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Structure–Property Comparison of Sulfonated and Carboxylated Telechelic Ionomers Based on Polyisoprene

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ABSTRACT: The structure and properties of polyisoprene-based telechelic ionomers having neutralized terminal sulfonate and carboxylate groups have been compared. In general, the mechanical properties of these materials suggest that metal sulfonates form stronger aggregates than the aggregates formed by metal carboxylates. This agrees with the results of previous workers who made similar comparisons for randomly substituted ionomers. Small-angle X-ray scattering data indicate that the periodic spacings between metal sulfonate aggregates are consistently higher than for the carboxylate ionomers, suggesting that the metal sulfonate aggregates may contain more ion pairs per aggregate than the metal carboxylate aggregates. The phase boundary between the ionic and nonionic regions is very sharp for both sulfonate and carboxylate ionomers.

Introduction

The utilization of ionic interactions in polymers has attracted widespread interest since it provides an additional means of controlling polymer structure and properties. One general class of ion containing polymers is known as "ionomers" which typically contain less than 15 mol % of ionizable groups. There have been many theories and models proposed to elucidate the microstructure of these systems;[1–7] however, an acceptance of any generalized theory or model has not yet been reached. Much of the earlier work has been conducted on ionomers where the ionic groups are located randomly along the polymer backbone. This uncertainty regarding the placement of the ions may be partially responsible for the controversy surrounding the nature of ion aggregation. Of particular interest to the present study are those ionomers where the placement of the ionizable groups is well defined—these being the telechelic ionomers. Here, the ionic groups are located only at the chain ends. This facilitates the task of correlating their bulk behavior to the observed structural and morphological features.

For conventional random ionomers, there have been a number of studies published in the literature dealing with carboxylate ionomers[8–10] and sulfonate ionomers.[11,12] Very few studies have attempted to make a direct comparison between the ionomers having an identical backbone and ion content but different functionalized acid groups. The best examples are the work of Lundberg and Makowski,[13] Visser and Cooper,[14] and Clas and Eisenberg.[15] In the work of Lundberg and Makowski comparing sodium carboxylated and sodium sulfonated polystyrene ionomers, it was shown that the sulfonate ionomers associate more strongly than the analogous carboxylated systems. The stronger association has been attributed to the greater polarization present in the sulfonate groups relative to the carboxylates. Therefore, the "softening point" of the sulfonate ionomer is about 50–100 °C above that of the corresponding carboxylated ionomer. In addition, the melt viscosities of the sulfonate ionomers at a given level of functionality and temperature are about 2–3 orders of magnitude greater than the carboxylated analogs. One of the limitations of these studies was that the placement of the ionic groups was not known (random). The purpose of this publication is to make a comparison between the performance of carboxylated and sulfonated ionomers in a well-defined network microstructure. The comparison has been made in terms of mechanical, thermal, and morphological properties for the two types of ionomers having identical polyisoprene (PIP) backbones and neutralized with different cations. As will be shown, the general observations are in good agreement with the earlier studies.[13–15] The effect of different cations on the ionomer properties will be discussed first followed by a comparison of the behavior of the two types of ionomers.

Experimental Section

Synthesis. Telechelic polymers were prepared by anionic polymerization. Pure and carefully dried monomers and solvents were used. Polymerization was performed in previously flamed and nitrogen-purged flasks equipped with rubber septums. Hypodermic syringes and stainless steel capillaries were used to handle liquid products under a nitrogen atmosphere.

Tetrahydrofuran (THF; pure grade) was dried by refluxing over benzophenone–sodium and distilled under a nitrogen atmosphere. α-Methylstyrene and isoprene (pure grade) were dried over CaH_2 at room temperature and distilled under reduced pressure just before use. Isoprene was mixed with *n*-BuLi and again distilled before polymerization. The commercially available propane sulfone (PS) was first boiled under reduced pressure for ca. 10 min in order to eliminate water by reaction with PS and formation of the related hydroxysulfonic acid. PS was then separated from that byproduct by distillation (120 °C/1 mmHg). A solution of 20% of the pure PS was prepared in dry THF.

The anionic polymerization of isoprene was carried out in THF at 200 K. α-Methylstyrene sodium tetramer was used as a difunctional initiator. The molecular weight of the final polymer was controlled by the monomer conversion (usually complete). After a 1-h polymerization time, the living macrodianions were deactivated by anhydrous CO_2. The resulting Na carboxylate end groups were converted to carboxylic acids by the addition of HCl. In order to prepare sulfonic acid terminated polyisoprene, the living macrodianions at 200 K were first added to a

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dilute solution of α-methylstyrene in dry THF in such a ratio that each chain extremity was capped with an average of two α-methylstyrene units. The solution of PS was then added to the polymerization flask in order to provide the sodium sulfonate end groups. Perchloric acid was finally added so that the sulfonic acid end groups were generated. Telechelic polymers were recovered by repeated precipitation into methanol (at least three times). Due to the instability of the sulfonic acid end groups under anhydrous conditions, the related telechelic polyisoprene was never dried until the acid end groups were neutralized.

Titration of the acid end groups was carried out as follows: A part of the telechelic polyisoprene was dissolved in a toluene/methanol mixture (90/10 v/v). The polymer concentration of that solution was determined by withdrawing a well-known volume, letting the solvent evaporate, drying the polymer to constant weight, and then weighing it. Another known volume of the polymer solution was titrated by a standard solution of tetramethylammonium hydroxide in the same solvent mixture. From the titration data and the molecular weight determined by vapor pressure osmometry, the functionality was calculated and considered to be acceptable when at least equal to 90%.

Carboxylic acid end groups were neutralized by metal alkoxides as reported elsewhere.[16] Sulfonic acid end groups were neutralized in nonanhydrous toluene by adding the stoichiometric amount of a metal acetate. The acetic acid byproduct was removed by repeated azeotropic distillation of the solvent. Finally, approximately 1 wt % of the antioxidant Irganox 1010 was added to prevent the oxidative cross-linking of polyisoprene.

Characterization. Film Preparation. The PIP carboxylated ionomer samples were compression molded between 120 and 130 °C for 2 min to form films from which samples were cut for further testing. The sulfonated ionomers were molded at higher temperatures (a 20 °C higher temperature was required for the sulfonated material relative to that of the carboxylated ionomer). Also, for materials with greater than stoichiometric amounts of neutralizing agent, slightly higher temperatures and/or molding times were needed to obtain a uniform film.

Mechanical Properties. The tensile studies were conducted using an Instron Model 1122 instrument. Dog-bone samples measuring 10 mm in length (gauge) and 2.8 mm in width were tested at an initial strain rate of 20 mm/min. Young's modulus was calculated from the initial portion of the load-time profiles. The load-time profiles were digitized to obtain the stress-strain (or elongation) curves for the different materials.

Stress relaxation experiments were carried out on a Tensilon Model UTM-II (Toyo Measuring Co.) instrument due to its the excellent stability over long periods of time. Samples were strained at 400%/min to 25%, and the stress was monitored as a function of time at 23 ± 3 °C.

The creep experiments were conducted at room temperature by applying a specified load and monitoring the sample displacement as a function of time using a LVDT (linear voltage displacement transducer). The tensile creep compliance, $D(t)$, was calculated from these data.

Thermal Analysis. Thermomechanical analysis (TMA) was performed using a Perkin-Elmer TMS-2 instrument. The samples were scanned in the temperature range from −100 °C until softening (up to 200 °C) at a heating rate of 10 °C/min, and the penetration of the probe under a 10-g load was monitored. TMA experiments were performed under a nitrogen atmosphere.

X-ray Scattering. The small-angle X-ray scattering (SAXS) experiments were conducted on an automated Kratky slit collimated camera. The primary X-ray source was obtained from a Philips PW1316/91 Cu tube operated at 40 kV and 20 mA by a Philips generator PW1729. Cu Kα radiation with a wavelength of 1.542 Å was obtained from a copper target after nickel-foil filtering. The scattered intensity was monitored by a one-dimensional position-sensitive detector (M. Braun—Innovative Technology Inc.).

Results and Discussion

Mechanical Properties. It is known from electrostatics that the force of attraction, F, between an anion of charge e_a and a cation of charge e_c is directly proportional to the product of these charges and is inversely proportional to both the dielectric constant of the medium, ϵ, and the square of the distance of separation, a, between their centers of charge, i.e.

$$F = (1/\epsilon)(e_a e_c/a^2) \quad (1)$$

With the assumption that a primarily electrostatic or ionic interaction is present, it is apparent that the two variables of importance are the size (i.e., the radius of the cation which determines size) and the valence of the cation. The force of attraction should, therefore, increase with increasing valence and decreasing size of the cation.

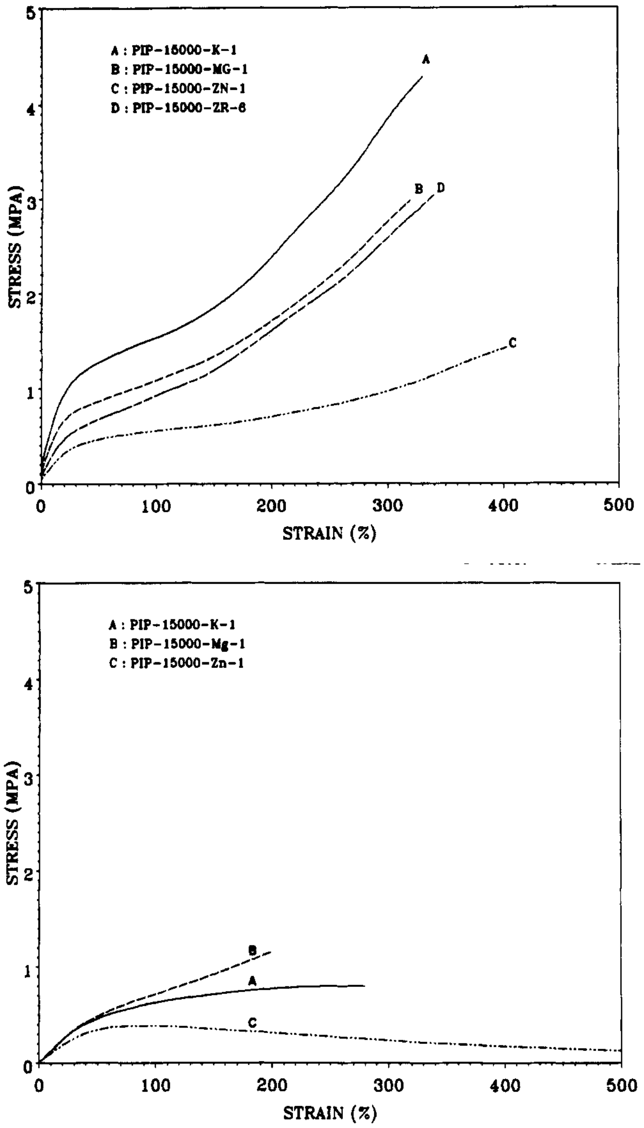

Figure 1. Stress strain curves for the 15 000 $\bar{M}_n$ PIP telechelic ionomers (experiments conducted at 23 °C): (a, top) sulfonated ionomers; (b, bottom) carboxylated ionomers.

The stress-strain profiles of the telechelic 15 000 $\bar{M}_n$ sulfonated ionomers and that of the carboxylated ionomers which have been neutralized with different cations are shown in Figure 1a,b, respectively. All the ionomers shown in Figure 1 have been neutralized to the stoichiometric amount with the exception of the Zr^{4+} ionomer. In this case 6 times the stoichiometric amount was utilized. It has been estimated by Jérôme and Broze[17] that at least one Zr^{4+} alkoxide per chain end is necessary for complete neutralization. Comparing the effect of the various cations on the stress-strain behavior of the sulfonated ionomers, shows that the K^+ ionomer exhibits the highest stress at a given strain followed by the Mg^{2+}, Zr^{4+}, and Zn^{2+} ionomers, respectively. From eq 1, it is expected that the attractive forces within the Mg^{2+} (0.65 Å) ionic domains would be larger than in the K^+ (1.33 Å) ionic domains, due to both a higher valence and smaller ionic radius (hence smaller a). Therefore, it is speculated that the Mg^{2+} ions may aggregate to form smaller domains than the K^+ ions. For example, when two chain ends interact, two K^+ counterions would be involved in the association but only one Mg^{2+} ion is needed for bridging the two ends. Furthermore, the ionic radius of a Mg^{2+} ion is smaller than that of the K^+ ion which potentially leads to a smaller domain being formed. At shorter time scales (as in the stress-strain experiments) these larger ionic aggregates may act as reinforcing fillers which are then at least partially responsible for the higher stress at a given strain (at least in those systems where effects of chain entanglements do not dominate). For longer experimental time scales (such as in stress relaxation and creep tests) the smaller Mg^{2+} ionic aggregates are more stable because of the greater mutual attractive forces existing within these aggregates. This greater network stability is indeed reflected in the observed behavior of the Mg^{2+} ionomers from both creep and stress relaxation experiments, as will be presented later. Returning to Figure 1a,b, the Zn^{2+} ionomers exhibit the lowest stress at a given strain of all the four cations studied. It is believed that this is primarily due to the coordination tendency of Zn^{2+} which results in a weaker mutual association of the ions in the ionic domains. The Zr^{4+} ionomer, however, exhibits a higher stress at a given strain than the Zn^{2+} ionomer; this may be due to the higher functionality of the Zr^{4+} ionomer that produces a more stable network structure than the Zn^{2+} ionomer. Also, the excess neutralizing agent not only ensures complete neutralization of the acid groups, but these excess ions also tend to aggregate near the ionic domains, enhancing the overall coulombic forces of attraction within the ionic domains.[18]

To note the effect of the functionalized acid groups, a comparison can also be made between the performance of the sulfonated ionomers and the carboxylated ionomers that had been neutralized with the same cations (K^+, Mg^{2+}, and Zn^{2+}). All the carboxylated materials exhibit a lower stress at a given strain than their sulfonated counterpart (compare parts a and b of Figure 1). The observed behavior clearly indicates that the sulfonated ionomers tend to associate more strongly than the carboxylated systems. This is in good agreement with the results obtained by Lundberg et al.[13] for the randomly sulfonated or carboxylated polystyrene ionomers neutralized with sodium.

Figures 2A,B and 3A,B show the tensile creep and stress relaxation response of both the sulfonated and carboxylated ionomers, respectively. From the tensile creep response (Figure 2A,B), the carboxylated ionomers displayed a strong tendency to flow in the time interval between 10 and 1000 min. However, for the sulfonated ionomers, only the material neutralized with Zn^{2+} displayed a comparably strong tendency to flow within this time interval. The other three sulfonated materials displayed, in general, distinctly less flow behavior. The greater network stability of the sulfonated ionomers was also evident from the stress relaxation curves (Figure 3A) where the sulfonated materials maintained a significant amount of the stress over the entire time interval investigated (see Figure 3B). The carboxylated ionomer, however, relaxes considerably within this same time interval. The results from both the tensile creep and the stress relaxation measurements support the earlier conclusion that the sulfonated ionomers associate more strongly, providing a more stable network structure than the carboxylated ionomers.

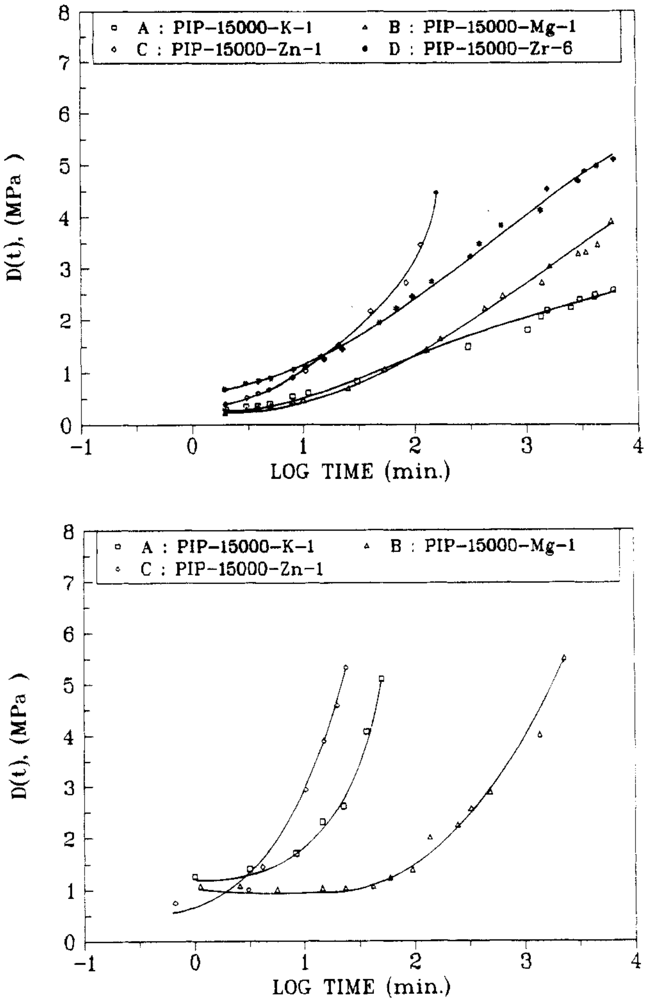

Figure 2. Tensile creep curves for the 15 000 $\bar{M}_n$ PIP telechelic ionomers (experiments conducted at 23 °C): (a, top) sulfonated ionomers; (b, bottom) carboxylated ionomers.

As shown by Lundberg et al.,[13] the softening temperatures for the sulfonated ionomers are expected to be shifted to higher temperatures due to the stronger association of the sulfonate groups. The thermomechanical behavior of both the sulfonated and carboxylated ionomers neutralized with K^+ and Mg^{2+} are shown in Figure 4. Complete penetration of the sulfonated ionomer neutralized with K^+ (curve B in Figure 4) occurs nearly 60 °C higher than the corresponding carboxylated ionomer (curve A). Also, a rubbery plateau extending for over 80 °C is observed for the sulfonated ionomer, while it is absent in the carboxylated ionomer. A short rubbery plateau is observed for both the carboxylated and sulfonated ionomers neutralized with Mg^{2+}. This behavior is again consistent with the earlier conclusion that sulfonated ionomers associate more strongly than their carboxylated analogs. What is somewhat surprising is that the carboxylate neutralized with potassium shows flow even sooner than either the carboxylate or sulfonated materials neutralized with magnesium and the magnesium systems undergo a flow nearly of the same temperature. This behavior is difficult to easily account for, but it is in line with the stress-strain results which show the same general ranking in terms of tensile strength (at ambient temperature). Further work, however, is needed regarding the temperature sensitivity of ion pair (or cluster) formation in order to fully understand the flow data behavior in Figure 4.

Small-Angle X-ray Scattering (SAXS) Behavior. Small-angle X-ray scattering (SAXS) is a powerful tech-

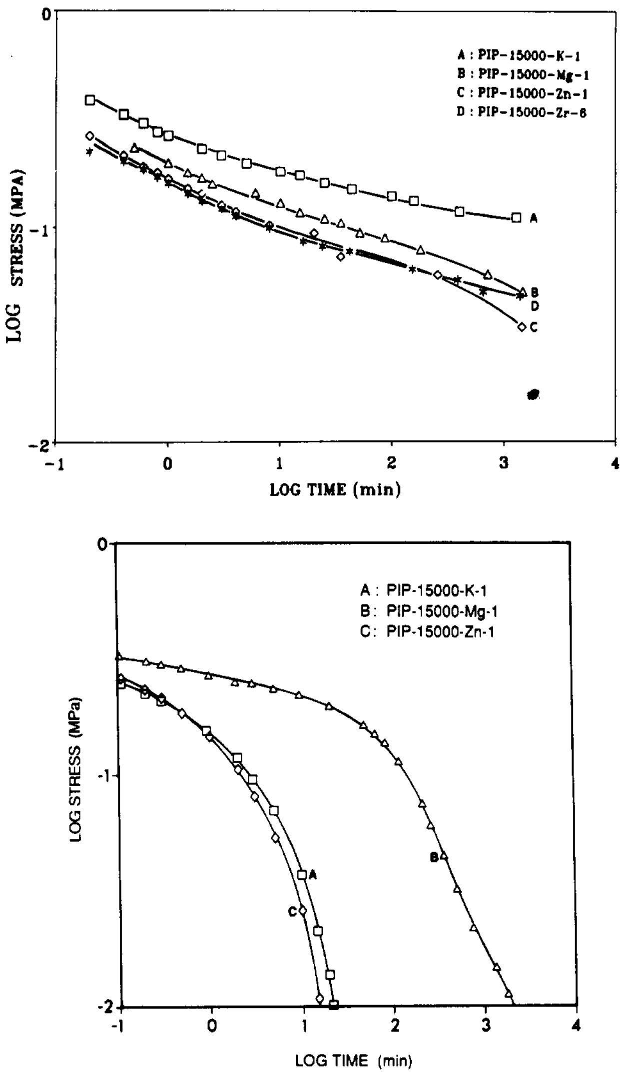

Figure 3. Stress-relaxation curves for the 15 000 $\bar{M}_n$ PIP telechelic ionomers (experiments conducted at 23 °C): (a, top) sulfonated ionomers; (b, bottom) carboxylated ionomers.

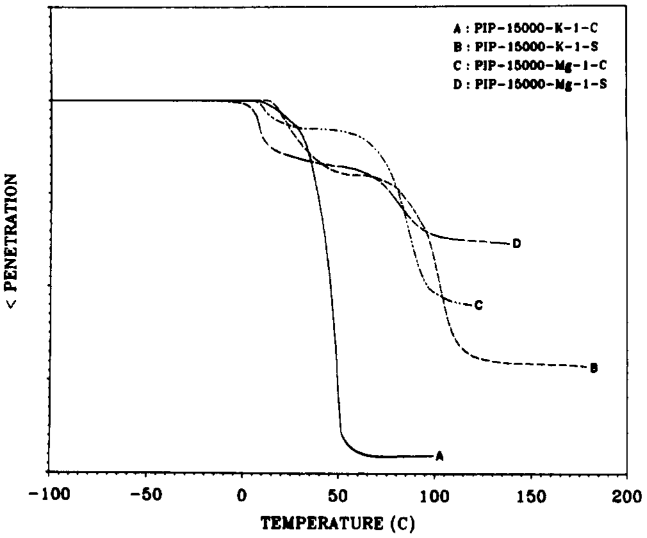

Figure 4. Thermomechanical behavior of PIP-15000-M-X ionomers. S represents sulfonated ionomers while C represents carboxylated ionomers. Only the behavior of the potassium (K) and magnesium (Mg) ionomers are shown.

nique which provides information regarding the morphology of the system based on the differences in the local electron density. For a two-phase system, scattering theory has been well developed and has been discussed in detail elsewhere.[19-22] It has been proposed that there are essentially two principal types of environments existing in ionomers, namely, ionic domains and the nonpolar matrix. The difference in the electron density between the two environments provides the contrast necessary for X-ray scattering. Any possible free ions, if distributed randomly in the matrix, would tend to increase the electron density of the matrix and thus decrease contrast between the two phases. Indeed, SAXS has been routinely applied to obtain information regarding the periodic spacing between regions of similar electron density as well as the nature of phase separation of the dispersed phase (ionic domains in the present study).

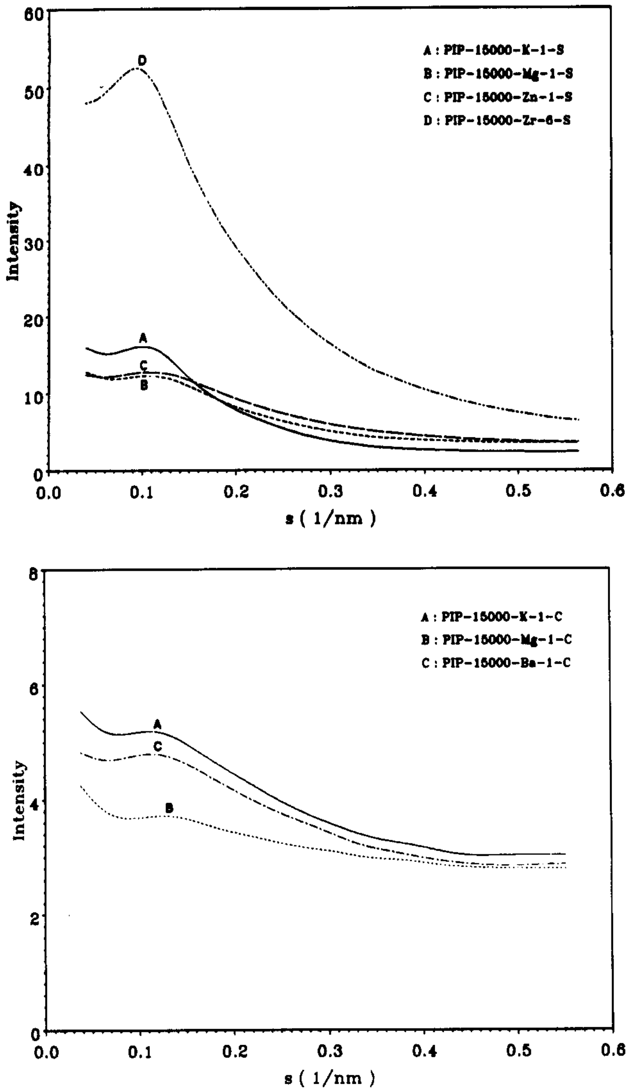

Figure 5. Smeared SAXS profiles for the 15 000 $\bar{M}_n$ PIP telechelic ionomers: (a, top) sulfonated (s) ionomers; (b, bottom) carboxylated ionomers (c).

The smeared small-angle X-ray scattering profiles of 15 000 $\bar{M}_n$ sulfonated and the carboxylated ionomers are shown in Figure 5A,B. The parameter $\tilde{I}(s)$ represents the smeared slit scattered intensity, and it is plotted against the angular variable s where s is defined as $(2 \sin \theta)/\lambda$ where λ is the wavelength (1.54 Å) and θ is half the radical scattering angle. A distinct "ionic peak" is observed for all the ionomers irrespective of the nature of the acid groups. The nature of the cation has very little effect on the periodic (or the d) spacing between the ionic domains in either the sulfonated or the carboxylated ionomers (ca. 7.2–8.7 nm for the sulfonated ionomers and between 6.9 and 7.6 nm for the carboxylated ionomers). Table I provides the period distances (interdomain or d spacing) for the 15 000 $\bar{M}_n$ carboxylated and the sulfonated tele-

Table I
Periodic Spacing between the Ionic Domains in 15 000 M_n PIP

sample	periodic spacing between the ionic domains (nm)		
	d_{smeared}	$d_{\text{desmeared}}$	γ_3(D)[a]
PIP-15000-K-1-S	9.5	8.2	8.9
PIP-15000-Mg-1-S	8.8	7.6	8.8
PIP-15000-Zn-1-S	8.4	7.2	8.8
PIP-15000-Zr-1-S	10.4	8.7	8.9
PIP-15000-K-1-C	8.5	7.4	*b*
PIP-15000-Mg-1-C	7.1	6.9	*b*
PIP-15000-Ba-1-C	7.9	7.6	*b*

[a] γ_3(D) represent the spacings estimated from the maximum in the three-dimensional correlation function obtained by a Fourier inversion of the SAXS profile. [b] Not available.

Table II
Diffuse Boundary Thickness Values Estimated Utilizing Different Interfacial Analysis[a]

sample	interfacial thickness values, σ (nm)			
	Bonart	exponential	Koberstein	Ruland
PIP-1500-K-1-S	0.11	0.07	0.07	0.07
PIP-15000-Mg-1-S	0.03	0.02	0.02	0.02
PIP-15000-Zn-1-S	0.06	0.05	0.05	0.05
PIP-15000-Zr-6-S	0.08	0.05	0.06	0.05
PIP-15000-K-1-C	0.14	0.09	0.10	0.06
PIP-15000-Mg-1-C	0.17	0.10	0.11	
PIP-15000-Ba-1-C		0.02	0.02	

[a] Methods for the 15 000 $\bar{M}_n$ carboxylated and sulfonated ionomers.

chelic ionomers. The spacings were obtained by a desmearing procedure and also from the analysis of the three-dimensional (3D) correlation functions. In the sulfonated ionomers, the K^+ and the Zr^{4+} ionomers have a slightly larger spacing. Although the relative sizes of the different aggregates are not known, the K^+ and the Zr^{4+} ionomers might form larger aggregates. This would necessarily lead to a longer interdomain spacing. However, we have no data to support a difference in domain size and thus this is merely speculation.

From Table I, it is noticed that the *d* spacings obtained for the sulfonated ionomers are consistently larger (ca. 11%) than those of the corresponding carboxylated ionomers when all other structural parameters are the same. Fontaine et al.[23] and Ledent et al.[24] have also observed a similar trend in a related series of telechelic ionomers. This suggests that the supermolecular morphology of the sulfonated ionomers may be somewhat inherently different from the carboxylated ionomers. However, this would not be unexpected since, as mentioned in the synthesis procedure, the sulfonated ionomers are end capped with an average of two units of α-methylstyrene. These units are fairly rigid when compared to the isoprene backbone and hence might contribute to a slightly partial extension of the polymer backbone or promote a slightly larger domain. This is tentatively speculated to be the cause of the slightly larger value of *d* for the sulfonated ionomers compared to the carboxylated ionomers.

Diffuse Boundary Analysis. The estimation of the diffuse boundary thickness was made in terms of the Porod law behavior. For an ideal two-phase system with sharp phase boundaries, Porod's law states that the scattered intensity decreases with the fourth power of the scattering vector *s* for a pinhole collimated system (or with the third power of *s* for a slit collimated system) at large *s* values. For a slit collimated system, however, a plot of $\tilde{I}(s)*s^3$ vs s^3 provides information regarding the nature of the phase boundary. For an ideal two-phase system (sharp phase boundary) the slope of the plot in the tail region is zero. For real systems, however, deviation from this ideal behavior is frequently encountered. A negative slope in the tail region is indicative of the presence of a diffuse phase boundary while a positive slope often indicates isolated mixing of one component in the other. Further details regarding the diffuse boundary analysis utilizing the methods of Bonart, Koberstein, and Ruland can be found elsewhere and will not be reviewed here.[20-22,25]

From our SAXS analysis, a near-ideal behavior is exhibited as was the case for all the ionomers investigated in this study. It was found that the interfacial or diffuse boundary thickness value for both the carboxylated and the sulfonated ionomers is <0.1 nm for all the materials studied, and this value is within the limits of experimental accuracy. This suggests that the interfacial region between the ionic and the organic phase is indeed very sharp and that very few ionic moieties are dissolved in the nonionic matrix, at least in the interfacial boundary region. This result is quite similar to that obtained on carboxylated telechelic ionomers.[26] Table II lists the interfacial or the diffuse boundary thickness values estimated from the different approaches. It appears that the coulombic forces within the ionic domains prevent any significant interfacial mixing between the polar ionic domains and the nonpolar organic matrix.

Summary

The results obtained from this study clearly indicate that the sulfonated ionomers form much stronger associations than the corresponding carboxylated ionomers when the two types of ionomers are compared under conditions as similar as possible. This observation further supports the conclusions suggested previously by several workers[13-15] for randomly substituted ionomers. A distinct SAXS or ionic peak was observed for both the sulfonated and carboxylated ionomers for the 15 000 $\bar{M}_n$ PIP ionomers, but surprisingly, the periodic spacings obtained for the sulfonate ionomers were slightly but *consistently higher* than for the carboxylate ionomers. On the basis of the SAXS analysis, it has been shown that the phase boundary between the ionic phase and the nonionic matrix is very sharp irrespective of the nature of the functionalized acid groups. It is believed that the coulombic forces of interaction in the system prevent any significant mixing between the ionic domains and the nonionic matrix in the interfacial region.

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