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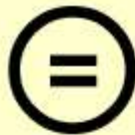
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February 2008
PhD Thesis

Dynamic Mechanical Properties and Morphology of Organic Additives- Containing Styrene Ionomers

by

Mohammad Luqman

Under the supervision

of

Professor Joon-Seop Kim

Department of Polymer Science and Engineering
Graduate School, Chosun University
South Korea

유기 첨가제를 함유하고 있는
스타이렌 아이오노머의 동적
기계적 성질 및 형태학

Dynamic mechanical properties and morphology of organic
additives-containing styrene ionomers

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朝鮮大學校大學院

高分子工學科

MOHAMMAD LUQMAN

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高分子工學科

MOHAMMAD LUQMAN

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A thesis submitted to the Graduate School of Chosun
University in partial fulfillment of the requirements for
the award of the Degree of Philosophy (PhD)

by

Mohammad Luqman

Under the supervision
of

Professor Joon-Seop Kim

17th October 2007

Department of Polymer Science and Engineering
Graduate School, Chosun University
South Korea

MOHAMMAD LUQMAN의
博士學位論文을 認准함.

委員長 朝鮮大學校

教授 조 병 욱 印

委 員 朝鮮大學校

教授 최 재 곤 印

委 員 朝鮮大學校

副教授 유 지 강 印

委 員 朝鮮大學校

教授 유 정 아 印

委 員 朝鮮大學校

教授 김 준 섭 印

2007 年 12 月 6 日

朝 鮮 大 學 校 大 學 院

Dynamic Mechanical Properties and Morphology of Organic Additives- Containing Styrene Ionomers

A thesis approved by the Guidance Committee in partial
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Degree of Philosophy (PhD)

Approved by:

Chair person:	Prof. Byung-Wook Jo
Member:	Prof. Jae-Kon Choi
Member:	Prof. Ji-Kang Yoo
Member:	Prof. Jeong-A Yu
Thesis advisor:	Prof. Joon-Seop Kim

6th December 2007

Department of Polymer Science and Engineering
Graduate School, Chosun University
South Korea

*To my parents, wife, son, PhD advisor and
the cause of Humanity*

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ABSTRACT

유기첨가제를 함유한 스타이렌 아이오노머의 동적, 기계적 성질과 형태학

모하메드 루크만

지도 교수 : 김준섭

고분자공학과

조선대학교 대학원

아이오노머는 보통 15 mol%의 이온기가 고분자 사슬에 직접 혹은 간접적으로 결합되어 있는 이온성 고분자이다. 이온기 사이의 정전기적인 상호작용과 이온기와 전기적으로 중성인 고분자 매트릭스 사이의 커다란 유전상수의 차이는 이온기들이 비극성 고분자 매트릭스로부터 상분리 되는 것을 야기 시킨다. 즉, 이온기들은 고분자 매트릭스 안에서 “multiplet” 이라고 불리는 이온회합체를 형성한다. Multiplet 의 견고함은 많은 요인에 의해 영향을 받는데 주로 이온기 사이의 상호작용의 세기에 영향을 받는다. 이온기에 직접 연결된 고분자 사슬 부분은 그 부분이 multiplet 에 고정되어 있기 때문에 그 움직임이 제한된다. 결과적으로 움직임이 제한된 커다란 연결된 영역이 영형이 되는데 이를 “cluster”라고 한다. Cluster 는 그들 자신의 유리전이를 비이온성 고분자가 보여주는 매트릭스 유리전이온도 보다 훨씬 더 높은 온도에서 보여준다. Cluster 는 또한 저장 탄성률/온도 그림에서 전이와 비슷한 새로운 plateau 를 보여주고 소각 X-선 산란 그림에서 피크를 보여준다.

이 논문에서, 우리는 구조-형태학 사이의 관계와 동적, 기계적 열적 분석 장치(DMTA), SAXS, XRD 그리고 DSC 테크닉을 이용하여 랜덤 아이오노머와 무정형인 폴리 스타이렌의 특성을 연구하였다. 이 논문은 5 장으로 구성되었다. 제

1 장은 고분자들과 아이오노머들, 그리고 이들의 특성을 알기위한 실험적 테크닉에 대한 소개를 하였다.

제 2 장에서는 methacrylate 그리고 술폰화된 폴리스타이렌 아이오노머를 지방화합물인 디카본산의 염을 포함하는 아이오노머와 각각 블렌드한 아이오노머의 기계적 그리고 형태학적 연구들에 대해서 논의하였다. 이 연구의 목적은 다른 이온 그룹들과 이온농도를 가진 폴리스타이렌 아이오노머에서 지방화합물인 디카본산의 염의 양과 종류를 달리 했을 때의 효과에 대해 알아보는 것이었다. 유기염 첨가제를 포함한 대부분의 아이오노머에서는 아이오노머 주사슬의 종류, 아이오노머와 첨가제의 이온기들의 종류, 첨가제의 성질(예를 들면, 작용성, 지방성 화합물과 방향족 화합물, 짧거나 또는 긴 사슬) 보다 오히려 첨가하는 유기염의 양이 아이오노머들의 모듈러스 증가에 영향을 미친다. 이상의 결과로부터 알 수 있었던 것은 첨가제는 소량을 넣어도 아이오노머에서는 상분리를 일으킨다는 것이었다.

아이오노머의 기계적 성질들 그리고 형태학은 이온기들의 형태, 종류, 크기, 위치, 중화 정도 그리고 양이온의 종류, 첨가제들 그리고 가소제들을 포함한 다양한 인자들에 의해 변화될 수 있다. 따라서 제 3 장에서는 DMTA 를 이용하여 poly(styrene-co-styrene sulfonate) 아이오노머의 동적.기계적 특성에 따라 짧고 긴 사슬을 가진 지방족 화합물인 디카본산 바륨과 코발트 염의 첨가 효과를 연구하였다. 첨가된 유기염의 양이온의 종류와 탄소 원자 수는 아이오노머 기계적 특성에 큰 영향을 미치지 않고, 2 가 양이온으로 중화된 유기염들은 아이오노머에서 충전제로서 주된 역할을 한다고 결론지을 수 있었다.

제 4 장에서는 술폰화된 폴리스타이렌 아이오노머들의 동적.기계적 성질 그리고 형태학적 연구에 대하여 양친성 물질인 diamine 의 효과가 논의 되었다. Diamine 의 첨가는 cluster T_g 를 크게 감소시켰으나, matrix T_g 에는 거의 영향을 미치지 않았다. 게다가 낮은 농도의 아이오노머의 경우, 클러스터링을 야기하는 diamine 의 첨가는 이온 모듈러스에서 약간의 증가를 보인다. 다른 한편으로, 높은 이온 농도의 아이오노머의 경우, diamine 은 multiplet 을 해체시켜 이온

모듈러스를 감소시켰다. 아이오노머 시스템의 특성은 diamine 의 탄소 원자 수와 관계있고, 그리고 diamine 은 중화제와 동시에 이온 영역의 가소제로서 행동한다.

술폰화 폴리스타이렌 아이오노머는 술폰기 사이의 강한 이온성 결합 때문에 높은 온도에서 흐름 현상을 보여주므로 가공이 쉽지 않다. 기계적 특성에 큰 불리한 효과 없이 공정온도를 감소시키기 위하여 긴 알킬 사슬 끝에 술폰기가 달린 단량체를 간단한 내부의 가소제로 사용 할 수 있다. 따라서, 우리는 최초로 폴리 스타이렌을 주사슬로한 poly(styrene-co-3-sulfopropyle methacrylate)라 이름 지어진 새로운 아이오노머를 합성했고, 동적.기계적 특성을 연구하였다. 새로 만든 아이오노머에는 한 공단량체 단위에 ester/carboxylated 와 술폰기가 같이 있기 때문에 이들의 성질들을 기존에 연구된 아이오노머 시스템[ester/carboxylate 를 가진 폴리스타이렌 아이오노머(예를들어, poly(styrene-co-methacrylate))와 술폰화된 폴리스타이렌 아이오노머]의 성질들과 비교 할 수 있다. 실험결과들을 제 5 장에서 이야기 했고, 논문 전체의 결론과 감사의 글이 뒤에 이어진다.

ABSTRACT

Dynamic Mechanical Properties and Morphology of Organic Additives-Containing Styrene Ionomers

Mohammad Luqman
Academic Advisor: Prof. Kim Joon-Seop
Dept. of Polym. Sci. and Engg.
Graduate School of Chosun University
South Korea

Ionomers are the ion containing polymers having usually up to 15 mol% of the ions attached directly or indirectly to the polymer chains. The electrostatic force of the attraction between the ionic groups and the significant difference in the dielectric constants of the ionic groups and the electrically neutral polymer matrix lead to the phase separation of the ionic groups into the non-polar polymer matrix, i.e. the ionic groups tend to form aggregates, called “multiplets” in the polymer matrix. The rigidity of the multiplets depends on many factors, but mainly on the strengths of the interactions between the ionic groups. A part of the polymer chains directly attached to the ionic groups feels reduction in the chain mobility due to the anchoring of that part with the multiplet. As the ion content increases, the number of the multiplets increases leading to the overlapping of the multiplets. As a result, larger contiguous regions of restricted mobility are formed, termed “clusters”. The clusters show their own glass transition (T_g) at higher temperatures than that of the usual matrix T_g of the non-ionic polymers. The clusters also lead to the development of a new plateau like

transition, called “ionic plateau” in the storage modulus plots and a peak in the small-angle X-ray scattering (SAXS) profile.

In this thesis, the relationship between the structure-morphology and property of polystyrene-based amorphous, random ionomers using DMTA, SAXS, XRD and DSC techniques have been presented. The thesis comprises five chapters. The first chapter deals with a brief introduction of the polymers, ionomers and instrumental techniques for their characterizations.

The second chapter discusses about the dynamic mechanical and morphological studies of methacrylate and sulfonated polystyrene ionomer blends containing salts of aliphatic dicarboxylic acids. The aim of this study was to know the effects of the type and amounts of the salts of aliphatic dicarboxylic acids on polystyrene-based ionomers. It was found that, in most of the ionomer systems, mainly the amounts of the additives rather than the nature of the ionomer chains, nature of the ionic groups of the ionomers and additives, the nature of the additives (e.g. functionality, aliphatic or aromatic, short or long chains), were responsible for the increase in the modulus of the ionomers. From the results, it was concluded that the additives have tendency to phase-separate even at low weight concentrations in the ionomers.

The mechanical properties and morphology of ionomers can be tailored by varying a number of factors including types, size, position and degree of neutralization of the ionic groups, and types of neutralizing cations, additives and plasticizers. Thus, in chapter third, the effects of the addition of barium and cobalt salts of short to long chain aliphatic dicarboxylic acids on the dynamic mechanical properties of poly(styrene-*co*-styrene sulfonate) ionomers using DMTA have been presented. It was concluded that the type of the cations and number of the carbon atoms of the added organic salts have no significant effect on the mechanical properties of the resulting ionomers, and that the organic salts acted mainly as filler in divalent systems.

In fourth chapter, the effects of the amphiphilic diamines on the dynamic mechanical properties and morphology of sulfonated polystyrene ionomers were analyzed. It was observed that the incorporation of the diamines led to a significant decrease in the cluster T_g , while the matrix T_g was almost unaffected. In addition, it was observed that on one hand, at low ion contents of the ionomer, the addition of diamines induced the clustering leading to a slight increase in the ionic modulus. On the other hand, at high ion contents, the diamines disrupted the multiplets of the ionomers leading to a decrease in the ionic modulus. It was also suggested that the properties of the ionomer systems were related with the number of the carbon atoms, and that the diamines acted as neutralizing agent-cum-ionic domain plasticizers.

It is not easy to process the sulfonated polystyrene ionomers due to their high flow temperatures, which in turn, due to the strong inter-ionic association of the sulfonate groups. In order to reduce the processing temperature without getting significantly adverse effects on the mechanical properties of sulfonated ionomers, long alkyl chains having sulfonate group at the chain end in one of the monomers may be used as a typical and simple internal plasticizer. Thus, for the first time, new polystyrene based ionomers namely poly(styrene-*co*-3-sulfopropyle methacrylate) have been synthesized, and studied their properties dynamic mechanically. The presence of the ester/carboxylate and sulfonate groups in the same comonomer unit led us to compare the properties of the current system with those of the styrene based ester/carboxylate, e.g. poly(styrene-*co*-methacrylate) ionomers, etc., and sulfonated, e.g. poly(styrene-*co*-styrenesulfonate) ionomers, etc. The results are discussed in fifth chapter, followed by the conclusion of the thesis and acknowledgements.

Chapter 1

Introduction

1. Short Introduction to Polymers

This chapter deals with a brief introduction about the polymers and subsequently to the ionomers and techniques to characterize them.

1.1. Basic Definitions

Ionomers are a part of the polymer family. Thus, in order to have indepth knowledge about the ionomers, we should be well aware about the basics of the polymers. Polymers (from Greek: *polu*, “many”; and *meros*, “part”), also known as ‘macromolecules’ are substances composed of molecules with large molecular mass composed of repeating structural units, or monomers, connected by covalent chemical bonds [1-4]. Usually they represent organic compounds, containing carbon atoms together with hydrogen, oxygen, nitrogen, halogens, etc. Polymers can be divided into many categories depending on the type of the monomer units, chemical structures, origins, physical properties, mechanical behavior, thermal characteristics, etc. Depending on the monomer units, polymers can be categorized into homopolymers, copolymers and terpolymers. When monomer units are same, the polymer is called homopolymer. If polymer consists of two types of the monomer units, the material is known as copolymer. If three different monomer units are connected together to form the polymer, the polymer is called terpolymer [4].

As most of the ionomers prepared by us are copolymers, it will be suitable to mention about the copolymers in more details. Copolymers can have four different types of the chain configurations, for example, linear, branched, cross-linked and 3-D network. When each monomer unit is linked with two other monomeric units on either side that can form a straight chain, the polymers are called linear polymers. During the synthesis of the polymers, if some side reactions also occur, some of the monomer units are linked to the main chains, and this type of polymers are termed branched polymer. In cross-linked polymers,

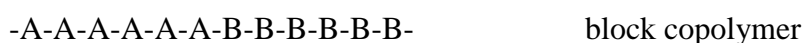
adjacent linear chains are joined to one and another at various positions along their lengths. Trifunctional monomer units, having three active covalent sites, form three-dimensional networks. Polymers consisting of trifunctional units are termed network polymers. Schematic representations of polymer molecular structures are shown in Fig.1 [5]. Other types of the classification of the copolymers are based on the type of distribution of the monomers to each other. When two different repeating units in a copolymer are distributed randomly throughout the chain, the polymer is termed random copolymer.



When two repeating units are distributed alternatively in the chains, the polymer is called an alternating copolymer.



In a block copolymer, a block of one repeating unit is followed by a block of another repeating unit, which, in turn, followed by a block of the first repeating unit and the sequence continues.



Graft copolymers are branched molecules where the main chain is made up entirely of one repeating unit, while the branch chains are made from another repeating unit.



Among the various types of the copolymers, our group mainly deals with the random copolymers/ionomers. The next section deals with a brief description of the synthesis of the polystyrene homopolymer and random copolymers (1.2.). This section will be followed by the section dealing with the various techniques used for the characterization of the polymers.

1.2. Synthesis

Polymers can be synthesized by three methods: organic synthesis, biological synthesis, or by chemical modification of natural polymers.

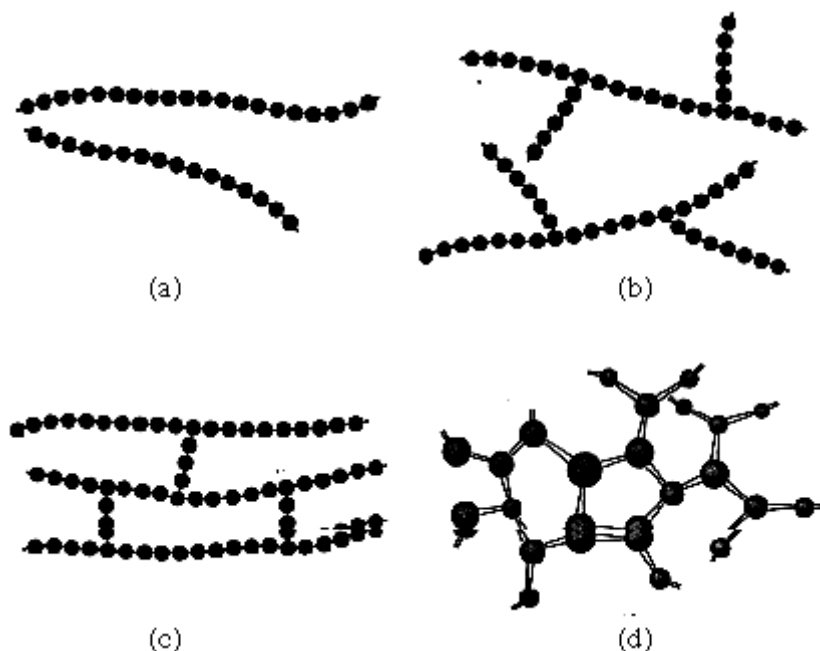


Figure 1. Schematic representation of (a) linear, (b) branched, (c) cross linked, and (d) network polymer structures. The individual monomer units are shown as dark circles.

Organic synthetic methods can be divided into two categories, addition or chain growth polymerization, and step or condensation polymerization [4]. Chain growth polymerization is characterized by a self-addition of the monomer units, to each other, very rapidly through a chain reaction. No byproduct is formed; the product has the same elemental composition as that of the monomer. Compounds containing reactive double bonds that can be changed into single bonds by the

free radicals or an ionic initiator can undergo this type of the polymerization. In step polymerization, the polymer buildup proceeds through a reaction between the functional groups other than the double bonds of the monomers in a step-wise manner. It is a slow process as compared to the chain growth polymerization. This polymerization is mostly accompanied by the elimination of the small molecules like water, etc. The elemental composition of the resulting polymer generally differs from those of the monomers.

Free radical polymerization; the most common type of chain growth polymerization was used in the present work. Thus, it would be useful to describe it briefly. It involves three kinetic steps: initiation, propagation and termination [3]. In initiation step, the initiator, e.g. azo compounds, peroxides, peracids, etc. decomposes into two free radicals with the help of heat energy, light energy, or catalysts, followed by the free radical attack to the monomers. As a result, the unsaturated monomers also decompose into radical monomers having unpaired electron at one end and the free radical at the other end. In the propagation step, the radical site at first monomer unit attacks the double bond of a fresh monomer molecule, resulting in the enlargement of the chains by the addition of the second monomer and transfer of the radical site from first monomer unit to the second. Since the decomposition of the initiator produces many free radicals at the same time, each one of them can initiate and propagate a chain growth simultaneously. In termination step, two growing chain ends may react with each other either by coupling or disproportionation, and the reaction stops. There is another method of chain termination, which takes place by a number of “transfer reactions”.

1.3. Characterization

There are several parameters which should be specified for the characterization of a polymer. It is due to the fact that a polymer consists of a statistical

distribution of chains of different lengths, and each of the chains consists of monomer residues that affects the polymer properties. There are many techniques to characterize the polymers. Only one of them will be described here, and few of the important techniques used in the present work, that are common to both for non-ionic polymers and ionomers will be described in detail in section dealing with the characterization of the ionomers. In a particular analysis, one may want to know the composition and the molecular weight of the polymers. There are many techniques that can be used to characterize the compositions of the polymers, for example, elemental analysis, infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR) [1-4,6]. The molecular weight of the polymers can be obtained using various techniques that can be divided into two groups, depending on whether these are absolute or relative methods [3]. In absolute methods, direct determination of the molecular weight of the polymers is possible, while in relative methods it is must to calibrate the procedure based on the absolute method. The number average molecular weight (M_n) and weight average molecular weight (M_w) are the most commonly used terms to define the molecular weights of the polymers. Some of the absolute methods based on ebulliometry, cryoscopy, end group analysis and osmometry, which are colligative in nature, can be used to determine the number average molecular weight. A few measurements in which the polymer molecules contribute to the measure property according to their size also exist. The weight average molecular weight can be determined from these measurements. ultracentrifugation and Light scattering techniques are examples of these type of the measurments. Size exclusion chromatography and viscometry are examples of relative methods.

It will be suitable to give the definitions of the number and weight average molecular weight, M_n and M_w , respectively. These are as follows:

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

where N_i is the number of the molecules having a molecular weight M_i . The weight average molecular weight, M_w is defined below:

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} = \frac{\sum W_i M_i}{\sum W_i}$$

where W_i is the weight fraction of each type of the polymer molecules. Weight fraction of the individual polymer molecules is the mass of each polymer molecule ($N_i M_i$) divided by the total weight of the polymer ($\sum N_i M_i$). The polydispersity index (PI) is the ratio of the M_w/M_n [1-4].

2. Ionomers

2.1. Definitions

Ion containing polymers can be divided into two categories: ionomers and polyelectrolytes. The definition of the word “ionomer” has been the subject of some uncertainty. Ionomers, generally, contain relatively low ion content (usually up to 15 mol% of the ions), while polyelectrolytes contain significantly higher ion content. This definition is commonly accepted, but at the same time, under certain conditions ionomers may behave like polyelectrolytes and vice versa. Thus, the boundary between the ionomers and polyelectrolytes is not certain. To avoid these problems, Eisenberg and Rinaudo [7] have proposed a new definition for these families of the polymers. **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”.

2.2. General Background

Due to the unique physical, mechanical and transport properties of the ionomers, these have long been used in applications as diverse as packaging film, resilient covers for golf balls, golf ball inlayers, synthetic drilling muds, proton exchange membranes, compatibilizing agents in polymer blends, reactive additives in composite materials, compatibilizers in polymer-clay nanocomposites, semi-permeable membranes and shape-memory materials [8-11]. The unique changes in the properties of the ionomers as compared to the analogous non-ionic polymers are due to the presence of low amounts of the ionic groups, which have a much higher dielectric constant than that the polymer phase. The aggregates of the ionic groups lead to a dramatic changes in the morphology of the system. The ionic aggregates are known as “multiplets”, at the same time, “clusters” are also used to describe them [12].

Numerous studies have been performed on the morphology and viscoelastic properties of a wide range of the random ionomers. These studies have been discussed in a many conferences proceedings [8,9,11-15], review articles [16-21], and books [22-24]. There are many instrumental techniques that can be used to study the morphology and mechanical properties of the ionomers. These are classified into five groups. The first groups belongs to scattering techniques, e.g. small angle X-ray scattering (SAXS) [25-29], extended X-ray absorption fine structure (EXAFS) [30,31], and small angle neutron scattering (SANS) [32]. The second one comprises spectroscopic techniques such as Raman spectroscopy [33], nuclear magnetic resonance spectroscopy (NMR) [34-36], Fourier transform infrared spectroscopy (FTIR) (37,38), electron spin resonance spectroscopy (ESR) [39-43], fluorescence (or luminescence) spectroscopy [44,45], and Mossbauer spectroscopy [46]. The third group comprises the viscoelastic or dielectric properties of the ionomers, such as, stress relaxation [47-49], dynamic mechanical thermal analysis [50-53], rheometry [54-59], and

dielectric analysis (DEA) [60-62]. The fourth group belongs to the thermal analysis techniques, e.g. differential scanning calorimetry (DSC) [63-68], and thermogravimetric analysis (TGA) [69]. The microscopic techniques [70-75], for example, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and scanning-transmission electron microscopy (STEM) comprise the fifth group of the techniques. In this work, DMTA, XRD, SAXS, DSC and FTIR have been used. For the sake of the concise Introduction, a brief discussion about the most commonly used techniques in present works, such as SAXS, DMTA and DSC are described below.

2.3. Important Techniques Used in the Present Work

2.3.1. Small-angle X-ray Scattering (SAXS)

There are different regions of varying electron densities in polymers. The main purpose of using the SAXS technique is to get insight about the electron density differences in the materials. SAXS is a technique in which the elastic scattering of X-rays of wavelength 0.1-0.2 nm by a sample having heterogeneities in the nano-meter range, is recorded at very low angles, typically 0.1-10°. In this range of angles, we can get the information about the distances of partially ordered materials, pore sizes, shape and size of particles. SAXS can deliver structural information of polymers between 5 to 25 nm, of repeat distances in partially ordered systems of ca. 150 nm [76-79].

There are two main groups in SAXS instruments: point-collimation and line-collimation instruments:

a) Point-collimation instruments have pinholes which are responsible for shaping the beam of X-ray to a circular or elliptical spot that illuminates the sample. Thus, the scattering is centro-symmetrically distributed around the primary X-ray beam, and the scattering pattern in the detection plane consists of circles around the primary beam. As a small volume of the sample is illuminated, the intensity of

scattered beam is small, and hence, the measurement time is in the order of hours or days. Point-collimation can be used to determine the orientation of the non-isotropic systems, e.g. fibres, sheared liquids, etc.

b) Line-collimation instruments confine the beam in one dimension only, and hence, the beam profile is a long but narrow line. The time of measurements with these instruments are significantly shorter as compared to the point-collimation, and take only few minutes to hours [79].

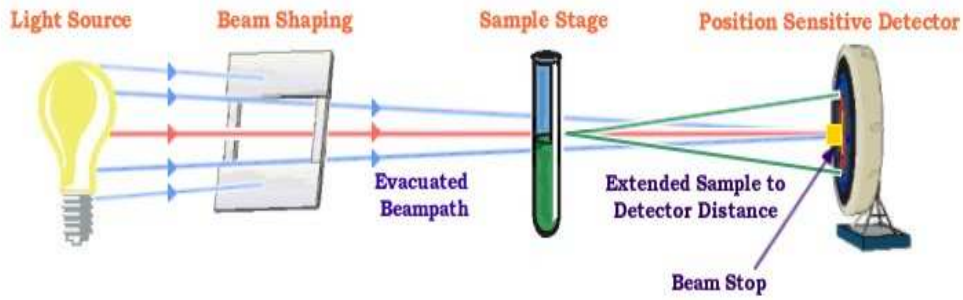


Figure 2. Schematic SAXS apparatus [80].

The SAXS utilizes the radiation diffraction on whole particles having interphase boundaries and the mean electron density (ρ) difference from that of the medium (ρ_0) [81]. The intensity of the scattered radiation (I) by the particles is proportional to:

$$I(K) \approx (\rho - \rho_0)^2 (\Sigma K)^2$$

where K is a wave vector, $K = 4\pi\sin\theta/\lambda$ and λ is wavelength of the X-ray [82]. The total radiation intensity scattered in the small-angle region, can be expressed as:

$$I(K) = \int_0^\infty D_r(R)m^2(R)\Phi(KR)dR$$

where $D_n(R)$ is a function of the particles size distribution which depends on their linear parameter R . For spherical particles, R is the radius of a sphere. $m^2(R)$ is an integral over excess density in the medium surrounding the particle, $\phi(KR)$ is the particle shape factor [83]. On considering the correction for the wavelength effect and the collimation effect, the equation can be written as:

$$I_{\text{exp}}(K) = 2 \int_0^\infty dR \int_0^\infty d\lambda \int_0^\infty dt \int_0^\infty dx \\ \times Q(x)P(t)W(\lambda')D_n(R)m^2(R)\Phi(\beta)$$

where $\lambda' = \lambda/\lambda_0$ and $W(\lambda')$ is the wavelength distribution; $Q(x)$ is a weight function for the aperture width effect; $P(t)$ is a weight function for the aperture length effect;

$$\beta = R[|h-x|^2 + f^2]^{1/2}/\lambda \quad (1)$$

From Equation 1, it is possible to calculate the function $D_n(R)$ by the inverse Fourier transform method. 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_{max} value. For very small angles, q_{max} is equal to the $2\pi/d_{\text{Bragg}}$ where d_{Bragg} is the Bragg distance ($= n\lambda/2\sin\theta$, where θ is the X-ray diffraction angle, and $n=1, 2, 3, \dots$).

SAXS is used for determining the micro to nano scale structure of particle systems in terms of parameters such as shapes, distribution, averaged particle sizes, and surface to volume ratio. SAXS is non-destructive, accurate and generally requires a minimum of sample preparation. SAXS can be used for the research and developmemt as well as in quality control for all types of colloids, oil, cement, metals, polymers, proteins, foods, pharmaceuticals, etc [79].

2.3.2. Dynamic Mechanical Thermal Analysis (DMTA)

DMTA is used to measure the mechanical properties of materials subjected to a periodic, sinusoidally stress. A low stress is applied sinusoidally so that the sample can always be within the elastic region of its stress-strain curve. For a perfectly elastic material, the stress and strain are in phase. A material may flow instead of reversibly being deformed under load. In this condition, the stress-strain curves will be 90° out-of-phase since the strain is proportional to the stress. Most of the polymeric materials show both types of the behavior, i.e. they react elastically, and at the same time, they flow to some extent, and hence, are termed "viscoelastic". Thus, the stress-strain curves are out of phase, but by an amount less than 90° (refer to Fig. 3) [1-4, 85,86, 87]. DMTA measures the amplitudes of the stress and strain as well as the phase angle (δ) between them. It is used to separate out the modulus into an in-phase component, the storage modulus (E'), and an out-of-phase component, the loss modulus (E''). An Argand diagram can represent the relationship between these quantities and the dynamic (or complex) modulus (E^*), as shown in Fig. 4 [87].

The damping factor or loss tangent ($\tan \delta$) is related with the amount of mechanical energy dissipated as heat. For a perfectly elastic material and a perfectly viscous material, $\tan \delta$ is equal to zero and infinite, respectively. In DMTA, a sinusoidal stress on the sample can be applied in various modes, e.g. tensile, bend and shear [88]. Thus, the DMTA can determine the moduli and $\tan \delta$ at different frequencies as a function of temperature. A typical DMTA instrument can deform the sample in a number of ways. The sample is deformed by the sinusoidal stress applied by a force motor, while the resulting strain is measured by a position transducer. There are many sample-mounting arrangements in DMTA. For solid samples of low to medium stiffness, the

cantilever bending mounts can be used. For soft materials or even liquids of high viscosity, the compression and shear mounts can be used. The tension mounts are useful for fibers or films and elastomers.

In DMTA, when the frequency of the chain motion coincides with the measurements frequency, the peak maximum in the plot of the loss tangent vs. temperature is observed. The materials can be scanned at various frequencies at the same time as a function of the temperature. The peak position is dependent on the frequency, i.e. at a higher frequency, the position of the loss tangent will be obtained at a higher temperature, since the faster chain motion is expected at higher frequency.

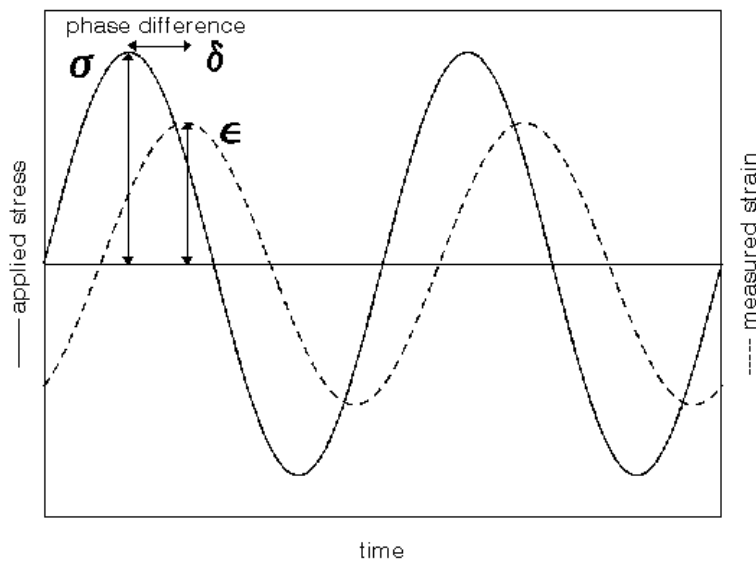


Figure 3. Schematic representation of the stress-strain phase behavior.

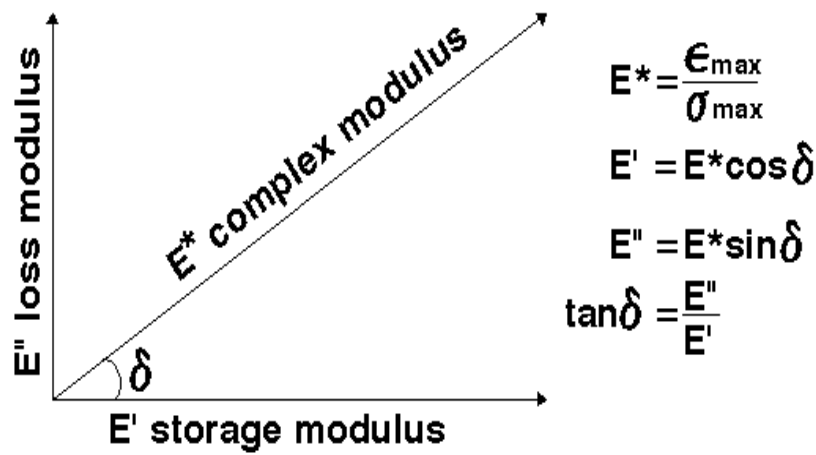


Figure 4. Argand Diagram representing the storage, loss and dynamic modulus.

The DMTA can be used for 1) the determination of the temperature and frequency dependence of the storage modulus (E' , G'), the loss modulus (E'' , G'') and the mechanical loss factor ($\tan \delta$), 2) the determination of the dynamical glass transition and secondary relaxation processes, 3) the characterization of the phase structure of multi-component polymeric materials, 4) the determination of cross-link densities (from the height of the rubber plateau), 5) the characterization of the influence of water on thermo-mechanical properties, 6) the characterization of physical and chemical aging processes and, 7) the determination of the degree of curing for duromers [89].

2.3.3. Differential Scanning Calorimetry (DSC)

DSC is a technique in which the difference for the heat required to increase the temperature of a sample and reference are measured as a function of temperature.

The temperature of both the sample and reference are maintained same throughout the experiment. The principle of this technique is that, when the sample undergoes a phase transitions, heat needs to flow to the sample to maintain both the sample and reference at the same temperature. The heat flow to the sample depends on whether the process is exothermic or endothermic. For example, as a sample melts from solid to a liquid, it will require more heat to flow to the sample to raise its temperature at the same rate as the reference. It is because of the absorption of heat by the sample as it undergoes the endothermic phase-transition from solid to liquid. Likewise, as the sample undergoes exothermic processes, e.g. crystallization, less heat is required to increase the temperature of the sample. Thus, the difference in heat flow between the sample and reference makes the DSC to measure the energy absorbed or released by the sample. An exothermic or endothermic process results in a significant deviation in the difference between the two heat flows. This results in a peak in the DSC curve. An exothermic process will result in positive peaks above the baseline, while the peaks resulting from an endothermic process are negative, i.e. below the baseline. DSC can be used to measure a number of parameters, characteristic to the sample. We can observe fusion and crystallization events as well as glass transition temperatures (T_g). In addition to these applications, DSC can be used to study oxidation as well as other chemical reactions [90-92].

2.3.4. Morphological Models

A wide range of experimental studies has been performed on the ionomers using above-mentioned techniques. Due to the presence of the ionic groups, the ionomers show significantly different mechanical and morphological properties than those of their non-ionic counter parts. The appearance of additional plateau like transition, one additional glass transition at higher temperatures other than

usual matrix glass transition in storage modulus and loss tangent curves, a peak in small angle X-ray scattering profile, and unusual high melt viscosities and high relaxation times are the various mechanical and morphological differences between the ionomers and non-ionic polymers [93-102]. The two loss tangent peaks are related with the glass transitions of two different phases of some of the ionomers [51,93-112]. The appearance of additional plateau like transition in the storage modulus plots vs. temperature is thought to be due the presence of the additional phase in the materials. The SAXS profiles of some ionomers show a SAXS maximum [26-29] that refers to an ionic peak arising from intraparticle [26] or interparticle interferences [27]. At this point, it should be mentioned that the morphological studies address only the distribution of the ions or ionic aggregates in the materials. A successful model for the ionomer morphology must also account for the mechanical properties of the ionomers.

A number of attempts have been made to propose a model that can reasonably explain the structure-property relationships, e.g. Multiplet-Cluster model, so-called EHM model by Eisenberg et al [12], Core-Shell model by MacKnight et al [113], Hard-Sphere model by Yarusso and Cooper [25]. I would like to describe briefly about the EHM model as the morphological and mechanical properties of most of the ionomers can most probably be explained on the basis of the assumptions made in this model. According to this model (see Fig. 5), the electrostatic interaction between the ion-pairs leads the ion-pairs to aggregate to form the multiplets having small number of the ion-pairs. At this point, it should be mentioned that the ion-pairs within the loopback distances reside in one multiplet. The loopback distance is the critical distance for the adjacent ion-pairs along the same chain to end up in the one multiplet. As the ion-pairs are attached to the polymer chains, the anchoring of the chains to the ionic cores (i.e. multiplets) take place, leading to a considerable reduction in the mobility of the

chains in the immediate vicinity of the multiples. The thickness of the restricted mobility regions is thought to be the equivalent of the persistence length of the polymer chains. The persistence length is one half of the Kuhn length, the length of hypothetical segments that the chain can be considered as freely joined. The persistence length equals the average projection of the end-to-end vector on the tangent to the chain contour at a chain end in the limit of infinite chain length [114,115]. It can also be defined as the distance over which the local inflexibility in a polymer chain persists [114]. On increasing the ion contents of the ionomers, the number and size of the multiplets increase, that leads to the overlapping of the adjacent restricted mobility regions. Once the size of the restricted mobility regions reach or exceed ca. 50-100 Å, the regions start to act as an independent phase, and thus are able to show a new glass transition peak in loss tangent plots, a new plateau like transition in storage modulus curve, and a peak in the SAXS profile for many ionomers. At this stage, these regions are called “clusters”. On further increasing the ion contents, the volume fraction of the clusters increases, while that of the matrix regions decreases. At the same time, the position of the two loss tangent peaks shifts to higher temperatures. The distance between the multiplets called “preferred spacing” can be related with the SAXS peak position. Thus, within the clusters, the distance between the multiplets is expected to be more or less regular.

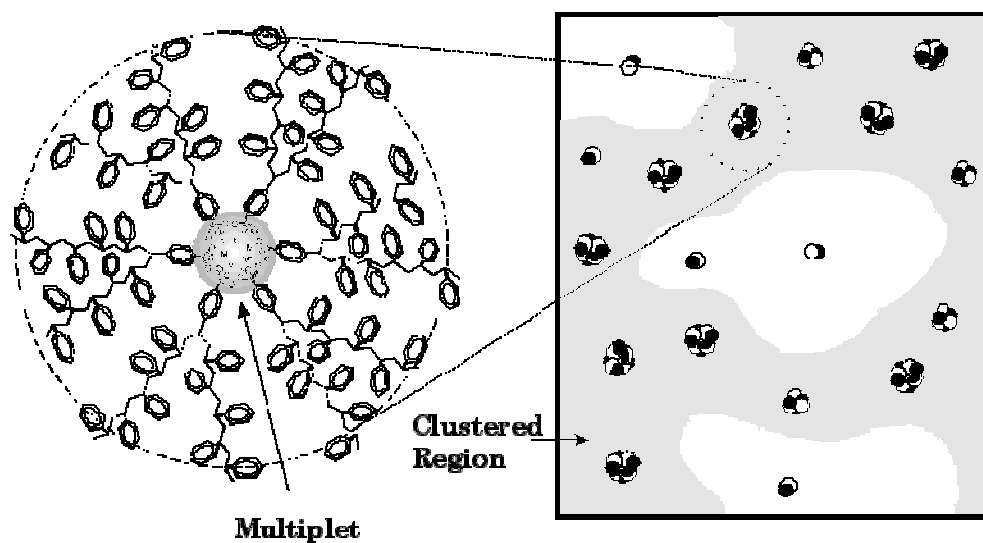


Figure 5. The Eisenberg, Hird and Moore's Multiplet-Cluster model of ion aggregation in random ionomers.

In addition to the effectiveness of EHM model in successfully interpreting many phenomenon encountered in the ionomers, numerous studies conducted later on proved the predictions made in that model to be true [35,36,52,90,93-116].

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Chapter 2

**Dynamic mechanical and morphological studies of
methacrylate and sulfonated polystyrene ionomer blends
with salts of aliphatic dicarboxylic acids**

Abstract

The effects of the addition of sodium salts of aliphatic dicarboxylic acids (DCAs) on the dynamic mechanical properties and morphology of poly(styrene-*co*-sodium methacrylate) MNa and poly(styrene-*co*-sodium styrenesulfonate) SNa ionomers were studied using DMTA, DSC, SAXS and XRD techniques. The addition of small amounts of the DCAs led to a considerable and slight increase in the ionic modulus and a negligible change in the matrix and cluster glass transition (T_g) temperatures of the MNa and SNa systems, respectively. It was also found that the rate of increasing the ionic modulus was higher in low ion content system, compared to that in high ion content systems. However, at large amounts of the DCAs, the ion contents and type of the ionic groups of the ionomers, number of the carbon atoms of DCAs had no significant effect on increasing the ionic modulus. At the same time, in both the systems, the addition of large amounts of the sodium succinate (DCA4) increased the matrix and cluster T_g s slightly and considerably. However, large amounts of the sodium hexadecanedioate (DCA16) decreased the matrix and cluster T_g s of SNa systems slightly and significantly, with no effect on the T_g s of the MNa systems. DSC thermograms showed no crystalline melting peaks in any of the systems below the decomposition temperatures of the ionomers, whereas, X-ray patterns showed crystalline peaks for the DCAs. The absence of the DSC melting peaks and the presence of X-ray peaks indicated the phase-separation of the DCAs in the ionomers. Now, it can be suggested that DCA4 acted as reinforcing additive by increasing the modulus and T_g s to some extent in both MNa and SNa systems. The DCA16, however, in addition to acting as reinforcing additive, acted as preferential plasticizer for the cluster phase at least at its large amounts in the SNa systems. It can also be concluded that it is mainly the amounts of the additives rather than the nature of the ionomer chains, nature of the ionic groups of the ionomers and additives, ion contents of the ionomers to some extent, the

nature of the additives, e.g. functionality, aliphatic or aromatic, short or long chains, which is responsible for the increase in the modulus, provided that the additives have tendency to phase-separate even at low weight concentrations in the ionomers.

Keywords: PS ionomers, aliphatic dicarboxylic acids, phase-separation, reinforcing filler

1. Introduction

Ionomers are polymeric materials containing small amounts of (usually up to 15 mol %) of ionic groups embedded with relatively less or non-polar polymer matrix [1-6]. The presence of the ionic groups in the polymer matrix generally causes ion aggregation, leading to the phase-separation of materials into ion-poor and ion-rich domains and, hence, resulting in materials with significantly different physical properties as compared to their non-ionic forms. The interpretation of mechanical data and morphology of random ionomers can possibly be done with the help of the multiplet-cluster or so-called EHM model [7]. Since 1970s, the mechanical properties, morphology and spectroscopy of ionomers have been extensively studied by varying a number of factors such as the type, size, position and degree of neutralization of functional repeat units (i.e. ionic units), type of plasticizers, additives and neutralizing agents, and other experimental conditions [1-6,8-11]. However, little is known about the effects of bi-functional additives on the morphology and mechanical properties of polystyrene (PS)-based ionomers.

Plante et al. performed dynamic mechanical studies on the matrix- and cluster-dominant carboxylated PS ionomers blended with chemically identical mono- and bi-functional styrene oligomers [13]. Mono-functional oligomers were found to plasticize both the matrix and cluster regions. In the matrix-dominant system,

the bi-functional oligomers showed anti-plasticization behavior at low oligomer contents. However, in the cluster-dominant system, the oligomers were phase-separated because of the insufficient weight percentage (amounts) of the non-ionic polymer matrix needed for the non-polar oligomer segments. In a subsequent study, Plante and Bazuin investigated the effects of the addition of mono-dispersed, tertiary amine-terminated oligomers of styrene on the properties of lightly sulfonated PS (PSSSA) [14]. Mono-functional styrene oligomers plasticized the PSSSA, but considerably less than the mono-functional alkyl chains did, which might be due to the greater bulkiness and stiffness of the styrene segments. The bi-functional oligomers showed a very little plasticization effect and, at their higher concentrations, became phase-separated despite extensive inter-component interactions, owing to the copolymer effects. Recently our group investigated the dynamic mechanical properties and morphology of poly(styrene-*co*-sodium methacrylate) ionomers containing sodium salts of aliphatic dicarboxylic acids (DCAs) [18]. It was found that the DCAs disrupted the formation of the multiplets of the ionomer. However, later on, authors came to know that the disruption of the multiplets was partly due to the under-neutralization of the acid groups of both the acid copolymers and aliphatic dicarboxylic acids. Jeon et al. investigated the effects of mono- to multi-functional carboxylated benzene salts on the morphology and mechanical properties of poly(styrene-*co*-sodium methacrylate) ionomers [19]. They found that the additives got phase-separated at all the weight concentrations ranging from 5 to 46 wt % and, hence, acted mainly as reinforcing fillers. Wakabayashi et al. studied the effects of few fatty acid salts (C_{16} - C_{22} in chain lengths) on morphology and mechanical properties of ethylene/ (meth) acrylic acid ionomers [21]. They showed that the structural and property modification in the ionomers induced by the addition of the additives were complex, and depend both on the neutralizing cation and on degree of the crystallinity of the hydrocarbon tails of

the fatty acid salts and polymer chains. In a recent paper, we showed that the mono-functional organic salts in PS-based ionomers acted both as plasticizers and fillers, while bi-functional organic salts behaved only as fillers [22]. Few other groups had also studied the effects of the organic acids (salts) on various properties of the ionomers. For the sake of the precise Introduction, reader is referred to the concerned articles [12,15-17,20].

Despite extensive studies on the behavior of the mono- to multi-functional oligomers, and aliphatic to aromatic compounds with or without the functional groups and alkyl chains, only a few studies have been performed on the effects of the aliphatic dicarboxylic acids (salts) on the properties of amorphous PS-based random ionomers. Now we have known that bi-functional organic salts (adipate and dodecanedioate) became phase-separated and act as fillers in methacrylate PS ionomers having ionic groups similar to those of the DCAs [22]. However, at this point we are not aware about the effects of chain lengths of DCAs from very short to sufficiently long in alkyl chain lengths, and of the differences in the types of the ionic groups of the additives (DCAs) and those of the ionomers (e.g. carboxylate vs. sulfonate). Despite known morphology of few of the DCAs in methacrylate PS ionomers, DCAs may have different morphology in sulfonated PS ionomers having the ionic groups different to those of the additives (DCAs). They may act either as polar (because of the presence of ionic groups at both the ends of alkyl chain), non-polar (because of the presence of aliphatic chains) plasticizers or fillers. Thus, the above-mentioned factors provoked us to further investigate the roles of DCAs in the PS-based ionomers. To do so, in the present study, we used sodium salts of succinic acid [$\text{NaOOC}-(\text{CH}_2)_2-\text{COONa}$], adipic acid [$\text{NaOOC}-(\text{CH}_2)_4-\text{COONa}$], dodecanedioic acid [$\text{NaOOC}-(\text{CH}_2)_{10}-\text{COONa}$], and hexadecanedioic acid [$\text{NaOOC}-(\text{CH}_2)_{14}-\text{COONa}$] as additives. As the study related to the addition of the adipate and dodecanedioate to the methacrylate PS ionomers has already been performed by

Luqman et al. [22], the detailed study in this work, however, will be performed using only two of these additives; DCAs of very short (e.g. succinate) to significantly long (hexadecanedioate) alkyl chains. We have selected ionomers having different ionic groups (i.e. carboxylate vs. sulfonate groups) to analyze the effects of the two DCAs, if any, on the morphology and mechanical properties of the ionomers.

2. Experimental Details

2.1. Sample Preparation

PS homopolymer (MW= ca. 500,000) and poly(styrene-*co*-methacrylic acid) SMAA copolymers (MW= ca. 500,000) were synthesized by the method described elsewhere [23-27]. The Poly(styrene-*co*-styrenesulfonic acid) SSA copolymers were made by the sulfonation of PS with the method reported by Makowski et al. [31]. To determine the acid contents, the copolymer samples were dissolved in a benzene/methanol (9/1, v/v) mixture to make a 5% (w/v) solution and titrated with methanolic NaOH solution to the phenolphthalein end point. The acid contents were found to be 4.5 and 7.1 mol% for the SSA and SMAA copolymers. In order to prepare the ionomers containing DCAs, the acid forms of the additives and copolymers were dissolved in a benzene/methanol (9/1, v/v) mixture. After complete dissolution of both the components, the acid groups of both the additives and acid copolymers were fully neutralized with methanolic NaOH solution. In this study, we prepared two sets of the samples. In the first set of samples, the mole ratio of the ionic groups of the DCAs to those of the ionomers was kept to be 1:1. Since the MW of the DCAs increased with increasing number of the carbon atoms of DCAs, the amount of the DCAs in the samples increased with the number of the carbon atoms to maintain the mole ratios of the ionic groups at 1:1 (see Table 1). Thus, the changes in the properties of the ionomers by the addition of the DCAs might be due to the variations in

both the number of the carbon atoms of DCAs and the amounts of DCAs in the ionomers. To prepare the second set of the samples, we chose the DCAs of the low and high numbers of the carbon atoms, i.e. DCA4 (sodium salt of succinic acid) and DCA16 (sodium salt of hexadecanedioic acid), and varied their amounts in the ionomer samples to see solely the effects of the amounts of that particular DCA on the properties of the ionomers. The samples were freeze-dried and further dried under a vacuum at ca. 150 °C for 24 h. For the dynamic mechanical property measurements, the samples were compression molded at ca. 240 and 260 °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 24 h. The notations used in plots for the samples are SNa-Cx-Y and MNa-Cx-Y, where MNa and SNa are the sulfonated and methacrylate ionomers, respectively, containing DCAs of “x” number of the carbon atoms, e.g. 0 (i.e. an ionomer), 4 (sodium succinate), 6 (sodium adipate), 12 (sodium dodecanedioate), and 16 (sodium hexadecanedioate), and “Y” denotes either the mol ratio of the ionic groups of DCAs to that of the ionomer or weight percentage (wt%) of the DCAs in the ionomer blends.

Name	Acronym	Structure	Wt% (Mol ratio =1)	
			MNa	SNa
Disodium Succinate	DCA04	NaOOC-(CH ₂) ₂ -COONa	3.94	2.44
Disodium Adipate	DCA06	NaOOC-(CH ₂) ₄ -COONa	4.83	2.96
Disodium Dodecanoate	DCA12	NaOOC-(CH ₂) ₁₀ -COONa	7.40	4.60
Disodium Hexadecanoate	DCA16	NaOOC-(CH ₂) ₁₄ -COONa	9.01	5.64

Table 1. Characteristics of the sodium salts of dicarboxylic acids.

2.2. Dynamic Mechanical and Thermal Properties Measurements

A TA dynamic mechanical thermal analyzer (DMTA, Mark II) was used to measure the storage modulus (E') and loss tangent ($\tan \delta$) of each sample as a function of the temperature in a dual cantilever-bending mode at five different frequencies. The heating rate was 1 °C/min. To analyze the loss tangent plots, curve de-convolutions were performed using the Peakfit computer program (SPSS Inc.). The plots were best fitted using the exponential equation as the baseline and Gaussian functions for fitting the matrix and cluster loss tangent peaks. For the thermal property study, a TA differential scanning calorimeter (DSC 3000) was used. The samples were scanned from 30 °C to 300 °C, with a heating rate of 10 °C/min.

2.3. X-ray Experiments

The SAXS experiments were conducted at Station 4C1 of the Pohang Light Source, Korea [32]. The generated critical beam energy was 2.8 keV (at 2.5 GeV operation modes). The size of the beam at the sample was smaller than 1 mm². The position-sensitive one-dimensional Si diode-array detector was used. The sample-to-detector distance was 400 mm, which allowed SAXS data to be obtained in the q range from ca. 0.4 to 5.7 nm⁻¹, where $q = 4\pi \sin \theta / \lambda$; θ is half the scattering angle, and λ is the X-ray wavelength ($\lambda = 0.1608$ nm). The SAXS data were plotted as relative intensity vs. q after correction for the sample absorption and a background. The XRD patterns were recorded using a Philips PANalytical X-ray diffractometer (X' pert PRO MPD). The scanning speed and the sampling width were 0.3 °/sec and 0.018 °, respectively.

3. Results and Discussion

The storage moduli (E') as a function of temperature for the P(S-7.1-MANa) MNa ionomer, P(S-4.5-SSNa) SNa ionomer and their systems containing DCAs

are shown in Figs. 1 (a) and (b), respectively. In these systems, the mole ratio of the ionic groups of the DCAs to those of the ionomers is 1:1. It is seen that with increasing temperature, the modulus curve changes its shape from a plateau (i.e. glassy plateau), through a first drop (i.e. matrix glass transition), through a first descending plateau (i.e. ionic plateau), through a second drop (i.e. cluster glass transition), to a second descending plateau (i.e. rubbery and flow regions). It is observed that below ca. 135 °C there is almost no difference in the modulus plots for all the samples including the pure ionomers. Above that temperature, there is a slight increase in the heights of modulus plots of both ionomer systems with increasing number of the carbon atoms of the DCAs. It should be mentioned that the widths of the ionic plateaus of the ionomers are found to be almost independent of the number of the carbon atoms of DCAs. The width of the ionic plateau is treated as a symbol for the strength of interactions between the ionic groups in the multiplets of the ionomers [5]. Thus, the similar widths of the ionic plateaus imply that the addition of the DCAs having the $\text{-COO}^-\text{Na}^+$ ionic groups negligibly affects the formation of the multiplets of the MNa and SNa ionomer systems having the $\text{-COO}^-\text{Na}^+$ and $\text{-SO}_3^-\text{Na}^+$ ionic groups, respectively. Also, shown in Figs. 1 (a) and (b) are the plots of loss tangent as a function of temperature for the ionomers. Each of the two ionomer systems shows two loss tangent peaks; one for the ion-poor phase (i.e. matrix phase) at low temperatures and the other for the ion-rich phase (i.e. cluster phase) at high temperatures [3-7,33-35]. It is seen that the addition of DCAs does not change significantly the position, shape and width of the matrix and cluster loss tangent peaks of both ionomer systems. Only the heights of the two peaks seem to decrease with increasing number of carbon atoms of DCAs.

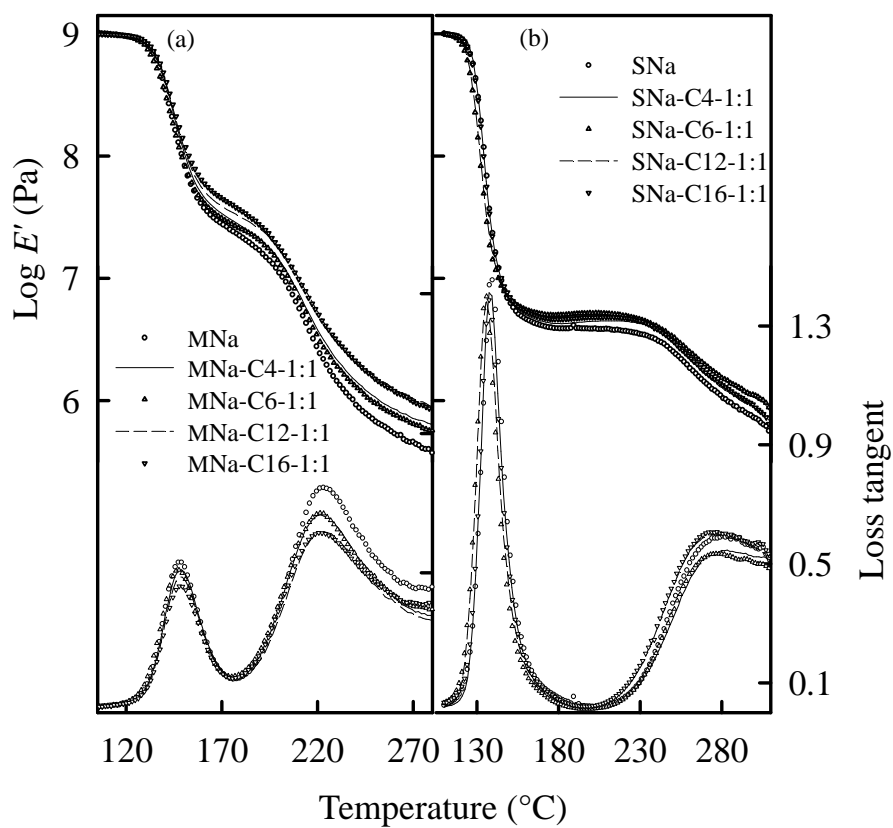


Figure 1. Storage moduli and loss tangents as a function of the temperature for the P(S-7.1-MNa) and P(S-4.5-SSNa) ionomers and their systems containing DCAs at 1:1 mol% of the ionic groups of DCAs to those of the pure ionomers, at 1 Hz.

The modulus at a point of minimum slope in the ionic plateau region is termed ionic modulus (E'_{ionic}) [5,7]. Figs. 2 (a) and (b) show the plots of the E'_{ionic} as a function of (a) the number of the carbon atoms of the DCAs and (b) the amounts of the DCAs in both ionomer systems. It is seen that the values of the E'_{ionic} for the MNa ionomer system increase considerably and almost linearly with increasing number of the carbon atoms and the amounts of the DCAs. Thus, we tried to fit the E'_{ionic} data with the first order polynomial equation as follows:

$$\text{Log } E'_{\text{ionic}} (\text{Pa}) = 7.4 + 0.014 \times (\text{number of the carbon atoms of the DCAs}) \quad (r^2 = 0.9730) \text{ and}$$

$$\text{Log } E'_{\text{ionic}} (\text{Pa}) = 7.4 + 0.023 \times (\text{weight percentage of the DCAs}) \quad (r^2 = 0.9449)$$

Here, r^2 is a linear least-squares correlation coefficient. In the case of the SNa system, it is evident that on increasing number of carbon atoms of DCAs from 0 to 6, there is an increase in the E'_{ionic} , but on the further increase in the number of carbon atoms of DCAs, the E'_{ionic} remains almost constant. It is observed that the initial slopes of the fitted lines for the E'_{ionic} data of both systems as a function of the number of the carbon atoms seem to be similar to each other. This indicates that the initial rates of increasing E'_{ionic} are more or less independent of the type of the ionomer systems (i.e. methacrylate vs. sulfonate). When the E'_{ionic} data for the SNa system were plotted as a function of the weight percentage of the DCAs, however, it is seen that the initial slope appears to be slightly higher than that for the MNa system.

The glass transition temperatures (T_g s) obtained from the positions of the loss tangent peak maxima for the matrix and cluster phases are shown in Fig. 2 (c) as a function of the number of the carbon atoms of DCAs. It is evident that on the addition of DCAs the matrix and cluster T_g s of the ionomer systems remain almost constant with increasing number of the carbon atoms of DCAs.

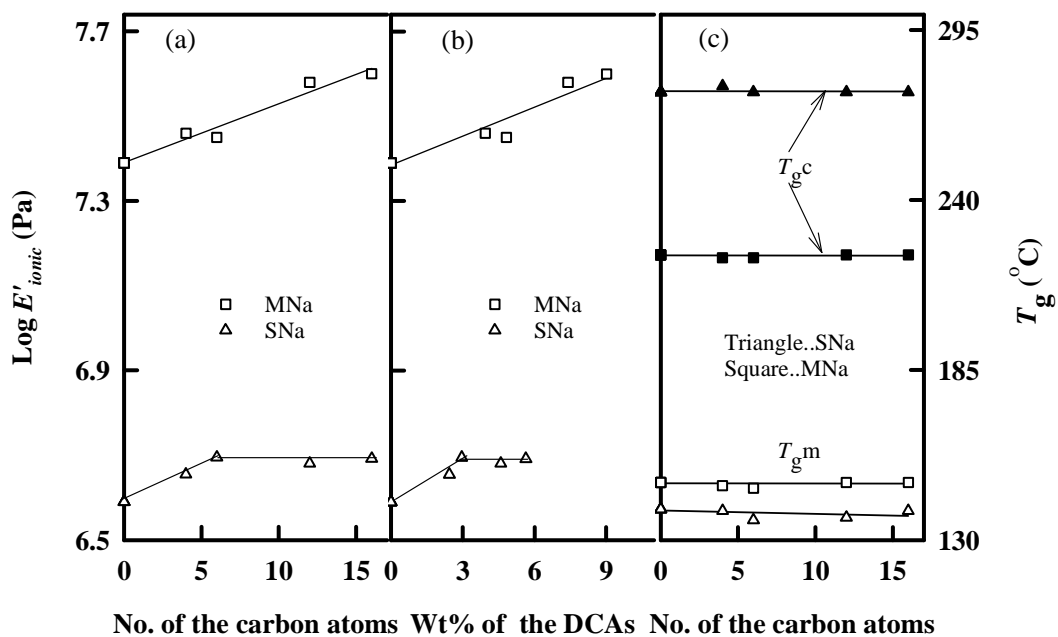


Figure 2. Ionic moduli and glass transition temperatures for the MNa and SNa ionomers and their systems containing DCAs at 1:1 mol% of the ionic groups of DCAs to those of the pure ionomers, at 1 Hz.

At this point, it should be mentioned that in some of the filled systems including chloride-filled polyurethanes [36,38], glass-fiber reinforced methacrylate polymers [37], alumina-filled polystyrenes [70], silica-filled EPDM rubbers [68] and wood-fiber reinforced styrene-maleic anhydride polymers [69], the T_g s of the systems were found to be independent of the filler content and/or the filler size. This implies that the DCAs-containing MNa and SNa ionomer systems might resemble some of the filled systems showing no changing in the T_g , but improved E'_{ionic} .

Now, let us discuss the second set of the ionomer systems. Figs. 3 (a) and (b) show the storage modulus and loss tangent plots for the MNa and SNa ionomer systems containing different amounts of the DCA4 as a function of temperature. Above ca. 135 °C, the heights of the ionic plateau increase significantly with increasing amounts of the DCA4 in both systems. In the loss tangent plots, the positions of matrix peaks do not change strongly, but those of the cluster peaks shift to slightly high temperatures with increasing DCA4 amounts. However, the heights of the two loss tangent peaks decrease significantly. Shown in Figs. 4 (a) and (b) are the storage modulus and loss tangent plots of the ionomers containing different amounts of the DCA16. In the storage modulus plots, again, the heights of the ionic plateau increase considerably with increasing amounts of the DCA16. In the loss tangent plots for the MNa system, it is observed that the positions of the peak seem to remain more or less constant with increasing the amounts of the DCA16. However, in the case of SNa system, the position of the matrix peak shifts negligibly to low temperatures and independent of the amount of the DCA16. The position of the cluster peak, however, shifts slowly and then significantly to low temperatures with increasing the DCA16 amounts. We will describe this effect later.

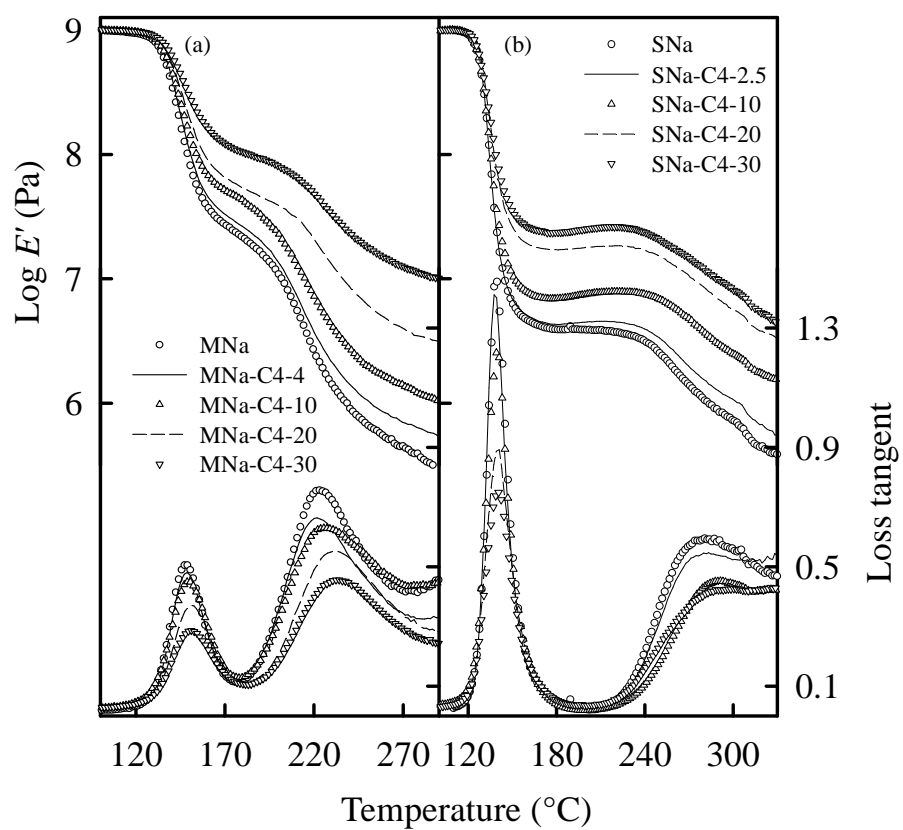


Figure 3. Storage moduli and loss tangents as a function of the temperature for the MNa and SNa ionomers and their systems containing varying amounts of the DCA4 at 1 Hz.

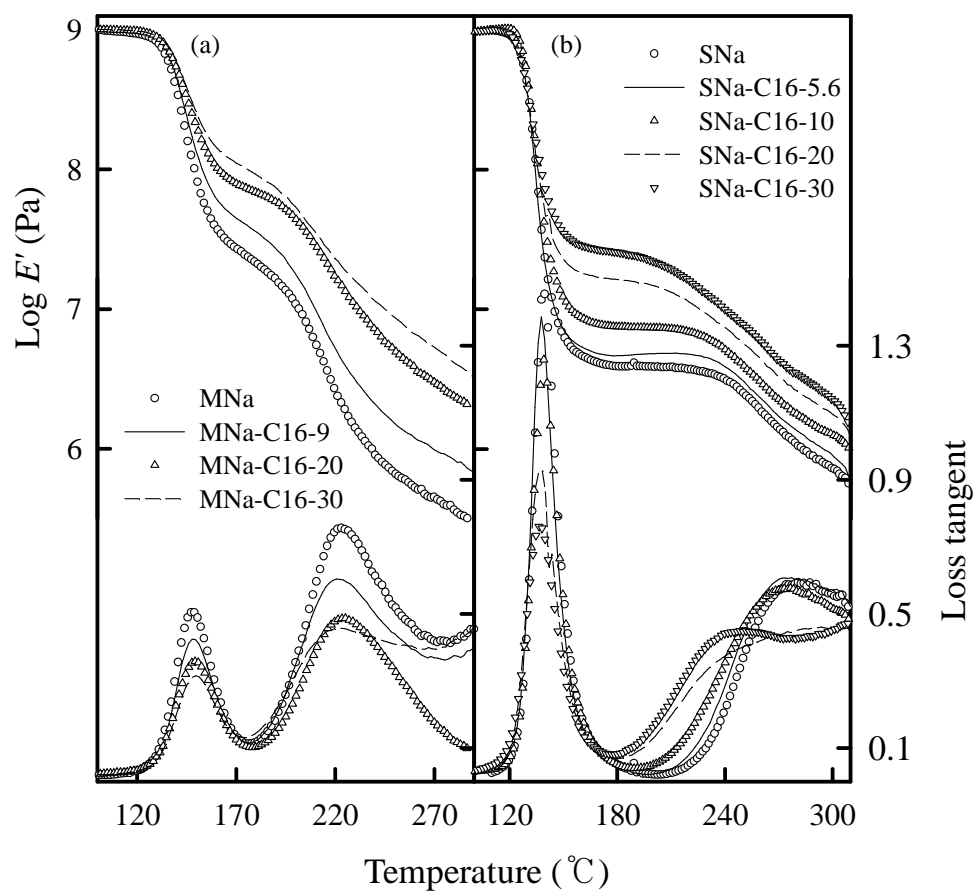


Figure 4. Storage moduli and loss tangents as a function of the temperature for the MNa and SNa ionomers and their systems containing varying amounts of the DCA16 at 1 Hz.

Shown in Fig. 5 (a) are the E'_{ionic} plots as a function of the amounts of the DCAs in the ionomer systems. It is observed that with increasing amounts of the DCAs, the E'_{ionic} values of the ionomer systems increase almost linearly. It should also be noted that for a particular ionomer system, the plots of the E'_{ionic} of the ionomers containing DCA4 and DCA16 are seen to be almost superimposed on each other. This implies that the type of the DCA salts does not affect the E'_{ionic} value of the ionomer, but only the amount of the DCAs does. The E'_{ionic} data can be best fitted with the first and second order polynomial equations for DCA4 and DCA16-containing systems, respectively. For the qualitative analysis, however, E'_{ionic} data for DCA16-containing systems are also fitted with the first order polynomial equations as follows:

For MNa system,

$$\text{Log } E'_{\text{ionic}} (\text{Pa}) = 7.39 + 0.022 \times (\text{weight percentage of the DCA4}) \quad (r^2 = 0.9947),$$

$$\text{Log } E'_{\text{ionic}} (\text{Pa}) = 7.4 + 0.023 \times (\text{weight percentage of the DCA16}) \quad (r^2 = 0.9834),$$

$$\text{Log } E'_{\text{ionic}} (\text{Pa}) = 7.39 + 0.034 \times (\text{weight percentage of the DCA16}) - 0.000410 \times (\text{weight percentage of the DCA16})^2 \quad (r^2 = 0.9947),$$

and for SNa system

$$\text{Log } E'_{\text{ionic}} (\text{Pa}) = 6.60 + 0.03 \times (\text{weight percentage of the DCA4}) \quad (r^2 = 0.9985),$$

$$\text{Log } E'_{\text{ionic}} (\text{Pa}) = 6.61 + 0.03 \times (\text{weight percentage of the DCA16}) \quad (r^2 = 0.9894),$$

$$\text{Log } E'_{\text{ionic}} (\text{Pa}) = 6.60 + 0.041 \times (\text{weight percentage of the DCA16}) - 0.000397 \times (\text{weight percentage of the DCA16})^2 \quad (r^2 = 0.9982)$$

The similarity in the slopes of the fitted lines (first order polynomial equations) for the two ionomer systems indicates again that the rates of increasing E'_{ionic} depend mainly on the amounts of the DCAs, and not on the types of the ionic groups of the PS-based ionomers.

Figs. 5 (b) and (c) show the T_g s as a function of the amounts of the DCA4 and DCA16 in the ionomer systems, respectively. It is seen that the addition of both DCA4 and DCA16 does not change the matrix T_g s significantly.

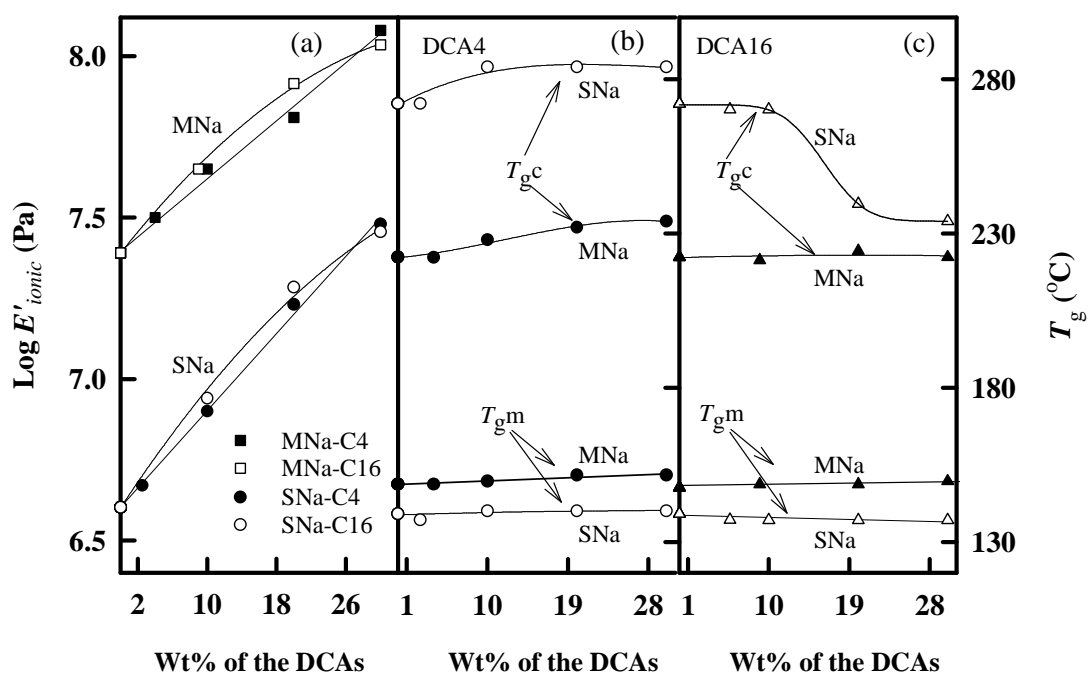


Figure 5. Ionic moduli and glass transition temperatures for the ionomers and their systems containing DCAs as a function of the weight percentage of the DCA4 and DCA16 in the ionomers, at 1 Hz.

In the case of the cluster T_g s of the DCA4 system, the T_g does not change much up to ca. 3 wt% of the salt, then increases slightly, and above ca. 10 wt% it remains almost constant. The similarity in the trends in the cluster T_g s indicates that the role of the DCA4 might be the same in both systems. In the case of DCA16 systems, with increasing the amounts of the salt, a negligible change in the cluster T_g s is observed in the MNa system. However, in the SNa system, on increasing the amount of DCA16 from 0 to ca. 10 wt%, only a slight decrease in the cluster T_g s is found. On further increasing the amount of DCA16, a drastic decrease followed by a gentle decrease in the T_g is observed.

At this point, it should be mentioned that all the samples except for the pure ionomers, were opaque; the degree of the opaqueness increased with increasing amounts of the DCAs. The degree of the opaqueness of the MNa system was higher than that of the SNa system. Since the phase-separated polymer blends showed opaqueness, we investigated the possible phase-separation of DCAs in the ionomers using DSC. The DSC thermograms are shown in Fig. 6. There is no crystalline melting peak for the DCAs in all the systems below the decomposition temperature of the ionomers, i.e. ca. 280 °C. It would be worthy to mention that the thermal decomposition of the sodium adipate and the sodium dodecanedioate started at ca. 320 and 308 °C, respectively [22]. Thus, the possible reason for the absence of the melting peak for the DCAs would be the occurrence of the melting of the crystalline domains of the DCAs above ca. 280 °C.

Shown in Fig. 7 are the SAXS profiles for the ionomer systems containing DCA4 and DCA16. For the MNa system, a small angle upturn (SAUT), probably representing the compositional heterogeneity in the ionomers [42-45], is shown at very low angles.

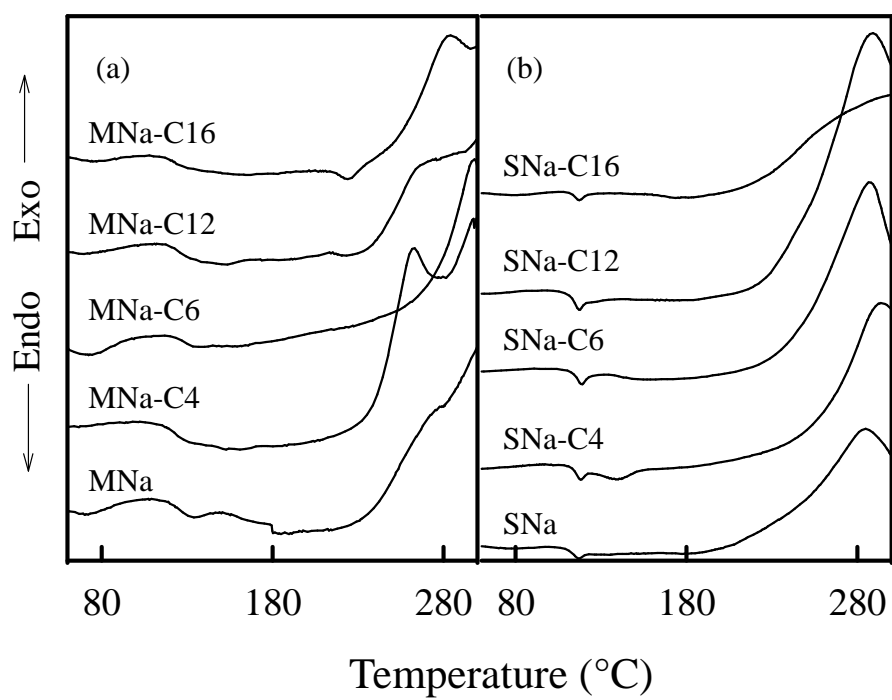


Figure 6. DSC thermograms for the ionomers and their systems containing DCAs at 1:1 ionic mole ratio.

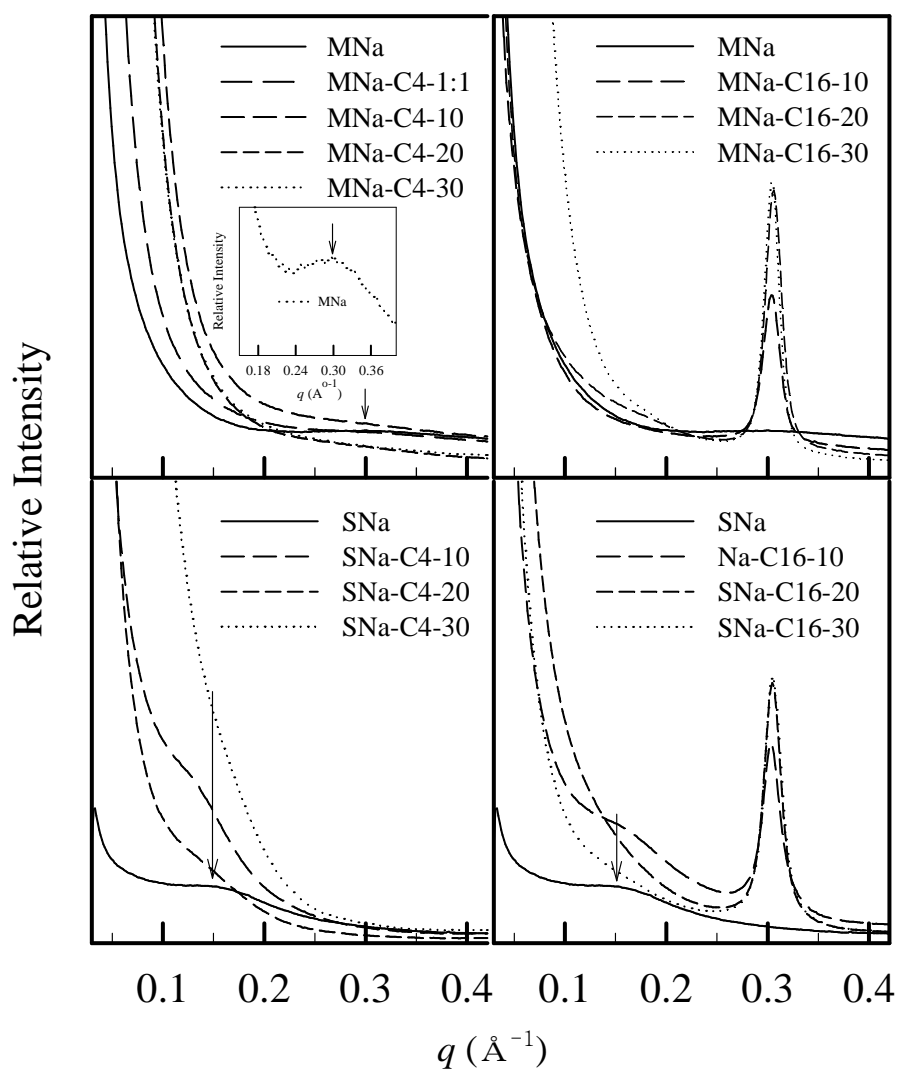


Figure 7. SAXS profiles as a function of the scattering vector for the ionomers and their blends with DCA4 and DCA16.

A very broad weak scattering (SAXS) peak, attributed to the inter-multiplet distances [46,47], also appears for the pure MNa ionomer at q (scattering vector) $= 0.3 \text{ \AA}^{-1}$ corresponding to a d_{Bragg} (Bragg distance) of ca. 21 \AA . In the case of the DCAs-containing MNa ionomers, a sharp peak for the DCA16 systems is seen at $q = 0.3 \text{ \AA}^{-1}$, while for the DCA4 system, no well-developed peak is observed. It should also be noted that the sharp peak position is coincided with that of the very broad SAXS ionomer peak. In the case of the SNa ionomers, the SAUT is also seen with a SAXS ionomer peak for the pure SNa ionomer at $q = 0.15 \text{ \AA}^{-1}$. For the DCA16 system, again a sharp peak at $q = 0.3 \text{ \AA}^{-1}$ is observed, while no well-developed peak is observed in DCA4 system. The intensity of the sharp peak of both ionomer systems containing DCA16 increases initially, followed by no significant increase with increasing the amounts of the DCA16. It is observed that the position of the SAUT shifts to higher angles for the ionomers containing the DCAs. This indicates that the heterogeneity of the systems increases upon the addition of the DCAs. The positions of the broad ionomer peak for the pure ionomers are in good agreement with the results reported in previous studies related to the methacrylate [7,26,34,35] and sulfonated [44,48-58] polystyrene ionomers. It is seen that the addition of the DCAs does not considerably change the positions of the broad SAXS ionomer peak. This suggests that the multiplet formation has not been affected by the addition of DCAs. The absence of a sharp peak for DCA4- containing systems leads us to investigate wide-angle X-ray patterns for the ionomers. The XRD patterns are shown in Fig. 8. In the case of the DCA4 systems, a sharp peak, which might indicate the presence of the crystalline domains of the DCA4 in the ionomers, is observed at $2\theta = \text{ca. } 12^\circ$ ($d_{\text{Bragg}} = \text{ca. } 7.4 \text{ \AA}$). For the DCA16 systems, a sharp peak is also seen at $2\theta = \text{ca. } 4.3^\circ$ ($d_{\text{Bragg}} = \text{ca. } 21 \text{ \AA}$), the position of which is identical to that of the sharp peak found in the SAXS profiles at $q = 0.3 \text{ \AA}^{-1}$.

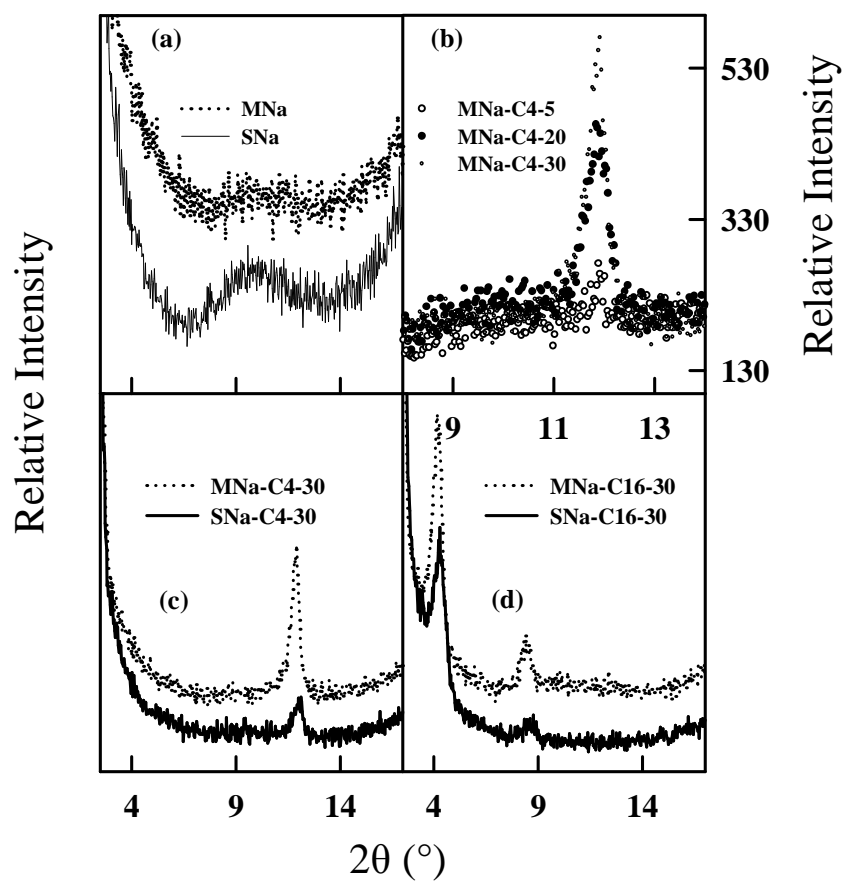


Figure 8. XRD patterns as a function of the scattering angle (2θ) for the ionomers and their blends with DCA4 and DCA16.

It should be noted that the values of the d_{Bragg} of ca. 7.4 and 21 Å are more or less same as the distances between the ionic groups of the fully extended DCAs, which might be ca. 7 and 22 Å for the DCA4 and DCA16, respectively. This implies that the occurrence of the XRD crystalline peaks for the ionomers containing DCAs is due to the presence of the DCAs in the form of phase-separated and ordered entities in the ionomers. It is also seen that in the XRD patterns for particular amount of the DCAs, the intensity of the XRD peaks is lower in SNa system than that in MNa system. This indicates that the DCAs are phase-separated and crystallized to a slight lower extent in SNa systems than that in the MNa systems.

Since the modulus of the polymers increases by the addition of the filler [39], the increase in the modulus of the ionomer systems by the addition of the DCAs might also be due to the filler effects. The X-ray results have shown that the DCAs are phase-separated into the matrix of the ionomer, which may act as filler. An attempt was made to fit the experimental E'_{ionic} data points with the Guth equation for calculating the modulus of the composites having rigid spheres. It should be mentioned that this equation is applicable for the systems having the non-elastic, spherical filler particles up to ca. 30 vol% of the fillers in the sample. The Guth equation shows the relationships between the Young's modulus of the polymer and the volume fraction of the filler as follows:

$$E^*/E = 1 + 2.5V_f + 14.1V_f^2$$

where E^* and E are the Young's modulus of the filled and unfilled polymer, respectively, and V_f is the volume fraction of filler in the composite [39,71]. In the present work, the ionic modulus (E'_{ionic}) of the ionomer systems having DCAs is taken as E^* , and that of the pure ionomers as E . To calculate the V_f of the DCAs, we need the densities (d) of the ionomers and the DCAs. The density of the pure MNa ionomer is ca. 1.13 g/cm³, which is obtained using a pycnometer in our lab.

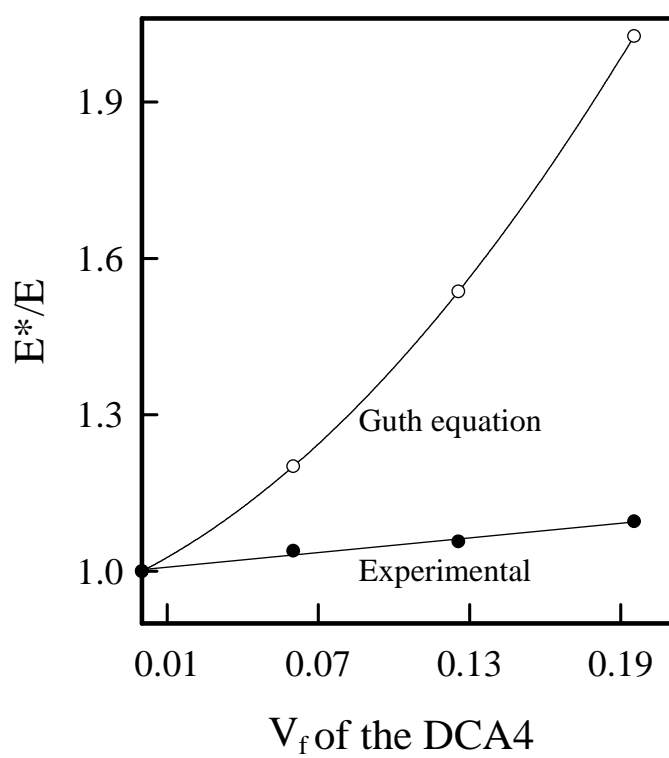


Figure 9. The ratio of the ionic modulus of pure ionomer to that of the ionomer blend containing DCA4 as a function of the volume fraction of the DCA4 in the ionomers.

The densities of the DCAs used in this study are unfortunately not available. Thus, we have used an indirect method to evaluate the density of DCA4, by analyzing the densities of some of the organic acids and their salt forms, whose chemical structure resembles with those of the DCAs. These are formic acid ($d=1.22 \text{ g/cm}^3$)/sodium formate ($d=1.92 \text{ g/cm}^3$), acetic acid ($d=1.049 \text{ g/cm}^3$)/sodium acetate ($d=1.53 \text{ g/cm}^3$), and oxalic acid ($d=1.65 \text{ g/cm}^3$)/sodium oxalate ($d=2.34 \text{ g/cm}^3$) [76]. Thus, we roughly assumed that the density of sodium salt of the succinic acid (DCA4) would be ca. 2.0 g/cm^3 . With the density and weight fractions of the DCA4, it is possible to calculate the volume fractions of the DCA4 in the ionomer blends. A major deviation between the experimental data and calculated one is observed in Fig. 9. The curvatures of the plots are different and the experimental values are significantly low as compared to the values obtained from the Guth equation. This indicates that the DCAs do not behave as “typical” filler, and the effect of DCAs in increasing modulus is considerably weaker, compared to those of the typical fillers. Despite the behavior of the DCAs as non-typical fillers, the DCAs surely have reinforcing effects on the modulus of the ionomers in the present systems.

In the section dealing with the T_g s, we have shown that the addition of the large amounts of the DCA4 leads to a slight and considerable increase in the matrix and cluster T_g s, respectively, of both MNa and SNa systems. However, the large amounts of the DCA16 lead to a negligible change in T_g s of the MNa system, and to a slight and significant decrease in the matrix and cluster T_g s of SNa systems, respectively. Let us discuss the possible reasons for the increase and decrease in the cluster T_g s upon the addition of DCA4 and DCA16, respectively. At this point, it would be worthy to recall that at low ion contents, some of the ion-pairs of the ionomers are not able to take part in multiplet formation, because these ion-pairs are beyond the loopback distances for the ion aggregation [5,7]. As the DCAs are phase-separated in the matrix of the ionomers, the DCAs will

push the isolated ion-pairs of the ionomers to come close to each other to form the multiplets, leading to a more clustering, and increasing T_g s. Thus, we predict that the increasing degree of the clustering upon the addition of DCA4 in both ionomer systems is responsible for the increase in the T_g s of the ionomers.

In the case of the DCA16-containing systems, we have shown that the intensity of the sharp peaks in SAXS profiles for the DCA16 in both ionomer systems increases initially, followed by no significant increase on increasing amounts of the DCA16. This suggests that at large amounts of the DCA16, some of the DCA16 molecules have not been fully phase-separated and exist singly or as imperfect crystallites in the matrix of the ionomers. It should also be noted that the DCAs being relatively non-polar compounds will naturally prefer to reside in relatively non-polar parts of the ionomers, i.e. bulk matrix, and restricted mobility regions in the cluster phase. On comparing the polarity of the restricted mobility and the bulk matrix regions, the restricted mobility regions are expected to be relatively less non-polar because of the presence of the polar multiplets surrounded by the restricted mobility regions in the clusters, compared to the bulk matrix regions. Upon the addition of the DCA16 molecules into the ionomers, initially, the majority of the DCA16 molecules will prefer to fully phase-separate into the bulk matrix regions. Upon further increasing the amounts of the DCA16, the major portion of the additional amounts of the DCA16 will probably shift to the restricted mobility regions. As per the SAXS and XRD results, these additional amounts of the DCA16 molecules most probably contain both perfect and imperfect crystallites, i.e. the amounts of the imperfect crystallites or singly existing DCA16 molecules will be more in restricted mobility regions, compared to the bulk matrix regions. The non-linear increase in the E'_{ionic} in the case of the DCA16-containing systems can be correlated with this factor, i.e. the imperfection of the crystallites. In the case of DCA16-MNa system, the increased degree of the clustering due to the additional multiplet

formation should increase mainly the cluster T_g as observed in the case of the DCA4-containing systems. However, there is negligible increase in the cluster T_g of the DCA16-MNa system. At the same time, the singly existing DCA16 molecules whose ion-pairs are supposed to be in ionic interaction with the ion-pairs of the ionomers in the multiplets, are expected to create additional free volumes in the restricted mobility regions, causing the relatively easy movements of the polymer chains in the vicinity of the multiplets leading to decreasing cluster T_g . Thus, these two opposite factors (i.e. improved degree of the clustering and relatively easy movements of the polymer chains) will try to balance each other, and, hence, negligible change in the cluster T_g seems natural.

In the case of DCA16-SNa system, one may expect that, similar to the DCA16-MNa system there should not be any significant change in the cluster T_g of the ionomers. However, the case is different here, i.e. there is a significant decrease in the cluster T_g of the ionomers. The two opposite factors responsible for the negligible change in the cluster T_g in the DCA16-MNa system are expected to be in operation here too. In addition, from the XRD results we know that the phase-separation of the DCAs is less in SNa system, compared to that in the MNa system. It suggests that the amounts of the fully phase-separated DCA16 is less, or in turn the amount of the singly existing DCA16 molecules are more in SNa system than that in MNa system at a particular amount of the DCA16. Thus, the chains in the restricted mobility regions of SNa system will have more easy movements, compared to those in MNa system. Other than the factors mentioned above, it would be worthy to remind that the ion-pairs of DCA16 (i.e. $-\text{COO}^- \text{Na}^+$) and SNa ionomer ($-\text{SO}_3^- \text{Na}^+$) are different from each other. Thus, the ion-pairs of some of the singly existing molecules are expected to be in ionic interaction with the ion-pairs in the multiplets of the ionomers. Therefore, the ion-pairs of the DCA16 will decrease the strength of interaction between the $-\text{SO}_3^- \text{Na}^+$ ion-pairs because the strength of interaction between $-\text{SO}_3^- \text{Na}^+$ and $-\text{COO}^- \text{Na}^+$

COO⁻Na⁺ ion-pairs will be significantly less than that of the -SO₃⁻Na⁺ and -SO₃⁻Na⁺ ion-pairs. If our explanations approved to be the close to the reality, then these may be the most probable reasons for the decrease in the T_g s in DCA16-SNa system. Agarwal et al. have also shown that the incorporation of the zinc stearate having carboxylate ion-pairs to the zinc sulfonate EPDM system, weakened the strength of ion interactions between the zinc sulfonate ion-pairs [61] leading to the decrease in the T_g s.

Now, it can be suggested that DCA4 acts as reinforcing additive by increasing the modulus and T_g s in both MNa and SNa systems. The DCA16, however, in addition to acting as reinforcing additive by increasing the modulus of both systems, acts as preferential plasticizer for the cluster phase at least at its large amounts in the SNa systems.

It would be useful to compare the effectiveness of the similar additives in changing the modulus of various ionomer systems. We have selected ionomers rather than non-ionic polymers, and additives having only carboxylate ion-pairs for effective comparison with our systems. Another criterion for selecting the additives containing systems was the full neutralization of both the additives and ionomers, so we found only a few systems fulfilling this criterion. The additives range from mono- to multi- functional, aliphatic to aromatic, and salts of mono- to di- valent cations. It would be worthy to mention that at least two properties are common to all of these additives. The first one is that these additives have carboxylate ion-pairs, and the second one is their phase-separation in the respective ionomer matrixes. The data has been taken from the enlarged version of the modulus vs. weight percentage plots from the respective papers. Fig. 10 shows the E'_{ionic} data for various ionomer systems having carboxylate additives as a function of the amounts of the additives. The slopes of the plots are listed in Table 2.

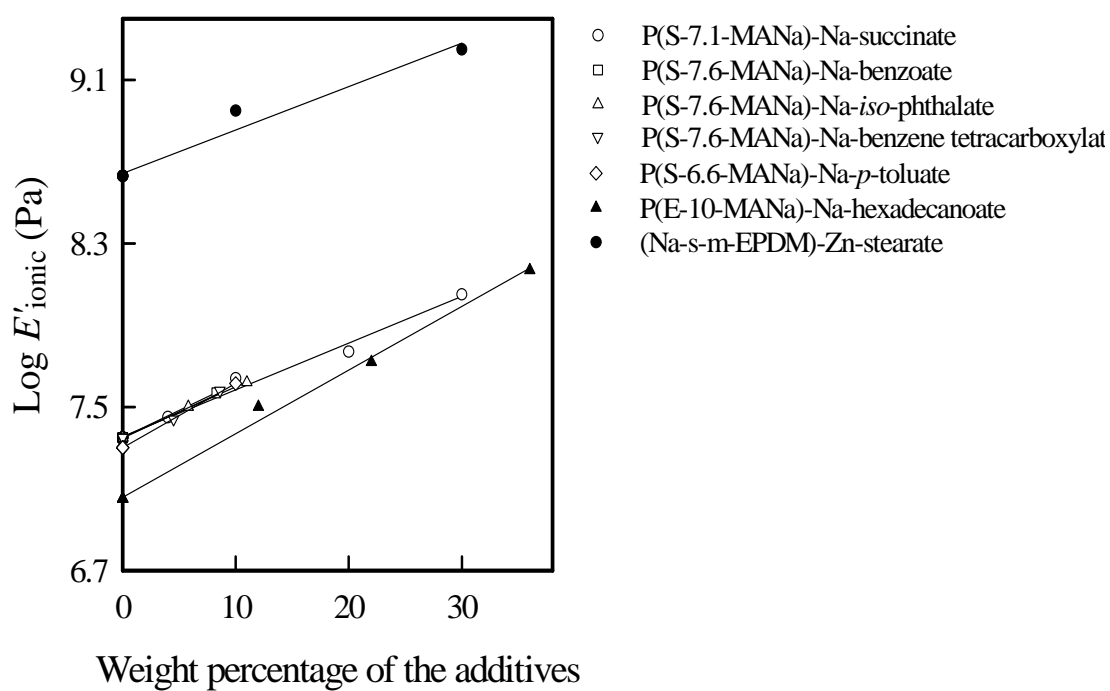


Figure 10. Ionic moduli for the various ionomers and their systems containing carboxylate additives as a function of the weight percentage of the additives.

Ionomer/Polymer blends	Slope
P(S-7.1-MANa)- <i>Na-succinate</i>	0.023
P(S-7.6-MANa)- <i>Na-benzoate</i>	0.026
P(S-7.6-MANa)- <i>Na-iso-phthalate</i>	0.025
P(S-7.6-MANa)- <i>Na-benzene tetracarboxylate</i>	0.026
P(S-6.6-MANa)- <i>Na-p-toluate</i>	0.031
P(E-10-MANa)- <i>Na-hexadecanoate</i>	0.031
(Na-s-m-EPDM)- <i>Zn-stearate</i>	0.021

Table 2. Comparison of the slopes of the modulus plots for the effectiveness of additives on increasing modulus.

It can be observed from Table that the slopes of the plots are more or less same to the slope of the plot of DCA4; the one of the additives used in the present study. This suggests that the rate of increase in the values of the modulus is more or less same irrespective of the types of the ionomer chains and additives, at least to these selected systems.

On combining these results with rest of the results of modulus obtained from our systems, it can be concluded that in most of the cases, it is mainly the amounts of the additives rather than the nature of the ionomer chains, nature of the ionic groups of the ionomers, similarity or difference in the nature of the ionic groups of the ionomers and additives, the nature of the additives, e.g. functionality, aliphatic or aromatic, short or long chains, which is responsible for the increase in the modulus, provided that the additives have tendency to phase-separate even at low weight concentrations in the ionomers and the additives have sufficiently high melting points so that they may not affect the properties of the polymers owing to the melting of the additives.

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Chapter 3

**Dynamic mechanical properties of lightly sulfonated
polystyrene ionomer blends with salts of dicarboxylic
acids, neutralized with divalent cations**

Abstract

We studied the effects of the addition of barium and cobalt salts of short to long chain aliphatic dicarboxylic acids on the dynamic mechanical properties of poly(styrene-*co*- styrene sulfonate) ionomers using DMTA. At 1:1 mol ratio of the ionic groups of the organic salts to that of the ionomers, the addition of organic salts led to a negligible change in the matrix glass transition temperatures, T_{gm} in both the barium and cobalt systems, with little effect of the number of the carbon atoms of the salts. The cluster glass transition temperatures, T_{gc} , however, almost remained constant in cobalt system, and increased slightly in barium system with increasing number of the carbon atoms of the salts up to C-12. Above C-12, however, the T_{gc} in both the systems decreased slightly. The ionic modulus increased with increasing number of the carbon atoms of the salts in both the systems. On increasing the mol ratio of the ionic groups, and in turn the weight percentage of the salts in barium-ionomers, the T_{gs} remained almost constant or increased slightly irrespective of the number of the carbon atoms. The ionic modulus of the systems having low and high number of the carbon atoms increased significantly and the plots almost superimposed on each other. These results were compared with those of the sulfonated ionomer system neutralized with mono-valent cation (e.g. sodium). Similar effects were observed in the ionic modulus and matrix T_{gs} for the systems having the DCAs of low and high number of the carbon atoms, while the effects of the DCA of high number of the carbon atom was much more significant in the mono-valent ionomer systems. Thus, we concluded that the type of the cation and number of the carbon atoms of the added organic salts has no significant effect on the modulus of the resulting ionomers, and that the organic salts acted mainly as filler in divalent systems.

Key words: polystyrene ionomers, aliphatic dibasic salts, mono and divalent cations, filler effects

1. Introduction

During the last 4 decades, extensive studies on the mechanical properties and morphologies of the ion containing polymers have been performed [1-6]. Polymers having small amount of the ionic groups, called ionomers, show important and enhanced mechanical properties as compared to their non ionic counter parts, owing to the significant interaction between the ionic groups, and polarity difference between the ion-poor and ion-rich regions. As per the EHM model, the ionic groups tend to aggregate in the polymer matrix, leading to the formation of multiplets [7]. The size and number of these multiplets increase with increasing the ion contents of the polymers, and they start to overlap each other, hence the mobility of the chains surrounding these multiplets decreases. Once, the size of restricted mobility regions along with the multiplets attains or exceeds a certain size ca. 50-100 Å, they lead to the phase separation of the materials into ion-poor and ion-rich domains. The ion-rich regions are termed “clusters” [7]. Now, the materials show two glass transitions, the one is usual matrix glass transitions, and the other is attributed to the cluster regions.

The mechanical properties and morphology of ionomers can be tailored by varying a number of factors including types, size, position and degree of neutralization of ionic groups, and types of additives, plasticizers, neutralizing agents [8-11]. However, little is known about the effects of bi-functional additives on the morphology and mechanical properties of amorphous PS based ionomers neutralized with multivalent cations. Agarwal *et al* studied the mechanical properties of Zn-sulfonated ethylene-propylene-ethylidene norbornene terpolymer (Zn-EPDM) containing Zn-stearate [12]. They showed that the crystalline zinc stearate phase separated, acted as filler and, thus, raised the matrix T_g of the ionomer. On the other hand, the zinc stearate also acted as a “multiplet” plasticizer at higher temperatures. Dynamic mechanical studies on the matrix- and cluster- dominant polystyrene (PS) ionomers containing

chemically identical mono- and di-functional oligomers were carried out by Plante *et al* [13]. Mono-functional oligomers decreased the T_g s. In matrix-rich system, di-functional oligomers were found to increase the T_g s at low oligomer contents. However, in the cluster-rich system, oligomers were phase separated due to the lack of sufficient amount of the non-ionic polymer matrix to accommodate the non-polar oligomers. Subsequently, Plante and Bazuin studied lightly sulfonated PS ionomers containing mono-dispersed, tertiary amine-terminated oligomers of styrene [14]. They showed that mono-functional oligomers plasticized the ionomer but considerably less than did alkyl chains. It was attributed to the greater bulkiness and stiffness of the styrene segments. The di-functional oligomers, however, showed a little plasticization effect, and, at higher amount of the oligomers, became phase separated despite extensive inter-component interactions owing to the copolymer effects. Recently, our group investigated the dynamic mechanical properties of PS-based ionomers containing disodium salts of aliphatic dicarboxylic acid [15,21]. It was found that the DCAs phase separated, and, hence, increased the modulus rather than significantly affecting the T_g s. Wakabayashi *et al* studied the effects of the addition of few of the fatty acid salts on morphology and mechanical properties of ethylene-based ionomers neutralized with mono to divalent cations [16]. They observed that the changes in the structure and properties of the ionomers induced by the additives were complex, and depend both on the cation and on whether the chains of the fatty acid salts and ionomers were crystallizable. This literature survey shows that there is a lack of sufficient information about the effects of the addition of difunctional additives on the properties of PS-based ionomeric systems. Thus, we decided to investigate the roles of DCAs neutralized with divalent cations to tailor the properties of SPS ionomers. In the present study, barium and cobalt salts of succinic acid [NaOOC-(CH₂)₂-COONa], adipic acid [NaOOC-(CH₂)₄-COONa], dodecanedioic acid [NaOOC-(CH₂)₁₀-COONa] and hexadecanedioic

acid $[\text{NaOOC}-(\text{CH}_2)_{14}-\text{COONa}]$ were used as additives. By selecting short to long chain additives, we may be able to see the effects of alkyl chain lengths on the dynamic mechanical properties of the ionomers. The results obtained will be compared with those of ionomers and DCAs neutralized with mono-valent cation, e.g. sodium.

2. Experimental Details

2.1. Sample Preparations

PS homopolymer of molecular weight ca. 500,000 was synthesized by the method described elsewhere [17,18]. The poly(styrene-*co*-styrenesulfonic acid) SSA copolymer was prepared by the sulfonation of PS with the method reported by Makowski *et al* [19]. In order to determine the sulfonic acid content, the copolymer sample was dissolved in a benzene/methanol (9/1, v/v) mixture to make a 5% (w/v) solution. The resulting solution was titrated with methanolic NaOH solution to the phenolphthalein end point. The acid content was found to be 4.0 mol%. To prepare the blends of the ionomer containing DCAs, the acid form of the DCAs and copolymer was dissolved in a benzene/methanol (9/1, v/v) mixture. After complete dissolution of both the components, the acid groups of both the DCAs and acid copolymer were fully neutralized with methanolic $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ solutions. The mole ratio of the acid groups of the copolymers to those of the DCAs was kept constant to 1/1. The samples were freeze-dried and dried further under a vacuum at ca. 150 °C for 24 h. For the dynamic mechanical studies, the samples were compression molded at ca. 260 °C with a pressure of ca. 25 MPa. The molded samples were annealed under a vacuum at 150 °C for 24 h. The notations used for the samples are SBa/SCo-Cx, where SBa and SCo are the SPS ionomers neutralized with Ba^{2+} and Co^{2+} ions, respectively, having DCAs of “x” number of the carbon atoms,

e.g. 0 (i.e. an ionomer), 4 (sodium succinate), 6 (sodium adipate), 12 (sodium dodecanedioate), and 16 (sodium hexadecanedioate).

2.2. Dynamic Mechanical Property Measurements

The storage modulus (E') and loss tangent ($\tan \delta$) of each sample were measured as a function of the temperature using a TA's (Thermal Analysis) dynamic mechanical thermal analyzer (DMTA Mark II) in a dual cantilever-bending mode at five different frequencies. The samples were heated at a rate of 1 °C/min. The detailed study was performed using the data obtained at 1 Hz.

3. Results and Discussion

In Fig. 1, it is seen that with increasing temperature, the modulus plots pass through the glassy region, to the matrix glass transition, to the ionic plateau (the plateau between the glass transitions of the matrix and cluster phases) [7], to the cluster glass transition, to the rubbery plateau and flow region. It can be observed in the modulus plots that the values of glassy modulus are almost same for all the samples including the pure ionomer. It is clearly seen that above matrix glass transition, there is a significant increase in the height of the modulus plots for the ionomers containing DCAs. It is also seen that the width of ionic plateau is almost same for all the samples including the pure ionomer. It suggests that there is a negligible interaction between the ionic groups of the pure ionomer and additives, i.e. $-\text{SO}_3^- \text{Ba}^{2+} \text{SO}_3^-$ and $-\text{COO}^- \text{Ba}^{2+} \text{COO}^-$, respectively. It may indicate that the multiplets of the ionomer are negligibly affected by the addition of DCAs. In the loss tangent plots, we can observe that the ionomer system represent characteristic two phase behavior, the first one is ion-poor phase at lower temperatures, i.e. matrix phase, and the second one is the ion-rich phase at higher temperatures, i.e. clustered phase.

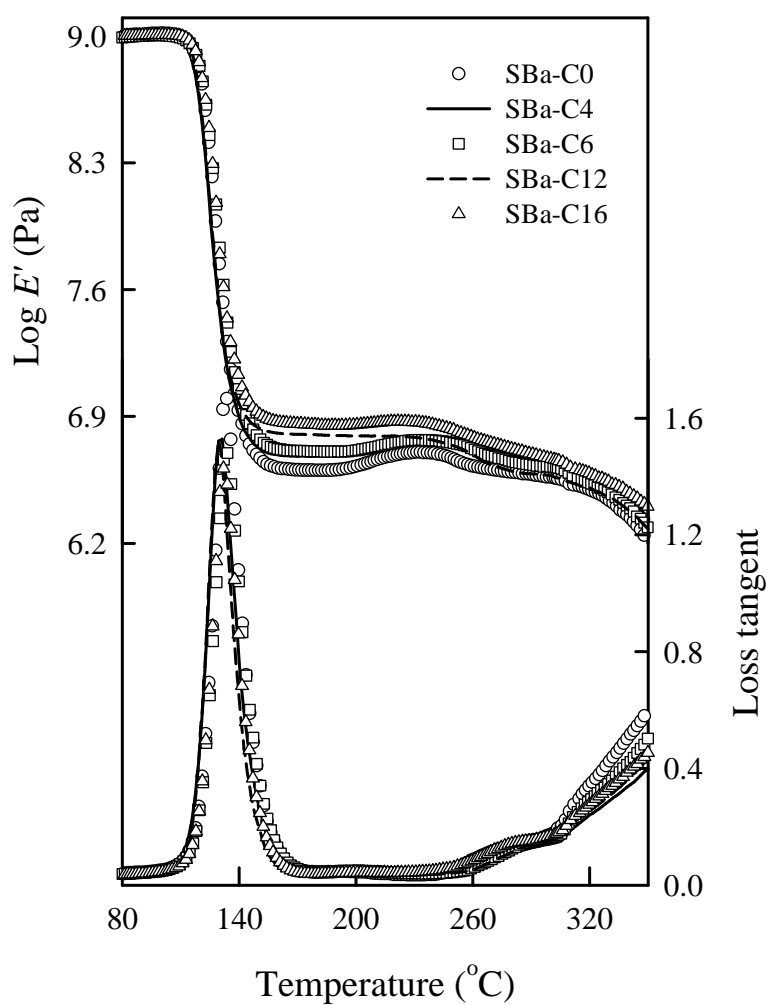


Figure 1. Storage moduli (E') and loss tangents as a function of the temperature for the P(S-*co*-SSBa) ionomer and its system containing salts of organic acids at 1 Hz.

It is observed from the figure that on the addition of the DCAs, there is a negligible change in the position of the matrix glass transition peaks with increasing alkyl chain lengths of the DCAs. However, the position of the cluster glass transition peaks shifts to higher temperatures by the addition of DCAs up to carbon number 12. On further increasing the number of the carbon atoms, the position of the cluster glass transition peak shift to slight lower temperatures as compared to the loss tangent peak positions of the ionomers having the rest of the DCAs, but the peak position is still higher than that of the pure ionomers.

Like the SBa system, it can be seen in the modulus plots in Fig. 2 that there is no considerable difference in the values of modulus up to the matrix glass transitions for all the samples including the pure ionomer. On the addition of the DCAs, the height of the modulus plots in the ionic plateau region increase slightly. Contrary to the SBa system, the height of the rubbery plateau decreases significantly on the addition of DCAs, with no proper order of the alkyl chain lengths. It can be seen in the loss tangent plots that there is no significant change in the shape, size and width in matrix loss tangent peaks. The trends in the position of the cluster loss tangent peaks are almost same to that in SBa system. The height of the peaks increases significantly, and seems almost independent of the alkyl chain lengths. On comparing the width of the ionic plateau of SBa and SCo pure ionomers, it can be observed that it is wider for the SBa ionomer than that of the SCo ionomer. The width of the ionic plateau is treated as a symbol for the strength of ion interactions between the ion-pairs in the multiplets of the ionomers [3,5,7], i.e. the wider the ionic plateau, the stronger the ion interactions between the ion-pairs. The wider ionic plateau in the SBa ionomer implies that the strength of interaction between the ion-pairs ($-\text{SO}_3^- \text{Ba}^{2+} \text{SO}_3^-$) in SBa ionomer is more than that of the ion-pairs ($-\text{SO}_3^- \text{Co}^{2+} \text{SO}_3^-$) in SCo ionomer.

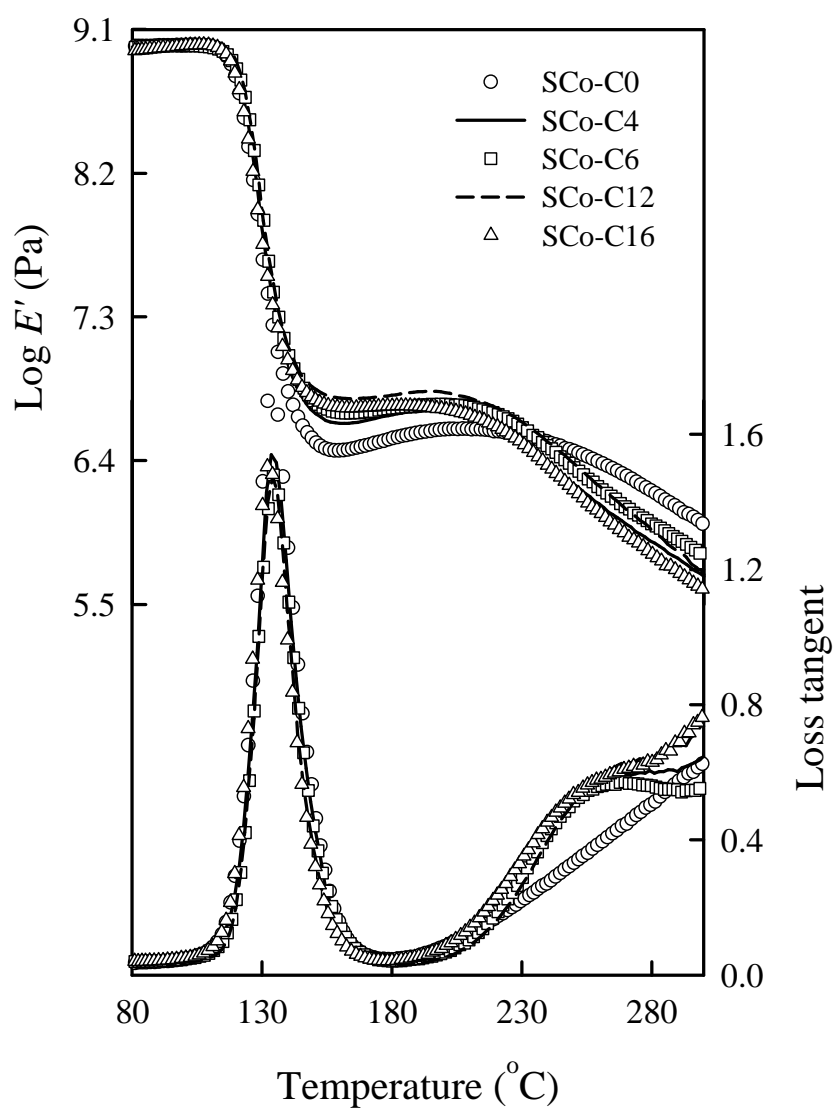


Figure 2. Storage moduli (E') and loss tangents as a function of the temperature for the P(S-co-SSCo) ionomer and its system containing salts of organic acids at 1 Hz.

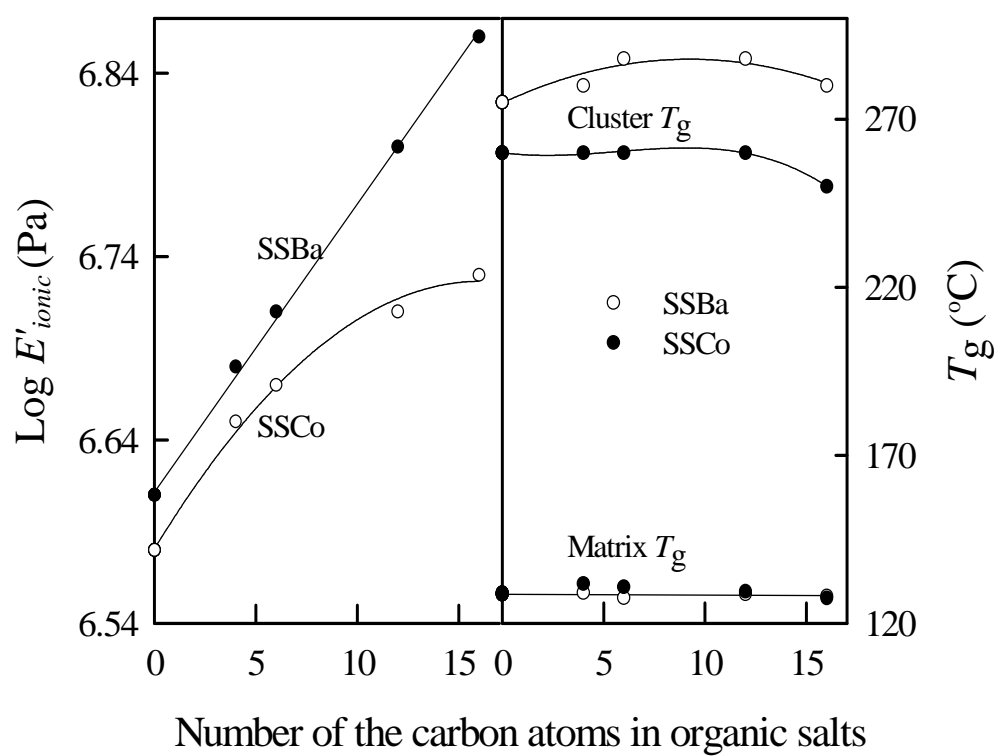


Figure 3. Ionic moduli and glass transition temperatures as a function of the number of carbon atoms of DCAs for the ionomers and their systems containing DCAs at 1 Hz.

It is observed from Fig. 3 that ionic modulus (the values of modulus in the ionic plateau regions at a point of minimum slope) of pure SCo ionomer is less than that of the pure SBa ionomer. It is known that the ionic modulus is associated with the degree of clustering; that is, the higher the degree of clustering, the higher the ionic modulus [3,5-7]. As mentioned earlier that the strength of interaction between the ion-pairs in SBa ionomer is more than that of the ion-pairs in SCo ionomer, then clustering will be easy in SBa ionomer, and, hence, the number of the multiplets will be more in the SBa ionomer as compared to the SCo ionomer. Thus, the total area of the clustered regions will be more in SBa ionomer than that of the SCo ionomer. This may be the reason for the lower ionic modulus in SCo ionomer, compared to the SBa ionomer. It is seen that on addition of the DCAs there is a significant increase in the ionic modulus in both the SBa and SCo systems. In SCo system, however, after DCA6, on further increasing the number of the carbon atoms, the rate of the increasing the ionic modulus slightly lowers. The values of the ionic modulus seem to be more or less same in both the systems having DCAs of low number of the carbon atoms. It suggests that the effects of the DCAs on the rate of increasing the ionic modulus are almost independent on the type of the cations, at least, to some extent if the valency of the cations is same.

It is also clear from the Fig. 3 that there is a negligible change in the matrix T_g s by the addition of the DCAs in both the ionomer systems, irrespective of the alkyl chain lengths. The cluster T_g s, however, increase slightly by the addition of DCAs of up to carbon number 12 in SBa system. On further increasing the number of the carbon atoms, the cluster T_g decreases slightly but it is still higher than that of the pure ionomers. In SCo system, the cluster T_g s remains almost constant up to DCA12, followed by a slight decrease on increasing the number of the carbon atoms of the DCAs.

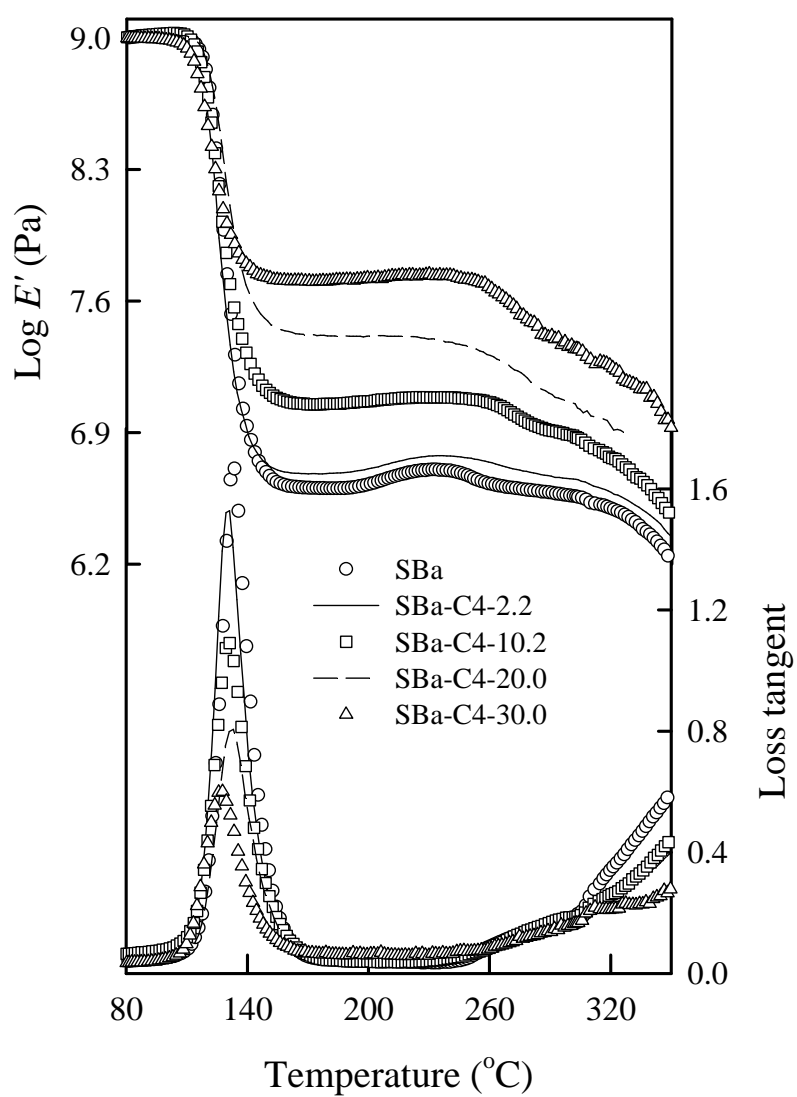


Figure 4. Storage moduli (E') and loss tangents as a function of the temperature for the P(S-*co*-SSBa) ionomer and its system containing varying weight percentage of the DCA4 at 1 Hz.

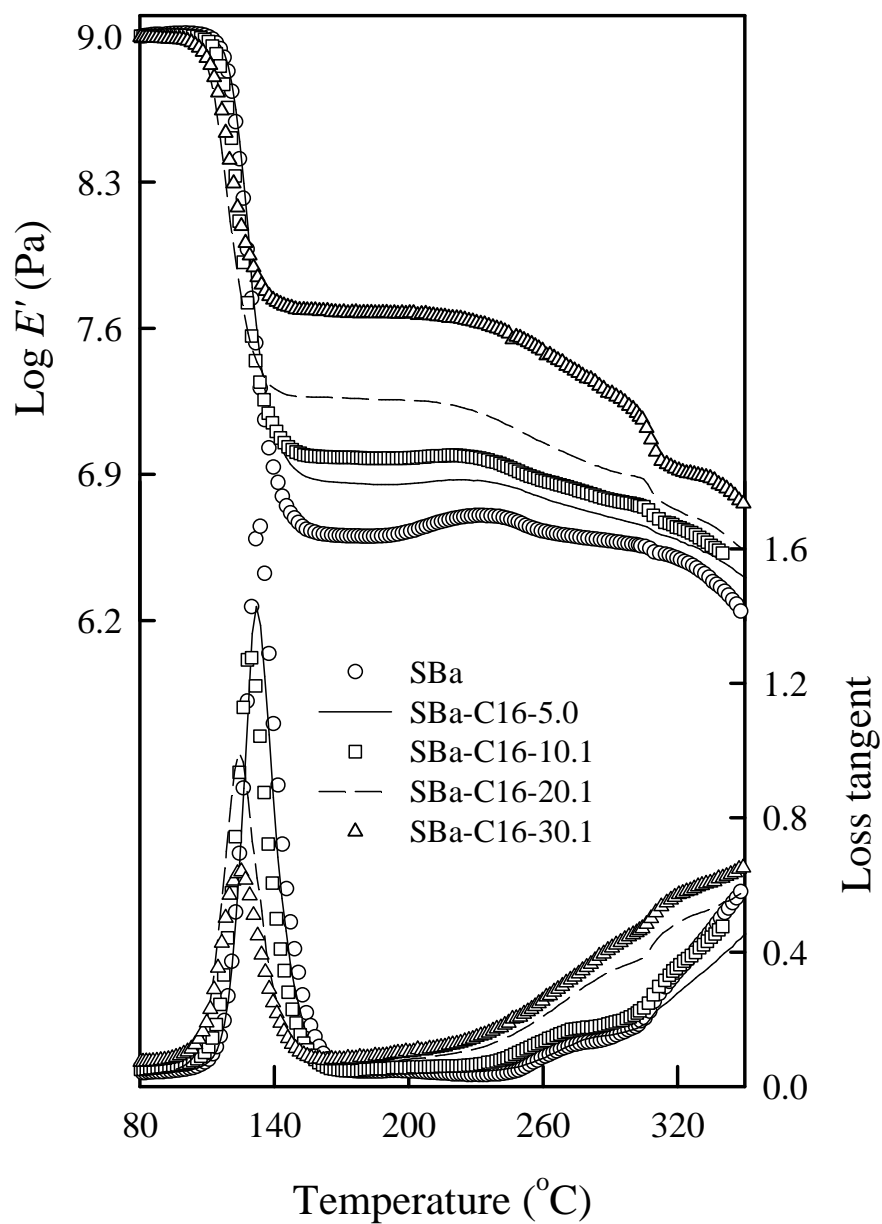


Figure 5. Storage moduli (E') and loss tangents as a function of the temperature for the P(S-*co*-SSBa) ionomer and its system containing varying weight percentage of the DCA16 at 1 Hz.

Let us analyze the effects of the high amounts of the DCAs on the mechanical properties of the ionomers. To do so, we prepared the SBa ionomers having up to 30 weight percentage of the DCA4 (the DCA having the lowest number of the carbon atoms used in this study) and DCA16 (the DCA having the highest number of the carbon atoms). As the effects of the DCAs on the mechanical properties of the SBa system seem slightly better than that for the SCo system, so we have selected SBa systems for further study. Fig. 4 and 5 show the modulus and loss tangent plots for the SBa systems having DCA4 and DCA16, respectively, as a function of the temperature. It is seen that on the addition of DCAs, there is a significant increase in the heights of the ionic plateaus in both the systems.

From the loss tangent plots, it is observed that there is a significant decrease in the heights of the matrix loss tangent peaks in both the systems. However, there is no considerable change in the heights of the cluster loss tangent peaks in DCA4 systems, but significant increase is seen in the DCA16 system on increasing the weight percentage of the DCA16.

Fig. 6 and 7 show the ionic modulus and glass transition temperatures as a function of the weight percentage of the DCAs in SBa and SNa systems, respectively. It is seen that there is a significant increase in the ionic modulus in both the SBa and SNa systems on increasing the weight percentage of the DCAs. Moreover, it is interesting to note that the ionic modulus plots of the DCA4 and DCA16 in both the SBa and SNa systems almost superimpose on each other. This suggests that the effects of the addition of DCAs on the rate of increasing the ionic modulus is independent of the type of the DCAs, i.e. short or long alkyl chain lengths, and the type of the cations, i.e. mono and divalent cations. It is shown in the glass transition temperature plots that there is a slight change in the matrix T_g in both the SBa and SNa systems, and it seems independent of the alkyl chain lengths of the DCAs.

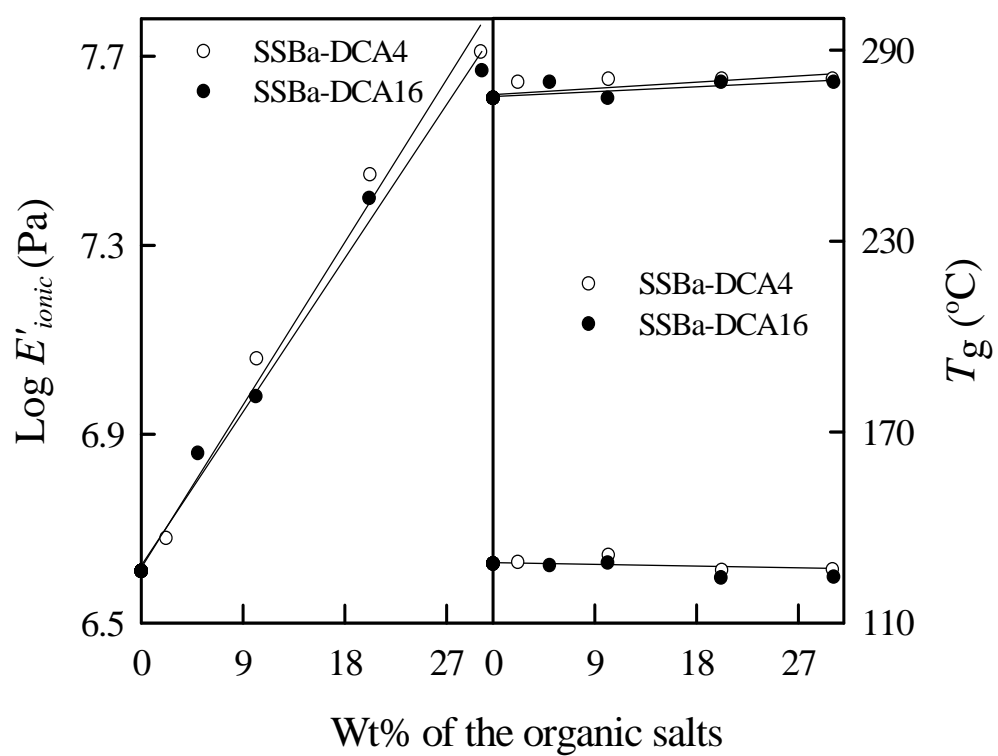


Figure 6. Ionic modulus and glass transition temperatures as a function of the weight percentage of the DCA4 and DCA16 for the SBa ionomers and their systems at 1 Hz.

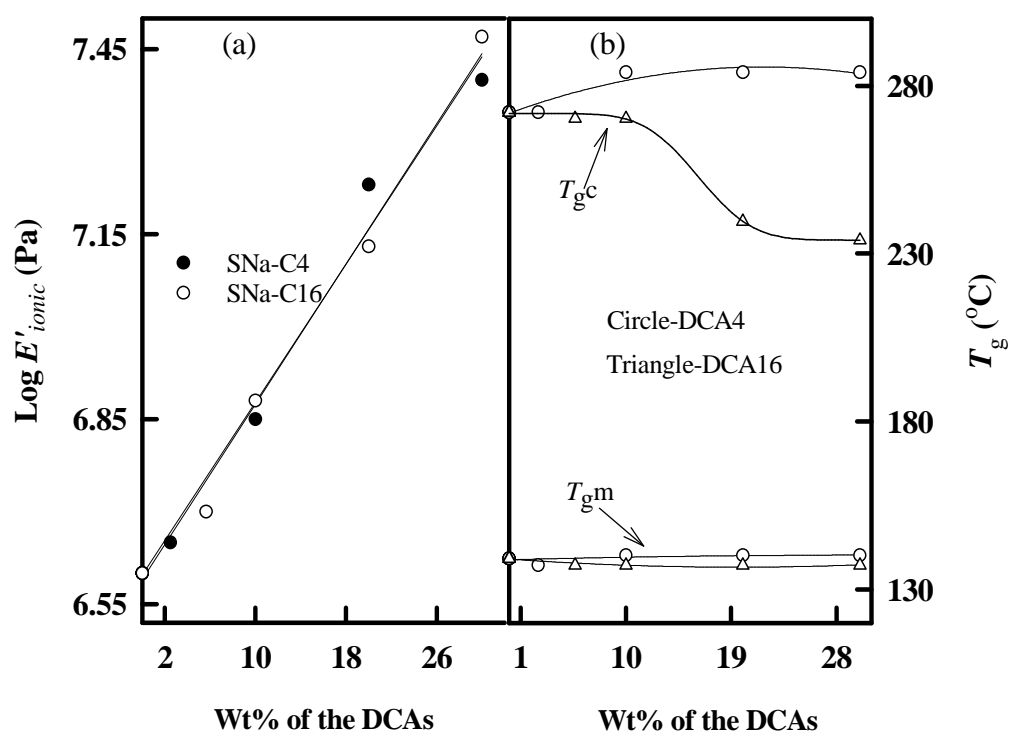


Figure 7. Ionic modulus and glass transition temperatures as a function of the weight percentage of the DCA4 and DCA16 for the SNa ionomers and their systems at 1 Hz (Refer to Chapter 2).

The cluster T_g s increased slightly with the addition of DCA4 in both the systems. However, it remained more or less same or increased slightly in DCA16 containing SBa system, and decreased significantly in DCA16 containing SNa system. Thus, it can be inferred that DCA4 has approximately same effect in both the systems in slightly increasing the cluster T_g , where as the effect of the DCA16 in decreasing the cluster T_g is much more significant in SNa system, compared to that in the SBa system. This is most probably due to the less strength of the ionic interaction between the ionic groups of the SNa system, compared to that of the SBa system. The another prominent reason for this is as follows: sodium cation is mono-valent, so it can interact with only one anion to make electrically neutral ion pair, whereas barium is divalent, and, hence, needs two anions to form electrically neutral ion-pairs. We know from the EHM model that the formation of the ionic aggregates creates steric hindrance to the movement of the adjacent polymer chains. The ion hopping, i.e. the movement of the ion-pairs from one multiplet to another is the most important mechanism for the occurrence of the cluster glass transition. Thus, for the ion hopping, less energy is needed for the ion-pairs having two ionic groups (SNa system) than that for the ion-pairs having three ionic groups (SBa system) due to the less steric hindrance in SNa systems compared to the SBa system. Therefore, for the DCA16 it will be easy to facilitate the plasticization of the restricted mobility regions in SNa system that that in the SBa system.

4. Conclusions

The effects of the addition of divalent salts of short to long chain aliphatic dicarboxylic acids on the dynamic mechanical properties of poly(styrene-*co*-styrene sulfonate) ionomers neutralized with barium and cobalt were studied using DMTA. At low weight percentage of the DCAs, the addition of DCAs led to a negligible change in the T_g m in both the barium and cobalt systems, with

negligible effect of the number of the carbon atoms of the salts. The T_{gc} , however, almost remained constant in cobalt system, and increased slightly in barium system with increasing number of the carbon atoms of the salts up to C-12. Above C-12, however, the T_{gc} in both the systems decreased slightly. The ionic modulus increased with increasing number of the carbon atoms of the salts in both the systems. At high weight percentage of the salts in barium-ionomers, the T_{gs} remained almost constant or increased slightly irrespective of the number of the carbon atoms. The ionic modulus of the systems having DCAs of low and high number of the carbon atoms, i.e. DCA4, and DCA16 increased significantly, and the plots almost superimposed on each other. On comparing these results with those of the sulfonated ionomer system neutralized with mono-valent cation (e.g. sodium), similar effects were observed in the ionic modulus and matrix T_{gs} for the systems having the DCA4 and DCA16, while the effects of the DCA16 in decreasing the cluster T_{gs} were significantly higher in mono-valent ionomer systems, compared to that in divalent system. Thus, we concluded that the type of the cations and number of the carbon atoms of the added organic salts has no significant effect on the mechanical properties of the resulting ionomer, and that the organic salts acted mainly as filler in divalent systems.

5. References

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Chapter 4

**Dynamic mechanical studies on sulfonated polystyrene
ionomers neutralized with amphiphilic diamines**

Abstract

As part of a series of investigations of different families of ionomeric systems containing bi-functional linear aliphatic molecules, the study reported here focused on the effects of short to long chain aliphatic diamines (ADAs) on the morphology and dynamic mechanical properties of poly(styrene-*co*-styrenesulfonic acid) SSA copolymers having 4.1, 7.3 and 11.5 mol% of the acid groups. Dynamic mechanical thermal analysis and small angle X-ray scattering techniques were used in this study. Upon blending-cum-neutralization of the copolymers with aliphatic diamines, a negligible change in the shape, size and position of the matrix loss tangent peaks was observed in the case of the ionomeric systems having 4.1 and 7.3 mol% of the ionic groups. However, only a little change in the position of the matrix loss tangent peaks, and a significant increase in their height were observed in the case of the system having 11.5 mol% of the ionic groups. A drastic shift in the position of the cluster loss tangent peaks to low temperatures in all systems was found to be related with the number of the carbon atoms of the ADAs. On increasing the number of carbon atoms of the ADAs, a negligible, and a significant decrease in the size of the cluster loss tangent peaks were observed in the ionomeric systems having 4.1 and 7.3, and 11.5 mol% of the ionic groups, respectively. The width of the ionic plateau decreased significantly with increasing number of carbon atoms of the ADAs, indicating the ion interactions between the ion-pairs of ionomer decreased in a similar order. There was a slight increase, a negligible decrease, and a considerable decrease in the ionic modulus in the ionomeric systems having 4.1, 7.3, and 11.5 mol% of ionic groups, respectively. Thus, it was concluded that on one hand, at low ion contents of the ionomer, the addition of ADAs induced the clustering leading to a slight increase in the ionic modulus. On the other hand, at high ion contents, the ADAs disrupted the multiplets of the ionomers leading to a decrease in the ionic modulus. It was also suggested that

the properties of these SSA systems were related with the number of the carbon atoms, and that the ADAs acted as neutralizing agent-cum-ionic domain plasticizers.

Keywords: sulfonated polystyrene ionomers, aliphatic diamines, clustering, plasticization

1. Introduction

Ionomers are polymers having a small amount of ionic groups attached directly to backbones or as pendant groups attached to side chains [1-7]. Because of the presence of attractive electrostatic forces between the ionic groups in the ionomers and high degree of incompatibility between the ionic groups and the relatively non-polar hydrocarbon polymer matrix, the ionic groups tend to aggregate. These ionic aggregates, called “multiplets” [8], lead to the reduction in the mobility of the polymer chain segments surrounding them [9]. Based on the extensive studies by many research groups using various experimental techniques, it is now well established that at very low ion contents only a few of the multiplets exist. At this stage, the ionomers show one-phase behavior. 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 contiguous regions. When the restricted mobility regions reach or exceed ca. 10 nm in their size, they exhibit their own glass transition at higher temperatures than that for the hydrocarbon rich regions (i.e. matrix phase). At this point, the restricted mobility regions along with the multiplets are termed “clusters”, and the ionomers behave like biphasic materials. At much higher ion contents, the cluster regions become dominant [10,11], and the ionomers again behave like monophasic materials, showing only one glass transition at much higher temperatures than the glass transition of the ionomers of very low ion

contents.

It is well known that the mechanical properties and morphology of the ionomeric systems are influenced by various factors including ion contents, type of the counter-ions, type and position of the ionic pendant groups, and type of the backbone chains [1,9]. In this paper, our study was focused on the roles of the neutralizing agents in changing the mechanical properties and morphology of lightly sulfonated polystyrene (SPS) ionomers. To convert the acid groups of the copolymers into the ionic groups, one could use various neutralizing agents. In the case of anionic ionomers, counter-ions can be alkali, alkaline earth, transition and rare earth metal cations. In addition, positively charged organic molecules can also be used as counter-ions. In the case of metal cations, an effective charge density of the ions is the main factor that affects the packing of the ion-pairs in the multiplets, which, in turn, can influence the mobility of the polymer chains emanating from the multiplets. However, for the organic cations, their functionality, shape and size play the dominant role in tailoring the properties of the ionomers. Thus, the selection of the counter-ion is one of the important factors to control the visco-elastic properties and morphology of ionomers. When multi-functional organic molecules are added to the ionic polymers, they introduce ionic cross-linking sites to the polymer chains, and the resulting ionomers get enhanced physical properties. Most probably, it was for the first time that Brown recognized this effect in the course of the preparation of the elastomers containing carboxylic acid and hexamethylene diamine [12]. Rees studied the ethylene-methacrylic acid copolymers neutralized with the aliphatic diamines and those with metal cations [13]. He concluded that the diamine salts of the copolymer showed weaker ion interactions than the metal salts. The thermal, mechanical and rheological properties of SPS ionomers neutralized with mono-, di- and tri-substituted alkyl amines, the alkyl chain lengths of which range from C₀ (ammonia) to C₂₀, were studied by Weiss et al [14]. The authors

demonstrated that the properties of the ionomers were affected by the chain lengths of alkyl amines, the number and size of the substituents. Smith and Eisenberg studied the effects of neutralization of SPS ionomers with either flexible or rigid mono-functional amines of low molecular weight (MW) on the mechanical properties of the ionomers [15]. They found that the flexible amines plasticized the system, and that the decrease in the glass transition temperatures (T_g) of the ionomers was proportional to the number of the carbon atoms of the amines. However, the rigid amines showed anti-plasticization effects (i.e. increase in the T_g) by acting like physical grafts. Few other groups had also studied the effects of the organic compounds, having functional groups used in the neutralization of the acid copolymers, on various properties of the ionomers. For the sake of the precise Introduction, the interested readers are referred to the concerned articles [16-25].

The above-mentioned literature survey shows that the small organic molecules can be used as neutralizing agents, plasticizers, or neutralizing agents-cum-plasticizers, depending on the functionality, shape and size of the molecules. In addition, amine-containing compounds among other small organic compounds can also be used as neutralizing agents as well as counter-ions to tailor the physical properties of the ionomers. Although, the effects of a few of the organic diamines on the properties of the crystalline ethylene-based ionomers had been studied, little attempts had been made to explore the effects of short to long chain aliphatic diamines (ADAs) on the morphology and dynamic mechanical properties of the amorphous polystyrene-based ionomers. The additives that are expected to show many applications at the same time may be more interesting and useful candidates as compared to the additives showing only a single application. Four aliphatic diamines, the alkyl chains of which range from ethyl (C_2) to dodecyl (C_{12}) in number of the carbon atoms, were selected for this study. All the ADAs have one amino functional group at each of the alkyl chain end.

The copolymers of low, medium and high acid contents were chosen to explore the effects of the degree of clustering on changing the mechanical properties of the ionomers containing ADAs.

2. Experimental Details

2.1. Polymer Synthesis

Polystyrene (PS) homopolymer (MW= ca. 500,000) was synthesized by the free radical polymerization of purified styrene at 60 °C using benzoyl peroxide as the initiator. After the pre-calculated polymerization time to give the conversion of ca. 30% by weight, the polymer solution was cooled and diluted with tetrahydrofuran. The polymer was recovered by the precipitation of the solution into an excess amount of methanol. Lightly SPS random copolymers were made by the sulfonation of PS with the method reported by Makowski *et al* [26,27]. The sulfonation reaction was carried out in 1,2-dichloroethane at 60 °C for 1 hr. By controlling the amount of the sulfonating agent, the degree of sulfonation was achieved as per need. The reaction was terminated by the addition of methanol into the reaction mixture. The PSSSA copolymers were recovered by steam stripping in boiling water followed by pulverization in a blender. The resulting powder samples were washed several times with de-ionized water and with methanol. To determine the acid contents, the copolymer samples were dissolved in a benzene/methanol (9/1, v/v) mixture to make a 5% (w/v) solution and titrated with methanolic NaOH solution to the phenolphthalein end point. The ion contents were found to be 4.1, 7.3 and 11.5 mol%.

2.2. Sample Preparation

For blending-cum-neutralization of the acid copolymers with ADAs, the solid and acid form of the copolymer and the ADAs were dissolved in a benzene/methanol (9/1, v/v) mixture to make a 5% (w/v) solution. The

copolymer solutions were freeze-dried and dried further under a vacuum at ca. 130 °C for 24 h. The ratio of the moles of ionic groups of the copolymers to that of the amino groups of the ADAs was kept at 1/1. For comparing the results of ionomers neutralized with ADAs to those of the metal neutralized ionomers, we also prepared sodium-neutralized ionomers. The acid copolymers were dissolved in a benzene/methanol (9/1, v/v) mixture to make a 5% (w/v) solution. A pre-determined amount of methanolic NaOH solution was added to the copolymer solutions for complete neutralization. The copolymer solutions were freeze-dried and dried further under a vacuum at ca. 130 °C for 24 h. The acronym used for these samples is x-Na/ADAY, where “x” stands for the mol% of the ionic groups in SPS ionomers neutralized with either sodium ion or ADAs, and “y” stands for the number of the carbon atoms in a particular ADA molecule, e.g. 2 (ethylene diamine), 6 (hexamethylene diamine), 10 (decamethylene diamine) and 12 (dodecamethylene diamine). For the dynamic mechanical property measurements, samples were compression molded at ca. 150-250 °C, and at a pressure of ca. 25 MPa. All the molded samples were transparent. The molded samples with approximate dimensions of $2.5 \times 7.0 \times 30.0 \text{ mm}^3$ were annealed under a vacuum at 130-150 °C for 24 h.

2.3. Dynamic Mechanical Thermal Analysis

To measure the dynamic mechanical properties of the ionomers, a TA dynamic mechanical analyzer (DMTA Mark II) was used. The dual cantilever-bending mode at frequencies of 0.3, 1, 3, 10 and 30 Hz was utilized. The heating rate was 1 °C/min. For each sample, the storage moduli (E') and loss tangents were obtained as a function of the temperature. Although dynamic mechanical measurements for each sample were conducted at five different frequencies, the detailed analysis was performed only on 1 Hz data.

2.4. X-ray Experiments

The small angle x-ray scattering (SAXS) experiments were conducted at Station 4C1 of the Pohang Light Source (PLS) synchrotron radiation source (Pohang, Korea). The generated critical beam energy was 2.8 keV (at 2.5 GeV operation modes). The size of the beam at the sample was smaller than one mm². The position-sensitive one-dimensional Si diode-array detector was used. The sample-to-detector distance was 400 mm, which allowed SAXS data to be obtained in the q (scattering vector) ranging from ca. 0.4 to 5.7 nm⁻¹, where $q = 4\pi \sin \theta/\lambda$; θ is half the scattering angle, and λ is the x-ray wavelength ($\lambda = 0.1608$ nm) [28]. The SAXS data were plotted as relative intensity vs. q after correction for sample absorption and a background.

3. Results and Discussion

Fig. 1 (a) shows the storage moduli (E') as a function of temperature for the SPS ionomers containing 4.1 mol% of the ionic groups neutralized with sodium, SNa (4.1-Na), and ADAs, SADAs (4.1-ADAs). With increasing temperature, the modulus curve shows a glassy plateau, a steep matrix glass transition, an ionic plateau, a cluster glass transition, a rubbery and a flow region. The ionic plateau (i.e. the region between the glass transitions of the matrix and the cluster phases) [6] extends up to ca. 225 °C for the 4.1-Na ionomer, to ca. 170 °C for 4.1-ADA2 and 4.1-ADA6, to ca. 145 for the 4.1-ADA10 and to ca. 150 °C for the 4.1-ADA12 ionomers. This indicates that the width of the ionic plateau decreases with increasing number of the carbon atoms of the ADAs. The width of the ionic plateau is treated as a symbol for the strength of the interactions between the ion-pairs in the multiplets of the ionomers based on the same non-ionic monomer [8,17,21,27]; the smaller the ionic plateau, the weaker the ion interactions between the ion-pairs.

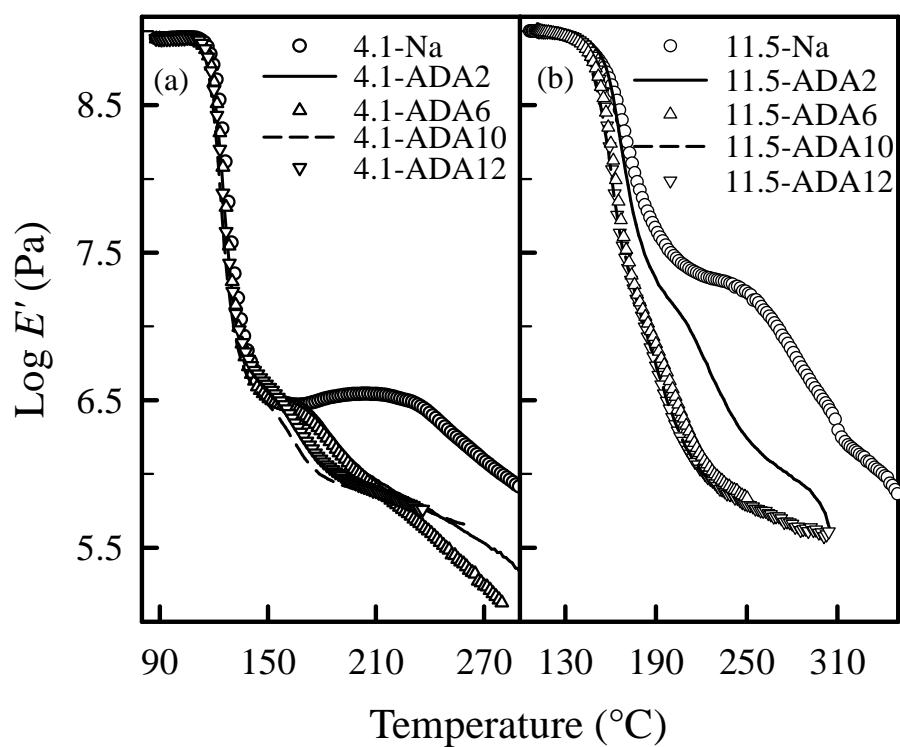


Figure 1. Storage moduli as a function of the temperature for the P(S-4.1-SSA) and P(S-11.5-SSA) ionomers neutralized with sodium and ADAs, at 1 Hz.

This suggests that the strength of the interactions between the ion-pairs in the multiplets of the ionomers neutralized with the ADAs decreases with increasing number of the carbon atoms of the ADAs. It will be worth mentioning that the height of the ionic plateau in the ionomers generally reflects the development of the cluster phase to some extent [1,9,10,29,31]. Clearly, it is the highest for the 4.1-Na ionomer, suggesting the highest stability of the cluster phase of the ionomer neutralized with the sodium. It is also seen that the curve for the cluster glass transition of SADAs becomes steeper and shifts to low temperatures with increasing number of the carbon atoms of the ADAs. Similar trends in the storage modulus plots (not shown here) are observed in the case of the ionomeric system containing 7.3 mol% of the ionic groups. Shown in Fig. 1 (b) are the storage modulus plots for the ionomeric system having 11.5 mol% of the ionic groups. Here, again, the trends are similar to that of the lowest ion content (i.e. 4.1 mol% of the ionic groups) system in this study, except that once the number of the carbon atoms of the ADAs is higher than two, the modulus curves seem to be similar to each other.

Fig. 2 (a) and (b) show the storage modulus as a function of temperature for the three SPS ionomers having 4.1, 7.3 and 11.5 mol% of the ionic groups neutralized with the sodium, and the ADAs having the lowest and the highest number of the carbon atoms in this study, e.g. ADA2 and ADA12, respectively. It is evident that the height of the ionic plateau is increasing with increasing the ion content of the SNa ionomers. It is also seen that the width of the ionic plateau decreases and its slope becomes steeper with increasing number of the carbon atoms of the ADAs. It may be interesting to note that on increasing the ion content of the ionomer, the gap between the ionic plateau of the SNa ionomers and the ionomers neutralized with the ADAs increase significantly. This will be described later.

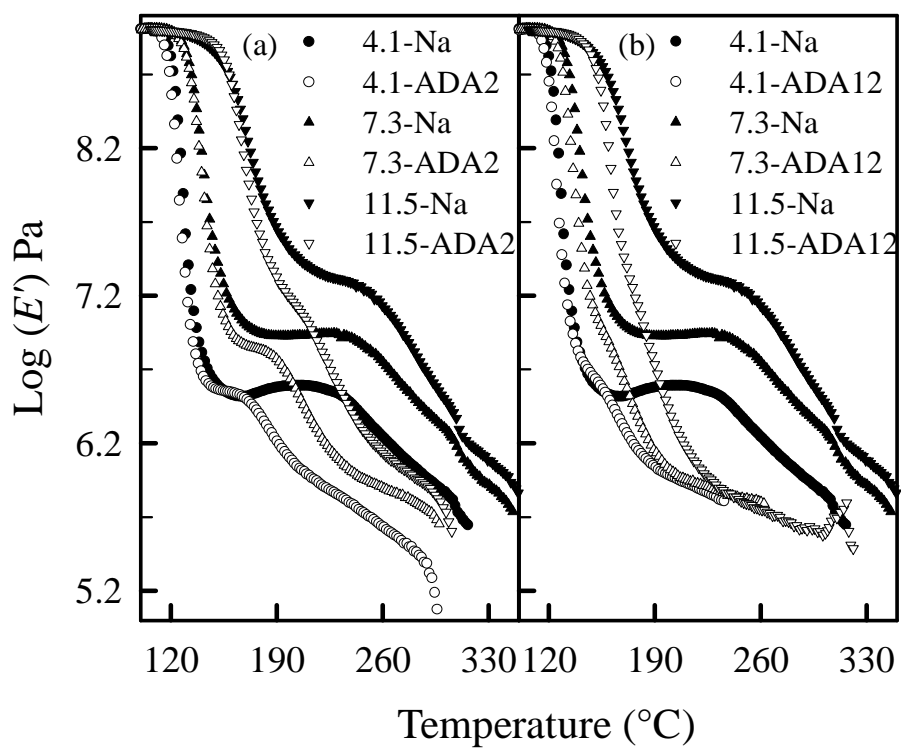


Figure 2. Storage moduli as a function of the temperature for the P(S-4.1-SSA), P(S-7.3-SSA) and P(S-11.5-SSA) ionomers neutralized with sodium and ADAs, at 1 Hz.

Let us focus on the loss tangents plots. The loss tangent as a function of temperature for the SNa ionomers and the SADAs are shown in Fig. 3 (a) and (b) for the ionomeric systems having 4.1 and 11.5 mol% of the ionic groups. From Fig. 3 (a), it is clear that these ionomers represents biphasic behavior by showing loss tangent peaks for the ion poor phase, i.e. matrix phase at low temperatures, and ion rich phase, i.e. cluster phase at high temperatures. It is found that with the addition of ADAs, there is a no change in the shape, size and position of the matrix loss tangent peaks. However, a drastic shift in the position of the cluster peaks to low temperatures is clearly seen, for example, the cluster peak appears at ca. 260 °C for the 4.1-Na ionomer, at ca. 190 °C for 4.1-ADA2 and 4.1-ADA6 ionomers, and at ca. 170 °C in the case of 4.1-ADA10 and 4.1-ADA12 ionomers. At this point, it will be useful to remind that the intensity (i.e. the height) of the loss tangent peaks does appear to be related with the degree of neutralization, the proton transfer, and the development of matrix and cluster phases [18]. No significant change in the size and intensity of both the phases is observed with increasing number of the carbon atoms of the ADAs. As shown in the Fig. 3 (b), the loss tangent plots in the case of the ionomeric system having 11.5 mol% of ion contents are quite different than that of the systems having 4.1 mol% of the ionic groups. The cluster phase is well dominated over the matrix phase. Like the systems having 4.1 mol% of the ionic groups, a negligible change in the position of the matrix phase, while drastic shift in the position of cluster phase is observed here, too. A significant decrease in the size of the cluster peak, with a subsequent increase in the size of the matrix peak with increasing number of the carbon atoms of ADAs is also seen. The shift in the position of the cluster loss tangent peaks towards lower temperatures in all the systems seems to be more or less related with the type (i.e. number of the carbon atoms) of the ADAs.

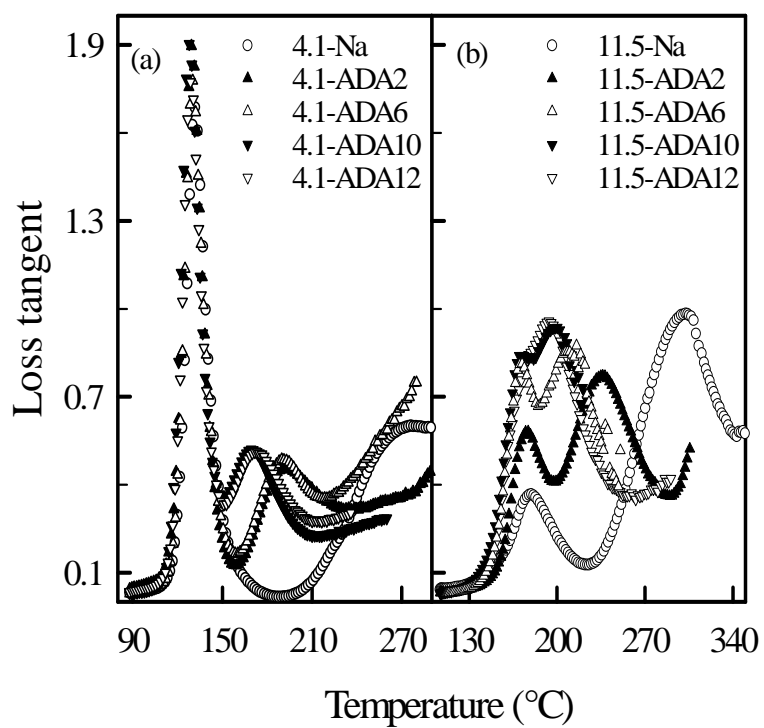


Figure 3. Loss tangents as a function of the temperature for the P(S-4.1-SSA) and P(S-11.5-SSA) ionomers neutralized with sodium and ADAs, at 1 Hz.

Fig. 4 shows the values of the ionic modulus, i.e. the modulus at the point of minimum slope in the ionic plateau region [9,10,30] as a function of number of the carbon atoms of the ADAs. The overall trend in these three systems shows that there is a slight increase, a negligible decrease, and a considerable decrease in the ionic modulus in the ionomeric systems having 4.1, 7.3 and 11.5 mol% of ionic groups, respectively. For a better understanding of these trends of the ionic modulus in these systems, the plots of ionic modulus for SADA2 and SADA12, shown in the Fig. 5 (a) and (b), respectively are worthy to see. Shown in the Fig 6 are the plots of glass transition temperatures (T_g s) vs. number of the carbon atoms of the ADAs in all the three systems. It is seen that on increasing the ion content, the T_g s of ionomers increase significantly. It is evident that there is a significant decrease in the cluster T_g s, while a negligible change in the matrix T_g s are observed in the SADAs. Initially, the cluster T_g drops significantly but on increasing the number of carbon atoms of the ADAs, it becomes less significant on the type of the ADAs.

Let us discuss the possible reasons for the change in the properties of the ionomeric system by the incorporation of the aliphatic diamines. It is found that the length of the ionic plateau decreases with increasing number of the carbon atoms of the ADAs. According to the law of electrostatic force of attraction between the ions, the electrostatic force is inversely proportional to the square of the distance between the ions. The ionic groups in the SNa ionomer are Na^+ and SO_3^- , while those in the SADAs are -NH_3^+ and -SO_3^- . It is worth reminding that all the ADAs are bi-functional, having one amino group at each of the alkyl chain end, and, hence, one molecule of an ADA seems to be capable of neutralizing two ionic groups of the copolymers. Because of the relatively long distance between the two alkyl chain ends of the ADAs, the ADAs are expected to naturally increase the distance between the ion-pairs in ionomers, either in the fully or partially extended or folded form of the ADA chains.

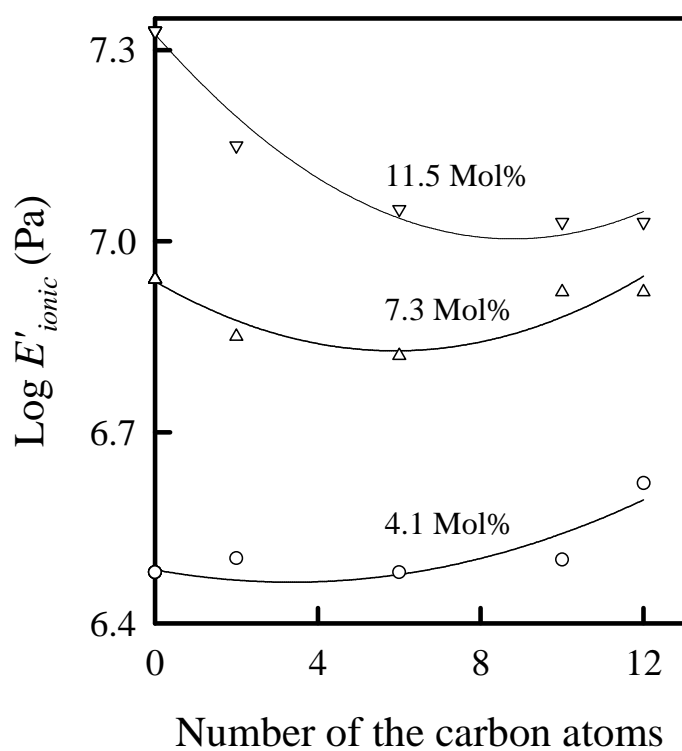


Figure 4. Ionic modulus as a function of the number of the carbon atoms of the ADAs for the P(S-4.1-SSA), P(S-7.3-SSA) and P(S-11.5-SSA) ionomers neutralized with sodium and ADAs, at 1 Hz.

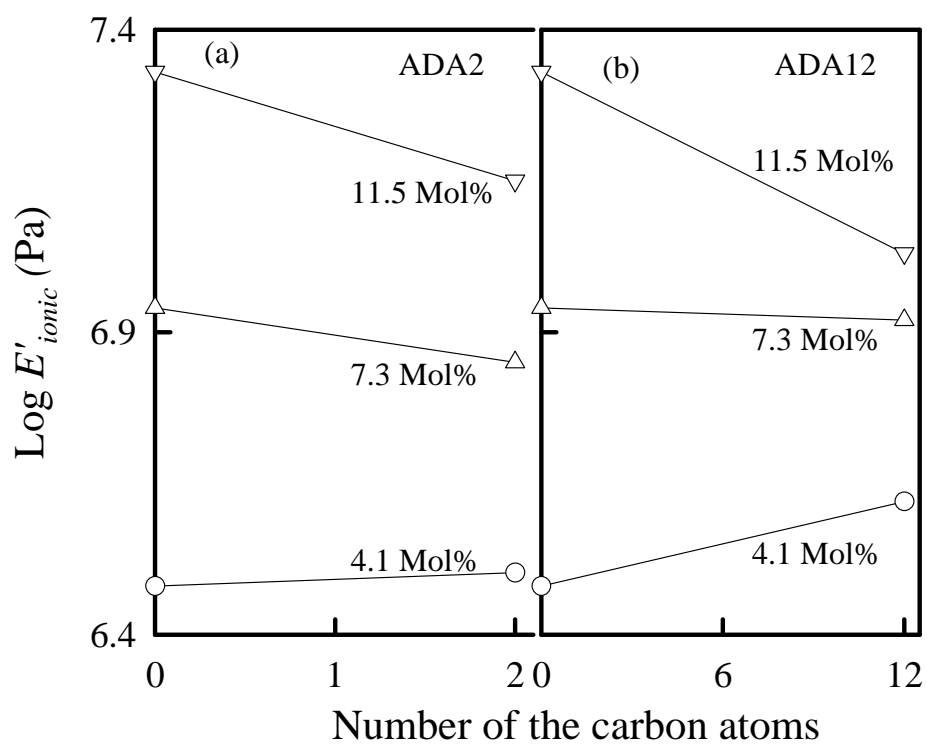


Figure 5. Ionic modulus as a function of the number of the carbon atoms of the ADA2 and ADA12 for the P(S-4.1-SSA), P(S-7.3-SSA) and P(S-11.5-SSA) ionomers neutralized with sodium and ADAs, at 1 Hz.

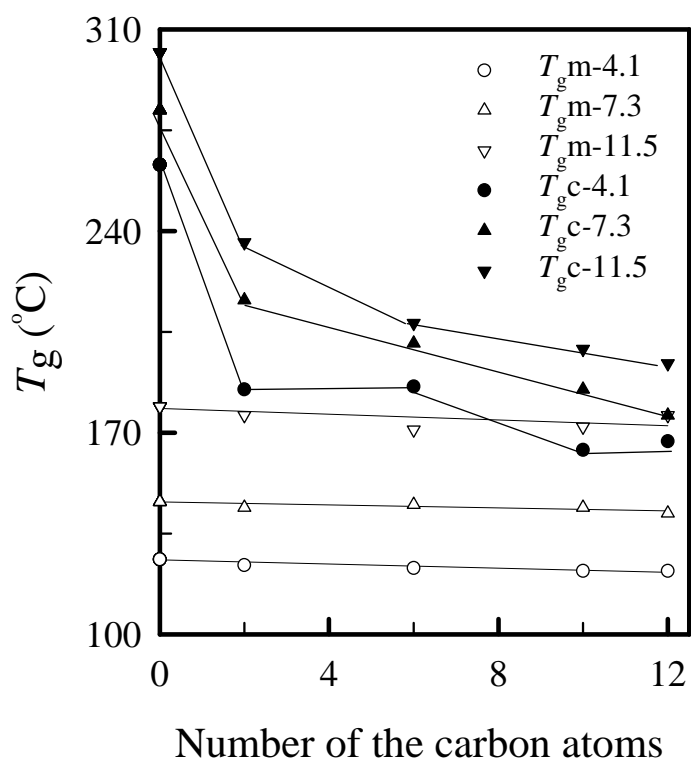


Figure 6. Glass transition temperatures as a function of the number of the carbon atoms of the ADAs for the P(S-4.1-SSA), P(S-7.3-SSA) and P(S-11.5-SSA) ionomers neutralized with sodium and ADAs, at 1 Hz.

The long and flexible aliphatic chains of the ADAs, and the large size of amine-sulfonate ion-pairs; acting as mechanical grafts [33,34], are expected to naturally decrease the ion aggregations by preventing the close approach of the amine-sulfonate ion-pairs. As a result, the strength of interactions between the adjacent ion pair will decrease with increasing number of the carbon atoms of the ADAs. The decreasing width of the ionic plateau with increasing number of the carbon atoms is in accordance with this expectation. As far as the effect of aliphatic diamines on the modulus is concerned, it is interesting to remind that a slight increase in the ionic modulus is observed in the case of the ionomeric system having 4.1 mol% of the ionic groups. The ionic modulus is probably related with the degree of the clustering, which depends on the type and size of the multiplets, contact surface area, persistence length of the polymer chains and restricted mobility regions surrounding the multiplets [6,7,9,10,30]. The mechanism involved in the neutralization of the ionic groups of the copolymers by the small organic molecules is the creation of the ion pair by the proton transfer from the ionic groups of the copolymers to the basic groups of the organic molecules usually having amine or related groups. As the ionic groups of the copolymers have been neutralized with the ADAs, the size of the multiplets is expected to increase because of the long chains of the ADAs and large size of amine-sulfonate ion pair, i.e. the ion aggregation is expected to decrease with increasing number of the carbon atoms of the ADAs. We conducted the SAXS experiment in order to know the whereabouts of the ADAs and other morphological details of the blends.

Shown in the Fig. 7 are the SAXS profiles for the ionomer system having 4.1 mol% of the ionic groups. No well developed peak but only a broad plateau like appearance is seen at q (scattering vector) = 0.17 \AA^{-1} , which corresponds to a Bragg spacing of 36 \AA . These Bragg spacings are almost same as compared to the results obtained in the previous studies (35-46).

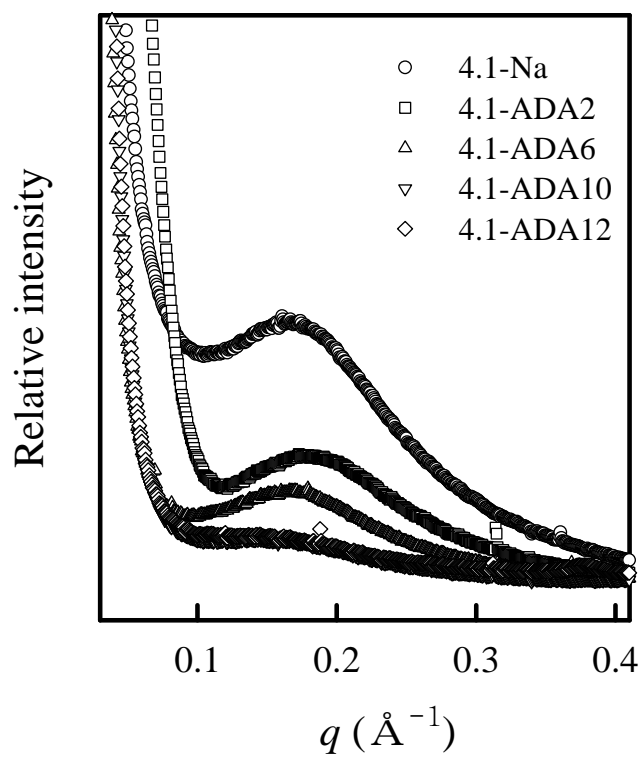


Figure 7. SAXS profiles as a function of the scattering vector for the P(S-4.1-SSA) ionomers neutralized with sodium and ADAs.

A broad plateau like appearance for the SAXS peak is not much surprising because of the fact that the ion content in this system is only ca. 4.1 mol%. The SAXS peak is ascribed to the inter-multiplet distances [2,26]. Almost the same Bragg spacing for all the samples, most probably indicates that the intermultiplets distance remained almost same even after the incorporation of the ADAs into the copolymer, which, in turn, shows that the process of the multiplet formation had not been disturbed much by the addition of the ADAs in this system. At the same time, the intensity of the broad peaks decreased with increasing number of the carbon atoms. The decreasing trend in the intensity and broadening of the peak with increasing number of the carbon atoms may be because of the following two factors: 1) the number density of the scattering centres, i.e. multiplets at prevalent distances may be very low in SADAs, and 2) the scattering centres may have different or broad-cum-distributed electron density. As the intermultiplet distance is almost same in each case, so it indicates that the number density of the multiplets is also similar in each case including the SNa ionomer, hence the first speculation is ruled out. The rejection of the first possibility leads us to most probably the last and the only remaining possibility. It seems to be applicable here by considering that the ionic groups of the copolymer had been neutralized with the ADAs, as a result, the size of the multiplets will increase because of the long chains of the ADAs and large size of the amine-sulfonate ion pair. Therefore, ion aggregation will decrease with increasing number of the carbon atoms of the ADAs, and, hence, the electron density will naturally disperse over a larger area, so the decrease in the intensity with increasing number of the carbon atoms of the ADAs can be understood.

From the morphological picture, now it is clear that by the addition of the ADAs, no disruption of the multiplets but only an increase in the size of multiplets took place in the case of the system having 4.1 mol% of the ionic groups. In the case of SADA2 and SADA6, the distance between the two alkyl

chain ends of the ADAs seems not to be too much to create multiplets of very large size; otherwise it might result in the overcrowdings of the polymer chains surrounding the multiplets. But, crowding of polymer chains will surely be more in these samples because of the larger size of the multiplets as compared to the SNa ionomer. As the ion interactions decrease with increasing the distance between the ion pair, so these two opposing factors (i.e. the crowding of the polymer chains and a decrease in the ion interactions) will try to nullify the effects of each other, and, as a result, the ionic modulus will change slightly. Whereas, in the case of SADA10 and SADA12, the multiplet size is expected to increase significantly, so severe crowding will decrease the mobility of the chains surrounding the multiplets, and, hence, modulus is expected to increase significantly, but at the same time, the ion interactions also decrease drastically with increasing number of the carbon atoms of the ADAs. Again, these two opposing factors seem to reduce the effects of each other, so the ionic modulus increased slightly. Here, in the case of SADA10 and SADA12, the overcrowding seems to play the dominant role in changing the ionic modulus. Gauthier and Eisenberg also observed similar results in their studies of alkylated styrene ionomers with variable length spacers [47]. They showed that the clustering is extensive for the materials of either very short or very long side chains. In the case of long chains, clustering is extensive because of the reduced mobility of the chains, which, in turn, because of the very large size of the multiplets.

Let us discuss the difference in the behavior of ADAs in changing the properties of the ionomers of higher ion contents. It is well known that the degree of the clustering increases with increasing the ion content of the ionomer and the cluster phase start to dominate over the matrix phase at ca. 8 mol% of the ionic groups in lightly SPS ionomers [9,10,30]. As was mentioned in the previous paragraphs that there is no disruption of the multiplets but only an increase in the size of multiplets took place by the addition of the ADAs in the

system having 4.1 mol% of the ionic groups. It may be because of the fact that the number of the ion-pairs per multiplet and overall number density of the multiplets may not be very much due to the less ion content. If there is an increase in the size of either the cation or anion, then the distance between the ion-pairs will reduce, leading to the enhanced entanglement of the polymer chains, and, hence, will increase the degree of clustering [2,9,10]. On incorporation of the ADAs, the distance between the ion-pairs, and, hence, the size of multiplets will definitely increase because of the larger size of the ADAs. It is evidenced by the well-developed loss tangent peaks for the cluster phase in SADAs. Therefore, on the addition of the ADAs, the ADAs may enlarge rather than exploding the multiplets into further smaller one. Similar results are also seen in the case of the system having 7.3 mol% of the ionic groups. The similar explanation seems to be applicable here, too. The loss tangent plots in the case of the ionomeric system having 11.5 mol% of ionic groups are slight different than those of the low ion content systems. As shown in the Fig. 3 (b), the cluster phase is well dominated over the matrix phase. It is well known that the size of the multiplets, the number of the ion-pairs per multiplet, and the number density of the multiplets itself may increase significantly on increasing the ion contents [2,9,10]. At this point, it would be worth reminding that the multiplets have an upper limit in their size [8]. In this case, the ion content itself seems to be too high to let further increase in the size of the multiplets by the addition of foreign elements of large size in the multiplets. So, we expect that due to the large size of the ADAs, the multiplets may not accommodate the same number of the ion-pairs as accommodated before the addition of the ADAs. Therefore, it will surely explode, leading to the decrease in the size of the cluster phase and subsequent increase in the matrix phase. This explanation seems true on analyzing the DMTA plots.

We have already described about the slight increase in the ionic modulus by the incorporation of the ADAs in the ionomeric system having 4.1 mol% of the ionic groups. Let us think about the effects of the ADAs on the ionic modulus of the ionomeric systems having 7.3, and 11.5 mol% of the ionic groups. A 7.3 mol% of the ionic groups seems to be an average ion content in the sense that the multiplets of whose may neither be too small to be enlarged significantly by the addition of the ADAs to increase the chain entanglement which may considerably increase the modulus, nor, too high to be much exploded by the presence of the large size of ADAs to decrease the clustering leading to the decrease in the modulus. So, overall there is a negligible decrease in the ionic modulus in this case. In the case of 11.5 mol% of the ionic groups, the well dominance of the cluster phase over the matrix phase is evident from the loss tangent plots. As there is an upper limit for the size of the multiplets, then the multiplets may not be able to accommodate the same number of the ion-pairs as was before the addition of the ADAs. So, it will surely explode, leading to the decrease in the clustering, and, hence, the ionic modulus. The higher the number of the carbon atoms of the ADAs, the more the disruption of the multiplets is expected. The ADAs having lower number of the carbon atoms seem to be sufficient to disrupt the multiplets so the increase in the number of the carbon atoms of the ADAs may not have the corresponding effect on disrupting the multiplets as was the trend expected naturally.

It is clear from the Fig. 1 (a) that above ca. 160 °C, the steepness of the modulus curve increases significantly with increasing number of the carbon atoms. At higher temperatures, the movements of the polymer chains will increase. The higher movements of the chains and the decrease in the ion interactions between the ion pair will decrease the chain entanglements, leading to the steepness of the slope, i.e. the rubbery modulus decreases significantly. The results in this study most probably support this explanation. It is also

observed that the flow region started at lower temperatures on increasing the number of the carbon atoms. The very early attainment of the flow region can also be understood by the same explanation.

4. Conclusions

The effects of the aliphatic diamines (ranging from C₂ to C₁₂ in number of the carbon atoms) on the morphology and dynamic mechanical properties of SPS copolymers had been studied. Upon blending-cum-neutralization of the copolymers with aliphatic diamines, a negligible change in the shape, size and position of the matrix loss tangent peaks was observed in the case of the ionomeric systems having 4.1 and 7.3 mol% of the ionic groups. However, only a little change in the position of the matrix loss tangent peaks, and a significant increase in their height were observed in the case of the system having 11.5 mol% of the ionic groups. A drastic shift in the position of the cluster loss tangent peaks to lower temperatures in all the systems was found to be related with number of the carbon atoms of the ADAs. A negligible change in the size of the cluster loss tangent peaks, while a significant decrease in their size on increasing the number of the carbon atoms of the diamines were found in the ionomeric systems having 4.1 and 7.3, and 11.5 mol% of the ionic groups, respectively. There was a slight increase, a negligible decrease, and a considerable decrease in the ionic modulus in the ionomeric systems having 4.1, 7.3, and 11.5 mol% of ionic groups, respectively. Thus, it was concluded that at lower ion contents of the ionomer, the addition of ADAs induced the clustering leading to a slight increase in the ionic modulus, while at higher ion contents, the ADAs disrupted the multiplets of the ionomers leading to a decrease in the ionic modulus. Finally, it was suggested that the properties of these systems were found to be related with number of the carbon atoms, i.e. the alkyl chain lengths of the ADAs, and that the ADAs acted as ionic domain plasticizers.

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Chapter 5

**Dynamic mechanical properties measurements of newly
synthesized polystyrene-based ionomers**

Abstract

Ionomers show unique mechanical properties owing to the presence of small percentage of the ionic groups in one of the monomer units. It is not easy to process the sulfonated polystyrene ionomers due to their very high flow temperatures. In order to reduce the processing temperature without getting significantly adverse effects on the mechanical properties, various types of plasticizers, additives, etc are used. Rather than adding plasticizers in the ionomers, we tried to use the comonomer unit itself as the internal plasticizer. For the same purpose, we have synthesized new polystyrene based ionomers namely poly(styrene-*co*-3-sulfopropyle methacrylate) SPMANa. On comparing its mechanical properties with poly(styrene-*co*-styrenesulfonate) SSNa and poly(styrene-*co*-methacrylate) MANa ionomers, we found that at low ion contents, the ionic modulus for SPMANa is higher than SSNa and MANa, but at high ion contents, the ionic modulus shows the reverse trend. The matrix T_g increased with increasing ion content and is more or less similar to SSNa and MANa systems specially at low ion contents. However, surprisingly the cluster T_g either remained constant or decreased slightly with increasing ion content, and it is essentially intermediate to SSNa and MANa systems. Thus, we concluded that poly(styrene-*co*-3-sulfopropyle methacrylates) ionomers showed good mechanical properties. Moreover, SPMANa ionomers have cluster T_g s intermediate to those of the SSNa and MANa systems. Therefore, the new ionomer may serve the purpose of the internal plasticization, at least to some extent, and may be helpful in understanding the distance effects of the ion pairs from the main polymer chain.

Keywords: polystyrene ionomers, internal plasticizers, ionic modulus, glass transition temperature

1. Introduction

The polymers having small amounts of the ionic groups attached directly or indirectly to the relatively less or non-polar polymer matrix are called ionomers [1]. The interaction between the ionic groups leads to the formation of small ionic aggregates, called “multiplets” [2]. At very low ion contents, the multiplets are treated as a part of the matrix phase. As the ion content increases, the number as well as the size of the multiplets increases leading to the reduction in the mobility of the adjacent polymer chains. At sufficiently high ion contents, the restricted mobility regions formed from the chains surrounding the multiplets start to overlap, forming contiguous restricted mobility regions, called “clusters” [2]. The mobility of the polymer chains in and around the clustered regions becomes so restricted that the clustered regions behave no longer as a part of the matrix phase. As the clustered regions host the majority of the ionic groups in addition to the part of the adjacent polymer chains, it creates significant difference in the polarity of the clustered regions and rest of the polymer matrix, leading to the phase separation of clustered regions into the matrix phase. Thus, it leads to the appearance of plateau like transition, and additional glass transition at higher temperatures than that of the usual matrix glass transition [3-6].

Due to the presence of the ionic groups, the ionomers show significantly different mechanical and morphological properties than those of their non-ionic counter parts. The appearance of plateau like transition, one additional glass transition at higher temperatures other than usual matrix glass transition in storage modulus and loss tangent curves, a peak in small angle X-ray scattering profile, and unusual high melt viscosities and high relaxation times are the various mechanical and morphological differences between the ionomers and non-ionic polymers [5-10]. The ionomers, being significantly different from their non-ionic counterparts, provide the polymer scientists a wide variety of options

to tailor the properties of the ionomers as per the need of the hour. Those options may be as follows: type, position and contents of the ionic groups, type of the backbone chains, comonomers, plasticizers, non plasticizing additives, counter ions, etc [1-10]. Various types of the plasticizers are widely used by polymer scientists and engineers to modify the properties of the polymers. Generally, three types of the external plasticizers can be used in the ionomers. First type is the plasticizers of low polarity for the polymer matrix, the second type belongs to the polar plasticizers for the multiplets, and the third type is the amphiphilic plasticizers for the multiplets and the restricted mobility regions adjacent to the multiplets [3-6,11-18]. We can also plasticize (without adding external plasticizers) the ionomers via direct or indirect attachment of the flexible side chains of low glass transitions to the polymer backbone, the technique called internal plasticization [3-6]. Wollman *et al* [19] had studied about the effects of the size of the counter ion, e.g., iodoalkanes having up to 10 carbon atoms in alkyl chains, on the mechanical properties of the styrene-co-4-vinylpyridinium ionomers. They observed a decrease in the glass transition temperature (T_g) of the backbone chains on increasing the chain length of the iodoalkanes. Similar studies of chain length spacers were also performed by Gauthier and Eisenberg [20], and Moore *et al* [21]. The plasticization effects of non ionic alkyl chains (e.g., 1-decene) as chain length spacers attached at *para* position of the benzene ring on the dynamic mechanical properties and morphology of the P(S-co-MANA) ionomer containing 7.0 mol% of the methacrylate units had also been studied by Gauthier and Eisenberg [22], and Moore *et al* [23]. They reported that the T_g of both the phases of the ionomers, i.e., matrix as well as the cluster dominated phases decreased with increasing level of the alkylation. They also found that at low level of the alkylation, the T_g for the clustered phase increased slightly and then dropped after further increasing the level of alkylation. It was attributed to the inducement of the

clustering by a low level of the plasticizer. Wollman *et al* [24] conducted a plasticization study using both the external (e.g., diethylbenzene, DEB) and internal (e.g., 1-decene attached at para position of the styrene ring) non-polar plasticizers in a low or unclustered random styrene-(*N*-alkyl-4-vinylpyridinium iodide) ionomers quaternized with varying chain lengths of the iodoalkanes. It was shown that plasticization of the styrene matrix led to the inducement of the clustering, and, hence, an unclustered system changed into the clustered one, while, quaternization of the pyridine group by the long chains of the counter ion (iodoalkanes) led to a decrease in the matrix T_g , and system remained unclustered. It was also reported that DEB; the external plasticizer was much more effective than that of the internal plasticizer at similar concentration in inducing the clustering in the unclustered system. The reason for the higher effectiveness of the external plasticizer was its non-attachment to the polymer chain, which led it to create higher free volume into the polymer chains than did an internal plasticizer of similar structure attached at one end to the polymer chain.

These are a few of the internal plasticization studies which had been carried out either by chemically attaching the ionic or non ionic alkyl chains directly or indirectly to the polymer backbone chains, or using counter ions of long alkyl chains. In most of these studies, the carboxylic acid group had been used to make the ionomers. However, up to our knowledge, no information is available on the similar systems having sulfonic acid as the ionic groups. In addition, we lack the information related to the ionomers having the ester (carboxylate) and sulfonate groups in the same monomer units with sufficiently long alkyl chains. Furthermore; sophisticated chemical processes were involved in adding the ionic groups at the end of the alkyl chains or attaching the alkyl chain itself to the backbone of the polymer chains, so for the same purpose, it will be better if we can find an easy method of adding the ionic groups at the alkyl chain ends. Thus, in order to

fill this knowledge gap, for the first time, we have synthesized new polystyrene based ionomers namely poly(styrene-*co*-3-sulfopropyle methacrylate), and studied their properties dynamic mechanically. It is not easy to process the sulfonated polystyrene ionomers due to their high flow temperatures, which in turn, due to the strong inter ionic association of the sulfonate groups. In order to reduce the processing temperature without getting significantly adverse effects on the mechanical properties, rather than adding or attaching, external or internal plasticizers, respectively in the sulfonated ionomers, long alkyl chains having sulfonate group at the chain end in one of the monomers may be used as typical and simple internal plasticizer. The presence of the ester/carboxylate and sulfonate groups in the same comonomer unit will lead us to compare the properties of the current system with those of the styrene based ester/carboxylated, e.g., poly(styrene-*co*-methacrylate) ionomers, etc., and sulfonated, e.g., poly(styrene-*co*-styrenesulfonate) ionomers, etc. Most probably, the properties of the current system may be similar or close to any of the carboxylated and sulfonated systems or intermediate to both of the systems.

2. Experimental Details

2.1. Polymer Synthesis

Poly(styrene-*co*-3-sulfopropyle methacrylate) copolymers were synthesized by the free radical bulk polymerization. We purified the styrene monomer by distilling it under reduced pressure and made it air tight until use. The 3-sulfopropyle methacrylate, potassium salt (98% pure) was used as received. As the reactivity ratios for these monomers are not available in literature, we used the reactivity ratios (0.6/0.37) of the related monomers, e.g., 2-sulfoethyl methacrylate and styrene [25]. As there is a major difference in the polarity of the monomers, so we used 2-methoxy ethanol (99.8% pure, anhydrous, was used as received) as the solvent [26] for dissolving the monomers, and the initiator,

e.g., benzoyl peroxide (75% pure, used as received). 3-sulfopropyle methacrylate, potassium salt was dissolved in 2-methoxy ethanol, followed by the complete mixing and dissolution of the styrene and the initiator in the 3-sulfopropyle methacrylate, potassium salt solution. The solution was then freeze and thawed three times to make it gas free, followed by the polymerization of the monomers at 70 °C for the calculated time to get the desired conversion of the monomers to the copolymer and to keep the degree of heterogeneity less than 0.1. The copolymer, poly(styrene-*co*-3-sulfopropyle potassium methacrylate) solution was poured into the excess volume of acetone to precipitate the copolymer and to dissolve polystyrene, if any, followed by washing the copolymer sample several times with excess volume of methanol. The obtained copolymer sample was dried at 60 °C for 12 h under reduced pressure. For the similar dynamic mechanical and morphological studies of the ionomers, many research groups including ours had used mainly the sodium ion for the neutralization of the ionomer, so it will be very easy to compare our results with the results available in the existing literature if we can also have the ionomers neutralized with the sodium ion. In order to know the exact ion content of the ionomer, and to change the potassium ionomer into acid copolymer and then to the sodium ionomer, we dissolved the potassium ionomer sample in a benzene/methanol (9/1 v/v) mixture to get 5% (w/v) solution. After complete dissolution of the ionomer sample, excess volume of 35% (v/v) aqueous hydrochloric acid solution was poured into the ionomer solution followed by strong stirring at least for half an hour. The color of the solution turned from colorless to milky. To precipitate the acid copolymer, two types of the non-solvents were used. Excess volumes of the *n*-hexane and methanol were used to precipitate, and wash the acid copolymers of expected high levels of the ion contents, respectively. For low levels of the ion contents, methanol was used to precipitate and wash the acid copolymer, followed by drying the copolymer samples at 60 °C for 12 h under reduced

pressure. To measure the acid content, the acid copolymer was dissolved in the benzene/methanol (9/1 v/v) mixture and titrated with methanolic NaOH solution to the phenolphthalein end point. The sulfonic acid contents were found to be 1.3, 2.5, 4.5, 8.6 and 10.5. To convert the acid copolymer into the sodium ionomer, a pre-calculated amount of the methanolic NaOH solution was added to the acid copolymer solution. The ionomer samples were freeze dried, and dried further under vacuum at 150 °C for at least 24 h.

2.2. Sample Preparation and Dynamic Mechanical Property Measurements

To prepare the samples for the dynamic mechanical thermal analysis (DMTA); depending on the ion contents, the samples were compression molded at ca. 210–240 °C, with a pressure of ca. 4 MPa, maintained for at least 5 min. The mold was cooled to room temperature followed by removing the sample from the mold. The samples were in the form of rectangular slab with dimensions of ca. 30×7.0×2.5 mm³. The annealing of the samples was performed under vacuum at ca. 150 °C for 24 h. For the dynamic mechanical property measurements, we used a Polymer Laboratories's dynamic mechanical thermal analyzer (DMTA, Mark II). The experiments were performed in a dual cantilever-bending mode at five frequencies ranging from 0.3 to 30 Hz. A heating rate of 1.0 °C/min was used to get the values of the storage modulus (E') and loss tangent (δ) as a function of temperature.

3. Results and Discussion

Fig. 1 shows the storage modulus (Log E') plots as a function of temperature for poly(styrene-*co*-3-sulfopropyle sodium methacrylate) SPMANa ionomers of various ion contents. With increasing temperature, the modulus plots goes through various transitions, e.g., through glassy region, to matrix glass transition,

to ionic plateau, to cluster glass transition, to rubbery plateau, and flow region. In line with the characteristics of the styrene-based ionomers, the values of the glassy modulus are found to be similar for all the samples irrespective of the ion contents [27]. The glassy region extends, and the position of the modulus plot related with the matrix glass transition shifts to high temperatures on increasing the ion content. It is well clear that the height of the ionic plateau [2,5,27] (i.e., the plateau, characteristics of the ionomers, emerged from the formation of ionic clusters due to the strong electrostatic force of attraction between the ionic groups) increases with increasing the ion content. There is no significant difference in the rest of the regions in the modulus plot.

In Fig. 2, the values of loss tangent (δ) are plotted as a function of temperature for the SPMANa ionomers of various ion contents. It is observed that the position of the matrix loss tangent peak shifts to high temperature with increasing ion content. Surprisingly, however, there seems no significant change in the position of the cluster loss tangent peaks. The height of the matrix loss tangent peak decreases, while the same for cluster loss tangent peak increases gently with increasing ion content.

Shown in Fig. 3 are the plots of ionic modulus as a function of the mole percent of the ionic groups for SPMANa, poly(styrene-*co*-sodium methacrylate) MANa, and poly(styrene-*co*-sodium styrenesulfonate) SSNa ionomers. It is observed that the value of the ionic modulus for the SPMANa ionomer increases with increasing ion content. On comparing the ionic modulus results of SPMANa ionomer with those of the MANa and SSNa ionomers of similar ion contents, we found that at low ion contents, the ionic modulus for SPMANa ionomers is higher than those of the SSNa and MANa systems. However, at high ion contents, the ionic modulus shows the reverse trend, i.e. the MANa and SPMANa systems have the highest and lowest ionic modulus values, respectively.

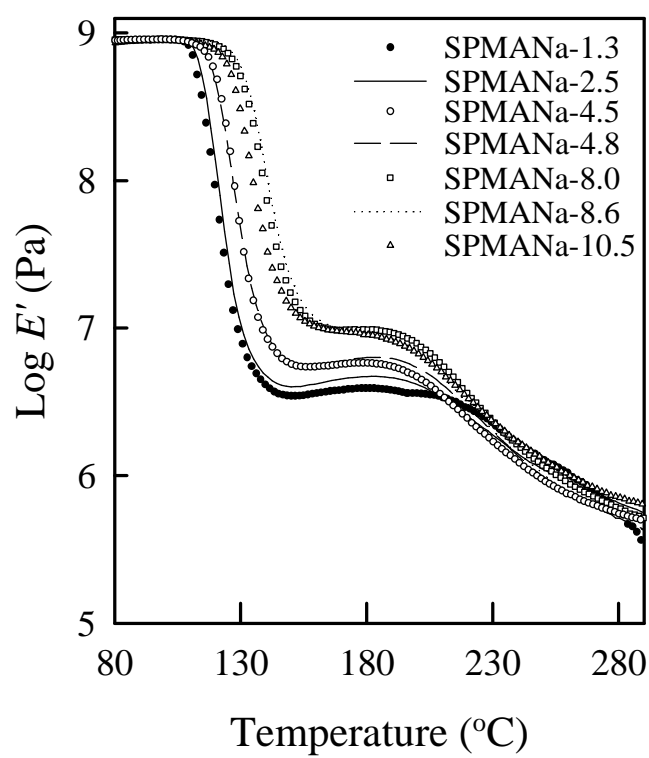


Figure 1. Storage moduli as a function of the temperature for the P(S-co-SPMANa) ionomers at 1 Hz.

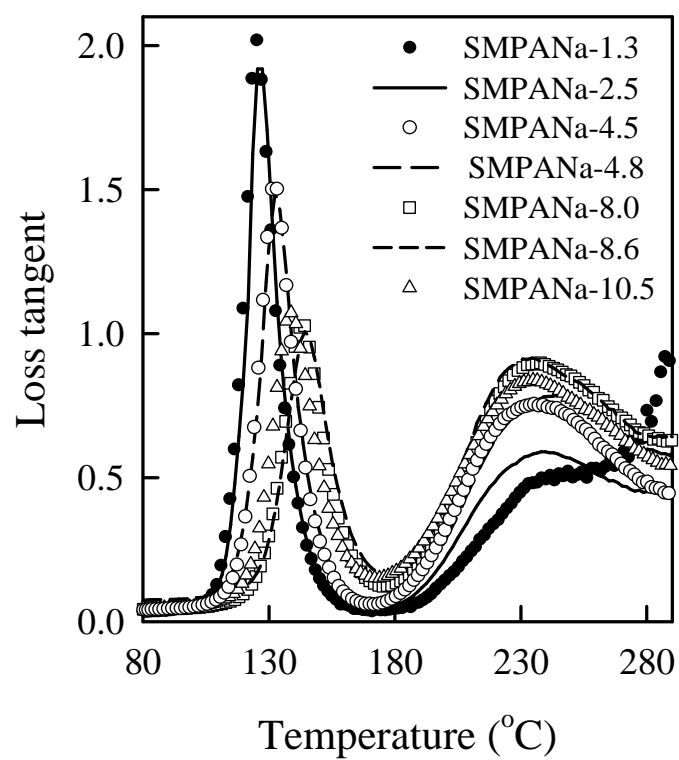


Figure 2. Loss tangent as a function of the temperature for the P(S-*co*-SPMANa) ionomers at 1 Hz.

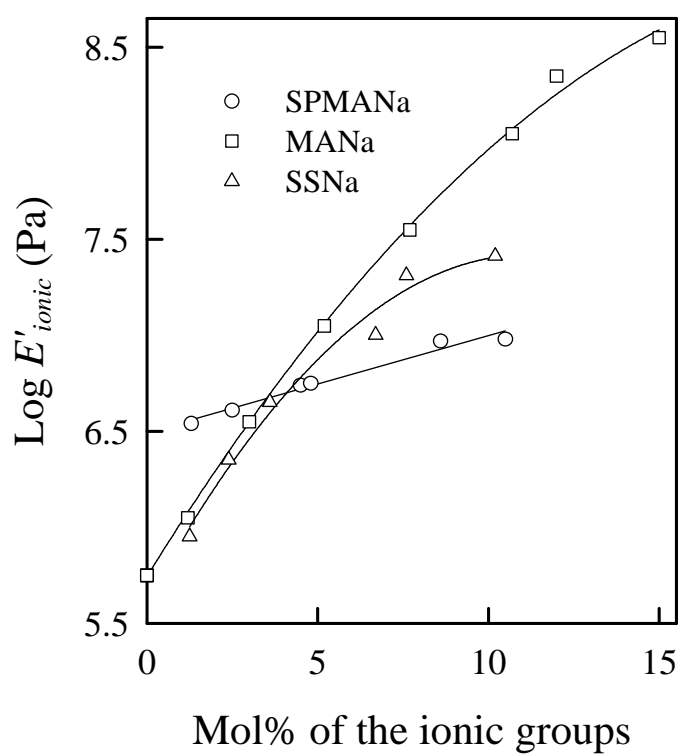


Figure 3. Ionic moduli as a function of the mol% of the ionic groups of the P(S-co-SPMANa), P(S-co-MANa) and P(S-co-SSNa) ionomers at 1 Hz.

The SSNa ionomer have slight higher value than that of the SPMANa ionomers.

The glass transition temperatures as a function of the mole percent of the ionic groups for SPMANa, MANa, and SSNa ionomers are shown in Fig. 4. From the SPMANa ionomer plot, it can be observed that the matrix glass transition temperature (T_{gm}) increases, while the cluster glass transition temperature (T_{gc}) remains almost constant on increasing the ion content. Up to almost 6 mol% of the ions, the T_{gm} is found to be almost same for each ionomer, while after that ion content, the T_{gm} for the SSNa ionomer increased, and differ significantly from the MANa and SPMANa ionomers. Moreover, above that ion content, the T_{gm} for MANa and SPMANa ionomers are almost same. In the case of the T_{gc} , however, the SSNa and MANa ionomers show the highest and the lowest values, respectively. It can be inferred that at low ion contents, the T_{gm} is almost independent of the type and position of the ionic groups. In addition, the T_{gc} of the SPMANa ionomer is found to be the intermediate to those of the SSNa and MANa ionomers.

From the results mentioned above, it is clear that the ionic moduli of the SPMANa ionomer are close but less than that of the SSNa ionomer at comparable ion contents. The T_{gc} of SPMANa ionomers, however, seems intermediate to those of the MANa and SSNa ionomers. At low ion contents, the T_{gc} resembles more with that of the SSNa ionomers, while at high ion contents it resembles more with the MANa ionomers. It is seen that the MANa ionomer shows the highest ionic modulus, but the lowest T_{gc} . Here, it will be worth mentioning that the ionic modulus is assumed to be related with the volume of the clustered regions in the ionomers [2,27-30]. It is well reported that the smaller the distance of the pendant ionic groups from the backbone chain of the ionomer, the smaller will be the size of the multiplets in the ionomers.

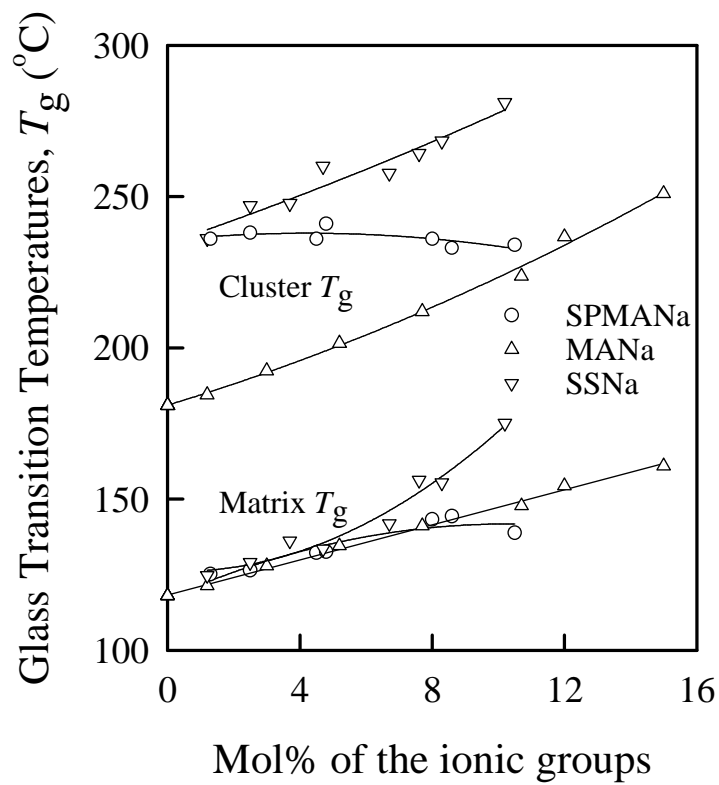


Figure 4. Glass transition temperatures as a function of the mol% of the ionic groups of the P(S-*co*-SPMANa), P(S-*co*-MANa) and P(S-*co*-SSNa) ionomers at 1 Hz.

Thus, at particular ion content, for the ionomers having the ion-pairs closer to the backbone chain, size will be smaller, but number of the multiplets will higher, leading to the higher volume of the clustered regions in the ionomers [2,5,6,28]. The $-\text{SO}_3^-\text{Na}^+$ pendant ionic group is common in both of the SPMANa and SSNa ionomers, but the distances of the ionic groups from the backbone chains are different in both the ionomers. In SPMANa ionomers, the $-\text{SO}_3^-\text{Na}^+$ pendant ionic groups are attached to the backbone chain through alkyl chains of four number of the carbon atoms, while in the SSNa ionomers, these ionic groups are attached at para position of the benzene ring. Because of the farther distance of the $-\text{SO}_3^-\text{Na}^+$ pendant ionic groups in SPMANa ionomers as compared to the SSNa ionomers, the size of the multiplets will be higher in SPMANa ionomer than that of the SSNa ionomer at particular ion content, and hence, the volume of the clustered regions in SPMANa ionomer will be relatively less than that of the SSNa ionomer. Thus, the results related to the ionic modulus are in full consistence with the reasons mentioned above. As mentioned earlier in this paragraph, the T_{gc} for the SPMANa ionomers is also close but less than that of the SSNa ionomer at particular ion content. It will be worth reminding that the T_{gc} is associated mainly with the strength of the interaction between the pendant ion (e.g., in this case, $-\text{SO}_3^-$ ion) and associated neutralizing ion (e.g., in this case, $-\text{Na}^+$ ion), and between the adjacent ion-pairs (e.g., in this case, $-\text{SO}_3^-\text{Na}^+$) in the ionomers [2,27,28,31-38]. The T_{gc} is also partly related with the distance of the ion-pairs from the backbone chain, bulkiness and the flexibility of the chain segment directly attached with the ion-pairs [31-38]. As the pendent ion-pairs are same in both the ionomers, then the strength of the interaction between the cation and anion in both the ionomers will be same, and hence, the T_{gc} should be the same in this respect. As this is not the case here, then now, it is the turn of the flexibility of the backbone chain segments attached with the pendent ion-pairs that may be responsible for the difference in the T_{gc} in both the ionomers. In

SSNa ionomers, the bulkiness of the benzene ring and closeness of the ion-pairs from the main backbone chains, will lead the ion-pairs less mobile to ion hopping (the process of inter-multiplets ion pair exchange, or movement of the ion-pairs into and out of the multiplets) [31-38]. Thus, the T_{gc} will be higher in SSNa ionomers than that of the SPMANa ionomers in which the ion-pairs are attached with long and flexible alkyl chains and are placed farther from the backbone chains. The reasons for the highest ionic modulus, but the lowest T_{gc} for the MANa ionomer among all the three ionomers in this study can easily be understood in the light of the discussion presented above.

From Fig. 4, we came to know that with increasing the ion content of the SPMANa ionomers, the height of the cluster loss tangent peaks increases, surprisingly; there is no considerable change in the T_{gc} . Currently, it is not easy for us to speculate the reasons behind this observation just by analyzing the results obtained from the dynamic mechanical properties measurements. In order to get the detailed insight into the morphology of these ionomers, we have to get the X-ray diffraction (XRD) and small angle X-ray scattering (SAXS) results. This will be a part of future study.

4. Conclusions

For the first time, we have synthesized new polystyrene based ionomers namely poly(styrene-*co*-3-sulfopropyle sodium methacrylate) SPMANa. Their properties were studied using dynamic mechanical thermal analyzer (DMTA). On increasing the ion content, the ionic modulus and the matrix T_g increased, while, the cluster T_g remained almost constant. On comparing the mechanical properties of these ionomers with poly(styrene-*co*-sodium styrenesulfonate) SSNa and poly(styrene-*co*-sodium methacrylate) MANa ionomers at particular ion content, the ionic modulus of SPMANa ionomer was found to be lower than those of the SSNa and MANa systems, but was more close to the SSNa system. The matrix

T_g was similar, while, the cluster T_g seemed to be the intermediate of the SSNa and MANa systems. Thus, we concluded that the mechanical properties of SPMANa ionomers seemed to be the intermediate of sulfonated and methacrylate polystyrene ionomer systems, but show more resemblance to the sulfonated system.

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CONCLUSIONS

This thesis presented studies related to the relationship between the architecture-morphology and properties of polystyrene-based amorphous, random ionomers using DMTA, SAXS, XRD and DSC techniques.

After the Introduction about the ionomers in chapter 1, the dynamic mechanical and morphological studies of polystyrene-based ionomer blends having aliphatic dicarboxylic acid salts have been discussed in the second chapter. It was found that, for most of the ionomer systems, it was mainly the amounts of the additives rather than the nature of the ionomer chains, nature of the ionic groups of the ionomers and additives, the nature of the additives, e.g. functionality, aliphatic or aromatic, short or long chains, which was responsible for the increase in the modulus of the ionomers, provided that the additives have tendency to phase-separate even at low weight concentrations in the ionomers.

In chapter third, the effects of the type of the cations on the dynamic mechanical properties of lightly sulfonated polystyrene ionomer blends with salts of dicarboxylic acids, neutralized with barium and cobalt cations were described. It was suggested that the organic salts acted mainly as fillers in divalent systems, while in the mono-valent systems, the organic salts acted both as fillers and as fillers-cum-plasticizers. In addition, rate of the ionic modulus values were almost independent of the type of the cations and number of the carbon atoms of the organic salts.

In fourth chapter, the effects of the amphiphilic diamines on the dynamic mechanical and morphological studies on sulfonated polystyrene ionomers were analyzed. It was concluded that the incorporation of the diamines led to a significant decrease in the cluster T_g , while the matrix T_g was almost unaffected. It was also observed that on one hand, at low ion contents of the ionomer, the

addition of diamines induced the clustering leading to a slight increase in the ionic modulus. On the other hand, at high ion contents, the diamines disrupted the multiplets of the ionomers leading to a decrease in the ionic modulus. In addition, it was suggested that the properties of the ionomer systems were related with the number of the carbon atoms, and that the diamines acted as neutralizing agent-cum-ionic domain plasticizers.

The processing of the sulfonated polystyrene ionomers is a tough job due to the occurrence of the flow of the materials at high temperatures. For reducing the processing temperature without getting significantly adverse effects on the mechanical properties of the sulfonated ionomers, long alkyl chains having sulfonate group at the chain end in one of the monomers may be used as typical and simple internal plasticizer. Thus, we have synthesized, for the first time, a new polystyrene-based ionomers namely poly(styrene-*co*-3-sulfopropyle methacrylate), and studied their properties dynamic mechanically. It was concluded that the mechanical properties of this ionomer seemed to be the intermediate of sulfonated and methacrylate ionomer systems, but show more resemblance to the sulfonated system.

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학 과	고분자공학과	학 번	20057819	과 정	박사
성 명	한글 : 모하메드 루크만 한문 : 영문 : Mohammad Luqman				
주 소	광주광역시 동구 서석동 조선대학교 공과대학2호관 4221호				
연락처	luqman_ionomers@yahoo.com , 010-5805-0045				
논문제목	한글 : 유기첨가제를 함유한 스타이렌 아이오노머의 동적·기계적 성질과 형태학 영문 : Dynamic mechanical Properties and morphology of organic additives-containing styrene ionomers				

본인이 저작한 위의 저작물에 대하여 다음과 같은 조건아래 -조선대학교가 저작물을 이용할 수 있도록 허락하고 동의합니다.

- 다 음 -

1. 저작물의 DB구축 및 인터넷을 포함한 정보통신망에의 공개를 위한 저작물의 복제, 기억장치에의 저장, 전송 등을 허락함
2. 위의 목적을 위하여 필요한 범위 내에서의 편집·형식상의 변경을 허락함.
다만, 저작물의 내용변경은 금지함.
3. 배포·전송된 저작물의 영리적 목적을 위한 복제, 저장, 전송 등은 금지함.
4. 저작물에 대한 이용기간은 5년으로 하고, 기간종료 3개월 이내에 별도의 의사표시가 없을 경우에는 저작물의 이용기간을 계속 연장함.
5. 해당 저작물의 저작권을 타인에게 양도하거나 또는 출판을 허락을 하였을 경우에는 1개월 이내에 대학에 이를 통보함.
6. 조선대학교는 저작물의 이용허락 이후 해당 저작물로 인하여 발생하는 타인에 의한 권리 침해에 대하여 일체의 법적 책임을 지지 않음
7. 소속대학의 협정기관에 저작물의 제공 및 인터넷 등 정보통신망을 이용한 저작물의 전송·출력을 허락함.

동의여부 : 동의(O) 조건부 동의() 반대()

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저작자: 모하메드 루크만 (서명 또는 인)

조선대학교 총장 귀하