Morphological Studies of a Triblock Copolymer Ionomer by Small Angle X-ray Scattering

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ABSTRACT: The block microstructure of a block copolymer ionomer, lightly sulfonated poly(*b*-styrene-*b*-(*r*-ethylene-*co*-*r*-butylene)-*b*-styrene) (S-SEBS), was investigated by small angle X-ray scattering. Sulfonation level was varied from 0 to 12 mol % of the polystyrene blocks and the sulfonic acid derivatives and Na and Zn salts were studied. Compression molded samples had a deformed spherical domain structure, and the extent of microphase separation was influenced by ionic aggregation that occurred in the sulfonated polystyrene domains. The extent of microphase separation decreased with increasing sulfonation level and with increasing strength of the ionic interactions, i.e., $Na^+ > Zn^{2+} > H^+$. Solution-cast samples exhibited a lamellar microstructure for the Zn salts and a spherical microstructure for the Na salts. Samples swollen with a paraffinic oil that plasticizes the rubber phase exhibited a spherical domain structure with a cubic arrangement of the domains. The development of microphase separation, however, decreased with increasing ionic strength of the ion dipoles.

Introduction

Various self-assembled microstructures occur in block copolymers as a result of microphase separation of thermodynamically immiscible constituent blocks. Typical microphase separated structures include spheres, cylinders, lamellae, and a bicontinuous double-diamond morphology.[1–3] The formation of these ordered microstructures is known to be affected by composition, interactions between the component blocks, sample preparation, and the addition of diluents or another homopolymer. A transition from an ordered microstructure to a disordered, homogeneous phase, called the order–disorder transition, is often observed at elevated temperature.[4]

Block copolymer ionomers, where one block is fully or partially ionized, have been the subject of recent studies in several laboratories directed especially at their morphology and physical properties.[5–9] For example, Gouin et al.[6] and Venkateshwaranet al.[7] investigated fully ionized block ionomers with small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM), and they found that the materials exhibited an ordered two-phase morphology, similar to that expected for a nonionic block copolymer. Weiss et al.,[8,9] however, reported a unique three-phase morphology for block copolymer ionomers of lightly sulfonated poly(*b*-styrene-*b*-(*r*-ethylene-*co*-*r*-butylene)-*b*-styrene), S-SEBS, that consisted of ionic microdomains distributed within polystyrene microdomains that were dispersed in a rubbery continuous matrix. The sizes of the two types of microdomains differed by an order of magnitude.

The introduction of blocks containing ion dipoles into a relatively nonpolar block copolymer significantly affects the thermodynamics and kinetics of the block microphase separation. On the one hand, ionization of one component of a block copolymer may increase the repulsive interactions between the ionic block and nonionic block, which promotes microphase separation and increases the temperature of the order–disorder transition, T_{od}. On the other hand, ionic aggregation within the ionic-block microdomain limits the diffusion of the ionic blocks, which may impede microphase separation and promote the formation of nonequilibrium block microstructures. The former effect is expected to dominate for fully ionized block copolymers, i.e., where nearly every repeat unit of the block contains an ion dipole,[6,7] and the latter effect should become more important for lightly ionized block copolymers. In a previous paper,[10] we described the morphology of the ionic microphase separation for a series of S-SEBS block copolymer ionomers. In this paper, we discuss the SAXS characterization of the block microstructure of S-SEBS as a function of the sulfonation level, counterion, and solvent and temperature histories.

Experimental Section

Materials. The SEBS used in this work was a hydrogenated triblock copolymer of styrene and butadiene, Kraton 1652, from Shell Development Co. After hydrogenation, the midblock is essentially a random copolymer of ethylene and butylene. The number average molecular weight, M_n, of the copolymer was 50 000 and the composition was 29.8 wt % styrene. Sulfonated SEBS block copolymer ionomers, S-SEBS, were prepared by sulfonation of the SEBS with acetyl sulfate in 1,2-dichloroethane at 50 °C.[8] The resulting styrenesulfonic acid groups were neutralized with a 10% excess of a metal hydroxide or acetate. The nomenclature used to identify the block copolymer ionomer samples was *x.yM*-S-SEBS, where *x.y* is the degree of sulfonation of the polystyrene blocks (i.e., mol % styrene sulfonated) and M is the counterion.

Two methods of sample preparation, solution casting and compression molding, were used to study the effect of sample history on the microstructure of the block ionomers. The solvents used for casting sample were tetrahydrofuran (THF) for the free-acid form of the ionomers and toluene/dimethylformamide (DMF) mixtures for the metal salt derivatives. Films were cast on glass at room temperature and were peeled off after air-drying for 24 h. Residual solvent was removed in a vacuum oven at 50 °C for 48 h. The compression molding conditions depended on the cation and sulfonation level, varying from 150 °C for 2 min at 2.5 MPa for the unsulfonated SEBS to 250 °C for 10 min at 75 MPa for some sodium salts.

Oil-extended compounds containing 50 parts polymer and 50 parts of Kaydol paraffinic oil were prepared by adding the oil directly to a crumb of the polymer and allowing it to diffuse into the polymer until a homogenous materials was obtained. The samples were compression molded at 130–160 °C.

SAXS Measurements. SAXS experiments were performed on beam line I-4 at the Stanford Synchrotron Radiation Lab-

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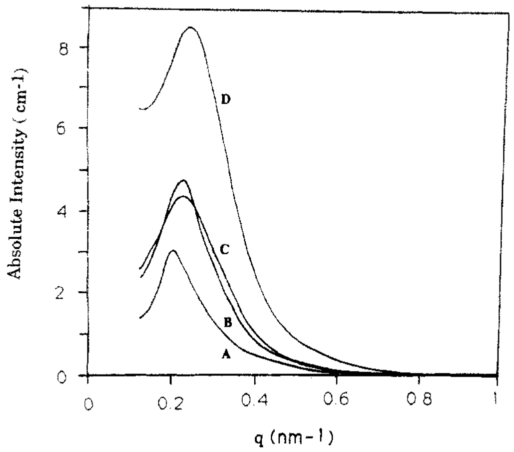

Figure 1. Effect of the counterion on the SAXS profiles for compression molded block copolymer ionomers: (A) SEBS; (B) 12H-S-SEBS; (C) 12Na-S-SEBS; (D) 12Zn-S-SEBS.

oratory (SSRL) and on beam line X3A2 at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratories. The sample-to-detector distance was varied to cover a q-range from 0.1 to 6.0 nm^{-1} at SSRL or 0.07–6.3 nm^{-1} at NSLS, where $q = 4\pi \sin \theta/\lambda$, 2θ is the scattering angle and λ was the X-ray wavelength ($\lambda_{SSRL} = 0.143$ nm and $\lambda_{NSLS} = 0.154$ nm). The data were corrected for dark current, detector homogeneity, parasitic and background scattering, and sample absorption. Details of the beamlines and data acquisition systems can be found elsewhere.[11,12]

Results and Discussion

The block copolymer ionomers exhibited two distinct microphase separated morphologies: (1) a block microstructure with a characteristic dimension of ca. 10–20 nm and (2) ionic aggregation of ca. 3–4 nm within the microdomains formed by the polystyrene blocks. Because the characteristic sizes of the two microstructures differed by an order of magnitude, they can be studied separately using two different SAXS geometries. Only the block microstructure is considered in this paper; the ionic microstructure was described elsewhere.[10]

Compression Molded Samples. Figure 1 shows the SAXS profiles of four compression molded samples: neat SEBS, 12H-S-SEBS, 12Zn-S-SEBS, and 12Na-S-SEBS. All the materials exhibited only a single intensity maximum. The Bragg-spacing associated with that peak represents the average separation, D_{AN}, between neighboring microdomains. Sulfonation of the PS block affected the intensity and the position of the scattering peak, and the magnitude of the changes depended on the counterion used.

The most notable change in Figure 1 was a stronger and broader scattering peak for the block copolymer ionomer compared with that for the unmodified SEBS. Two effects arising from ionic aggregation within the sulfonated PS phase may account for the peak broadening: (1) the ionic aggregates produce additional electron density fluctuations within the polystyrene block microdomains and (2) the hinderance of the block microphase separation due to longer relaxation times arising from the ionic aggregation may result in a broader distribution of the center to center distance between neighboring microdomains and a more diffuse interphase boundary. The higher intensity of the scattering peak for the ionomers is due to an enhancement of the electron density contrast between the rubber and the sulfonated PS phases. The observed variation of the peaks intensity with the counterion used, $I_{Na} < I_H < I_{Zn}$, however, was not consistent with the atomic weights of the counterions. That is, if the microstructures of the ionomers were equivalent, the intensity of the peak in the different materials should have increased as the atomic number of the cation was increased, i.e., $I_H < I_{Na} < I_{Zn}$. The deviation from the expected trend indicates that the choice of the counterion also affected the extent of block microphase separation in the block ionomers.

Table I. Q, Q_0, and K for Compression-Molded SEBS and Block Copolymer Ionomers

samples	Q (10^{-3})	Q_0 (10^{-3})	K
SEBS	0.47	1.1	0.43
12H-S-SEBS	0.71	1.9	0.37
12Zn-S-SEBS	1.05	3.7	0.28
9Zn-S-SEBS	0.89	2.9	0.31
5Zn-S-SEBS	0.69	2.0	0.35
12Na-S-SEBS	0.68	3.5	0.19
9Na-S-SEBS	0.59	2.7	0.22
5Na-S-SEBS	0.61	1.9	0.32

The extent of microphase separation can be calculated from the scattering invariant, Q, which for an ideal two-phase system with sharp interfaces is related to the mean square electron difference between the phases[13]

$$Q_0 = \phi_1\phi_2(\rho_1 - \rho_2)^2 V \tag{1}$$

where ϕ_i is the volume fraction of phase i with electron density ρ_i and V is the sample volume. The electron density of each microphase was estimated from the mass density of the corresponding component polymer.[13,14] For a *real* two-phase material, where there may be an interphase region and/or phase separation is not complete, Q may be calculated from SAXS data[15]

$$Q = \frac{1}{2\pi^2 I_e} \int_0^\infty q^2 I(q) \mathrm{d}q \tag{2}$$

where I_e is the Thomson scattering constant for an electron. The ratio, $K = Q/Q_0$, provides a quantitative measure of the extent of microphase-separation of the block copolymer.

The values of Q, Q_0, and K for different counterions and sulfonation levels are summarized in Table I. For a constant sulfonation level, e.g., 12M-S-SEBS, Q_0, increases in the order of H-S-SEBS < Na-S-SEBS < Zn-S-SEBS, but the values of K followed the order Na-S-SEBS < Zn-S-SEBS < H-S-SEBS. The order of the K values was, however, consistent with the relative strengths of the ion-dipole, which was found to vary as Na-S-SEBS > Zn-S-SEBS > H-S-SEBS.[10] It follows, that it becomes more difficult to develop microphase separation during compression molding as the intensity of the ionic associations in the melt becomes stronger. The high viscosity of the melt limits the kinetics of microphase separation, which is manifest here as a decrease in the extent of block microphase separation. For example, 12H-S-SEBS had the weakest ion–dipole interactions, but the largest K, while 12Na-S-SEBS exhibited the strongest ionic associations and the smallest K; see Table I. Also, K for a given cation, e.g., Zn-S-SEBS, decreased with increasing sulfonation level for the same reason, i.e., increasing melt viscosity.

The SAXS peak position was also affected by sulfonation of the PS block. The domain separation, D_{AN}, calculated from the peak position, decreased from 28.8 nm for SEBS to 25.8 nm for 12Na-S-SEBS, 25.8 nm for 12H-S-SEBS, and 24.7 nm for 12Zn-S-SEBS. D_{AN} is primarily governed by the chain dimension of the component blocks and the structure and arrangement of the microdomains. Sulfonation of the PS blocks is not expected to significantly affect the chain dimension of the component blocks,[10] but the structure and arrangement of the microdomains may

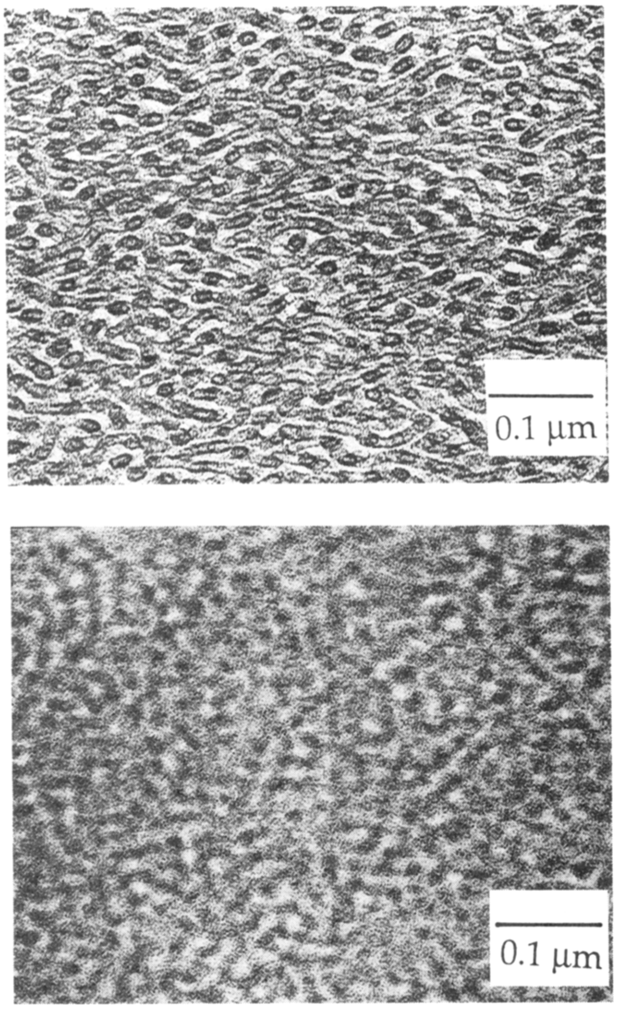

Figure 2. Transmission electron micrographs of (A, top) SEBS and (B, bottom) 12Zn-S-SEBS. Reprinted with permission from ref 9. Copyright 1991 Butterworth Publishers.

change as a result of the effects the strong associations of the sulfonate groups have on the kinetics of the block microphase separation process. This is especially expected to be the case for the compression molded samples, because of the effects of ionic association on the melt viscosity. In the absence of resolution of higher-order SAXS peaks, however, it is not possible to unambiguously identify the microstructure of the block copolymer by SAXS measurements alone.

TEM micrographs of the molded SEBS sample[8] stained by RuO_4, Figure 2A, revealed a two-phase morphology of 10–15 nm diameter PS microdomains (the dark phase) dispersed in a continuous EB rubber phase. The microstructure of the PS phase appeared to be intermediate between spherical and cylindrical, but without long range order. After sulfonation of the PS block, the dispersed phase microstructure appeared more like deformed spheres with a very diffuse phase boundary;[9] see Figure 2B. The average diameter of the dispersed sulfonated PS phase in 12Zn-S-SEBS was similar to that of the PS phase in SEBS, i.e., 10–15 nm. Therefore, although sulfonation modified the microstructure of a compression molded block copolymer, it did not appear to alter the dimensions of the PS chain.

The extent of block microphase separation was also influenced by the sulfonation level. Figure 3 shows the SAXS profiles for Na-S-SEBS samples with varying composition. The SAXS peak intensity and the scattering invariant decreased with increasing the sulfonation level.

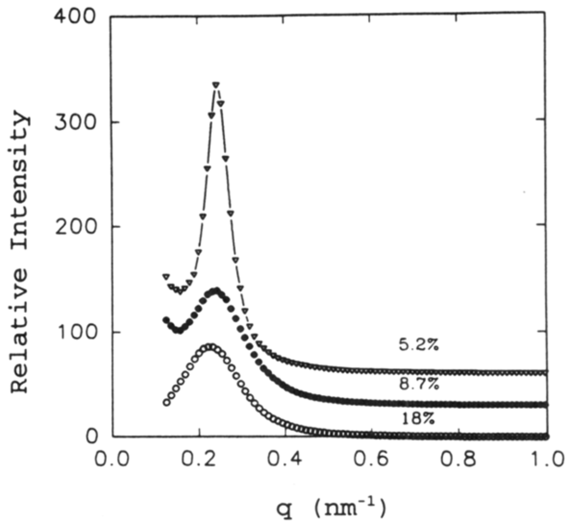

Figure 3. SAXS curves for compression molded Na-S-SEBS as a function of sulfonation level. (The curves are vertically displaced to improve clarity.)

This indicates a reduction in the extent of the block microphase separation; otherwise, one would have expected the electron density contrast between the two phases to increase as more sodium sulfonate groups were incorporated into the sulfonated polystyrene microphase. In a previous paper,[10] it was shown that ion–dipole associations in the Na-S-SEBS were thermally stable up to at least 250 °C, which was the temperature used to prepare the compression molded specimens used in this study. Therefore, one might expect that such strong ionic associations could significantly restrict the formation of a well-ordered block microstructure when the materials were compression molded.

The scattering maximum for the Na-S-SEBS samples also broadened as the sulfonation level increased. A relatively sharp scattering maximum was observed for 5.2-Na-S-SEBS, Figure 3, but the peak became increasingly broader for 8.7-Na-S-SEBS and 18-Na-S-SEBS, respectively. As stated earlier, the broadening of the scattering peak was the result of ionic aggregation that enhanced the electron density fluctuations in the sulfonated PS microdomains but which also favored a less ordered block microstructure in those samples. The concentration of ionic aggregates and the hindrance to development of a well-ordered microstructure increased with increasing sulfonation level, and accordingly, the SAXS peak broadened. In addition, the scattering vector associated with the maximum of the SAXS peak, q_{max}, decreased slightly with increasing sulfonation level, Figure 3, which suggests an increase in the interdomain spacing. An alternative interpretation of the change of q_{max} is that the texture of the block microstructure changed as the sulfonation level increased. Although the data in Figure 3 are insufficient to confirm that hypothesis, as will be discussed later in this paper, sulfonation did affect the microdomain texture for solution-cast specimens.

In contrast to the Na-S-SEBS data, the intensity of the SAXS maximum *increased* with increasing sulfonation level for the Zn-S-SEBS samples, see Figure 4, though as seen in Table I, the extent of microphase separation also decreased with increasing sulfonation for these ionomers. For a given sulfonation level, however, the development of the block microstructure was always greater for the zinc salt. Previous temperature-resolved SAXS studies of lightly sulfonated polystyrene[16] and S-SEBS[10] ionomers revealed that the ionic aggregates in the Zn salts were not

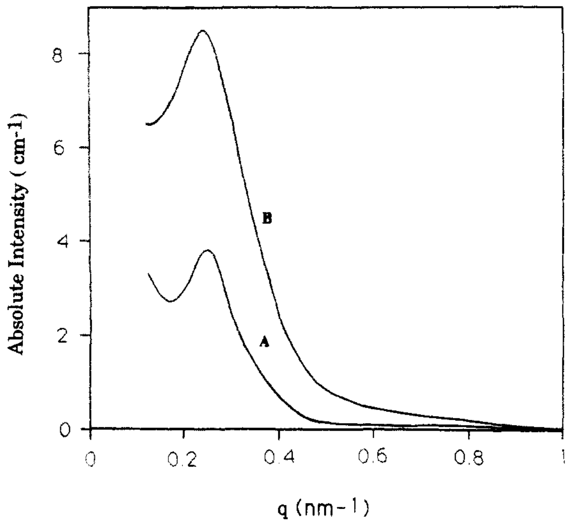

Figure 4. SAXS curves for compression molded block copolymer ionomers: (A) 5Zn-S-SEBS; (B) 12Zn-S-SEBS.

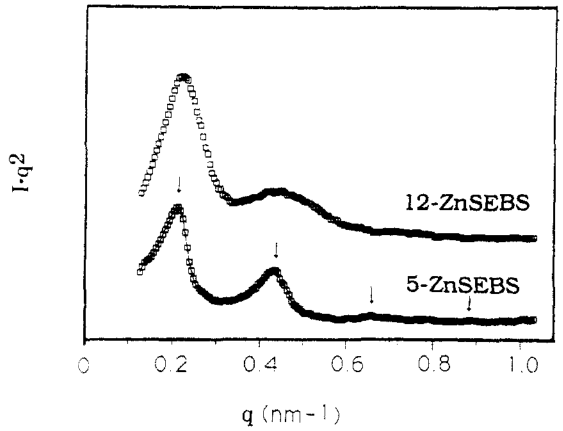

Figure 5. SAXS curves for solution-cast Zn-S-SEBS as a function of sulfonation level: (a) 5Zn-S-SEBS; (b) 12Zn-S-SEBS. (The curves were vertically displaced to improve clarity.)

as thermally stable as in the Na salts, and the extent of microphase separation of the ionic phase decreased with increasing temperature. Those results suggest that the influence of ionic associations at restraining self-assembly of the block microstructure at elevated temperatures, such as used for compression molding the block copolymer ionomer samples, should be less significant for the Zn-S-SEBS than for the Na-S-SEBS. That is consistent with the higher extent of block microphase separation found for the Zn salts, see Table I.

Solution-Cast Samples. It was expected that the increased molecular mobility of the block copolymer ionomer in solution would allow for the formation of a microstructure closer to equilibrium. Figure 5 shows the SAXS patterns in the block microstructure region for 5Zn-S-SEBS and 12Zn-S-SEBS cast from toluene/DMF solutions. Much more detail is seen in the scattering pattern compared with the corresponding molded samples; cf. Figure 4. Four SAXS maxima were resolved for the solution-case samples, which indicate more long-range order in spatial arrangement of the microdomains than in the compression molded samples, which exhibited a deformed spherical domain structure. The positions of the four scattering maxima in q-space corresponded to a ratio of 1:2:3:4, which corresponds to a lamellar microstructure.

The first-order maximum in the SAXS curves in Figure 5 is associated with the average distance between neighboring lamellae, D_{AN} which is calculated from Bragg's law

Table II. Lamella Microphase Structure Parameters for Solution Cast Zn-S-SEBS

samples	D_{NA} (nm)	L (nm)	Q (10^{-3} e-mol/cm^3)^2
SEBS	28.1	7.3	0.77
3Zn-S-SEBS	27.6	7.3	1.1
5Zn-S-SEBS	27.4	7.4	1.3
9Zn-S-SEBS	26.6	7.2	1.9
12Zn-S-SEBS	26.3	7.1	2.4

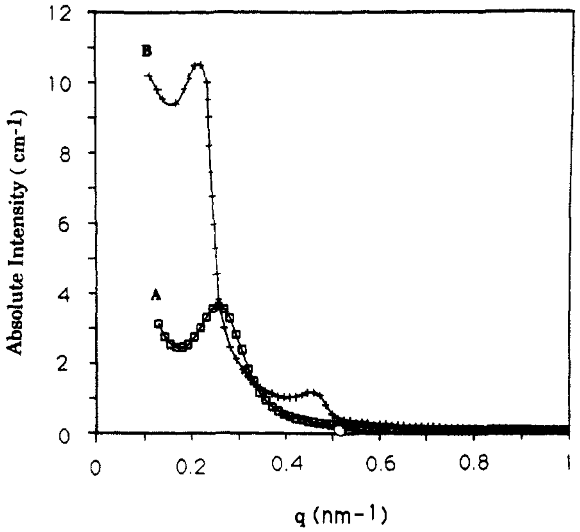

Figure 6. SAXS curves for 5Zn-S-SEBS: (A) compression-molded; (B) solution-cast.

$$D_{AN} = 2\pi/q \qquad (3)$$

The lamellar thickness L is given by

$$L = D_{AN}V_2 \qquad (4)$$

where V_2 is the volume fraction of the sulfonated block in the copolymer. The values of D_{AN} and L for different samples are listed in Table II; both D_{AN} and L were relatively insensitive to the sulfonation level.

The SAXS patterns for the solution-cast and compression-molded samples of 5-Zn-S-SEBS are compared in Figure 6. In addition to the different microstructures exhibited by the two samples, the scattering intensity and the invariant were much greater for the solution-cast specimen, which signifies that the extent of the block microphase separation was much higher for the solution cast sample. The K values, which denote the extent of the phase separation, are plotted against sulfonation level in Figure 7 for the solution cast and compression molded Zn salts. For the solution-cast samples, $K \sim 0.6–0.7$ and was almost independent of the sulfonation level, while for the compression-molded samples, K was almost 50% smaller, ~0.3–0.4, and decreased with increasing sulfonation of the block copolymer. The differences in the microstructures produced by the two different sample preparations may be attributed to the increased mobility of the chains in solution, especially when a polar cosolvent, such as DMF, was used. The polar cosolvent effectively solvates the ionic interactions, which were believed to be responsible for inhibiting the formation of a more ordered microstructure in the compression molded samples.

SAXS data of solution-cast Na-S-SEBS samples are shown in Figure 8. Unlike the data for the solution-cast Zn-S-SEBS samples, the Na-S-SEBS SAXS curves exhibited only a first-order scattering maximum, which indicates a lack of long-range order in the spatial arrangement of the block-microdomains in those materials. The less ordered microstructure in the Na-S-SEBS compared with Zn-S-SEBS probably reflects the poorer

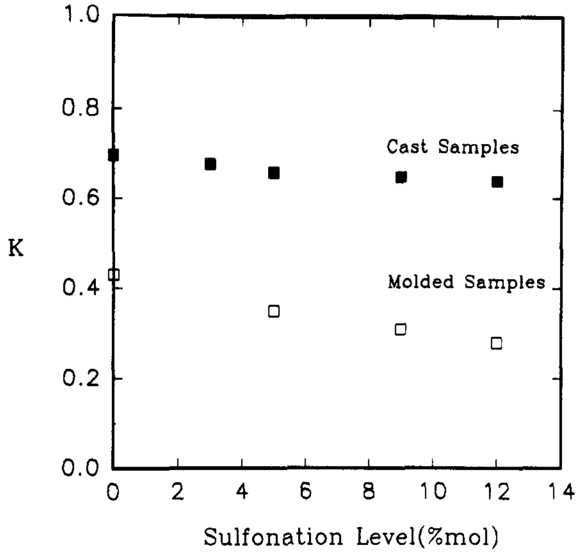

Figure 7. Extent of the microphase separation of Zn-S-SEBS as a function of sulfonation level and sample preparation.

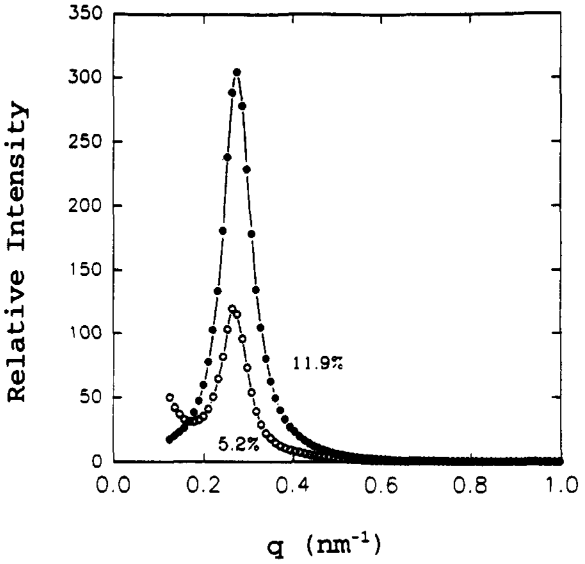

Figure 8. Effect of sulfonation level on SAXS curves of solution-cast Na-S-SEBS.

mobility of the ionomeric blocks in the Na-S-SEBS, even in solution. That hypothesis is consistent with the poorer solubility of Na-S-SEBS compared with Zn-S-SEBS and its higher viscosity at comparable sulfonation levels and polymer concentrations.[8] In general, the higher solution viscosities of ionomer solutions compared with their parent polymers reflect the presence of intermolecular associations of the ionic species. Thus, it is not surprising that the morphology resulting from solution-casting is dependent upon the aggregation structure of the solution, which, in turn, depends on the sulfonation level, the cation, the solvent used, and the polymer concentration. The solvent was less effective at solvating the ionic associations in the Na-S-SEBS solutions than in the Zn-S-SEBS solutions, and as a result, the ability of the chain segments to form an ordered structure was inhibited to a greater extent for the Na-S-SEBS polymers.

Although both the compression-molded and solution-cast Na-S-SEBS samples exhibited only a single SAXS peak, for a fixed sulfonation level, the latter sample preparation produced a narrower, but more intense SAXS peak; cf. Figures 3 and 8. In addition, whereas the scattering intensity and K decreased with increasing sulfonation level for the compression molded Na-S-SEBS specimens, both variables increased with increasing sulfonation level for the solution-cast specimens. For any sulfonation level, the scattering invariants of the solution-cast Na-S-SEBS samples were higher than for the compression molded samples, which confirms that solution-casting favored more complete block microphase separation. The higher level of the microphase separation is understandable, because the solvent enhanced the segmental motion of the block polymer chains and their ability to self-organize, even though the ionic associations of the ionomer segments suppressed mobility.

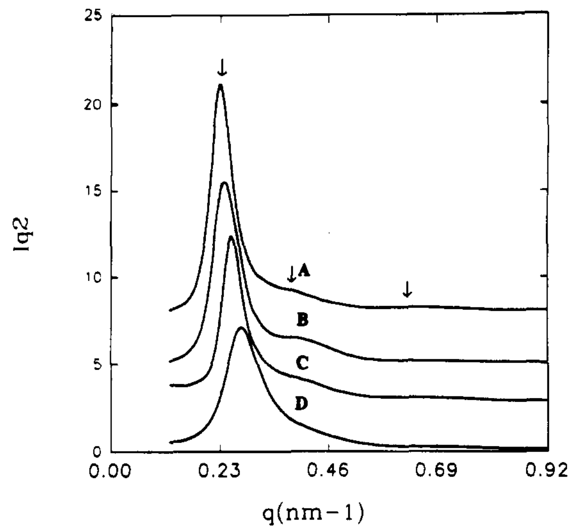

Figure 9. SAXS curves of oil-swollen block copolymer ionomers: (A) SEBS; (B) 5H-S-SEBS; (C) 5Zn-S-SEBS; (D) 5Na-S-SEBS.

Effect of Oil-Swelling. The morphology of a block copolymer can be altered by adding a second component that is miscible with one of the constituent blocks. Figure 9 shows the SAXS profiles for SEBS and several different 5.2-M-S-SEBS samples swollen by a paraffinic oil that was soluble in the EB-rubber phase. In the absence of ionic associations, the addition of the oil to the block copolymer was expected to increase the average PS domain spacing and possibly change the texture of the microstructure as a result of increased volume fraction of the rubbery phase. Figure 9A shows that the oil-swollen SEBS exhibited three SAXS peaks in contrast to the single peak seen in the compression molded neat block copolymer; cf. Figures 1 and 9. The sharp first-order maximum and the two relatively weak higher order peaks in Figure 9A corresponded to a ratio of scattering vectors of $1:\sqrt{2}:\sqrt{3}$, which is characteristic of a spherical microstructure with a cubic arrangement. That is in marked contrast to the ellipsoidal domain microstructure observed in the neat SEBS, but it is also consistent with the lower volume fraction of the PS microphase that resulted from preferentially swelling the rubber phase. The spacing of the spherical domains in real space also increased (i.e., q_{max} decreased) when the rubbery blocks were plasticized with oil.

A cubic arrangement of spherical domains was also observed for the oil-swollen block copolymer ionomers, though the first-order maximum broadened and the resolution of the higher order maxima became poorer as the ionic interactions increased, i.e., as the cation was changed from H^+ to Zn^{2+} to Na^+. Those results suggest that the development of microphase separation decreased in the order of H-S-SEBS > Zn-S-SEBS > Na-S-SEBS, which is consistent with the discussion in the previous section concerning the inhibited mobility of the chains due to ionic associations. The first-order scattering

Table III. Microphase Structure Parameters for Samples Swollen 50% (wt) with Paraffinic Oil

polymer	q (nm^{-1})	D_{NA} (nm)
SEBS	0.23	27.3
5H-S-SEBS	0.238	26.4
5Na-S-SEBS	0.276	22.8

maximum also shifted to higher q, or smaller average neighbor distance, as the cation was varied in the same order; see Table III. That result indicates that the increase in the volume of the rubbery phase decreased with increasing strength of the ionic associations.

The ability of the added oil to change the microstructure of the ionic aggregates suggests that the oil perturbed the ionic domain structure, since it is the relaxation behavior of the latter that is expected to control the morphology. The SAXS data, however, indicate the persistence of the ionic structure. Although the rheology of the block copolymer ionomers was not investigated, the explanation for the effect of the oil on the microstructure may be obtained from previous studies of the viscoelastic behavior of SPS ionomers.[17] Plasticizers that preferentially swell the nonionic phase, as would be expected of the oil in the present study, decrease all of the polymer relaxation times, even though the plasticizer does not dissociate the ionic aggregates. The effect of the *matrix-plasticizer* on the ionic aggregate relaxation times is a consequence of the connectivity of the two phases and the enhnaced mobility of the plasticized polymer chains. All the phases of the block copolymer ionomer are connected due to the fact that individual chains pervade the rubber and polystyrene block domains, as well as the ionic domains within the polystyrene microphase. The oil swells only the rubber phase, but motion of the EB chain segments create stresses at the boundary between the block microphases that may influence the relaxation behavior of the polystyrene domains. Similarly, changes in the polystyrene relaxation affect the relaxation behavior of the ionic aggregates. As a result, the relaxation times associated with the ionic aggregates may be lowered without solvating the ionic interactions. This facilitates formation of a better ordered ionic morphology, without sacrificing the mechanical benefits of the ionic associations.

Conclusions

The block morphology of a sulfonated SEBS ionomer was investigated by small angle X-ray scattering. Ionic aggregation within the polystyrene-rich microdomains had an important influence on the extent of block microphase separation and the texture of the block microstructure. A deformed spherical microstructure was observed when the samples were made by compression molding. In that case, the ionic aggregation impeded the diffusion of the block segments, and the extent of the block microphase separation decreased with increasing sulfonation level. This was especially the case for Na-S-SEBS ionomers in which the ionic aggregates were stable even at the molding temperature. The inhibition of the formation of the block microphase separation coincided with the strength of the ionic interactions for the different cations used, i.e., $Na^+ > Zn^{2+} > H^+$.

When the Zn salts of the block copolymer ionomers were cast from solution, four SAXS maxima were observed at scattering vectors corresponding to a ratio of 1:2:3:4, which indicated a lamellar microstructure. Such a well-defined microstructure, however, was not observed for the solution-cast Na salts. The morphological differences for the two salts is believed to be a due to differences in the persistence of ionic aggregation in solution. The poorer solubilities and higher viscosities of the Na salt solutions indicated that the solvent used (a mixture of toluene and DMF) was less efficient at solvating the ionic interactions in those ionomers than for the Zn salts.

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