents of ionomers are (a) 4.1 mol % and (b) 11.5 mol %.

at low temperatures for the glass transition of matrix regions and the other at high temperatures for that of cluster regions. It should be mentioned that, at first glance, the shapes of the matrix and cluster peaks of the 4.1-ADA and 11.5-ADA ionomers look different from each other. However, if one considers the deconvolutions of the peaks with baseline subtraction,<sup>35</sup> one may find not much different shapes and sizes of the matrix and cluster peaks for each ionomer. In Figure 3, it is clear that the addition of ADAs does not change the positions of the matrix loss tangent peaks of the 4.1 and 11.5 mol % ionomers noticeably. On the other hand, upon the neutralization with the ADAs, the cluster peak position moves to low temperatures progressively. For example, the cluster peak of the 4.1-Na ionomer at about 265°C shifts to about 200°C for the 4.1-ADA2 ionomer and further down to about 170°C for the 4.1-ADA12 ionomer. In the case of the 11.5-Na ionomer, the matrix and cluster peaks are smaller and larger, respectively, than those of the 4.1-Na ionomer because of the higher degree of clustering.<sup>35</sup> When the ionomer is neutralized with ADA, the cluster peak of the 11.5-Na ionomer at about 300°C shifts to about 235°C for the 11.5-ADA2 ionomer and further down to about 195°C for the 11.5-ADA12 ionomer.

Figure 4(a) is the plots of  $T_g$ s vs. the number of carbon atoms of ADAs (or DCAs or AMAs). As expected, with increasing ion content from 4.1 to 11.5 mol %, the matrix  $T_g$  ( $T_g$ , m) and cluster  $T_g$  ( $T_g$ , c) of the Na- and ADA-ionomers increase significantly. The increasing  $T_g$ , m is due to both the copolymerzation effect and the increasing degree of clustering and the increasing  $T_g$ , c is due mainly to the increasing degree of clustering with increasing ion content.<sup>3,4,6,35</sup> Now, let us look at the  $T_g$ s as a function of the number of carbon atoms of ADAs. It is evident that the matrix  $T_g$  changes only slightly as the number of carbon atoms of ADAs increases; however, the cluster  $T_g$  drops significantly. As mentioned before, at the  $T_g$ , c two mechanisms are operative simultaneously; the relaxation of the polymer ARTICLE

chains in clustered regions and the hopping of the ionic groups between multiplets.<sup>3,7</sup> Thus, stronger interactions between ionic groups require higher temperatures for ions to hope from one multiplet to another multiplet. Therefore, the type of cations affects a cluster  $T_g$  strongly, with only a marginal effect on a matrix  $T_{g}$ .<sup>38</sup> In the present work, since the size of Na<sup>+</sup> cation is smaller than that of a monosubstituted ammonium cation, the cluster  $T_g$  of Na ionomer is higher than that of the ADA ionomers. Furthermore, the cluster  $T_g$  of the ionomer decreases with increasing chain length of ADAs. At this point, it should be recalled that the type of ion pairs in ADA ionomers is similar to each other, i.e.  $-SO_3^- +H_3N-C_n-NH_3^+ -O_3S-$ . Thus, the electrostatic forces between  $-NH_3^+ -O_3S-$  ion pair and other -- NH3<sup>+</sup> -O3S- ion pairs in the multiplet are similar for all of the ADA ionomers, if the alkyl chain did not participate in the multiplet formation. However, this idea may not be fully applicable here, since the cluster  $T_g$  decreases with increasing chain length of ADAs. This implies that the alkyl chains of ADA may participate in the preferential plasticization of the cluster regions of the ionomer, to some extent, by residing in the multiplets and/or in the regions of restricted mobility. At this point, it can be mentioned that the alkyl chains in the vicinity of multiplets would reduce the number of polymer chains emanating from the multiplets, to some extent, and provide more room for the polymer chains to move, leading to the decrease in cluster  $T_{o}$ . On the other hand, if the thickness of restricted mobility regions surrounding the multiplet decreased, the amount of cluster region should decrease, leading to the decreasing size of cluster loss tangent peak; this is not observed here. Thus, the



**Figure 4.** Glass transition temperatures of matrix  $(T_{g, m})$  and cluster  $(T_{g, c})$  regions of SPS ionomers neutralized with either Na or ADAs (dashed lines) as functions of (a) number of carbon atoms of ADAs and (b) wt % of ADAs (1 Hz data) (the numbers near the symbols indicate the number of carbon atoms of the ADAs). The  $T_{g, m}$  and  $T_{g, c}$  of SPS ionomers (ion content = 4.5 mol %) containing DCA (dotted lines, data were obtained from Ref. 32) and those of SPS ionomers (ion content = 8.1 mol %) neutralized with AMA (data were obtained from Ref. 22) are also included in (a).





**Figure 5.** Temperature difference  $(\Delta T_g)$  between cluster  $T_g$  and matrix  $T_g$  of SPS ionomers neutralized with either Na or ADAs as functions of (a) number of carbon atoms of ADAs and (b) wt % of ADAs (1 Hz data) (the numbers near the symbols indicate the number of carbon atoms of the ADAs).

possibility of the decrease in the thickness of restricted mobility regions by the introduction of ADAs can be ruled out. The  $T_{es}$ of 4.5-DCA ionomers are also presented in Figure 4(a) (data were obtained from Ref. 32). Because the DCA acts mainly as filler, the matrix and cluster  $T_{g}$ s remain constant with increasing chain length of DCAs. In the same figure, the  $T_{gs}$  of monofunctional amine, AMA-neutralized SPS ionomers (8.1 mol % of ion content), are also shown (data were obtained from Ref. 22). It is seen that the matrix and cluster  $T_{gs}$  of AMA-ionomers decrease with increasing AMA chain length, and that the  $T_{gs}$ can be fitted to a linear function for the matrix  $T_{gs}$  and a quadratic function for the cluster  $T_{gs}$ . These results are quite different from what we observed here, that is, no significant change in the matrix  $T_g$  for ADA ionomers vs. a strong decrease in the matrix  $T_g$  for 8.1-AMA ionomer. This can be understood: The AMAs, being monofunctional amines and having relatively freely movable alkyl chains, act as normal "internal" plasticizers for both the matrix and cluster regions. However, the ADAs, being difunctional amines, behave like "cluster" plasticizers that decrease only a cluster  $T_g$ . This is due to the fact that the alkyl chain of ADA, unlike that of AMA, would reside inside the multiplet and/or outside but only in close proximity to the multiplet because most of the ion pairs of both ends of the ADA chain would form ionic aggregates; sometimes, two ion pairs of one ADA may reside in the same multiplet, making the alkyl chain stay outside the multiplet. In this case, the alkyl chains of ADA are too short to reside in matrix regions and, thus, stay in the regions of restricted mobility; therefore, the ADA acts as cluster plasticizer. Now, let us consider the effect of the amount of ADA on the  $T_{gs}$  of the ionomer. Because the amount of ADAs in the ionomers changes with the ion content of the ionomers and the chain length of the ADAs, the  $T_{gs}$  are also shown as a function of wt % of ADAs in Figure 4(b). It is seen that the cluster  $T_g$  seems to decrease more smoothly as a

function of wt % of ADAs in comparison with that shown in Figure 4(a), and the decreasing rates depend on the ion content of ionomers. This indicates that the dynamic mechanical properties of ADA ionomers are affected by the ion content of ionomers but more strongly by the amount of ADAs.

Figure 5(a) exhibits temperature differences between the cluster  $T_g$  and matrix  $T_g$  ( $\Delta T_g$ ) as a function of the chain length of ADAs. First of all, as expected, the  $\Delta T_g$  decreases with increasing chain length of ADAs. As mentioned before, this is possibly due to the preferential plasticization of the cluster regions by the alkyl chains of ADAs, which becomes more effective with increasing chain length of ADAs. Second, the  $\Delta T_g$  becomes smaller with increasing ion contents of the ADA ionomers. This means that the preferential cluster plasticization effect becomes more profound for the ionomers of higher ion content, which have more clustered regions. Because the cluster  $T_g$  changes more smoothly as a function of wt % of ADAs, we also obtained  $\Delta T_g$  as a function of wt % of ADAs [see Figure 5(b)]. Interestingly enough, the  $\Delta T_g$  data seem to be fitted to a single equation. This implies that the  $\Delta T_g$  depends more strongly on the amount of ADAs, which, in turn, depends directly on both the type of ADAs and the ion content of ionomers, simultaneously.

The morphological details of the ionomers were examined by SAXS experiments. Shown in Figure 6 are the SAXS profiles of 4.1-Na and 4.1-ADA ionomers. A well-developed peak is seen at q (scattering vector) = ca. 1.7 nm<sup>-1</sup> for the 4.1-Na ionomer, which corresponds to a Bragg spacing ( $d_{\text{Bragg}}$ ) of about 3.7 nm. This Bragg spacing, ascribed to an intermultiplet distance, is almost the same as the results obtained elsewhere.<sup>22,39-43</sup> In the present work, the increase of ADA chain length from  $C_2$  to  $C_{12}$  induces a shift of SAXS peak position from  $q = \text{ca. 1.8 nm}^{-1}$  to  $q = \text{ca. 1.5 nm}^{-1}$  with decreasing its intensity. The shift of the peak to smaller q values indicates that the distance between scattering centers increases, which, in turn, means that the



Figure 6. SAXS profiles of SPS ionomers (ion content = 4.1 mol %) neutralized with either Na or ADAs.



Figure 7. XRD patterns of SPS ionomers (ion content = 4.1 mol %) neutralized with ADA10 and ADA12.

number of scattering centers decreases since the number of scattering centers is inversely proportional to the distance between scattering centers. In addition, the decreasing intensity can be caused by the following two factors: the number of the scattering centers (i.e., multiplets) at prevalent distances decreases with increasing chain length, and the electron density contrast of the scattering centers decreases. It should be noted that the ADA molecules with long chains lead to the reduction of the short range order in multiplets arrangement in the cluster regions. Thus, for ADA10 and ADA12 ionomers, only a small number of multiplets of relatively low electron density may exist. Therefore, the size of the SAXS peak decreases drastically, and the peak position shifts to lower q value. In the present work, if some of the alkyl chains of the ADAs reside in multiplets, the sizes of the multiplets will increase as the chain length of ADAs increases. Then, the enlargement of multiplet sizes increases the distance between multiplets, to some extent, and decreases the effective electron density of multiplets, which, in turn, lowers the SAXS peak intensity. In addition, 4.1-ADA12 ionomer shows an additional small SAXS peak at  $q = ca. 3.8 \text{ nm}^{-1}$  ( $d_{\text{Bragg}} = ca. 1.7$ nm). This morphological difference suggests that the role of ADA12 may not be the same as that of the rest of ADAs. The XRD profile of the 4.1-ADA12 ionomer shows a small sharp peak at  $2\theta$  = ca.  $6^{\circ}$  ( $d_{\text{Bragg}}$  = ca. 1.5 nm) and a very broad peak at larger angles, associated with the amorphous phase of the polymers (see Figure 7). The rest of ionomers show only a very broad peak (only XRD pattern of ADA10 is shown here for comparison). At this time, it should be mentioned that the freezedried ADA12 ionomer in a powder form does not show the small peak, but the sample molded and annealed at high temperatures exhibits the peak. This indicates that the small XRD peak is originated from the thermal treatment of ADA12 ionomer. Interestingly enough, the Bragg spacing values calculated from

the positions of the small SAXS and XRD peaks are similar to the length of fully extended ADA12 molecules (i.e., ca. 1.6 nm). Thus, it can be suggested that the small peaks in the SAXS and XRD profiles are due to the presence of phase-separated quaternary ADA12 salts. This phase-separated ADA12 salt might act as filler that increases ionic modulus strongly; however, it does not affect the cluster  $T_g$  since the cluster  $T_g$  is related with both the strength of ionic interaction and the amount of cluster regions. At this point, it should be noted that the melting temperature of 1-dodecylamine is 28-30°C, but that of its quaternary form, 1dodecylamine hydrochloride, is 186-188°C; the melting temperatures of 1,2-diaminoethane and 1,4-diaminobutane are 8-11°C and 25-28°C, respectively, but those of their quaternary form 1,2-diaminoethane dihydrochloride and 1,4-diaminobutane dihydrochloride are over 300°C and 279-281°C, respectively.34 Thus, in the present work, with consideration of the melting temperature of pure ADA12 of 67-69°C, one can expect that the melting temperature of the quaternary ADA12 would be very high. This implies that the phase-separated quaternary ADA12 molecules can act as filler above matrix Tg. However, it should be mentioned that at this moment we do not have a clear explanation for the reason why the rest of ADAs are not phase-separated.

Let us discuss the possible reasons for the change in the properties of the SPS ionomers by the incorporation of the ADA. First of all, the addition of small organic molecules containing amine groups to copolymers containing sulfonic acid groups creates ion pairs by proton-transfer from the acid groups to the basic amine groups. Because the ADAs are bifunctional, one ADA molecule can form two ion pairs with two acid groups of the copolymers, resulting in physical crosslinks. In this case, the alkyl chains of the ADAs may reside both inside and outside the multiplets. The alkyl chains remaining inside the multiplet lead to the increase in the size of the multiplets. This prevents ammonium-sulfonate ion pairs from approaching closely each other. As a result, the strength of interactions between adjacent ion pairs becomes weak, and it becomes weaker with increasing chain length of ADAs. The decrease in the temperature range of the ionic plateau and the shift rate of the cluster loss tangent peak to lower temperatures with increasing chain length of ADAs are in accordance with this expectation. Furthermore, if the size of the multiplet increases upon the neutralization with ADA but the average number of anionic groups per multiplet is the same, the crowdedness of polymer chains emanating from the multiplet will be reduced due to the larger contact surface area of the multiplet per emanating polymer chain. This, in turn, makes the clustered regions relatively less crowded, compared to that of the Na ionomers, without changing the relative amount of clustered regions in the ionomer. If this is the case, the ionic modulus of ADA ionomer will decrease not by the decreases in the amount of clustered region but by the less crowdedness of the clustered region. In addition, the alkyl chains of ADAs can also reside in the regions of restricted mobility, which induces more free volume in the cluster regions. This also decreases the cluster  $T_{e}$ . In this case, one can expect the similar sizes of the deconvoluted matrix and cluster loss tangent peaks and the decreasing ionic modulus with increasing chain length of ADAs, which were what we observed here. If ADAs act as plasticizer for the multiplets



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and clustered regions, the amount of the ADAs must affect the  $T_{gs}^{44,45}$ ; the  $T_{g}$  data, indeed, show direct relation with the amount of ADAs, indicating the plasticization by ADAs. In the case of ADA12 molecules, some of them may be phase-separated and act as filler that increases ionic modulus, and the ADA12-neutralized ionomer shows a second SAXS peak and an XRD peak for the phase-separated regions.

## CONCLUSIONS

It was found that the ionic modulus decreased with increasing chain length of ADAs, except for the ADA12, indicating that the addition of ADAs induced more flexibility in the polymer chains in the restricted mobility regions surrounding multiplets. Upon the neutralization of the SPS with ADAs, only a small change in the shape, size and position of the matrix loss tangent peaks of the ionomers was observed. However, the position of the cluster loss tangent peaks, with similar sizes, shifted drastically to low temperatures. Thus, it was suggested that the alkyl chains of ADAs could reside both in multiplets and cluster regions and acted mainly as cluster plasticizer. In the case of ADA12 molecules, however, some of them might be phase-separated, acted as filler particles.

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## Tangible Plasticization/Filler Effects of Sodium Salts of Dimer Acids on the Mechanical Properties of Styrene Ionomers

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**ABSTRACT**: The effects of the presence of dimer acid (DA) molecules in Na-sulfonated polystyrene (PSSNa) and poly(styrene-co Na-methacrylate) (PSMANa) ionomers on the ionomer properties were investigated using a dynamic mechanical analysis technique. The DA decreased the matrix and cluster  $T_{gs}$  of PSSNa ionomer without changing the ionic modulus, suggesting that the DA resided both in the matrix and cluster regions of PSSNa ionomer and acted mainly as a plasticizer. On the other hand, the DA decreased the cluster  $T_{g}$  of PSMANa ionomer, without changing the matrix  $T_{g}$ , and also increased the ionic modulus, implying that the DA behaved like plasticizer only for the cluster regions. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2443–2450, 2013

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## INTRODUCTION

Ionomers are polymeric materials containing a relatively small amount of ionic groups (<15 mol %) embedded in a polymer matrix of low dielectric constant.<sup>1</sup> The presence of the ionic groups in the polymer matrix generally causes ion aggregation. The ionic aggregates (so-called multiplets) induce the restriction of the mobility of the polymer chains emanating from the multiplet and in the vicinity of the multiplets.<sup>2</sup> When the concentration of ionic groups of an ionomer is very low, the number of the multiplets is relatively small so that the restricted mobility regions of the polymer chains do not overlap, and the ionomer shows only the glass transition  $(T_g)$  of non-ionic polymer matrix (i.e. matrix  $T_g$ ). On the other hand, with increasing ion content, the number of the multiplets increases and the restricted mobility regions start overlapping. When the size of the restricted mobility regions becomes large enough to have their own  $T_g$  (i.e. cluster  $T_g$ ), the regions are called clustered regions. At this stage, the ionomer shows two  $T_{\rm g}$ s; the matrix  $T_{\rm g}$  is seen at low temperatures, and the cluster  $T_{\rm g}$  occurs at high temperatures. In addition, the ionomer exhibits an "ionic" plateau in the plots of log(storage modulus) vs. temperature, which is shown in the temperature range between the matrix and cluster  $T_{gs}$ .<sup>3,4</sup> The height and width of ionic plateau are mainly related with the amounts of clustered regions and the strength of interactions between ionic groups in the multiplets, respectively.<sup>1</sup>

Only a few studies have been performed on the effects of the aliphatic dicarboxylic acid salts on the properties of amorphous polystyrene (PS)-based random ionomers.<sup>5,6</sup> It was suggested that the di-functional organic salts became phase-separated and acted mainly as filler particles in poly(styrene-*co* Na-methacrylate) (PSMANa) ionomers.<sup>5</sup> It was also found that when a large amount of sodium hexadecanedioate was added to the poly (styrene-*co*-sodium styrenesulfonate) (PSSNa) ionomer, the organic salt acted both as a reinforcing filler and as preferential plasticizer for the clustered region of PSSNa ionomers.<sup>6</sup> On comparing these results with those of other systems, it was proposed that the amount of the additives was responsible for the increasing ionic modulus.

These days, the environmental regulations on industrial consumption have been tightened up, and there is an urgent need for the development of new eco-friendly materials. Thus, natural products (e.g. vegetable oil), non-toxic, and environmentalfriendly products have gained much attention in regard to the development of "green chemicals". Recently, we have conducted a research on the preparation and modification of bio-based monomers. In course of the research, various "dimer acids" (DA), e.g. monocyclic, bicyclic, acyclic DA (Scheme 1), have been prepared from waste fatty acid cooking oils (vegetable and animal oils) as raw materials; the detailed compositions of the DAs are not known at present, but it is known that the reaction

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Scheme 1. Chemical structures of dimer acids obtained from waste fatty acid vegetable oils.

condition could control the compositions. From our previous studies,<sup>5,6</sup> we have known that the DA obtained from the waste cooking oil, being eco-friendly additives, can also be utilized as filler/plasticizer for the PS-based ionomers. Thus, in this study, we attempted to investigate the effects of the addition of sodium salts of DA compounds to the PS-based ionomers on the mechanical properties and morphology of the ionomers.

## **EXPERIMENTAL**

## Sample Preparations

The preparation method of DA using the fatty acids of soybean oil, modified from the work by Paschke et al.7 and Wheeler and White,8 is described briefly below: Fatty acid, catalyst, hypophosphoric acid, and deionized water were placed in a high-pressure stainless-steel reactor that was equipped with a mechanical stirrer and a cooling water line equipped with a temperature controller. The reactor was sealed and purged with N<sub>2</sub> gas four times to remove O<sub>2</sub>, and then N<sub>2</sub> gas was released. The reactor was heated to 250°C, and kept at that temperature for 6 hr. When the reaction was complete, the products were taken out from the reactor, and the hypophosphoric acid was added to the products for the neutralization, which was then stirred at 80°C for 1 hr. Subsequently, diatom earth was added to the products: the solution was stirred sufficiently and, then, filtered. Finally, the DAs were separated from the monomer fatty acids by using a distillation process at 270°C. To prepare the ionomers, polystyrene (PS) homopolymer (MW = ca.

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300,000) and poly(styrene-co-methacrylic acid) PSMAA copolymer (MW = ca. 300,000) containing 7.0 mol% of methacrylic acid units were synthesized by the method described elsewhere.<sup>4</sup> Poly(styrene-co-styrenesulfonic acid) copolymer was prepared by the sulfonation of the PS using the method reported by Makowski et al.<sup>9</sup>; the content of the styrenesulfonic acid units was 7.7 mol%. To prepare the ionomer samples containing varying amounts of DA, the DA and copolymers were dissolved in a benzene/methanol (9/1, v/v) mixture, and the acid groups of the DA and copolymers were fully neutralized with methanolic NaOH solution. Then, the samples were freeze-dried and dried further in a vacuum oven at ca. 150°C for 24 hr. For the dynamic mechanical property measurements, the samples were compression-molded when the mold temperatures reached ca. 190 and 230°C for the methacrylate and sulfonated ionomers, respectively, at a pressure of ca. 25 MPa. The molded samples were annealed under a vacuum at 150°C for 12 hr. The sample denotation used in the present work is PSSNa-x and PSMANax, where PSSNa and PSMANa are Na-neutralized sulfonated polystyrene and poly(styrene-co-sodium methacrylate) ionomers, respectively, and x indicates the weight % of Na-neutralized DA. To compare the results obtained from the DA-containing ionomers with those obtained from the ionomers containing only one type of sodium salt of aliphatic diacids, we also prepared PSSNa and PSMANa ionomers containing varying amounts of sodium salt of aliphatic diacid, i.e. sodium hexadecanedioate (HD). An ASPECT 1000 Fourier transform infrared spectrometer (Bruker AXS, Madison, WI) was used to check the neutralization of PSSNa-x ionomers. The samples were pelletized with KBr and scanned 64 times, and the scanning range was from 4000 to 400 cm<sup>-1</sup>. It was found that in the wavenumber range of 900-1300 cm<sup>-1</sup> the IR spectrum of pure PSSNa ionomer was similar to those obtained by other researchers10-19 and was also similar to those of DA-containing ionomers (spectra are not shown here), indicating that the ionomers were fully neutralized. At this point, it should be mentioned that the PSMANa and PSSNa ionomers are known to be thermally stable well above 300°C,<sup>20</sup> but the thermal stability of Na-neutralized DA is not known yet. Thus, a TA instrument 2050 thermogravimetric analyzer (TGA) was utilized to study the thermal stability of the Na-neutralized DA in the ionomers. The experiments were carried out as a function of temperature, over the range of 50-500°C, at a heating rate of 10°C min<sup>-1</sup> under nitrogen and at a N<sub>2</sub> flow rate of 30 mL min<sup>-1</sup>. For a thermal property study, a TA DSC 2010 differential scanning calorimeter (TA Instruments, New Castle, DE) was used. The samples were scanned using the DSC from 30°C to 300°C, with a heating rate of 10°C  $\min^{-1}$ .

## Dynamic Mechanical Property Measurements

The storage modulus (E') and loss tangent (tan  $\delta$ ) of each sample were measured as a function of temperature using a TA Instruments Q 800 dynamic mechanical analyzer in a dual cantilever-bending mode. The samples were heated at a heating rate of 1°C min<sup>-1</sup>. The detailed data analysis was performed using the data obtained at 1 Hz. When deconvolutions on the loss tangent data were necessary, we performed the curve deconvolutions using PeakFit program (Jandel). The best fits were





Figure 1. TGA thermograms of PSMANa-0, PSSNa-0, PSSNa-6.5, and PSSNa-41.5 ionomers.

achieved by assuming an exponential background and fitting the matrix and cluster peaks with Gaussian Area peaks.

## Small Angle X-ray Scattering Experiments

The small angle X-ray scattering (SAXS) experiments were conducted at Station 3 C of Pohang Light Source (PLS) synchrotron radiation source (Pohang, Korea). The sample-to-detector distance was 1 m, which allowed SAXS data to be obtained in the q (scattering vector) ranging from ca. 0.2 to 4.2 nm<sup>-1</sup>, where  $q = 4\pi \sin\theta/\lambda$ ;  $\theta$  is half the scattering angle, and  $\lambda$  is the X-ray wavelength ( $\lambda = 0.1608$  nm).

## **RESULTS AND DISCUSSION**

Figure 1 shows the weight loss of PSMANa-0 and PSSNa-x ionomers as a function of temperature. At this point, it should be mentioned that we chose only one ionomer system that contains Na-neutralized DA, i.e. PSSNa-x ionomers, because the purpose of this TGA study was to investigate the thermal stability of the Na-neutralized DA, not those of the ionomers. The PSMANa-0 and PSSNa-0 ionomers are shown to be thermally stable well above 300°C.  $^{20}$  The temperatures of 2% and 5% weight loss for the PSSNa-0 ionomer are ca. 320 and 370°C, respectively, while those for the PSSNa-6.1 ionomer are ca. 270 and 370°C. On the other hand, the temperatures of 2% and 5% weight loss for the PSSNa-41.5 ionomer are ca. 260 and 310°C, respectively. Thus, in the present work, the mold temperatures of 190 and 230°C for the methacrylate and sulfonate ionomers are suitable for the sample preparation and for the measurement of dynamic mechanical properties of these ionomers, since residence times are short.

The loss tangents of PSSNa and PSMANa ionomers containing varying amounts of DA are shown in Figure 2 as a function of temperature. First of all, as expected, two loss tangent peaks are seen in the figure; the matrix peak at low temperatures and the cluster peak at high temperatures. The presence of well-developed two loss tangent peaks indicates that these ionomers are well clustered ionomers.<sup>1</sup> Secondly, it is observed that the

positions of the matrix and cluster peaks of the PSSNa ionomers shift to lower temperatures with increasing amounts of DA. In addition, the intensity of the matrix peak decreases gradually with increasing DA amounts, but that of the cluster peak seems to increase slightly. In the case of PSMANa ionomers, only the cluster peak position shifts to lower temperatures, but the matrix peak position seems to remain constant. The intensities of the matrix and cluster peaks of the PSMANa ionomers change in a similar way found in the PSSNa ionomers. In the case of the loss tangent and storage modulus curves of the PSSNa and PSMANa ionomers containing HD, even though we obtained them by using the samples that we prepared in the present work, we do not show them here because similar results had already been shown elsewhere.<sup>5,6</sup> We only use the  $T_{gs}$  and ionic moduli of HD-containing ionomers to compare them with those of the ionomers containing DA.

Figure 3 shows, as a function of the amounts of DA or HD, the  $T_{\rm g}$ s of the PSSNa and PSMANa ionomers obtained from the positions of the loss tangent peaks.

The data can be fitted to linear functions and the intercepts and slopes of the fitted lines for the  $T_{gs}$  of PSSNa and PSMANa ionomers containing either DA or HD are listed in Table 1.

The matrix and cluster  $T_{\rm g}$ s of the PSSNa ionomers decrease in similar rates with increasing amounts of DA. This suggests that the DA might act as plasticizer, at least to some extent, in the PSSNa ionomer. In addition, the decreasing rates of  $T_{\rm g}$ s (i.e., ca. 1°C/wt%) imply that the DA might be very effective plasticizer, which is one of very important factors for polymer processing.



Figure 2. Loss tangents of the PSSNa and PSMANa ionomers containing varying amounts of DA as a function of temperature, measured at 1 Hz.



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**Figure 3.** Matrix and cluster  $T_{gs}$  of PSSNa and PSMANa ionomers containing DA (left) or HD (right) obtained from the loss tangent peak positions (at 1 Hz) as a function of wt% of DA or HD.

In the case of PSMANa ionomer, the cluster  $T_{\rm g}$  also decreases but slowly. On the other hand, the matrix  $T_{\rm g}$  seems to remain constant at 125°C. The results mentioned above imply that the roles of DA in the PSSNA and PSMANa ionomers are not the same; the DA in the PSMANa ionomers might behave like plasticizer only for the cluster regions. In the cases of the ionomers containing HD, the decreasing rates of the matrix and cluster  $T_{\rm g}s$  are lower than those of the PS ionomers containing DA. These results clearly indicate that the effect of the presence of the DA on the  $T_{\rm g}s$  of PSSNa ionomers is stronger than that of the HD.

The storage moduli of the PSSNa and PSMANa ionomers containing varying amounts of DA are shown in Figure 4 as a function of temperature.

In the case of PSSNa-0 ionomer, it is seen that the modulus curve changes from a glassy modulus, a sharp modulus drop due to the glass transition of matrix regions, a relatively long and horizontal "ionic" plateau (the segment of the modulus curve between the matrix and cluster  $T_{\rm g}$ s), a second modulus drop due to the glass transition of the cluster regions, a slight downward slope related to a rubbery modulus and the last modulus drop related to sample flow. It is observed that, with increasing amounts of DA, the slopes of the modulus curve for

**Table I.** The Intercepts and Slopes of the Lines Fitted to the  $T_{gs}$  of PSSNa and PSMANa Ionomers Containing Either DA or HD

	Cluster (T <sub>g</sub> )		Matrix (T <sub>g</sub> )	
lonomers	Intercept	Slope	Intercept	Slope
PSSNa-DA	237	-1.2	124	-1.0
PSMANa-DA	209	-0.5	125	0
PSSNa-HD	245	-0.3	126	-0.2
PSMANa-HD	213	-0.4	127	0



Temperature (°C)

Figure 4. Storage moduli of the PSSNa and PSMANa ionomers containing varying amounts of DA as a function of temperature, measured at 1 Hz.

the matrix  $T_g$  and cluster  $T_g$  become less steep. This indicates that, with increasing amounts of DA, the glass transitions take place in a relatively wider temperature range. The onset points of the modulus drops for the matrix and cluster  $T_g$ s of the PSSNa ionomer shift to lower temperatures with increasing DA contents. It is also observed that the slope of ionic plateau becomes slightly steeper with increasing DA amounts. In the case of the PSMANa ionomers, it is seen that the changes of modulus curves with the amounts of DA are different from those found in the PSSNa ionomers. Especially, with increasing amounts of DA, the onset points of the modulus drop for the matrix glass transition of the PSMANa ionomers seems to remain at similar positions. The slope of ionic plateau of the PSMANa ionomers becomes also steeper with increasing amounts of DA.

The presence of ionic plateau is the unique characteristics of PS-based ionomers. Thus, it is useful to analyze the ionic plateau in more detail to gain an insight into the roles of DA in the ionomers. Before we start to discuss the ionic plateau of the ionomer containing DA, let us review the ionic plateau of pure PSSNa and PSMANa ionomers. Since some of amorphous ionomers show the ionic plateau between the matrix and cluster  $T_{\rm g}$ s, it can be thought that the cluster regions including multiplets act as cross-links as well as reinforcing filler particles.<sup>3,21–24</sup> If the multiplets remained intact in the temperature range between the matrix and cluster  $T_{\rm g}$ s, the ionomer would show a modulus plateau (i.e. ionic plateau), higher than the rubbery plateau, due to the filler effect of the clusters. The height and width of ionic plateau are related to the degree of clustering and the strength of the interactions between the ion pairs in the

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multiplets, respectively.<sup>1,3,20</sup> As can be seen in Figure 4, the ionic plateau of the PSSNa ionomer is lower but wider than that of the PSMANa ionomer of the same ion content. This is due to the differences in the position of ionic groups and the strength of interactions between the ion pairs in the multiplets. Firstly, the sulfonate anionic group of the PSSNa ionomer and the carboxylate anionic group of the PSMANa ionomer are attached to the para position of the benzene ring of a styrene unit and the main chain of the ionomer, respectively. Thus, the distance between the anionic group and the main chain is longer for the PSSNa ionomer, compared to the PSMANa ionomer. This implies that the ion pairs of the PSSNa ionomer can form larger multiplets, compared to the PSMANa ionomer,<sup>3</sup> because of less steric hindrance. Secondly, the interactions between the Na-sulfonate ion pairs are stronger than those between the Na-carboxylate ion pairs.<sup>3,25</sup> This leads to more ion pairs per multiplet of the PSSNa ionomer, compared to those of PSMANa ionomer of the same ion content. At this point, it should be mentioned that the ion-hopping is related to the strength of interactions between ion pairs in the multiplets and is one of the cluster glass transition mechanisms:<sup>3,4,26-33</sup> When the ion-hopping occurs, the storage modulus of the ionomer starts decreasing. Naturally, the more ion pairs per multiplet and the stronger interactions between ion pairs in the multiplets of the PSSNa ionomer make the ion-hopping occur at higher temperatures (i.e. higher cluster  $T_g$ ), compared to the PSMANa ionomer. This higher cluster  $T_{\rm g}$  causes a wider ionic plateau for the PSSNa ionomer. Now, let us talk about the height of ionic plateau in the modulus-temperature plots, which, again, is not directly related with the cluster  $T_{\rm g}$  that is mainly related with the strength of interactions between ion pairs. It is known that with increasing ion contents, the ionic plateau shifts to higher positions,<sup>4</sup> indicating that the ionic plateau position is associated with the degree of clustering. Since the PSSNa ionomer has more ion pairs per multiplet than the PSMANa ionomer, there must be fewer multiplets for the PSSNa ionomer, at the same ion content. If the thickness of reduced mobility regions surrounding the multiplets were constant, the size of the restricted mobility regions would be smaller for the ionomer having fewer multiplets. Thus, at the same ion content, the degree of clustering (i.e. the size of reduced mobility regions) of the PSSNa ionomer is lower than that of the PSMANa ionomer. As a result, the ionic plateau of the PSSNa ionomer is lower than that of the PSMANa ionomer, even though the cluster  $T_g$  of the PSSNa ionomer is higher than that of the PSMANa ionomer.<sup>3</sup> One should keep these aspects in mind when one interprets the modulus data of polystyrene ionomers.

To evaluate the position of ionic plateau, we obtained the ionic moduli ( $E'_{ionic}$ ) of the ionomers. The ionic modulus is a modulus at the point of a minimum slope in the ionic plateau region. Figure 5 shows the ionic moduli of the PSSNa and PSMANa ionomers containing various amounts of DA as a function of wt% of DA. This figure also includes the ionic moduli of styrene ionomers containing HD. It is seen that, with increasing DA amounts, the log $E'_{ionic}$  (Pa) of the PSSNa seems to remain constant at 7.0  $\pm$  0.008, but that of the PSMANa increases linearly. Figure 4 also shows that the ionic moduli of PSSNa and PSMANa ionomers containing HD also increase not



Figure 5. Ionic moduli of the PSSNa and PSMANa ionomers containing varying amounts of DA or HD as a function of wt% of DA or HD, measured at 1 Hz.

linearly but rather quadratically, with increasing HD amounts. It is clear that the increasing rates of log  $E'_{\rm ionic}$  of the ionomers containing HD are higher than those of the ionomers containing DA. At this point, it should be mentioned that the increasing ionic modulus of the PSSNa-HD or PSMANa-DA or PSMANa-HD ionomers might be due to the fact that the DA or HD in the ionomer might act as filler particles (the endothermic DSC peak for the  $T_{\rm m}$  of Na-neutralized HD and DA is seen at 222 and 228°C, respectively). In addition, the filler effect of the HD in the PSMANa ionomer is stronger than that of DA in the PSSNa and PSMANa ionomers on the increasing ionic moduli of the ionomers.

Shown in Figure 6 are the SAXS profiles of PSSNa and PSMANa ionomers containing varying amounts of either DA or HD. First of all, small-angle upturn is seen for all the ionomers. This upturn might be due to the compositional heterogeneity or the large-scale density fluctuations of scattering centers of the ionomers.34-40 In the case of PSSNa ionomer, a well-developed SAXS peak is seen at q (scattering vector) = ca. 1.5 nm<sup>-1</sup> and the peak position shifts to slightly higher q (indicating that the Bragg distance between scattering centers becomes slightly shorter) and the peak intensity increases, with increasing DA amounts. In addition, the width of the SAXS peak becomes narrower with increasing DA amounts. This implies that the DA molecules in the PSSNa ionomer act as plasticizer, which makes the  $T_{g}$ s of the matrix and cluster regions of the PSSNa ionomer lower, to some extent. This makes the formation of multiplets at relatively regular distances easier, which leads to the appearance of a narrower SAXS peak at higher q values. In the case of PSMANa ionomer, there is no well developed SAXS peak in the q range of 0.5–4  $\text{nm}^{-1}$ . However, upon the addition of DA, a peak is seen at  $q = ca. 2.0 \text{ nm}^{-1}$ , and the peak intensity increases progressively with increasing DA amounts, without changing the peak position and width, suggesting that the DA acts as plasticizer. In addition, a shoulder is seen at q = ca. 1.2









Figure 6. SAXS profiles of PSSNa and PSMANa ionomers containing varying amounts of DA or HD.

nm<sup>-1</sup> upon the addition of DA and becomes more visible with increasing DA amounts. This suggests that the shoulder is related to the formation of phase-separated DA molecules. In the case of PSSNa-HD ionomers, the SAXS peak at q = ca. 1.5nm<sup>-1</sup>, shifts to slightly higher q, but its intensity decreases strongly, with increasing HD contents. In addition, a new peak is seen at  $q = \text{ca. } 3.0 \text{ nm}^{-1}$ , and the peak intensity increases noticeably as the HD content increases. For the PSMANa, usually showing a very weak shoulder at  $q = \text{ca. } 3.0 \text{ nm}^{-1}$ , a new peak is also seen at the same position, with increasing its intensity, as the HD content increases. The above results imply that the appearance of the peak at  $q = \text{ca. } 3.0 \text{ nm}^{-1}$  is related with the presence of phase-separated HD that acts as filler particles and increases ionic modulus.

Figure 8. DSC thermograms of DA, PSSNa, and PSMANa ionomers containing varying amounts of DA.

The IR spectra of Na-neutralized DA, PSSNa and PSMANa ionomers in the wavenumber range of  $900-2000 \text{ cm}^{-1}$  are seen in Figure 7. We assigned IR bands with reference to others' interpretation.<sup>41,42</sup> In the case of PSSNa ionomers, the intensity of IR bands at ca. 1740 cm<sup>-1</sup> increases with increasing DA contents, but the intensities of the rest of IR bands decrease systematically. At this point, it should be noted that the IR band at ca. 1680 cm<sup>-1</sup> decreases drastically for the PSSNa-41.5 ionomer; we do not have clear explanation for this finding, yet. For the PSMANa ionomers, the IR spectra do not show any new IR band upon the addition of DA compound. Only the relatively intensities of the IR bands decrease with increasing DA contents. This different trend in IR band intensities also supports the idea that the roles of DA in PSMANa and PSSNa ionomers are not the same.



Figure 7. IR spectra of DA, PSSNa, and PSMANa ionomers containing varying amounts of DA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



The DSC thermograms of Na-neutralized DA itself, PSSNa and PSMANa ionomers are shown in Figure 8. It is seen that the DA shows a broad endothermic peak at 228°C, which is related to the melting of crystalized DA compounds. For the PSSNa ionomers, only the glass transitions of the matrix regions of the ionomers are seen at ca. 120°C. In the case of the PSMANa ionomers of low DA contents, they also exhibit only the matrix glass transition. In addition to the matrix glass transition, PSMANa-24.0 and PSMANa-41.5 ionomers show a small shoulder at ca. 245°C and a small, broad endothermic peak at ca. 240°C, respectively. This endothermic peak is probably related to the phase-separated Na-neutralized DA. These DSC results are in agreement with the findings in DMA results discussed earlier.

Now, let us talk about the roles of DA molecules in the PSSNa and PSMANa ionomers in more detail. The fact that the matrix and cluster Tgs of PSSNa ionomers decrease significantly in a similar way with increasing DA amounts suggests that the DA molecules may reside in both the matrix and cluster regions of PSSNa ionomer relatively evenly and act as effective plasticizer for both the matrix and cluster regions, which lowers the matrix and cluster  $T_{gs}$ . Naturally, some of Na-carboxylate ion pairs of the DA may participate in the formation of multiplets with Na-sulfonate ion pairs of the PSSNa ionomer. If this were the case, the interactions between ion pairs in the multiplets might become weaker due to the heterogeneous compositions of ion pairs in the multiplets, at least to some extent. Thus, the ion-hopping would occur at relatively lower temperatures, leading to a lower cluster  $T_{g}$ . In the case of ionic modulus, since the DA molecules in the PSSNa act mainly as plasticizer, the ionic modulus would not be expected to change; this is what we observed here. According to the dynamic mechanical data of the PSMANa ionomer containing DA, the presence of the DA does not change the matrix  $T_{\rm g}$ s, but it decreases the cluster  $T_{\rm g}$ , and it increases the ionic modulus strongly. This is due to the phase-separation of DA molecules. It should be recalled that the DA molecules in the present work are mixtures that consist of monocyclic, bicyclic and acyclic compounds, but the HD molecules have linear alkyl chains having Na-carboxylate ion pairs at both ends of the chain. Since aliphatic dicarboxylate can form the filler particles more easily, the filler effect of HD would be stronger than that of DA.<sup>5,6</sup> In addition, as expected, the plasticization effect of DA is more profound than that of HD because of the nature of DA, i.e. mixture of various DAs.

## CONCLUSIONS

The DA molecules resided in the hydrocarbon matrix and cluster regions of PSSNa ionomers, and acted mainly as plasticizer to decrease the matrix and cluster  $T_{\rm g}$ s without changing the ionic modulus. In the case of PSMANa ionomer, the monocyclic and bicyclic DA molecules in the PSMANa ionomer also acted as plasticizer, but the acyclic DA molecules were phase-separated to form filler particles that increased the ionic modulus of the PSMANa ionomer. The above findings suggested that the monocyclic and bicyclic DA molecules could be used as very effective plasticizer.

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# Effect of the number of methyl groups of the ionic repeat unit on the dynamic mechanical properties and morphology of poly(styrene-*co*-acrylate)-based ionomers



polyme



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## ABSTRACT

The dynamic mechanical properties of poly(styrene-*co*-Na tiglate) PSTANa, poly(styrene-*co*-Na methacrylate) PSMANa, and poly(styrene-*co*-Na acrylate) PSAANa ionomers were investigated to know the effect of the number of methyl groups of the acrylate unit on the mechanical properties and morphology of those ionomers. It was found that the ionic modulus of the PSTANa ionomers was much lower than that of the PSMANa ionomer but slightly lower than that of the PSAANa ionomers of comparable ionic unit content. The matrix and cluster  $T_g$ 's of the PSTANa ionomers were also found to be lower than those of the PSMANa and PSAANa ionomers. The PSTANa ionomers showed a very weak, broad shoulder-like feature at very small angles of X-ray diffraction or scattering profiles. Thus, it was suggested that the presence of two methyl groups on the alpha and beta carbons of an acrylate unit might induce the high energy barrier for the bond rotation, which made the formation of the multiplets difficult; therefore, the PSTANa ionomers became less clustered materials than the PSMANa and PSAANa ionomers.

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## 1. Introduction

Ionomers, copolymers that have a small fraction of ionic groups, have been used in a wide range of applications such as membranes, actuators, and packaging and coating materials [1-3]. The ionomers exhibit unique physical properties, compared with non-ionic polymers, due to the interactions between ion pairs. The ionic groups of the ionomer aggregate to form so-called multiplets; the ion aggregation is due to both the electrostatic interactions between ionic groups and the difference in polarities of polymer hydrocarbon matrix and ionic groups. According to the multiplet/ cluster model for amorphous random ionomers, the multiplets reduce the mobility of polymer chain segments surrounding the multiplets [4]. When the content of ionic monomer unit is relatively low, the number of multiplets is small, the size of the reduced mobility regions is relatively small, and, thus, the ionomer behaves like a non-ionic polymer. At this stage, the ionomers shows a typical glass transition of the non-ionic matrix regions. As the content of ionic monomer unit increases, the number of the multiplet increases, and the reduced mobility regions start overlapping. Above certain ionic unit content, the overlapping regions of the reduced mobility become large enough to show their own glass transition. These regions of reduced mobility are then called "clusters" [4]. Now, the ionomer behaves like a bi-phasic material and, thus, exhibits two glass transitions; the glass transition at low temperatures is due to the glass transition of polymer chains in the matrix (i.e. ion-poor) regions, while the glass transition at high temperatures to the glass transition of polymer chains in the cluster regions. At this time, it should be mentioned that two mechanisms are operative at the cluster glass transition; (1) the relaxation mechanism of polymer chains in the restricted mobility regions and (2) the hopping mechanism of ion pairs among multiplets [5–16].

It is well known that the chemical structures of ionomers are directly related with the properties of ionomers [1-3]. For example, if the size of counter-ion were small and the oxidation state of counter-ion were high, the attractive electric force  $F_{el}$  between the ion pairs in the multiplets would increase [17], and, thus, the cluster glass transition temperature ( $T_{g,c}$ ) of the ionomer would increase [5,13]. If the ionic groups were located farther from the polymer backbone chain, they would experience less steric hindrance, when they form multiplets, compared to the ionic groups attached directly to the polymer backbone chain [5]; thus, the former ionic groups form relatively larger but fewer multiplets [4,5]. If the thickness of the reduced mobility regions surrounding



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the multiplets were the same, the ionomer having larger but fewer multiplets would have smaller amounts of cluster regions than the ionomer containing smaller but more multiplets. In this case, the former ionomer would have a lower  $T_{g,c}$  due to the lower degree of clustering [5]. In addition, if the interactions between ionic groups became stronger, the ionomer would form large multiplets but would have a higher  $T_{g,c}$  [5]. Needless to say, many other factors also affect the mechanical and thermal properties of ionomers.

The mechanical properties of ionomers have been studied extensively because the information on the properties is necessary in order to use the ionomers as compatibilizers for polymer blends [18-20] or ion-exchange membranes [21-23] or ionomer membranes in polymer electrolyte membrane fuel cells [24-26]. Recently, the morphology and dynamics of various ionomers have also been investigated in more detail to provide new insight into the physical properties of the ionomers [14,16,27–30]. Prior to this work, one of the authors of this paper studied the mechanical properties and morphology of styrene-co-sodium acrylate (PSAANa) and its Cs-neutralized ionomers (PSAACs), respectively, and compared the mechanical and morphology data with those obtained from styrene-co-sodium methacrylate (PSMANa) and its Cs-neutralized ionomers, having a methyl group attached to the  $\alpha$ carbon of the acrylate unit [31]. It was found that the PSMANa ionomer showed a higher cluster  $T_g$  and a higher and longer ionic plateau in the plots of log(storage modulus (E')) vs. temperature in comparison with the PSAANa ionomer. Thus, it was suggested that the contact surface area occupied by two polymer chains emanating from the multiplet of the PSMANa ionomer was larger. compared with that of the PSAANa ionomer, because of the presence of the methyl group on the  $\alpha$ -carbon of the acrylate unit. Therefore, the number of ion pairs per multiplet was smaller for the PSMANa ionomer, and the average size of the multiplets of the PSMANa ionomer was slightly smaller than that of the PSAANa ionomer. It was also found that the Cs-neutralized PSMA ionomer (PSMACs) showed a small-angle x-ray scattering (SAXS) peak at slightly larger angles than the Cs-neutralized PSAA ionomer (PSAACs), indicating that the Bragg spacing between scattering centers of the PSMACs ionomer was slightly shorter than that of the PSAACs ionomer. Now, one question arises: what is the effect of the presence of two methyl groups attached to both the  $\alpha$ - and  $\beta$ -carbons of the acrylate unit on the dynamic mechanical properties and morphology of the ionomer? Thus, in this work, we prepared poly(styrene-co-sodium tiglate) (PSTANa) ionomers and compared their mechanical properties and morphology with those of PSMANa and PSAANa ionomers. The chemical structures of these three ionomers are shown in Scheme 1. Here, the sample denotations are PSTANa-y, PSMANa-y, and PSAANa-y, where y is the mole percentages of ionic repeat units.

## 2. Experimental section

#### 2.1. Sample preparation

For convenience, only a brief summary of a polymerization procedure is given here. To prepare poly(styrene-*co*-tiglic acid) PSTA random copolymers, we modified the method of bulk polymerization of poly(styrene-*co*-methacrylic acid) copolymers [32]. Purified styrene and tiglic acid monomers were used as monomers. Since the reactivity ratios of the two monomers had not been reported, we deduced the ratios from the reactivity ratios of styrene/acrylic acid (0.25/0.05), styrene/methacrylic acid (0.12/0.60) and styrene/itaconic acid (0.26/0.12) [33]; the reactivity ratios of the styrene/tiglic acid were assumed to be roughly 0.75/0.05. Detailed reaction conditions are listed in Table 1.



Scheme 1. The chemical structures of three ionomers studied in the present work.

The amount of benzoyl peroxide as the initiator was calculated to make the average molecular weight of copolymers of 300,000, and the reaction time was determined to make the heterogeneity of the mole fractions of acidic repeat units in each polymer chain less than 0.1. When the reaction was complete, the reaction solution was diluted with tetrahydrofuran, and the diluted solution was poured into a rapidly stirred excess of methanol to recover the copolymer samples. The precipitated polymer was filtered, and dried under a vacuum at 120 °C for 1 day. To determine the content of tiglic acid units, the PSTA acidic copolymers were dissolved in a benzene/methanol (9/1 v/v) mixture to make ca. 5% (w/v) solution, and the solution was titrated with standard methanolic NaOH solution to the phenolphthalein end point: the tiglic acid contents were found to be 3.4, 5.9, 7.1 and 11.1 mol%. To neutralize the acid groups, the acidic copolymers were dissolved in a benzene/methanol (9/1 v/v) mixture to make a 5% (w/v) solution, and a predetermined quantity of methanolic NaOH was added to the solutions to make poly(styrene-co-sodium tiglate) (PSTANa) ionomers. The solutions were freeze-dried and then dried further under a vacuum at 140 °C for at least 1 day. To compare the dynamic mechanical and morphological data of PSTANa ionomers with those of PSMANa and PSAANa ionomers, the PSMANa and PSAANa ionomers were also prepared in a similar way; the detailed copolymerization procedures were reported elsewhere [31,32]. For the dynamic mechanical analysis (DMA) experiments, the ionomer samples were compression-molded at a pressure of ca. 25 MPa for

Table 1				
Polymerization	conditions	for the	PSTA	copolymers

Content of ionic repeat units (mol%)	TA in monomer feed <sup>a</sup> (mol%/mass)	Benzoyl peroxide (g)	Reaction time (h)	Reaction temperature (°C)	Actual yield (%)
3.4	0.093/8.97	0.022	33.0	60	7
5.9	0.167/16.14	0.021	34.5	62	6
7.1	0.199/19.23	0.021	34.5	61	7
11.1	0.299/29.10	0.021	35.4	62	8

<sup>a</sup> Total monomer mass in all case was 100 g.



5 min when the mold temperature went up to ca. 200 °C. The samples were removed from the mold and annealed under a vacuum at 130 °C for 1 day. The dimensions of the molded samples were ca.  $2.0 \times 6.0 \times 30$  mm. For the SAXS experiments, the acidic copolymers were neutralized with CsOH to obtain higher electron density contrasts, compared to the ionomers neutralized with NaOH. The samples were also compression-molded. The molded samples in the form of a thin disk had the dimensions of ca. 10 mm (diameter)  $\times$  0.5 mm (thickness).

#### 2.2. Thermal property measurements

For the studies of the thermal stability of the PSTANa ionomer, a thermogravimetric analyzer (TGA) 2050 (TA Instruments, New Castle, DE) was utilized. The TGA experiment was carried out as a function of temperature, over the range of 50–550 °C, at a heating rate of 10 °C/min under N<sub>2</sub> atmosphere with a flow rate of 30 mL/min. A differential scanning calorimeter (DSC) 2010 (TA Instruments, New Castle, DE) was also used to detect the glass transition temperatures of the PSTANa ionomers. The samples were scanned from 30 °C to 300 °C at a heating rate of 10 °C/min.

## 2.3. Dynamic mechanical property measurements

For the measurement of the dynamic mechanical properties of the ionomers, a dynamic mechanical analyzer (DMA) Q-800 (TA Instruments, New Castle, DE) was utilized. The dual cantilever bending mode was used at five different frequencies; 0.3, 1, 3, 10 and 30 Hz, and the heating rate was 1 °C/min. For each sample, the storage moduli (E') and loss tangents were obtained as a function of temperature. The detailed data analysis was performed only on 1 Hz data.

#### 2.4. X-ray experiments

An X'pert PRO MPD X-ray diffractometer (PANalytical, Almelo, the Netherlands) using a Cu K $\alpha$  radiation source with a high purity Cu target was used to obtain the X-ray diffraction (XRD) patterns of the ionomers. The SAXS experiments at Station 3C of Pohang Light Source (PLS) synchrotron radiation source (Pohang, Korea) were also conducted. The generated beam energy was 10 keV (at 3.0 GeV operation modes), and the Rayonix 2D MAR165 detector was used. The sample-to-detector distance was 400 mm, which allowed SAXS data to be obtained in the q (scattering vector) range of 0.2–4.2 nm<sup>-1</sup>, where  $q = 4\pi \sin\theta/\lambda$ ;  $\theta$  was half the scattering angle, and  $\lambda$  was the x-ray wavelength ( $\lambda = 0.1608$  nm). The SAXS data were plotted as relative intensity vs. q after correction for sample absorption and a background.

## 3. Results

The TGA study reveals that the temperatures of 1% and 5% weight loss of the PSTANa-11.1 ionomer are 304 and 387 °C, respectively (TGA thermogram is not shown here). Thus, in the present work, the molding temperature of ca. 200 °C and the sample drying and annealing temperature of 140 °C are thought to be suitable for the sample preparation because residence times of the samples at such high temperatures are relatively short, and the temperatures of the samples.

Fig. 1 shows the DSC thermograms of the three selected PSTANa ionomers. Only one  $T_g$  is observed, the position of which is very close to that of the  $T_g$  of the matrix regions of polystyrene-based ionomers [31,32].



Fig. 1. DSC thermograms of PSTANa ionomers.

The  $T_g$  shifts from 109 °C to 123 °C with increasing ionic unit content. The presence of only the matrix  $T_g$  may be due to the small heat capacity change for the  $T_g$  of the cluster phase. At this point, it should be mentioned that Suchocka-Gałaś [34,35] and Kim et al. [31] also found only one  $T_g$  on DSC thermograms for the PSAANa and PSAACs ionomers, respectively, which was related to the glass transition of a predominant phase of the ionomers.

In Fig. 2, the log(storage moduli (E')) and loss tangents of PSTANa, PSMANa and PSAANa ionomers are seen as a function of temperature.

As the temperature increases, the storage modulus changes from a glassy modulus, to a glass transition of matrix regions  $(T_{g,m})$ , to an ionic plateau, to a glass transition of cluster regions  $(T_{g,c})$ , and to a rubbery modulus and sample flow. It is seen that, with increasing ionic unit content, the modulus curve shifts to higher temperatures progressively, and the modulus curve segment between two glass transitions, i.e. ionic plateau, shifts to higher modulus values. In the previous studies, it was found that the height of the ionic plateau was related with the degree of clustering, i.e. the amount and size of cluster regions, of the ionomer [4,5,13,32]. Thus, if the size of cluster regions increases, the ionic plateau will shift to a higher position. To discuss the height of ionic plateau quantitatively, we take the modulus value at the point of a minimum slope of ionic plateau in  $\log E'$  vs. temperature plots as "ionic" modulus  $(E'_{\text{ionic}})$ . The  $E'_{\text{ionic}}$  values of the three ionomer systems are shown in Fig. 3 as a function of ionic unit content.

It is seen that the  $E'_{ionic}$  increases with increasing ionic unit content, and the increasing rates of the  $E'_{ionic}$  values are in the following order: PSMANa > PSAANa  $\approx$  PSTANa. If the  $E'_{ionic}$  were solely related with the clustering degree, the above results might indicate that the degree of clustering of PSMANa ionomer is highest, that of PSTANa ionomer is lowest, and that of PSAANa ionomer is between them. In the cases of un-neutralized PSTA copolymers, they show only one modulus drop due to a matrix glass transition in the temperature range of ca. 100–130 °C; with increasing acidic unit content, the modulus drop moves to higher temperatures slightly (the dynamic mechanical data of PSTA copolymers are not shown here).



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Fig. 2. Storage moduli (E') and loss tangents of (a) PSTANa, (b) PSMANa, and (c) PSAANa ionomers as a function of temperature, measured at 1 Hz.

In Fig. 2, two loss tangent peaks are seen for all the ionomers, indicating that these ionomers behave like biphasic materials. As mentioned before, the loss tangent peak at relatively low temperatures is due to the matrix  $T_g(T_{g,m})$  and the peak at relatively high



**Fig. 3.** Log(ionic moduli) ( $E'_{\text{ionic}}$ ) of PSMANa, PSAANa, and PSTANa ionomers as a function of ionic unit content, measured at 1 Hz. This figure also includes the rubbery modulus ( $E'_{\text{rubbery}}$ ) of pure non-ionic polystyrene (PS).

temperatures is due to the cluster  $T_g(T_{g,c})$ . With increasing ionic unit content, the two peaks shift to higher temperatures with changing the relative areas under the peaks in the opposite direction, i.e. the area under the matrix peak decreases, but that under the cluster peak increases. Again, the PSTA acidic copolymers show only one matrix loss tangent peak, and the peak shifts to higher temperatures slowly with increasing acidic unit content (data are not shown here). From the positions of loss tangent peaks, one can obtain the glass transition temperatures ( $T_g s$ ) of the ionomers. The  $T_g s$  of the PSTANa, PSMANa and PSAANa ionomers, and PSTA acidic copolymers are shown in Fig. 4-(a) as a function of ionic (or acidic) unit content. It is obvious that the  $T_{g,m}$  and  $T_{g,c} s$  increase with increasing ionic unit content. The  $T_{g,m}$  and  $T_{g,c}$  data can be fitted to linear functions, and the fitting results are listed in Table 2.

It is clear that, at the same ionic unit content, the  $T_{g,c}$  is in the following order: PSMANa > PSAANa > PSTANa. In addition, the increasing rate of  $T_{g,c}$  (i.e. slope) of the PSMANa is highest, that of PSTANa is lowest, and that of the PSAANa is between them; but the slopes of the last two ionomers are not much different. In the cases of the matrix glass transition, the  $T_{g,m}$  is in the following order: PSMANa  $\approx$  PSAANa > PSTANa. The increasing rates of the  $T_{g,m}$  of both PSMANa and PSAANa are found to be not much different each other and higher than that of the PSTANa. In Fig. 4-(b), the temperature differences between  $T_{g,c}s$  and  $T_{g,m}s$  ( $\Delta T_g$ ) of the three ionomer systems are shown as a function of ionic unit content.

As expected from the difference in the increasing rates of  $T_{g,cS}$  and  $T_{g,mS}$ , the  $\Delta T_g$  of the PSMANa increases progressively, which is in accordance with the results reported elsewhere [32]. In the present work, it increases from ca. 70 °C to ca. 90 °C with increasing ionic unit content from 4.2 mol% to 13.5 mol%. For the PSAANa ionomers that have not methyl groups but only hydrogen atoms on





**Fig. 4.** (a) Matrix and cluster  $T_g s$  of PSTANa, PSAANa and PSMANa ionomers, and PSTA acidic copolymers as a function of ionic (or acidic) unit content, obtained from the loss tangent peak positions at 1 Hz. The matrix  $T_g s$  of PSTANa ionomers obtained from DSC experiments are also included in the figure. (b) Differences in the cluster and matrix  $T_g s$  of the three ionomers as a function of ionic unit content.

both the  $\alpha$ - and  $\beta$ -carbons of an acrylate unit, the  $\Delta T_g$  does not change much with ionic unit content, being 56  $\pm$  1.0 °C, which again coincides with the results reported elsewhere [31]. Interestingly enough, the PSTANa ionomers that have two methyl groups each on both the  $\alpha$ - and  $\beta$ -carbons of an acrylate unit also show a relatively constant  $\Delta T_g s$ , being 53  $\pm$  1.3 °C.

The activation energies ( $E_as$ ) for the glass transitions of the ionomers can be calculated using Arrhenius plots of log frequency vs. inverse temperature (confidence limits  $< \pm 30$  kJ/mol). Fig. 5 shows the plots of the  $E_as$  for the glass transitions of the matrix and cluster regions of some of PSTANa, PSMANa and PSAANa ionomers, and PSTA acid copolymers as a function of the ionic (or acidic) unit content.

The  $E_as$  for the matrix  $T_g$  increase slowly within the range of ca. 460–630 kJ/mol and those for the cluster  $T_g$  also increase within the range of ca. 210–390 kJ/mol, with increasing ionic unit content. The similar ranges of the  $E_a$  values for either the matrix  $T_gs$  or the cluster  $T_gs$  of PSTANa, PSMANa, and PSAANa ionomers suggest that their glass transition mechanisms are not much different from each other. The relatively large  $E_a$  values for the cluster  $T_g$  of PSTANa ionomer indicate that the loss tangent peak at high temperatures is related with a true glass transition [31,32].

It would be useful to have morphological data to understand the dynamic mechanical properties of the ionomers. Thus, we obtained the XRD patterns of PSTANa, PSMANa, and PSAANa ionomers. In Fig. 6-(a), it is seen that PSTANa-3.4 and PSTANa-5.9 ionomers do not show a peak.

However, PSTANa-7.1 ionomer shows a very broad shoulderlike feature, in the scattering vector q (=  $4\pi \sin\theta/\lambda$ ) range of

 Table 2

 Intercepts and slopes of the lines shown in Fig. 4.

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Ionomers	$T_{g,m}$		T <sub>g,c</sub>	
	Intercept (°C)	Slope (°C/mol%)	Intercept (°C)	Slope (°C/mol%)
PSTANa	107	2.7	157	2.9
PSMANa	114	3.3	178	5.1
PSAANa	106	3.9	170	3.1
PSTA	111	1.0	-	-



**Fig. 5.** Apparent activation energies for the glass transitions of PSTANa, PSMANa, and PSAANa ionomers, and of PSTA copolymers as a function of ionic (or acidic) unit content.

ca. 1.4–4.2 nm<sup>-1</sup>, related with the presence of multiplets. In the case of PSMANa ionomers (Fig. 6-(b)), only a very weak shoulderlike peak is observed at  $q = ca. 3.0 \text{ nm}^{-1}$  for PSMANa-9.8 ionomer. For PSAANa ionomers (Fig. 6-(c)), again, no XRD peak is seen for the ionomers of low ionic unit contents. However, a peak is observed for PSAANa-8.2 ionomer, with the position of the peak maximum at  $q = ca. 2.6 \text{ nm}^{-1}$ . Even though we could obtain XRD patterns of the Na-neutralized ionomers, the electron density of the small-sized multiplets containing Na<sup>+</sup> cations was too low to give us more defined morphological information, and, thus, we prepared ionomers, the multiplets of which contain Cs<sup>+</sup> cations instead of Na<sup>+</sup>, by neutralizing the PSTA copolymer with CsOH, and conducted SAXS experiments. At this point, it should be mentioned that the mechanical data of Na-neutralized ionomers may not be related directly to the morphology of Cs-neutralized ionomers. In case of poly(ethyl acrylate) ionomers, however, since the dynamic mechanical data of Cs-neutralized ionomers were found to be only slightly different from those of Na-neutralized ionomers [13], the SAXS study on the Cs-neutralized ionomers was thought to be very useful for the better understanding of the mechanical propertymorphology relationship of PSTANa ionomers. The SAXS profiles of the Cs-neutralized ionomers are shown in Fig. 6-(d), -(e) and -(f). Needless to say, the Cs-ionomers show a stronger X-ray peak, compared to the Na-ionomers, due to the much higher electron density of Cs<sup>+</sup> than that of Na<sup>+</sup>. It is seen that the PSTACs-3.4 ionomer exhibits only a small-angle upturn, which is due to a relatively small number of small-sized multiplets (Fig. 6-(d)). With increasing ionic unit content, however, the PSTACs ionomer starts showing a broad SAXS peak, and the peak shifts to higher angles with increasing its intensity. The PSMACs and PSAACs ionomers also show a similar trend, but their SAXS peak widths are narrower and the peak intensities are higher than those of PSTACs ionomer of comparable ionic unit contents. From the *q* value at which the peak shows its maximum (i.e.  $q_{max}$ ), one can calculate the Bragg distances ( $d_{\text{Bragg}} = 2\pi/q_{\text{max}}$ ) between the scattering centers, i.e. multipelts. The  $q_{\text{max}}$  and  $d_{\text{Bragg}}$  of the ionomers are presented in Fig. 7-(a) and -(b), respectively.

It is clear that the  $q_{\text{max}}$  is the highest for the PSMACs and the lowest for the PSTACs ionomer, and that the  $q_{\text{max}}$  shifts to higher q



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Fig. 6. XRD patterns of (a) PSTANa, (b) PSMANa, and (c) PSAANa ionomers; SAXS profiles of (d) PSTACs, (e) PSMACs, and (f) PSAACs ionomers.

values with increasing ionic unit content. As expected, the Bragg distance of the ionomers is the largest for the PSTACs and the smallest for the PSMACs ionomer of the same ionic unit content. This, in turn, implies that the number of scattering centers (i.e. multiplets) is the largest for the PSMACs and the smallest for the PSTACs ionomer. In addition, it is seen that the Bragg distance decreases with increasing ionic unit content, which is due to the fact that with increasing ionic unit content, more multiplets form, and, thus, the intensity of SAXS peak increases and the peak shifts to higher q.



**Fig. 7.** (a) SAXS peak positions and (b) Bragg distances as a function of ionic unit content of PSTACs, PSMACs and PSAACs ionomers.

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## 4. Discussion

At this point, it is useful to recall the SAXS data of poly(styreneco-Cs itaconate) (PSITCs) ionomers, having two carboxylate groups in the same ionic repeat unit, that also showed a very weak, broad SAXS peak in the q range of ca.  $1.0-1.7 \text{ nm}^{-1}$  [36], where the PSTACs ionomers exhibited a very weak SAXS peak. It was found that the position of a very weak, small SAXS peak of PSITCs ionomer shifted from  $q_{\text{max}} = \text{ca. 1.0 nm}^{-1}$  to  $q_{\text{max}} = \text{ca. 1.7 nm}^{-1}$  with increasing ionic unit content from 1.0 to 7.0 mol% [36]. Thus, the authors suggested that, in the case of the PSITCs ionomers, the two ion pairs of the same ionic unit experienced severe angle strain in course of a multiplet formation process. As a result, the formation of multiplets became very difficult, and, thus, the ionomer formed only a few multiplets, and most of the ionic aggregates might contain only a couple of ion pairs. Therefore, the SAXS peak intensity was very low, and the peak was located in a very low q range. Naturally, one can realize that this type of ion aggregation is not the same as that found in the PSMANa or PSAANa ionomers. The similar interpretation may also be applicable to the SAXS results of the PSTACs ionomers. Two bulky methyl groups attached to the  $\alpha$ - and  $\beta$ -carbons of acrylate unit cause the restriction in bond rotation, resulting in the difficulty for the ion pairs to form multiplets. Thus, each multiplet of the PSTACs ionomer might contain only a few ion pairs. The strength of the electrostatic interaction is the same for PSTANa, PSMANa, and PSAANa systems, because the ion pairs are identical. Therefore, those ion pairs which fail to form multiplets for energetic reasons in the PSTANa system will be able to do so in the PSMANa and PSAANa ionomers. Thus, it is not unreasonable that the PSTANa ionomers are less clustered than the PSMANa and PSAANa ionomers of comparable ion content. At this point, the work by the group of Winey is worth recalling [29]. They found that the width of the SAXS peak was related with the randomness of the positions of ionic groups on the polymer chain, which results in the

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irregular distances between scattering centers. In the case of the PSTACs ionomers, the ion pairs experience difficulty in the multiplet formation, and, thus, they might form multiplets not at their prevalent distances but irregular distances. Thus, the PSTACs ionomers show a very broad SAXS peak. At this point, it should be mentioned that if one knows the  $T_{gs}$  of poly(tiglate), poly(methacrylate), and poly(acrylate) polymers, one can explain the mechanical behavior and morphology of PSTANa ionomer more instructively. Unfortunately, however, the  $T_{gs}$  of poly(tiglate) has not been reported, yet. Thus, the T<sub>g</sub>s of poly(acrylate) polymer derivatives are compared here [37]. First of all, the  $T_g$  of poly(methyl acrylate) is 5 °C. Secondly, the  $T_g$  of poly(methyl methacrylate) that has a methyl group on the  $\alpha$ -carbon of acrylate is 105 °C. Thirdly, the  $T_g$  of poly(methyl crotonate) that has a methyl group on the  $\beta$ carbon is over 320 °C. This indicates that even a simple change in the position of methyl group from  $\alpha$ -carbon to  $\beta$ -carbon induces severe steric hindrance for bond rotation. From this information, one can infer that the presence of two methyl groups on the  $\alpha$ - and β-carbons makes even very high energy barrier for the bond rotation. Therefore, the PSTANa ionomer would form only a few smallsized multiplets, leading to a smaller amount of cluster regions. This morphological feature is supportive for our interpretation on the lower matrix and cluster  $T_gs$  and  $E'_{ionic}$  values of the PSTANa ionomers, compared to those of the PSAANa and PSMANa ionomers. At this point, it is worth recalling that the ratio of the areas under the matrix and cluster peaks is related to the relative amounts of the matrix and cluster regions of polystyrene-based ionomers, respectively [5,32,38,39]. In Fig. 2, one can find that, at similar ionic unit contents, the area under the cluster loss tangent peak of PSTANa ionomer is relatively smaller than those of PSMANa and PSAANa ionomers. This is also supportive information on the reduced degree of clustering of the PSTANa ionomer system, compared to those of the other two ionomer systems.

## 5. Conclusions

It was found that the ionic modulus and the matrix and cluster  $T_{gS}$  of the PSTANa ionomers were lower than those of the PSMANa and PSAANa ionomers. Thus, it was suggested that the presence of two methyl groups on the  $\alpha$ - and  $\beta$ -carbons of an acrylate unit would induce the high energy barrier for the bond rotation, which resulted in the formation of only a few of small-sized ionic aggregates. This, in turn, made the ionomer less clustered. The very broad and weak shoulder-like XRD and SAXS peak of PSTANa and PSTACs ionomers, respectively, suggested that the PSTANa ionomer formed small amounts of small-sized multiplets that were distributed in the matrix very unevenly. The above findings suggest that the number of methyl groups affects the dynamic mechanical property of PSAANa ionomers differently. That is, the presence of just one methyl group on the  $\alpha$ -carbon of an acrylate unit causes the larger contact surface area for the PSMANa ionomer, leading to more clustering. However, the presence of two methyl groups on the  $\alpha$ and  $\beta$ -carbons results in the restricted bond rotation for the PSTANa ionomer, reducing the degree of clustering.

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## Effects of the addition of dimer acid alkyl esters on the properties of ethyl cellulose



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## ABSTRACT

In this study, we synthesized dimer acid (DA) esters, having short to long alkyl chains,  $(DA-C_n)$  by the Diels–Alder reaction and subsequent esterification reaction of fatty acids that were prepared by the hydrolysis of waste vegetable oil. It was found that the DA-C<sub>n</sub> were thermally more stable than common petroleum-based plasticizer DOP. When the DOP, DA, or DA-C<sub>n</sub> with short alkyl chains were added to ethyl cellulose (EC), the optical clarity and SEM images of the samples showed their good miscibility with those additives in a micro-scale. It was also found that the rubbery modulus of the EC decreased with increasing amount of additives; the type of the additives did not affect the rates of the decrease in the rubbery modulus. The main transition temperatures of the EC containing either DA or DA-C<sub>1</sub> or DA-C<sub>4</sub> decreased with increasing amounts of those additives and were comparable to that of the DOP-containing EC. The above findings suggested that the DA and its esters with short alkyl chains could act as effective plasticizer and, thus, could be used instead of the DOP. In addition, the results obtained from tensile testing and leaching experiments implied that the DA might be better plasticizer than the DA-C<sub>1</sub> and DA-C<sub>4</sub>, at least in some cases, because of hydrogen-bonding with the EC.

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## 1. Introduction

In the 20th century, petroleum-based materials had become main row materials and chemicals in the field of material science and technology; however, eventually, they were recognized as a major cause of carbon dioxide emissions that is, now, widely blamed for global warming (Rem, Olsen, Welink, & Fraunholcz, 2009; Halden, 2010). In addition, the upsurge in oil prices due to the depletion of oil resources has also led us to the reduction of the use of petroleum-based fuel. Thus, many researchers continue and spur the development of materials from bio-based resources instead of petrochemical resources. Most of these eco-friendly bio-based materials made from renewable resources are bio-plastics and have

http://dx.doi.org/10.1016/j.carbpol.2014.12.029 0144-8617/© 2015 Elsevier Ltd. All rights reserved. the merits of solving the oil depletion problems and environmental pollution problems caused by plastics waste (Qin & Wang, 2010; Chen & Patel, 2012). The typical examples of the bio-plastics are poly(lactic acid) and poly(hydroxyalkanoate). However, the bio-plastics have the drawbacks of very high unit costs of production and deteriorating physical properties such as poor heat resistance (Lunt, 1998; Luckachan & Pillai, 2011). To overcome these short-comings, many researchers have been actively studying composite materials that consist of relatively cheap, abundant and renewable natural polymers (e.g. cellulose, starch, chitosan, etc.) and inorganic filler.

Ethyl cellulose (EC) is one of cellulose derivatives, some of the hydroxyl groups of the glucose units of cellulose are converted into ethyl ether groups, and shows excellent mechanical properties, stability, and biocompatibility (Rekhi & Jambhekar, 1995; Gupta & Sahoo, 2001). However, the hydrogen bonds between the hydroxyl groups of the repeating units make the processing of the EC difficult, which limits its applications (Bodmeier & Paeratakul, 1994). In plastics industry, phthalate plasticizers (e.g. di(2-ethylhexyl)phthalate (DOP) and diisodecyl phthalate) have been applied to weaken the intermolecular interactions and enhance the mobility of polymer



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chains, which leads to the easier processing of brittle polymer such as EC (Rahman & Brazel, 2004). Recently, however, it has been reported that some of the phthalates are endocrine disruptors and toxic. In addition, sometimes external plasticizers leach out of plastics in a certain period of time. Thus, in some countries the use of some of phthalates as external plasticizers has been strictly restricted for use in medical plastics, toys for children and child care items (Peña, Hidalgo, & Mijangos, 2000; Krauskopf, 2003), which urges the development of eco-friendly plasticizer (Labrecque, Kumar, Davé, Gross, & McCarthy, 1997). In this case, the ecofriendly plasticizer should meet the strict requirements in terms of better biocompatibility, biodegradability, and renewability, compared to petroleum-based plasticizer (Rahman & Brazel, 2004).

Dimer acid (DA), a yellow viscous liquid at room temperature, is renewable materials that can be synthesized by dimerization of fatty acids obtained from vegetable oils. The DA has noncrystallinity, high molecular weights and more than two reactive functional groups, and thus, the useful applications of the DA have been as oil additives, lubricants, and materials used in the preparation of resins, hot-melt adhesives, surfactants, inks or coatings (Fan, Deng, Waterhouse, & Pfromm, 1998). Furthermore, bio-based and non-toxic properties of DA allow its usage as eco-friendly materials. Thus, in the present work, we attempted to study DA and its ester forms that can be used as the eco-friendly plasticizer for the EC. Thus, we synthesized DA, using waste soybean oil as a raw material, and dimer acid derivatives, i.e. dimer acid alkyl ester (DA-C<sub>n</sub>, here *n* = the number of carbon atoms of alkyl group), and characterized them, and prepared the EC materials containing DA or DA-C<sub>n</sub>. Then, the thermal and mechanical properties and leachability of the EC materials were investigated.

#### 2. Experimental

## 2.1. Materials

The reagents such as ethyl cellulose, di(2-ethylhexyl)phthalate (99%), methanol (anhydrous, >99.8%), 1-butanol (anhydrous, 99.8%), 2-ethylhexan-1-ol (>99%), and p-toluenesulfonic acid monohydrate (>99%) were purchased from Sigma-Aldrich. Isotridecanol (>99%) was purchased from Sasol. Toluene (HPLC grade) and chloroform (HPLC grade) were obtained from Samchun. The reagents and solvents were used without further purification. The number-average molecular weight ( $M_n = 20,000$ ) and molecular weight distribution (MWD=2.22) of ethyl cellulose (viscosity 4 cP, 5% in toluene/ethanol 8/2 (v/v)) were determined at 35  $^{\circ}$ C using an Agilent 1260 LC system with one PLgel guard column  $(5 \,\mu\text{m}, 50 \times 7.5 \,\text{mm})$  and three PLgel Mixed-C columns  $(5 \,\mu\text{m}, 50 \times 7.5 \,\text{mm})$  $300 \times 7.5$  mm) connected in series with CHCl<sub>3</sub> as the solvent (flow rate of the eluent = 1 mL/min). Shodex SM-105 polystyrene standards were used for alibration of the columns. The degree of substitution (DS) of EC sample (2.45–2.57) was calculated using the ethoxyl labeling (48–49.5%) given by the manufacturer as follows:

$$DS = \frac{(\text{ethoxyl content} \times (246.3 - 29.1 \times 3))}{(45.1 - \text{ethoxyl content} \times 29.1)}$$
(1)

here 246.3 = molecular weight  $(M_W)$  of fully substituted ethyl cellulose unit,  $45.1 = M_W$  of ethoxyl group,  $29.1 = M_W$  of ethyl group.

#### 2.2. Characterization methods

The <sup>1</sup>H- and <sup>13</sup>C-nuclear magnetic resonance (NMR) spectra of the compounds dissolved in CDCl<sub>3</sub> were obtained using a Bruker DPX-300 spectrometer (300 MHz and 75 MHz, respectively). Tetramethylsilane was used as the internal standard. The Fourier transform infrared (FT-IR) transmittance spectra of the compounds were acquired in the range of 4000 to 550 cm<sup>-1</sup> using a



Bio-RAD FTS165 spectrometer. For the gas chromatography-mass spectrometry (GC/MS) study to determine the composition of fatty acids (FAs), an Agilent Technologies 7890 A GC/MS instrument, equipped with electron ionization and HP-1 capillary GC column (30 m (length) × 0.25 mm (inner diameter)) was used. A temperature range was 50-320 °C, a heating rate was 10 °C/min, a split ratio was 1:50, and injector and detector temperatures were ca. 250 and 300 °C, respectively. The molar mass and composition of FAs were also determined using size exclusion chromatograph at 40 °C using three Styragel columns (i.e. two HR 0.5 ( $7.8 \times 300$  mm) columns and one HR 1.0  $(7.8 \times 300 \text{ mm})$  column) connected in a series, with tetrahydrofuran as the solvent. Six of polyglycerol fatty acid ester standards (molecular weight = 280, 360, 620, 880, 1200, and 1500) were used for the calibration of the columns. The high-performance liquid chromatography (Waters HPLC system) for the quantitative analysis of the DA and DA- $C_n$  derivatives were also carried out. The total acid number (TAN) of the compounds was determined by a base titration technique (ASTM D664) using a Metrohm 888 Titrando titrator.

## 2.3. Synthesis of $DA-C_n$

As shown in Scheme 1, dimer acid (DA) (85%) containing a small amount of trimer acid (TA) (15%) were synthesized by the hydrolysis and subsequent Diels–Alder reaction of fatty acids (FAs). Then, DA and TA ester derivatives were prepared by the esterification between corresponding the DA and TA, respectively, and proper alcohols.

#### 2.3.1. Preparation of DA

FAs were prepared by the hydrolysis of waste soybean oil at 180-200 °C. The chemical composition of the FAs analyzed by GC/MS is C16:0 (4.7%), C16:1 (0.8%), C18:0 (0.7%), C18:1c (37.0%), C18:2c (50.4%), C18:3 (6.2%), others (balance); here, the number right next to capital "C" indicates the number of carbon atoms of the molecule, and the number right next to colon indicates the number of double bonds of the molecule, and "c" indicates cis isomer form. The preparation method, modified from the work by Paschke, Peterson, and Wheeler (1964) and Wheeler and White (Wheele & White, 1967), is described briefly here. For the preparation of the DA, the FAs (30 g), clay catalyst (2.4 g, 8 wt%), H<sub>3</sub>PO<sub>4</sub> (0.026 g, 0.085 wt%), and deionized water (0.6 g, 2 wt%) were put in a highpressure stainless-steel reactor equipped with a mechanical stirrer, a cooling water jacket, and a temperature controller. The reactor was sealed, evacuated for 30 min, and backfilled with N<sub>2</sub> four times to remove O<sub>2</sub> completely. The mixture in the reactor was heated to 250 °C and stirred for 12 h, and, then, cooled to room temperature and neutralized with H<sub>3</sub>PO<sub>4</sub>. After that, the mixture was heated again to 80 °C and stirred for 1 h. The mixture was cooled to room temperature and filtered to remove salts. The unreacted FAs in the filtrate were removed by vacuum distillation to obtain a product (27 g, yield = ca. 90%). HPLC analysis revealed that the product was composed of ca. 85 wt% of dimer acid and ca. 15 wt% of trimer acid. From now on, we use "DA" as a product notation instead of "the mixture of dimer acid (DA) and trimer acid (TA)" throughout the paper. At this point, it should be mentioned that the detailed studies on the effect of reaction conditions and source of fatty acids had already been conducted by our group and the findings have been reported elsewhere; interested readers are referred to the original article (Lee et al., 2013). For the sake of convenience, only brief results are given here. We found that the various waste vegetable oils, such as used soybean oil or by-products obtained in course of the production of edible oils, can be converted to fatty acids that can be used for synthesis of DA. Depending on oil sources, various fatty acids were obtained. With increasing the proportion of unsaturated fatty acids, overall yield percentages and the relative amount of TA were found



Scheme 1. Brief synthetic route of DA and TA and their ester derivatives.

to be increased. In addition, when the reaction time increased from 6 h to 24 h, the overall yield percentage increased from ca. 61% to ca. 90%. On the other hand, the relative amount of TA increased from ca. 10% to ca. 20%. Finally, we observed that the effect of the amount of catalyst was the same as that of the reaction time.

## 2.3.2. Preparation of $DA-C_n$

For the preparation of methyl ester of DA (DA-C<sub>1</sub>), the DA (30 g, 53.5 mmol) and *p*-toluenesulfonic acid (0.92 g, 5.35 mmol) were placed in a 4-neck round-bottom flask equipped with a Dean–Stark apparatus and a condenser. The mixture in the flask was stirred at 150 °C, and methanol (5.14 g, 160 mmol) was added to the mixture slowly for 2 h to produce the DA-C<sub>1</sub>. Then, the mixture was cooled to room temperature, neutralized with saturated NaHCO<sub>3</sub> solution, and finally washed with water three times. The product was dried using MgSO<sub>4</sub>, and the residual solvent was evaporated to dryness to afford brownish oily product (30 g, yield = ca. 96%). Other DA-C<sub>n</sub> esters were prepared using a similar method. The sample notations used here for the DA methyl ester, DA butyl ester, DA 2-ethylhexyl ester, and DA 11-methyldodecyl ester are DA-C<sub>1</sub>, -C<sub>4</sub>, -iC<sub>8</sub>, and -iC<sub>13</sub>, respectively.

## 2.4. Thermogravimetic analysis

For the thermogravimetric analysis (TGA) of DOP, DA, and DA-C<sub>n</sub> derivatives, a TA Q-500 TGA instrument was used. The samples were heated from 25 °C to 600 °C at a heating rate of 10 °C/min under N<sub>2</sub> at a flow rate of 20 mL/min. The temperature for 5% weight loss ( $T_{d-5\%}$ ) was determined.

## 2.5. Film preparation

To investigate the thermal properties of EC containing DA- $C_n$ , we prepared the samples in a film form by using a solution casting method, described in literature (Tarvainen, Sutinen, Peltonen, Tiihonen, & Paronen, 2002); the amounts of the DA- $C_n$  in the samples were 10, 20, 30, 40 and 50 phr. First of all, the EC and DA- $C_n$  were dissolved in chloroform to make 5% (w/v) solutions. The solutions were then stirred for 3 h at room temperature. Then the solutions were poured into clean Teflon petri dishes (diameter = 10 cm), and the dishes were covered with their lids. The solutions were dried in an ambient condition for 1 week, which led to the film formation. Subsequently, the films were dried further

under vacuum at 50 °C for another 1 week. The films were stored in a desiccator prior to use. The notations used for the EC containing either DOP or DA or DA- $C_n$  are either EC-DOP(x) or EC-DA(x) or EC-DA- $C_n(x)$ , respectively; x indicates the amount of additives in the material in phr. A Philips XL30S FEG scanning electron microscope (SEM) was utilized to monitor the surface morphology of the films. To determine the optical clarity of the film samples (film thickness = 0.2 mm), the digital camera (Samsung NX-mini) was used to take photos of the film samples against the scene of our laboratory as a background. In addition, for the quantitative analysis of the film clarity, the UV-vis spectrophotometer (Shimadzu) was also used to determine the transmittance of the films exposed to the light (wavelength = 600 nm).

## 2.6. Mechanical property measurements

The dynamic mechanical properties of the EC samples were evaluated using a TA dynamic mechanical analyzer (DMA, Q-800) in a temperature sweep mode from 30°C to 250°C at 1 Hz. The heating rate was 1 °C/min. The specimens for the DMA in the form of a rectangular bar  $(30 \text{ mm} \times 7 \text{ mm} \times 2 \text{ mm})$  were prepared by compression molding of samples at 200-230 °C and under a pressure of 20 MPa for 5 min. The tensile strength ( $\sigma$ ) and elongation  $(\varepsilon)$  of the sample were determined using an Instron 4482 testing machine with a 100 N load cell. The specimens in the form of a film for the tensile test  $(100 \text{ mm} \times 100 \text{ mm} \times 0.30 \text{ mm})$  were also prepared by compression molding at 160 °C and under a pressure of 7 MPa for 5 min, and the molded films were cut into strips (60 mm  $\times$  6 mm  $\times$  0.30 mm). The experimental condition was 25 °C and 50% relative humidity. The initial distance between the tensile grips and cross-head speed were 30 mm and 10 mm/s, respectively. The tensile strength was calculated as the maximum force at break divided by the cross-sectional area of the specimen, and the elongation at break was treated as the percentage of the length of specimen at break, compared to the initial length. An elastic modulus, i.e. Young's modulus, was calculated from the slope of the linear portion of the stress-strain curve in the elastic deformation region.

## 2.7. Leaching test

The measurement of the leachability of the DA or DA- $C_n$  from the EC film samples was conducted using a modified version of ASTM D1239 for Resistance of Plastic Films to Extraction by Chemicals.



Deionized water was used as the extraction solvent, and the EC films containing DA or DA-C<sub>n</sub> (50 mm × 50 mm × 0.20 mm) were also prepared by a casting method using chloroform as the solvent. For the leaching test, the film samples were immersed in deionized water for 24 h; the water container was placed in a chamber set to keep  $23 \pm 2$  °C and  $50 \pm 5\%$  relative humidity. Then, the films were fully dried in a vacuum oven at 50 °C for 1 week.

#### 3. Results and discussion

#### 3.1. Characterization of DA and DA- $C_n$ esters

#### The TAN of the DA and DA- $C_n$ are listed in Table 1.

First of all, it is clear that the TAN of the DA obtained by titration is almost the same as that (200.0 mg KOH/g) obtained by the calculation based on the chemical structures of dimer acid (85 wt%) and trimer acid (15 wt%). Second, zero or very small TANs of the DA- $C_n$ indicate that the esterification of the DA is successfully complete.

The <sup>1</sup>H- and <sup>13</sup>C-NMR, and FT-IR spectra of the DA and DA- $C_n$  were obtained to confirm their chemical structures. For the convenience of readers, only some of the <sup>1</sup>H NMR, <sup>13</sup>C-NMR and FT-IR spectra are discussed below. Figs. 1–3 show the <sup>1</sup>H- and <sup>13</sup>C-NMR, and FT-IR spectra of the FA, DA, and DA- $C_n$ , respectively. In Fig. 1,



Fig. 1.  $^1\text{H}$  NMR spectra of (a) FA, (b) DA, (c) DA-C\_1, (d) DA-C\_4, (e) DA-iC\_8, and (f) DA-iC\_{13}.



Fig. 2.  $^{13}C$  NMR spectra of (a) FA, (b) DA, (c) DA-C\_1, (d) DA-C\_4, (e) DA-iC\_8, and (f) DA-iC\_{13}.

one can find that, upon the Diels–Alder reaction of the FA, the NMR peaks for the olefinic protons of the FA at  $\delta$  = 5.3 ppm and methylene protons between two double bonds of the FA at  $\delta$  = 2.8 ppm disappear, and new peaks of low intensity, derived from cyclic olefinic protons, appear for the DA and DA-C<sub>n</sub> at  $\delta$  = 6.5–7.5 ppm. In addition, upon the esterification of the DA, new NMR peaks of the methyl protons of the DA-C<sub>1</sub> appear at  $\delta$  = 3.65 ppm, and those of the methylene protons of the DA-C<sub>4</sub>, DA-iC<sub>8</sub> and DA-iC<sub>13</sub> are present at  $\delta$  = 3.98 ppm. The positions of the <sup>1</sup>H NMR peaks of the DA and DA-C<sub>n</sub> are also summarized in Table 1.

In Fig. 2, it is seen that the <sup>13</sup>C NMR spectrum of the DA is very similar to that of the FA, except for the absence of the NMR peaks for the olefinic protons of the FA at  $\delta$  = 130 ppm. At this point, it should be mentioned that the NMR peaks for the cyclic unsaturated carbons are difficult to detect because of their low intensity. Upon the esterification, the NMR peak for the acid carbonyl group of the DA at  $\delta$  = 180.6 ppm shifts to  $\delta$  = 174.2 ppm for the ester carbonyl of the DA-C<sub>1</sub>. The peak for the ester carbonyl of other DA-C<sub>n</sub> with *n* = 4, 8, 13 appears in the range of  $\delta$  = 173.3–173.6 ppm. The NMR peaks for the new terminal methyl carbons adjacent to the ester group of the DA-C<sub>1</sub> appear at  $\delta$  = 51.3 ppm. In the case of other DA-C<sub>n</sub> with *n* = 4, 8, 13, the peaks appear in the range of  $\delta$  = 63.7–66.4 ppm. The positions of the <sup>13</sup>C NMR peaks of the DA and DA-C<sub>n</sub> are also summarized in Table 1.

The FT-IR spectra of the FA, DA and DA-C<sub>n</sub> are shown in Fig. 3. A typical strong IR band caused by the stretching mode of the acid carbonyl group of the FA and DA are shown at  $v = 1710 \text{ cm}^{-1}$ . This strong IR band is due to the cyclic dimerization of two carboxylic acid groups that can form hydrogen bonds. After the esterification reaction, the IR band for the carbonyl stretching of the DA-C<sub>n</sub> shifts to  $v = 1738-1743 \text{ cm}^{-1}$ . Also, a broad IR band for O—H stretching is not shown at  $v = 3083 \text{ cm}^{-1}$  for the DA-C<sub>n</sub>, whereas the spectra of the FA and DA show only the obscured O—H stretching band. The positions of the IR bands of the DA and DA-C<sub>n</sub> are also summarized in Table 1.

## 3.2. Optical properties of EC containing DOP, DA, or $DA-C_n$

Fig. 4 shows the photographs of the EC, EC-DOP(30), EC-DA(30), EC-DA-(30), EC-DA-(



**Fig. 3.** FT-IR spectra of (a) FA, (b) DA, (c) DA-C<sub>1</sub>, (d) DA-iC<sub>8</sub>, and (e) DA-iC<sub>13</sub>.



#### Table 1 TAN, NMR, IR, and T<sub>d-5%</sub> data of DA and DA-C<sub>n</sub>.

Compounds	TAN (mg KOH/g)	Positions of <sup>1</sup> H NMR peaks, $\delta$ (ppm)	Positions of <sup>13</sup> C NMR peaks, $\delta$ (ppm)	Positions of IR bands, $\nu$ (cm <sup>-1</sup> )	<i>T</i> <sub>d-5%</sub> (°C)
DA	198.5	2.54 (m, 1 <i>H</i> ), 2.32 (t, 4 <i>H</i> ), 1.98 (m, 3 <i>H</i> ), 1.62 (m, 6 <i>H</i> ), 1.26 (m, 33 <i>H</i> ) 0.88 (t, 6 <i>H</i> )	180.6, 34.1, 32.0, 29.8–29.1, 24.7, 22.8, 14.1	3083, 2925–2853, 1710, 1463, 1285, 937	294
DA-C <sub>1</sub>	0.0	3.65 (s, 6H), 2.53 (m, 1.2H), 2.30 (t, 4.5H), 1.97 (m, 2.3H), 1.62 (m, 7H), 1.26 (m, 38.2H), 0.88 (m, 7H)	174.2, 51.3, 34.0, 31.9, 29.6–29.1, 24.9, 22.7, 14.1	2926–2854, 1743, 1461, 1363, 1171	284
DA-C <sub>4</sub>	0.0	4.0 (t, 4H), 2.48 (m, 1H), 2.21 (t, 5.4H), 1.94 (m, 2H), 1.56 (m, 10.5H), 1.22 (m, 41H), 0.85–0.75 (m, 12H)	173.3, 63.7, 34.1, 31.9, 30.7, 29.6–29.1, 24.9, 22.6, 21.2, 19.1, 14.0, 13.6	2925–2851, 1736, 1460, 1356, 1177	267
DA-iC <sub>8</sub>	0.042	3.98 (d, 4H), 2.51 (m, 1H), 2.25 (t, 4.2H), 1.95 (m, 2H), 1.59 (m, 8.4H), 1.25 (m, 53H), 0.85–0.75 (m, 19H)	173.6, 66.4, 38.8, 34.3, 31.9, 30.4, 29.6–28.9, 25.0, 23.8, 22.9, 22.6, 13.9, 10.9	2926–2855, 1738, 1463, 1379, 1174	273
DA-iC <sub>13</sub>	0.006	3.98 (d, 4H), 2.49 (m, 1H), 2.28 (t, 4H), 1.97 (m, 2H), 1.58 (m, 2H), 1.24(65H), 0.88 (m, 27H)	173.5, 65.7, 38.2, 33.9, 32.1, 30.1, 29.9–28.4, 24.8, 23.7, 22.9, 22.6, 13.6, 10.8	2925–2855, 1738, 1462, 1378, 1176	271



Fig. 4. Photographs of the EC films containing DOP, DA, DA-C1, DA-iC8, or DA-iC13 against the scene of our laboratory as a background and SEM images of the film surface.

The SEM images suggest that the surface of the EC, EC-DOP, EC-DA and EC-DA-C1 films are smooth and uniform without micro-sized phase-separation, suggesting indirectly the relative transparency of the films. However, the SEM images of the EC-DA-iC<sub>8</sub> and EC-DAiC13 films show micrometer-sized holes dispersed in the EC matrix randomly; this might result in the film opaqueness.

The optical clarity of some of the films was quantitatively measured by using UV-vis spectrophotometer. The results are listed in Table 2.

It is seen that the UV-vis transmittance of the EC-DOP, EC-DA and EC-DA-C1 increases from ca. 56% to ca. 76-86% with increasing additive contents. This can be understood: If the DOP, DA, and

#### Table 2

UV-vis transmittance of EC, EC-DOP, EC-DA, and EC-DA-Cn.

Films	UV-vis transmittance (%)	Films	UV-vis transmittance (%)
EC	56.0	EC-DA-C1(20)	63.7
EC-DOP(10)	60.2	EC-DA-C <sub>1</sub> (30)	69.3
EC-DOP(30)	80.4	$EC-DA-C_1(40)$	73.6
EC-DOP(50)	85.6	$EC-DA-C_{1}(50)$	76.3
EC-DA(10)	50.0	$EC-DA-iC_8(10)$	39.5
EC-DA(20)	61.9	EC-DA-iC <sub>8</sub> (20)	39.8
EC-DA(30)	70.7	EC-DA-iC <sub>8</sub> (30)	39.2
EC-DA(40)	77.2	EC-DA-iC <sub>13</sub> (10)	40.4
EC-DA(50)	80.5	EC-DA-iC <sub>13</sub> (20)	39.9
$EC-DA-C_{1}(10)$	50.1	EC-DA-iC <sub>13</sub> (30)	39.2

DA-C<sub>1</sub> were miscible with the EC, the material could be homogeneous and relatively transparent. Then, with increasing amount of the additives the relative amount of the EC in the film decreases, which, in turn, leads to the dilution effect of the EC. If this were the case, it would be natural for the EC-DOP, EC-DA and EC-DA-C1 to exhibit an enhanced UV-vis transmittance of the EC films; this might be what we observed here. However, the UV-vis transmittances of the EC-DA-iC<sub>8</sub> and EC-DA-iC<sub>13</sub> are lower than that of the EC and remain constant at ca. 40%, which is due to the micro-sized phase-separation of the additives.

To investigate the interactions between the hydroxyl groups of the EC and the carboxylic acid groups of the DA or the ester groups of the DA- $C_n$ , we used an FT-IR technique. As seen in Fig. 5, the EC shows the IR bands for the hydroxyl groups and the ether groups at  $v = 3475 \text{ cm}^{-1}$  and  $v = 1050 \text{ cm}^{-1}$ , respectively, but no IR band for the carbonyl groups at  $v = 1710 \text{ cm}^{-1}$  because the EC does not have a carbonyl group. On one hand, as mentioned earlier, pure DA shows one strong IR band at  $v = 1710 \text{ cm}^{-1}$  for the stretching mode of the carbonyl group of carboxylic acids that take part in the formation of hydrogen bonds between them. On the other hand, the EC-DA shows two IR bands for the stretching mode of the carbonyl group at v = 1710 and  $1735 \text{ cm}^{-1}$ , which will be discussed later. Pure DA-C<sub>1</sub> exhibits a strong IR band for the stretching mode of the carbonyl group of methyl ester at  $v = 1743 \text{ cm}^{-1}$ , but the EC-DA-C1 exhibits only a weak IR band at the same wavenumber. This can be understood: the intensity of the IR band for the stretching mode of the carbonyl group should naturally be lower for the








**Fig. 5.** FT-IR spectra of (a) EC, (b) DA, (c) EC-DA(30), (d) DA-C<sub>1</sub> and (e) EC-DA-C<sub>1</sub>(30).

EC-DA-C<sub>1</sub>, compared to that for the DA-C<sub>1</sub>, because of a dilution effect. Now, let us discuss the two IR bands for the carbonyl groups of the EC-DA. The EC polymer chains contain a large amount of ether groups and a small amount of hydroxyl groups; the ether groups are poor proton acceptors (De Brabander, Van den Mooter, Vervaet, & Remon, 2002). This implies that there are two types of carbonyl groups in the EC-DA (Lizaso, Muñoz, & Santamaría, 1999). One is the carbonyl groups that form relatively strong hydrogen bonds with the hydroxyl groups of both the DA and EC, and the other is the carbonyl groups that form relatively weak hydrogen bonds with the ether groups of the EC. The IR band at  $v = 1710 \text{ cm}^{-1}$  might be due to the stretching mode of the strong hydrogen-bonding carbonyl groups, and that at  $v = 1735 \text{ cm}^{-1}$  might be due to the stretching mode of the weak hydrogen-bonding carbonyl groups. The above results suggest that the DA molecules in the EC-DA are relatively well distributed in the EC polymer matrix, and the DA molecules have relatively low chances to form hydrogen bonds with other DA molecules. Thus, the interactions between the EC polymer chains become weaker significantly as the DA molecules reside in the EC matrix, in which the DA acts as effective plasticizer. De Brabander et al. (2002) and Taylor and Zografi (1997) also observed similar results that the IR bands for the carbonyl stretching mode shifted due to the decrease or absence of the cyclic dimerization of acid functional groups in polymer dispersions.

# 3.3. Thermogravimetric properties

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Fig. 6 shows the weight percentage of the DOP, DA and DA- $C_n$  as a function of temperature. It is clear that the DA and DA- $C_n$  are thermally more stable than the DOP. For example, the 5% weight loss temperature ( $T_{d-5\%}$ ) of the DOP is ca. 198 °C, while those of the DA and DA- $C_n$  are in the range of 267–294 °C (see Table 1). This indicates that if one used the DA and DA- $C_n$  as the additives for the polymer processing, one could set the maxium temperature for the processing much higher temperatures, compared to that for the polymers containing DOP. In addition, it is seen that the weight % of the DA and DA- $C_n$  decreases slowly up to ca. 300 °C and then



**Fig. 6.** Thermogravimetric curves of DOP, DA,  $DA-C_n$ , and EC as a function of temperature.

strongly. It is also found that the weight % curve shifts to high temperatures with increasing alkyl chain length, *n*, from 1 to 13. At this point, it should be mentioned that the weight % of the EC seems to remain constant up to 300 °C, and decreases drastically, and the  $T_{d-5\%}$  of the EC is 307 °C that is not much different from the value reported elsewhere (Li, Huang, & Bai, 1999). The TGA data shown in Fig. 6 indicate that the thermal stability of the DA-C<sub>n</sub> might be, at least, comparable to or even better than that of the EC. Also, it should be noted that the DA seems to go through two decomposition mechanisms, compared to just one mechanism for the rest. However, the investigation on the two decomposition mechanisms is beyond the scope of this work, and, thus, we do not discuss it any more here.

Fig. 7(a) shows the weight percentage of EC and EC composites containing 30 phr of DOP, DA or DA-C1. The thermal decomposition of EC begins at ca. 300 °C and is completed at ca. 390 °C. On the other hand, the weight loss of the EC-DOP composite starts at ca. 200 °C, which is due to the presence of thermally unstable DOP; other than that, the thermal decomposition behaviour of the EC-DOP is similar to the that of EC. In the cases of the EC-DA and EC-DA- $C_1$ , major decompositions occur in the temperature range of ca. 320-380 °C, related with the thermal degradation of EC. It is also seen that above 380 °C, the wight percentages of EC containing DA or DA-C<sub>1</sub>, being more thermally stable than DOP, are higher than those of EC and EC-DOP. These findings indicate that the DA derivatives can be used as additives that allow the EC matrix to maintain its thermal stability. Fig. 7(b) exhibits that, as expected, with increasing amount of DA the onset temperature of degradation shifts to low temperatures progressively. However, it should be noted that even the EC-DA(50) is thermally stable at 300 °C, implying the possbile applications of DA as polymer additives used at high temperatures.

# 3.4. Dynamic mechanical properties

We measured the dynamic mechanical properties of the EC containing varying amounts of DOP, DA or DA-C<sub>n</sub>. Fig. 8 shows the storage moduli (*E'*) and loss tangents of the EC-DA as a function of temperature. In the log *E'* vs. temperature plots, it is seen that the EC shows a glassy modulus up to ca. 130 °C, and goes through a glass transition ( $T_g$ ) in the temperature range of ca. 130–160 °C, and exhibits a plateau at log *E'* (Pa) = ca. 7.4 up to ca. 200 °C. Above ca. 200 °C, the storage modulus of the EC starts to decrease drastically with increasing temperature, i.e. the EC begins to flow. At



Fig. 7. (a) (top) Thermogravimetric and (bottom) differential thermogravimetric curves of EC containing 30 phr of DOP, DA, or DA-C1 as a function of temperature. (b) (top) Thermogravimetric and (bottom) differential thermogravimetric curves of EC containing varying amounts of DA.

this point, it should be noted that the plateau modulus of the EC is much higher than the rubbery modulus of common polymers (e.g.  $\log E'$  (Pa) < ca. 6.0). This is due to the presence of intermolecular interactions (i.e. hydrogen bonds) in the EC, as was mentioned before (Rekhi & Jambhekar, 1995; Gupta & Sahoo, 2001). It is known that this type of interactions could increase the rubbery modulus (Nielsen & Landel, 1994).

In the case of the EC-DA, the glassy modulus decreases slowly, and the slope of the curve for the transition becomes more gradual with increasing amount of the DA, which is due to the increase in the heterogeneity of polymer phase (Nielsen & Landel, 1994). In addition, the rubbery modulus decreases progressively, which will be discussed later in more detail, and shifts to lower temperatures, but the temperature range for the rubbery state increases. Loss tangent



**Fig. 8.** Storage modulus (E') and loss tangent of the EC containing varying amounts of DA, measured at 1 Hz. The amount of DA in the sample is marked near each curve.

 $(\tan \delta)$  curves show that a single  $\tan \delta$  peak is seen for the EC at ca. 145 °C. Sakellariou, Rowe, and White (1986), Tarvainen et al. (2003), Crowley et al. (2004), and Lai. Pitt, and Craig (2010) also reported that the  $T_{g}$  of the EC determined by using differential scanning calorimetry (DSC) was in the range of ca. 120-130 °C. According to the fact that the  $T_g$  obtained by using the DSC (10 °C/min heating rate) was usually ca. 10-20 °C lower than that obtained by using the DMA (1 Hz data) (Kim, Wu, & Eisenberg, 1994), the tan  $\delta$  peak at ca. 145 °C for the EC of the present work would be related with the glass transition. With increasing DA content, the tan  $\delta$  peak shifts to lower temperatures, with increasing the peak width. Again, the broadening of the peak is assumed to be due to the increase in the heterogeneity of the polymer matrix phase (Nielsen & Landel, 1994). In the cases of the EC samples containing 30 or 40 phr of DA, they show an additional weak tan  $\delta$  peak at ca. 140 °C that is close to the peak position of the pure EC. The other  $EC-C_n$  series also show similar results (data are not shown here).

For the comparison of the effects of the alkyl chain length of the DA-C<sub>n</sub> on the dynamic mechanical properties of the EC-DA-C<sub>n</sub>, the storage moduli (E') plots of the EC and EC containing 30 phr of DOP, DA, or DA-C<sub>n</sub> as a function of temperature are shown in Fig. 9. It is seen that at room temperature the EC-DOP exhibits the lowest storage modulus, compared to the rest of samples. In addition, the EC-DOP shows the  $T_g$  in a temperature range of ca. 30–80 °C and a long descending plateau related to a rubbery modulus. Above ca. 150 °C, the sample starts to flow.

In the case of the EC-DA, the storage modulus value at ca. 30 °C is between those of the EC and EC-DOP. Interestingly, the modulus curve of the EC-DA looks similar to that of the EC-DOP, except for the differences in the onset temperatures of the sample flow. That is, the EC-DA begins to flow at 175 °C, but the EC-DOP starts to flow at ca. 150 °C. For the EC-DA-C<sub>1</sub>, the onset temperature for the flow is ca. 160 °C, which is only 10 °C higher than that of the EC-DOP and ca. 15 °C lower than that of the EC-DA. The rest of the EC-DA-C<sub>n</sub> samples show the shift of the modulus curve to high temperatures progressively with increasing alkyl chain length. However, the flow regions seem to merge into one point. In addition, it is seen that the temperature range of the descending plateau is either relatively





**Fig. 9.** Storage modulus (E') of the EC and EC containing 30 phr of DOP, DA, or DA- $C_n$  as a function of temperature, measured at 1 Hz.

short (e.g. ca. 30 °C) or relatively long (e.g. ca. 70 °C), depending on the samples. The above findings suggest that the DA or DA- $C_n$  could be promising candidates that can be used instead of the DOP.

Shown in Fig. 10 are the moduli at the point of a minimum slope in the descending plateau segment of the  $\log E'$  vs. temperature plots of EC-DOP, EC-DA and EC-C<sub>n</sub> as a function of additive amounts. It is seen that the plateau moduli of the additive-containing EC decrease with increasing amount of additives. The plateau modulus data can be fitted with a first order polynomial. The equation for the straight line is as follows:

$$\log E'$$
 (Pa) = 7.5 - 0.030w ( $r^2 = 0.9924$ ) (2)

here w is the amount of the additives in phr, and  $r^2$  is the linear leastsquares correlation coefficient. It should be noted that the data at high concentrations of additives scatter, to some extent. This might be due to the fact that the increase in the additive concentration makes the samples too soft to be kept their dimensions for the DMA study at high temperatures where the samples exhibit their plateau moduli. This might cause the slightly scattering data at high additive concentrations.



**Fig. 10.** Rubbery plateau of the EC-DOP, EC-DA and EC-DA- $C_n$  as a function of amounts of additives, measured at 1 Hz.

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**Fig. 11.** Loss tangents of the EC and EC containing 30 phr of DOP, DA, or  $DA-C_n$  as a function of temperature, measured at 1 Hz.

Fig. 11 shows the loss tangents of the EC and EC containing 30 phr of DA or DA-C<sub>n</sub> as a function of temperature. As mentioned before, the pure EC shows only one loss tangent peak at ca. 145 °C. On the other hand, a well-developed tan  $\delta$  peak is seen for the EC-DOP at ca. 90 °C. For the EC-DA, a well-developed but relatively broad peak and a shoulder are present at ca. 80 °C and ca. 145 °C, respectively. In the case of the EC-DA-C<sub>1</sub>, a very broad peak and a shoulder are seen at ca. 80 °C and ca. 125 °C, respectively.

At this point, it should be mentioned that some of the loss tangent curves seem to be a combination of two or three loss tangent peaks. Thus, we tried to de-convolute the peaks using a PeakFit software program (Systat Software, Inc.). Shown in Fig. 12 is one example of curve deconvolutions. The best fit curve for each of the samples can be obtained with an exponential background and Gaussian Areas for the peaks. The peak positions are the temperatures at the maxima of the low-temperature, middle-temperature, and high-temperature transition peaks. Present in Fig. 13(a) are the thermal transition temperatures obtained from the deconvolutions as a function of the amount of additives in the samples.



Fig. 12. Curve deconvolution results of EC-DA-iC<sub>8</sub>(30).





Fig. 13. (a) The thermal transition temperatures of the EC and EC containing varying amounts of DOP, DA, or  $DA-C_n$  as a function of the additive amounts, measured at 1 Hz. The straight solid line indicates the first order polynomial fitted to the data of EC-DOP. The dashed, dotted, and solid lines indicate the positions of the loss tangent peaks at high, middle, and low temperatures, respectively. (b) Filled symbols indicate the positions of the largest loss tangent peak among two or three de-convoluted peaks. The open symbols present the positions of the smaller loss tangent peaks. The straight solid line represents the first order polynomial fitted to the data of EC-DA, EC-DA-C<sub>1</sub>, and EC-DA-C<sub>4</sub>.

It is seen that two or three thermal transition temperatures are seen for the EC-DA and EC-DA- $C_n$  samples. On the other hand, the EC-DOP samples show only one transition temperature that shifts to lower temperatures with increasing amount of the DOP. The data for the EC-DOP can be fitted with a first order polynomial. The equation for the straight line shown in Fig. 13(a) is as follows:

Transition temperature (°C) = 144 - 1.76w ( $r^2 = 0.9654$ ) (3)

The transition temperatures can be categorized into three temperature ranges; high temperature range (110-145 °C), middle temperature range (70–130 °C), and low temperature range (40–90 °C), depending on the type of the additives. The tan  $\delta$  peak in the low temperature range might be involved in the disruption of the links between ester groups (Lizaso et al., 1999). It is also seen that the position of the peak of the EC-DA in the middle temperature range shifts to lower temperatures strongly with increasing additive amounts. Thus, it can be suggested that the peak might be involved in the glass transition of additive-rich phase. Lastly, the  $\tan \delta$  peak in the high temperature range is probably related with the glass transition of EC-rich phase. Fig. 13(b) shows the temperatures for the main transition as a function of the additive amounts. It is seen that the main transition peaks of the EC-DA, EC-DA-C<sub>1</sub> and EC-DA-C<sub>4</sub> shift to lower temperatures drastically as the additive amount increases, which is comparable to the peak shift of the EC-DOP (see Fig. 13(a)). In addition, when the amounts of additives are above 30 phr, the positions of the main peak of the EC-DA, EC-DA-C<sub>1</sub> and EC-DA-C<sub>4</sub> are close to that of the EC-DOP. It is clear that the transition temperatures for the EC-DA-iC<sub>8</sub> and EC-DA-iC<sub>13</sub> do not change much, except for the EC-DA-iC $_{13}(40)$ . The rest of the data also can be fitted with a first order polynomial. The equation for the straight line shown in Fig. 13(b) is as follows:

Transition temperature (°C) = 143 - 1.75w ( $r^2 = 0.9573$ ) (4)

Interestingly enough, this equation is almost identical to Eq. (3) for the EC-DOP. The above results indicate that the DA, DA-C<sub>1</sub> and  $DA-C_4$  in the EC can act as plasticizer like the DOP in the EC. In the case of the DA-iC $_8$  and DA-iC $_{13}$ , they show poor miscibility with the

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Fig. 14. Stress-strain curve and the Young's modulus of (a) EC, (b) EC-DOP(30), (c) EC-DA(30) and (d) EC-DA-C1(30).

EC, which might be due to their relatively low polarity. That is, the DOP has two alkyl chains, i.e. 2-ethylhexyl groups, but the DA has four alkyl chains, i.e. one hexyl chain, one octyl chain, and two heptyl chains. Thus, the increase in the alkyl chain length of the DA- $C_n$ (see  $R_1$  in Scheme 1) further induces the non-polarity significantly, and, thus, the DA-iC<sub>8</sub> and DA-iC<sub>13</sub> might be less miscible with the EC. This suggests that the DA-iC<sub>8</sub> and DA-iC<sub>13</sub> cannot behave like effective plasticizer like the DOP.

#### 3.5. Tensile properties

The plasticization efficiency of the  $DA-C_n$  was also evaluated by using the tensile testing. The tensile stress and strain of the EC-DOP(30), EC-DA(30) or EC-DA-C<sub>1</sub>(30) are compared in Fig. 14. From the tensile strength of the material, one can obtained the data on the mechanical resistance of the material due to the cohesion between the chains (Nielsen & Landel, 1994). On the other hand, the tensile strain at break gives us an idea on the material's plasticity that is related to the material's flexibility. The Young's modulus represents of the stiffness of an elastic material, which can be calculated from the initial stress/strain ratio. It is seen that the pure EC can be elongated only up to ca. 3% before failure, indicating its brittleness. However, the strain at break of the EC-DA(30) is found to be ca. 84%, which is more than twice that of the EC-DOP(30), keeping a little reduced stress at break, compared to that of the pure EC. The stress-strain properties of the EC-DA-C<sub>1</sub>(30) are seen to be similar with those of the EC-DOP(30). The detailed data are listed in Table 3 that also includes the data for 50 phr samples. It is found that with increasing amount of the additives the stress at break and Young's moduli decrease. On the other hand, as the amount of the additives increases, the strains at break of the EC-DOP and EC-DA increase slowly, but that of the EC-DA-C<sub>1</sub> decreases. The most important

Table 3 Stress-strain data of EC, EC-DOP, EC-DA, and EC-DA-Cn.

Samples	Stress at break (MPa)	Strain at break (%)	Young's modulus (MPa)
EC	$22 \pm 2$	$3\pm0.3$	$856\pm84$
EC-DOP(30)	$12 \pm 1$	$35\pm9$	$456 \pm 21$
EC-DOP(50)	$5\pm0.5$	$46 \pm 11$	$120 \pm 14$
EC-DA(30)	$18 \pm 1$	$84 \pm 14$	$405\pm20$
EC-DA(50)	$10 \pm 1$	$87 \pm 4$	$133 \pm 15$
EC-DA-C <sub>1</sub> (30)	$14\pm0.4$	$32 \pm 5$	$369\pm52$
$EC-DA-C_1(50)$	$5\pm0.6$	$15\pm5$	$135 \pm 19$



Fig. 15. Percentage of the weight loss of the EC films containing DOP, DA, or  $DA-C_1$ , extracted in deionized water for 24 h.

finding is that the EC-DA samples elongate more than any other samples. This is due to the presence of the DA in the EC. That is, as suggested in the section dealing with the IR data, the presence of the DA in the EC-DA leads to weaker interactions between the EC polymer chains, which results in the enhanced elongation of the EC.

#### 3.6. Leaching test

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The percentage of the weight loss of the EC films containing 30 phr of additives by extraction can be calculated as follows:

Weight loss (%) = 
$$\frac{W_1 - W_2}{W_1} \times 100$$
 (4)

here  $W_1$  and  $W_2$  are the weight of film samples before and after the extraction, respectively; Fig. 15 shows the results.

It is known that the leaching of additives from polymer (i.e. plastics) is affected strongly by the strength of interactions between the polymer chains and additives (Lardjane & Belhaneche-Bensemra, 2009; Kastner, Cooper, Marić, Dodd, & Yargeau, 2012). Therefore, the strong hydrogen bonds between the hydroxyl groups of the EC and the acid groups of the DA can increase the resistance to leaching. In the present work, the phthalate plasticizer, DOP, is vulnerable to leaching, resulting in ca. 4.2% weight loss of the EC-DOP; this is similar to the value obtained by Crosthwaite, Muldoon, Dixon, Anderson, and Brennecke (2005). The EC-DA and EC-DA-C<sub>1</sub> samples show weak leachability (i.e. 0.6% and 1.2% weight loss, respectively). The results obtained from the leaching tests indicate that two acid functional groups of the DA play a significant role than the ester functional groups of the DOP and DA-C<sub>1</sub>. Furthermore, the bulky structures and larger molecular weights  $(M_W)$  of the DA ( $M_W$  = 602.9) and DA-C<sub>1</sub> ( $M_W$  = 633.1) might be additional factors that reduce the leachability of the DA and DA-C<sub>1</sub>, compared to the DOP ( $M_W$  = 390.6).

### 4. Conclusions

In this study, we synthesized DA containing a small amount of TA using the waste vegetable oil. Then, we converted them into their alkyl ester DA- $C_n$  forms using an esterification reaction with proper alcohols. The DA and DA- $C_n$  were found to be thermally more stable than the DOP. As the main part of our study, we prepared the EC films containing either DOP or DA or DA- $C_n$ . We observed that the

EC containing either DOP or DA or  $DA-C_n$  with short alkyl chains did not show phase separation in a micro-scale. We also found that the rubbery moduli of the EC were affected not by the type of the additives but by the amount of the additives. On the other hand, the main transition temperatures of the EC containing either DOP or DA or DA-C1 or DA-C4 decreased with increasing amounts of the additives, and the rates of decreasing transition temperatures were very similar to each other, implying that those additives could be used as effective plasticizer like the DOP. Furthermore, it was observed that the elongation at break of the EC-DA was better that those of the EC or EC-DOP or EC-DA-C<sub>1</sub>, suggesting that the DA molecules, well-distributed in the EC matrix, weakened the interactions between the EC polymer chains. The results of the leaching test of the EC containing either DOP or DA or DA-C<sub>1</sub> revealed that the DA was released from the EC matrix more slowly than the DA-C<sub>1</sub>, and the DOP was released faster. This means that the DA, if there were no problem caused by the acidity of the DA, might be better eco-friendly plasticizer than the DA-C<sub>1</sub>, which, in turn, might be much better than the petroleum-based plasticizer, the DOP.

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