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Morphology and mechanical properties of styrene homoblends of methacrylate and sulfonate ionomers

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Summary

Dynamic mechanical properties and morphology of homoblends of sulfonated polystyrene and poly(styrene-*co*-methacrylate) ionomers were investigated. While two tan δ peaks were found in the unblended ionomer samples, three tan δ peaks were observed for the homoblend. The peak at 152 °C is thought to be due to the matrix T_g, and those at 194 and 261 °C probably represent the glass transitions of cluster regions, containing methacrylate-rich multiplets and sulfonate-rich multiplets, respectively. In SAXS profile, only a very broad plateau-type feature was seen for the homoblend. This result implies either that the number density of the scattering centers at prevalent distances is low or that each scattering center has a different electron density. Thus we suggest that in the present study the multiplets of the homoblend consist of random mixtures of sulfonate and carboxylate groups.

Introduction

Ionomers, i.e., ion-containing polymers with a small amount of ionic groups along the nonionic polymer chains, have been extensively investigated during the past three decades (1-6). Ionomers show significant changes in physical properties owing to the formation of ion aggregates, called multiplets (7). For example, most amorphous random ionomers show two glass transitions (*Tg*s) (6). It has also been known that, in general, ionomers exhibit an ionomer peak in the small-angle x-ray scattering (SAXS) profile (8-12).

Recently, Eisenberg et al. (13) postulated that the polymer chains in the immediate vicinity of the multiplets experience a reduction in their mobility. At very low ion contents, only multiplets are present. As the ion content increases, the restricted mobility regions start to overlap and form large contiguous regions of reduced mobility, the so-called clusters (13). When the dimensions of these regions exceed ca. 100 Å, the ionomer exhibits two T_gs; the T_g at lower temperature is due to the glass transition of matrix regions, while the T_g at higher temperature is due to the glass transition of cluster

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regions. The multiplets in the cluster regions act as scattering centers which give rise to the SAXS peak (9,11).

Extensive information on various ionomer blends has been accumulated over the years (14,15). One type of ionomer blend which has been studied is a homoblend, e.g. polystyrene ionomer containing anionic groups mixed with a polystyrene ionomers containing cationic groups (16-18). In this case, the ionic interactions between cation and anion improve the miscibility of polymers. However, no study has yet been reported on the homoblends that contain two different anionic groups on the chains. Thus, the present study explores the properties and morphology of homoblends of a poly(styrene-*co*-sodium styrenesulfonate) ionomer with a poly(styrene-*co*-sodium methacrylate) ionomer.

Experimental

Polymer synthesis

Polystyrene (M_n = 260,000, M_w = 450,000) was prepared by bulk free radical polymerization. The sulfonation method developed by Makowski et al. (19) was used to produce the poly(styrene-*co*-styrenesulfonic acid) (PSSA) samples. Poly (styrene-*co*-methacrylic acid) (PSMAA) samples were also prepared by bulk free-radical polymerization of styrene and methacrylic acid monomers (20). To determine the ion content, samples were dissolved in a benzene/methanol (9/1 v/v) mixture to make a 5% (w/v) solution, and titrated with standard methanolic NaOH to the phenolphthalein end point. The acid blends were prepared by mixing an equal amount by weight of PSSA and PSMAA copolymers. The acid form samples in a benzene/methanol mixture were neutralized with methanolic sodium hydroxide. The solution was freeze-dried and then dried further under vacuum at 150 °C for one day. In order to prepare samples for dynamic mechanical property measurements and SAXS experiments, the samples were compression molded in a mold at 230 °C under a pressure of 25 MPa. The molded samples were annealed under vacuum at 130 °C for one day.

Dynamic mechanical thermal analysis (DMTA)

A Polymer Laboratories DMTA Mark II was utilized for the measurement of the mechanical properties of ionomers. For each sample, the storage moduli (*E’*) and loss tangent (tan δ) were obtained in a dual cantilever bending mode as a function of temperature at a heating rate of 1 °C/min.

SAXS experiments

The SAXS experiments were conducted at D-22 station of the LURE-DCI synchrotron radiation source (Orsay, France). A detailed description of the X-ray spectrometer is given elsewhere (21). The sample-to-detector distance was 570 mm, which allowed SAXS data to be obtained in the q range from ca. 0.012 to 0.32 $Å^{-1}$, where $q = 4\pi\sin\theta/\lambda$, θ is half the scattering angle and λ is the X-ray wavelength. The SAXS data were plotted as relative intensity vs q after correction for background scattering.

Results and discussion

Figure 1 shows the storage modulus and loss tangent of two polystyrene-based ionomers and their homoblend against temperature. The modulus curve of poly(styrene-*co*-sodium methacrylate) containing 8.7 mol% of ions [PSMANa(8.7)] shows two drops in modulus at ca. 160 and ca. 210 °C. The modulus between these two drops is called an “ ionic modulus”. The loss tangent curve shows two peaks. To see the peak shape and

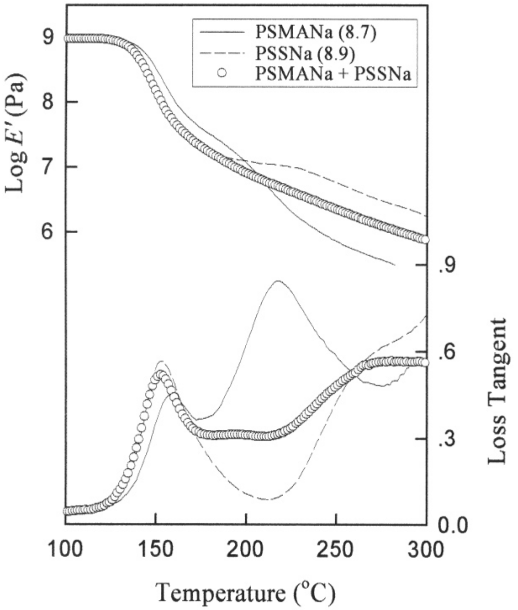

Figure 1. Storage modulus and loss tangent as a function of temperature for PSMANa (8.7 mol% of ions), PSSNa (8.9 mol% of ions), and their 50/50 blend, measured at 1 Hz.

position more precisely, curve deconvolutions were performed using the Peakfit computer program. The exponential function was chosen for the background, and the exponentially-modified-Gaussian function for the peaks (22). The matrix tan δ peak of PSMANa ionomer is centered at 158 °C, and the cluster tan δ peak at 219 °C.

In the case of poly(styrene-*co*-sodium styrenesulfonate) (8.9 mol% of ions) [PSSNa(8.9)], the ionic moduli are lower than that of the PSMANa(8.7); however, the length of the modulus plateau is longer for the PSSNa(8.9) ionomer. This is due to the difference in ionic interaction parameters. The ionic interactions are stronger in sulfonate ionomer than in methacrylate ionomer; as a result, at comparable ion contents, ion-hopping (23), one of mechanisms for cluster T_g, occurs at higher temperatures for the PSSNa ionomer. The result of the deconvolution (22) of tan 8 curve shows that the matrix peak maximum is located at 152 °C and the cluster peak maximum at 267 °C. In addition, in the sulfonate case the ionic groups are attached to the *para* position of benzene ring, while in the methacrylate case the ionic groups are attached directly to the polymer backbone. The proximity of the sodium carboxylate ion pair to the backbone means that the multiplets are smaller in the methacrylate case than in the sulfonate case (23). In that case, the amount of reduced mobility material should be larger in the methacrylate than in the sulfonate at a comparable ion content; the area under the loss tangent peak connected with the cluster glass transition should be larger in the PSMANa than in PSSNa. This is what was found in the present study. Similar effects have been observed in a number of other materials (23,24).

When one looks at the modulus curve for the homoblend, one finds that it is different from the curves of the individual ionomers. While the first drop in the modulus curve is similar to that of PSSNa, the ionic modulus does not extend to higher temperature, as seen in PSSNa ionomer; at higher temperature the modulus values are in between those of the PSSNa ionomer and those of the PSMANa ionomer. The loss tangent curve is even more instructive. Figure 2 shows the deconvolution result of the loss tangent curve; there are three peaks, and the maxima of the peaks are found to be at 152, 194, and 261 °C (linear least-squares correlation coefficient = 0.999). The peak at 152 °C represents the matrix T_g, while the peaks at 194 °C and 261 °C are probably due to the glass transitions of cluster regions, containing mainly methacrylate multiplets and mainly sulfonate multiplets, respectively. It should be pointed out that these cluster T_g values are lower than those of the unblended ionomers. The other blend sample in which the PSSNa(8.9) sample was mixed with PSMANa containing 4.0 mol% of ions [PSMANa(4.0)] showed similar results (not shown here). The cluster T_g of the PSMANa(4.0) was found to be ca. 190 °C. In the blend, two cluster T_gs were also observed at ca. 175 °C and ca. 260 °C, which can probably be ascribed to the cluster T_gs of the PSMANa(4.0) and PSSNa(8.9), respectively.

The SAXS profiles of the three ionomer systems are shown in Figure 3. A well-developed peak is seen at q = ca. 0.18 Å^{-1} for the sulfonate polystyrene containing 10.8 mol% of ions; a weak SAXS peak is seen at q = ca. 0.28 Å^{-1} for the polystyrene-methacrylate ionomer (10.6 mol% of ions). However, the homoblend sample shows no well developed peak but only a very broad plateau-type feature. This result means either that the number density of the scattering centers at prevalent distances is very low or that the scattering centers have very different electron densities. If the former possibility is operative here, no SAXS peak should be expected as there are few scattering centers of high electron density. In the latter case, no well-developed SAXS peak would be expected because the very high degree of heterogeneity in the electron densities of the scattering centers results in a very broad plateau-like feature in the SAXS profile.

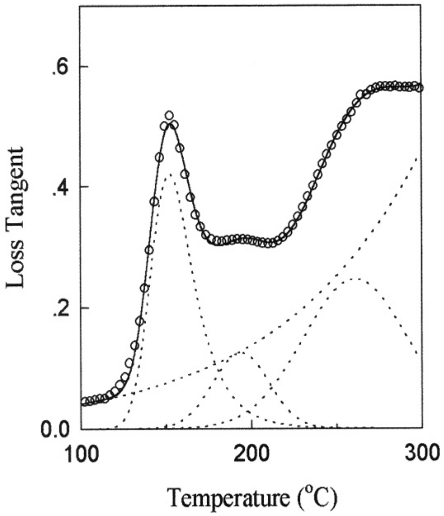

Figure 2. Deconvoluted loss tangent curve as a function of temperature for the ionomer homoblend, measured at 1 Hz.

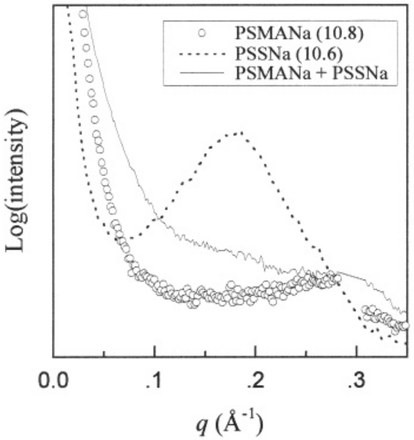

Figure 3. SAXS data for the PSMANa (10.8 mol% of ions), PSSNa (10.6 mol% of ions), and their homoblend.

Based on the above findings, we can suggest three morphological possibilities. First, if the sulfonate and the methacrylate ionomers are phase-separated, simple additivity rule should be operative; if so, the loss tangent curve should show two cluster T_gs at the temperatures where each ionomer exhibits its own cluster T_g, and we should also be able to see two SAXS peaks. However, this was not the case in the present study (see Figures 1 and 3). Second, if the ionomers were miscible on the multiplet level, new multiplets, consisting of Na-carboxylate and Na-sulfonate ionic groups, could form. If the sulfonate and carboxylate ionic groups were distributed evenly in the multiplets, only one SAXS peak and one loss tangent peak should be observed. This possibility is also rejected by the present study as shown in Figures 1 and 3.

The rejection of the first and the second possibilities brings us to the third and the only remaining possibility. It thus appears that in this homoblend, multiplets, consisting of random mixtures of sulfonate and carboxylate groups, form. The sizes of multiplets and the sulfonate/carboxylate ratio in each multiplet probably vary a great deal. Consequently, no SAXS peak but a very broad plateau-like feature would be expected, arising from the summation of scattering by centers of various scattering intensities at varying distances, i.e. the destruction of the relatively ordered arrangement of scattering centers by blending. The mechanical properties could also be understood within this frame. Two cluster T_gs should be seen; one for the T_g of cluster regions containing methacrylate/methacrylate-rich multiplets, and the other for the T_g of clusters containing sulfonate/sulfonate-rich multiplets. At this point, it should be mentioned that, because of the heterogeneity of the multiplets in size, type of ion attachment and chemical species, which leads to a decreased packing efficiency within the multiplets, the cluster T_gs of the homoblend would be lower than those of the ionomers. This is, indeed, explanation supported by the present study.

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