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Preferential Cluster-Phase Plasticization of Ionomers Containing Surfactant Molecules

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Introduction

Considerable changes in the chemical and physical properties of organic polymers can be achieved by incorporating a small quantity of ionic groups either directly onto the polymer backbone or as pendent groups along the polymer chains.[1,2] In ionomers (i.e., organic copolymers usually containing less than ca. 15 mol % of charged comonomers), strong Coulombic attractive forces cause the ionic groups to aggregate into small structures of tightly packed ion pairs, termed "multiplets".[3] Since multiplets act as multifunctional electrostatic cross-links, polymer chains emanating directly from the multiplet surfaces experience a significant reduction in relative mobility.[4,5] As shown in Figure 1, the thickness of this layer of restricted mobility is postulated to be on the order of the persistence length of the polymer (i.e., about 10 Å in polystyrene).[4] Beyond this restricted layer, the segmental mobility is expected to be similar to that of the same polymer segments in a lightly cross-linked system. For example, ionomers which contain a significant quantity of multiplets often show increases in glass transition temperature, tensile strength, and melt viscosity.

As the ion content in an ionomer is increased, the size and/or quantity of multiplets increases. Once a sufficient quantity of multiplets is developed, the regions of restricted mobility surrounding multiplets in close proximity begin to overlap and to form larger contiguous regions of restricted mobility. These large regions of closely spaced multiplets may exhibit phase-separated behavior (e.g., a separate glass transition temperature from that of the ion-poor regions) and are termed "clusters". Experimental evidence for the existence of both multiplets and clusters in ionomers have been obtained by correlating the results of morphological studies using techniques such as small-angle X-ray scattering (SAXS)[6–8] and dynamic mechanical analysis (DMA).[9,10]

Numerous plasticization studies of ionomers[11] have demonstrated the dual nature of plasticization by incorporation of either nonpolar plasticizers (e.g., dioctyl phthalate)[12–14] or polar plasticizers (e.g., glycerol).[14] Nonpolar plasticizers have been shown to plasticize both the unclustered and clustered regions, leading to a marked, and sometimes parallel, decrease in the glass transition temperatures of the unclustered, or "matrix" regions, $T_{g,m}$, and the clustered regions, $T_{g,c}$.[12,14,16] According to the model shown schematically in Figure 1, the nonpolar diluent is able to plasticize the regions of restricted mobility between the multiplets in the cluster as well as the nonpolar material in the regions of high mobility.[4] It is important to note that an analogous decrease in both $T_{g,m}$ and $T_{g,c}$ has been observed with internally plasticized polystyrene-based ionomers containing covalently-attached alkyl chains.[17]

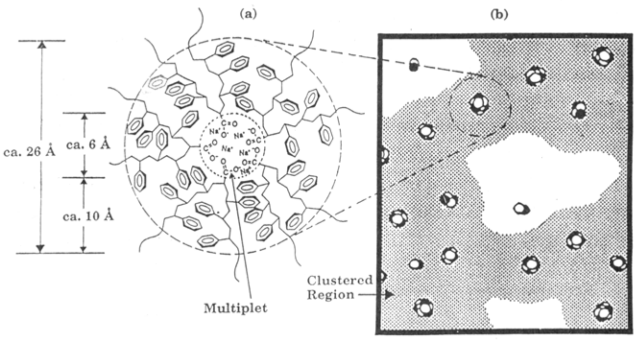

Figure 1. Schematic diagram of (a) a multiplet and the region of restricted mobility and (b) a cluster composed of closely spaced multiplets in a typical polystyrene-based ionomer.

Polar plasticizers, on the other hand, have been shown to selectively reduce the $T_{g,c}$ of the clusters in random ionomers. This has been attributed to the incorporation of the plasticizer into the multiplets, which, in turn, reduces the firmness with which the ion pairs in the multiplet are anchored.[4] As the electrostatic interactions between the ion pairs in the multiplet are shielded by the solvating diluent, the multiplets themselves are plasticized, and the mobility of the hydrocarbon chains attached to the ion pairs increases. This increase in chain mobility near the multiplets thus decreases the $T_{g,c}$, which is accompanied by ion hopping.[10]

To match the nonpolar/polar nature of ionomers, other studies have utilized plasticizers which contain both nonpolar and polar functionalities. For example, studies of monofunctionalized styrene oligomers containing sodium carboxylate end groups blended with sulfonated polystyrene showed significant plasticization of both the clustered and nonclustered phases.[11] In addition, plasticizers such as zinc stearate[18] or hexadecanoate[19] were found to form phase-separated, crystalline domains which acted as reinforcing fillers and were capable of interacting with the ionic domains only at temperatures in excess of their respective melting points.

In this investigation, we are using surfactant molecules with ionic head groups identical to the ionic groups on the ionomer to plasticize selectively the regions of restricted mobility which exist in polystyrene-based ionomers containing ionic multiplets. It should be stressed that, because of the identity of the functional groups on the polymer and plasticizer, no "plasticization" of the multiplet is to be expected, only the regions of reduced mobility surrounding it. The regions which are not in the immediate vicinity of multiplets should experience no plasticization.

Experimental Section

Materials. Polystyrene was prepared by bulk free-radical polymerization using benzoyl peroxide as the initiator. The weight-average molecular weight was determined to be 485 000 by GPC. Three samples of the polystyrene were sulfonated with acetyl sulfate in 1,2-dichloroethane as previously described.[20] The degree of sulfonation for the three poly(styrenesulfonic acid) (PSSA) samples was determined to be 4.7, 8.4, and 10.6 mol % by titration of 0.5 g of samples of each in a 90:10 (v/v) benzene–methanol mixture. The solutions were titrated to the phenolphthalein end point with methanolic NaOH.

Sodium dodecylbenzenesulfonate (SDBS), obtained from Aldrich, was purified by dissolving 15 g of the surfactant in 100 mL of deionized water and reprecipitating in 1 L of methanol. This reprecipitation was facilitated by cooling the mixture to ca.

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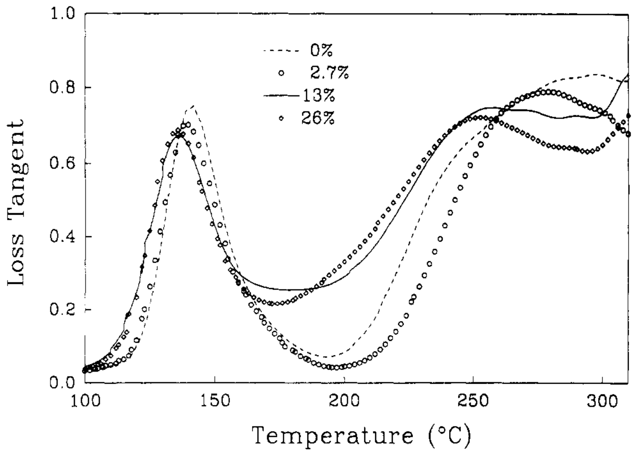

Figure 2. Loss tangents (tan δ) as a function of temperature for the 8.4 mol % sulfonated polystyrene, measured at 1 Hz, containing variable weight percents of added surfactant. The weight percent of added surfactant is indicated for each sample.

Table I. Sulfonated Polystyrene–Surfactant Blend Compositions

degree of ionomer sulfonation (mol %)	mol % of surfactant in blend	wt % of surfactant in blend
4.7	10	1.5
4.7	100	15
8.4	10	2.7
8.4	50	13
8.4	100	26
10.6	10	3.2
10.6	50	17
10.6	100	33

10 °C overnight. The purified surfactant was then filtered and dried in a vacuum oven, at 60 °C, for ca. 12 h.

The sulfonated polystyrene–surfactant blends were prepared by first dissolving accurately weighed portions of the three PSSA samples in 90:10 (v/v) benzene–methanol and quantitatively neutralizing with methanolic NaOH. On the basis of the equivalent weight (i.e., grams of polymer per mole of sulfonate groups) of the neutralized ionomers, samples of the purified surfactant were added to the poly(styrene-*co*-sodium styrenesulfonate) solutions on a 10, 50, and 100 mol % basis (i.e., moles of surfactant per moles of sodium styrenesulfonate units). The ionomer–surfactant blends were freeze-dried and then thoroughly dried, at 60 °C, in a vacuum oven. The blend compositions for the samples used in this study are listed in Table I.

Dynamic Mechanical Experiments. For dynamic mechanical thermal analysis, the samples were dried under vacuum at 140 °C for 1 day. Each sample was then molded at 240 °C and a pressure of approximately 20 MPa into a bar with dimensions of 6 × 27 × 2.5 mm. The samples were stored in a vacuum oven at 110 °C for 1 day prior to use.

A Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) was used to measure the mechanical properties of the samples. The dual cantilever mode was used with a 5-mm free length. The storage moduli (E'), loss moduli (E''), and loss tangents (tan δ) were measured for each sample as a function of temperature for frequencies in the range of 0.3–30 Hz. All dynamic mechanical experiments were conducted under a nitrogen atmosphere at a heating rate of 0.5 °C/min.

The tan δ peaks were deconvoluted using Peak Fit (Jandel Scientific) software, and the best fits to the data were obtained by assuming an exponential base line and an exponentially modified Gaussian distribution for each of the two peaks. The apparent activation energies were calculated according to the Arrhenius equation from the temperatures of the loss tangent maxima at five frequencies.

Results and Discussion

The ionic head group of the surfactant molecules used in this investigation (i.e., sodium dodecylbenzenesulfonate) is identical to the ionic moiety on the poly(styrene-*co*-sodium styrenesulfonate) ionomers. Since the multiplets are expected to be formed by aggregation of the sodium sulfonate ion pairs, the surfactant head group is not expected to perturb dramatically the multiplet size. Moreover, since the fully extended chain length of the surfactant tail is ca. 14.5 Å, the tail is not expected to extend much beyond the region of restricted mobility surrounding the multiplets. It should be noted that no evidence of surfactant phase separation and/or crystallization was observed in the DSC thermograms of these ionomer–surfactant blends.

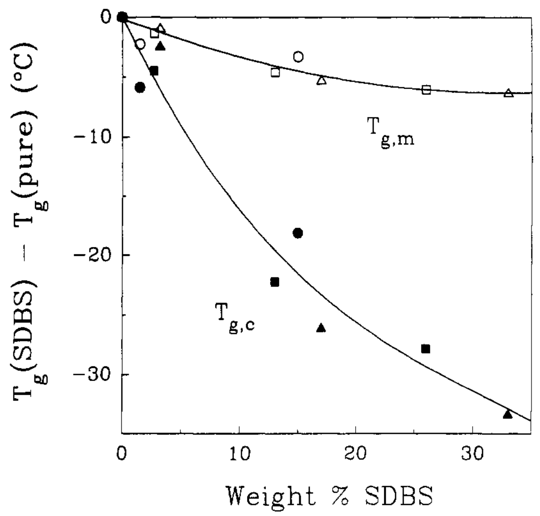

Figure 3. Effect of added sodium dodecylbenzenesulfonate (SDBS) on the matrix (open symbols) and cluster (filled symbols) glass transition temperatures for the (○) 4.7, (□) 8.4, and (△) 10.6 mol % ionomers. T_g(SDBS) and T_g(pure) refer to the glass transition temperatures with and without added surfactant, respectively. The smooth curves are fitted by using second- and third-order polynomials for the matrix and cluster T_g's, respectively.

Figure 2 shows the loss tangent versus temperature plots for the 8.4 mol % ionomer–surfactant blends containing variable contents of added surfactant. For each blend sample, two characteristic relaxation peaks were observed. These relaxations have been attributed to the glass transition of the nonclustered domains (i.e., the low-temperature peak) and the glass transition of the clustered domains (i.e., the high-temperature peak).[4] It is important to note that, as the surfactant content in the blend increases, there is a significant decrease in the peak temperature of the relaxation attributed to the cluster phase, $T_{g,c}$, whereas only a minimal decrease in the matrix $T_{g,m}$ is observed.

The trends in $T_{g,m}$ and $T_{g,c}$ versus surfactant content observed with the 8.4 mol % ionomer are also observed with the 4.7 and 10.6 mol % ionomers. Figure 3 shows the effects of surfactant content on the glass transition temperatures of the clustered phase and nonclustered phase relaxations for all of the ionomer samples. Note that data are plotted as the difference in the T_g's between the plasticized, T_g(SDBS), and the nonplasticized, T_g(pure), ionomers. As the weight percent of surfactant is increased, the glass transition temperatures of the clustered phase decrease sharply relative to those of the nonclustered phase. In contrast to the behavior of typical nonpolar plasticizers,[12–14] these data clearly indicate that the nonpolar portions of the surfactant molecules preferentially plasticize the regions of restricted mobility surrounding the multiplets in the clustered phase.

The preferential plasticization of the clustered phase is attributed to the incorporation of ionic head groups of the surfactant molecules into the ionic multiplets, while the tail groups reside in the proposed regions of restricted mobility surrounding them. The presence of the tail

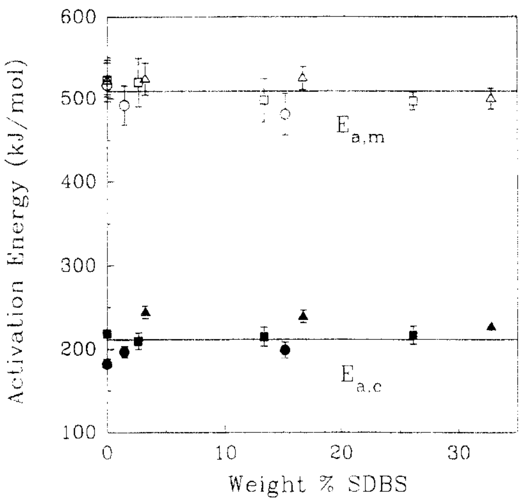

Figure 4. Effect of added sodium dodecylbenzenesulfonate (SDBS) on the activation energies of the matrix (open symbols) and cluster (filled symbols) glass transitions for the (○) 4.7, (□) 8.4, and (△) 10.6 mol % ionomers. Error bars are derived from ± the standard error of the slope in the Arrhenius plot.

groups extending from the multiplet surface increases the free volume in the regions of restricted mobility. This increase in free volume thus causes the decrease in $T_{g,c}$ with increasing surfactant content.

While the majority of multiplets are believed to exist in the clustered phase,[4] a significant quantity of lone multiplets and lone ion pairs may exist in the nonclustered phase.[7] Since the ionic aggregates in the nonclustered phase simply act as multifunctional electrostatic cross-links, the matrix glass transition temperature in many ionomeric systems has been observed to increase with ionic content.[4] In keeping with the above argument for the incorporation of the surfactant head groups within the multiplets, some of the electrostatic cross-links in the ionomer–surfactant blends may now be associated with a nonpolar plasticizer (i.e., the surfactant tail). Thus, it is not surprising that the matrix $T_{g,m}$ slightly decreases at high surfactant contents.

Figure 4 shows plots of the apparent activation energies, E_a, for the glass transitions of the clustered and nonclustered phases versus the surfactant content. These data indicate that the activation energies for the two glass transitions remain constant, within experimental error, as the surfactant content increases. It is of interest to note that identical behavior has been observed for poly(ethyl acrylate)-based ionomers plasticized to variable degrees with 4-decylaniline.[16] Since these transition activation energies are not significantly influenced by the incorporation of the surfactant molecules, it is reasonable to assume that the plasticizers do not induce any changes in the multiplets which would alter the mechanism of the observed relaxations.

Conclusions

Plasticization of polystyrene-based ionomers with surfactant molecules having head groups identical to the ionic groups along the polymer chains causes a large decrease in the glass transition temperature associated with the ionic clusters. In contrast, the glass transition temperature of the polystyrene matrix is much less dependent on the amount of added surfactant. This preferential plasticization of the ionic cluster phase is attributed to the incorporation of surfactant head groups into the multiplets, while the tail groups reside in the proposed regions of restricted mobility surrounding the multiplets. The surfactant tail groups lower the $T_{g,c}$ of the clustered phase by adding free volume to the regions surrounding the multiplets. Furthermore, constant activation energies of the glass transitions as a function of added surfactant suggest that the surfactant molecules do not change the rigidity of the multiplets or the morphology of the clustered phase. Since the clustered phase is proposed to consist of overlapping regions of restricted mobility, these experimental observations support the new multiplet-cluster model for the morphology of random ionomers.[4]

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