Effect of Preferential Plasticization on the Crystallization of Lightly Sulfonated Syndiotactic Polystyrene Ionomers

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ABSTRACT: The incorporation of 2.2 mol % sodium sulfonate groups along the backbone of syndiotactic polystyrene dramatically inhibits crystallization from the melt. However, small amounts of a surfactant, such as sodium dodecylbenzenesulfonate (DBSNa), may be used to selectively plasticize the ionic domains of sulfonated polystyrene ionomers. On the basis of ^{23}Na SSNMR results and the dynamic mechanical behavior of these ionomers, this preferential plasticization is postulated to perturb the electrostatic interactions within the ionic multiplets (i.e., electrostatic cross-links), destabilize the dynamic network, and thus increase the molecular mobility of the crystallizable chain segments. With enhanced chain mobility, a higher degree of crystallinity and an elevated rate of crystallization are observed. In contrast to the effect of DBSNa, the incorporation of phenyldodecane or sodium benzenesulfonate (i.e., the separate nonpolar and polar components of DBSNa, respectively) into the ionomer does not significantly affect the electrostatic network or enhance crystallization of sulfonated, syndiotactic polystyrene.

Introduction

Ion pairs that are covalently attached to the backbone of nonpolar organic polymers have been shown to aggregate as the ionic content along the chains is increased.[1−8] For typical random ionomers, the state of ionic aggregation ranges from isolated ion pairs[7−11] to multiplets (i.e., aggregates containing several ion pairs).[2,12−23] Since the polymer chains are covalently attached to the multiplets, the backbone mobility near the aggregates is restricted.[2,24−28] For very low ion contents, these regions of restricted mobility are isolated, and the ionomer behaves as a lightly cross-linked polymer (i.e., a modest increase in the matrix T_g relative to an un-cross-linked system).[6,29,30] With increasing ion contents, however, more multiplets are formed, and the regions of restricted mobility surrounding these multiplets begin to overlap to form a larger contiguous "cluster phase" with a separate and distinctly higher T_g.[2,6,13,19,31−34]

The heterogeneous morphology of random ionomers allows the properties of these materials to be tailored by manipulation of either the nonpolar polymer matrix or the polar ionic domains. One method of tailoring the properties of ionomers is by "preferential plasticization" of the matrix and/or ionic cluster phase.[30,33,35−48] Polar plasticizers affect primarily the cluster T_g,[35,41,43,46] while nonpolar plasticizers usually affect the T_g's of both the cluster phase and the matrix.[35−37,47]

Kim et al.[33] investigated the preferential plasticization of sulfonated atactic polystyrene (SaPS) ionomers with the sodium salt of dodecylbenzenesulfonic acid (DBSNa). With increasing surfactant content, there was little effect on the matrix T_g; however, there was significant plasticization of the cluster phase. This behavior was attributed to a preferential incorporation of the ionic headgroup of the surfactant into the multiplet (i.e., the headgroup is structurally identical to the ionomeric functionality). Consequently, the hydrocarbon tail of the surfactant was suggested to effectively plasticize the region of restricted mobility and lower the cluster-phase T_g. Plante and co-workers observed similar results in studies of plasticized carboxylated polystyrene ionomers with monofunctional polystyrene oligomers containing carboxylic headgroups.[39,40]

Recently, we have been investigating the effect of ionic aggregation on the crystallization of sulfonated syndiotactic polystyrene (SsPS) ionomers.[49−51] These studies have shown that the incorporation of small quantities of ionic groups reduces the rate and degree of crystallization of these materials. Moreover, the rate of crystallization was found to decrease with an increase in the strength of the electrostatic cross-links (i.e., the multiplet stability). To obtain a greater understanding of the link between ionic aggregation and crystallization in these strongly interacting systems, the strength of the electrostatic cross-links may be affected by the selective incorporation of surfactant molecules into the ionic domains.[33] By systematically disrupting the stability of the ionic aggregates, the mobility of the chain segments should be increased, yielding enhanced crystallization. Therefore, the purpose of this investigation is to determine the influence of preferential plasticization by a surfactant molecule on the crystallization of SsPS ionomers.

Experimental Section

Materials. The syndiotactic polystyrene (with greater than 99% purity) was obtained from the Dow Chemical Co. and had a weight-average molecular weight of 609 000 g/mol. Sulfonated atactic polystyrene samples were prepared as described previously.[52] Chloroform (pentene stabilized) and sulfuric acid were obtained from Fisher; all other chemicals were obtained from Aldrich and used without further purification.

Preparation of the Sulfonating Reagent. Concentrated sulfuric acid (0.018 mol) was slowly added, with vigorous stirring, to 25 mL of a chilled chloroform solution containing 0.03 mol of caproic anhydride. After complete mixing, these reagents were equilibrated at room temperature and then diluted with chloroform to 50 mL in a volumetric flask.

Sulfonation of Syndiotactic Polystyrene. The syndiotactic polystyrene (7.5 g) and 200 mL of pentene stabilized

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chloroform were placed in the glass liner of a Parr pressure reactor. The sPS was dissolved by heating the reactor to 100 °C for 1.5 h. The reactor was allowed to cool to room temperature, and the solution was diluted in a 1000 mL round-bottom flask with 300 mL of chloroform. The flask was heated to reflux, and the sulfonating reagent was slowly added to the sPS solution with rapid stirring. The reaction was allowed to proceed for 1 h at 60 °C and then terminated by the addition of 10 mL of methanol. To facilitate the complete removal of residual sulfonating reagent from the functionalized polymer, the sulfonated syndiotactic polystyrene (SsPS) samples were steam stripped into deionized water. The precipitate was then ground into a fine slurry in methanol using a Waring blender. The polymer was filtered and washed twice in hot deionized water. Finally, the polymer was filtered and dried in a vacuum oven, at 90 °C, for 48 h. The degree of sulfonation was determined titrimetrically, and the samples were neutralized with NaOH and CsOH as described previously.[51] The nomenclature for the sulfonated polystyrene (PS) ionomers used throughout this paper will be StPS-xM$^+$, where, t is the polymer tacticity (a = atactic, s = syndiotactic), x is the mole percent of sulfonation, and M$^+$ represents the alkali metal counterion.

Preparation of Ionomer/Additive Mixtures. The additives utilized in this investigation were phenyldodecane (DB) and sodium salts of benzenesulfonic acid (BSNa) and dodecylbenzenesulfonic acid (DBSNa). SsPS/additive mixtures were prepared by mixing the appropriate amount of 0.01 M additive solution with SsPS-2.2Na$^+$ in a 95:5 (v/v) chloroform/methanol solution. The additive contents were chosen to represent a 0.5:1, 1:1, and 2:1 molar ratio of additive to sodium sulfonate groups along the ionomer chains. The ionomer/additive mixtures were solution-cast under a nitrogen purge and dried at 80 °C for 48 h under vacuum.

Thermal Analysis. The effects of the additive molecules on the thermal properties and isothermal crystallization kinetics of SsPS-2.2Na$^+$ were studied using a Perkin-Elmer DSC-7 differential scanning calorimeter using a nitrogen purge. For thermal scans, the heating rate was 20 °C/min. For the isothermal studies, all samples were initially heated to 330 °C for a period of 3 min to equalize the thermal history. These samples were then rapidly cooled at a rate of −200 °C/min to the isothermal crystallization temperature, and the crystallization exotherms were monitored as a function of time.

Dynamic Mechanical Analysis. Dynamic mechanical measurements were performed on sulfonated *atactic* polystyrene ionomer samples using a Seiko Instruments SDM 5600 series dynamic mechanical spectrometer (DMS 210). All samples were compression molded at 180 °C, and the sample cross-sectional areas were ca. 8 mm^2. The samples were analyzed in the tensile mode at a deformation frequency of 1 Hz and a strain amplitude of 6.5 μm.

^{23}Na SSNMR Investigations. ^{23}Na SSNMR measurements were conducted on a Bruker MSL-400 operating at 105.8 MHz. The external reference of NaCl (crystalline solid), which has a chemical shift $\sigma = 7.1$ ppm relative to the standard NaCl (aqueous solution), was used to set the frequency axis. All solid samples were run in zirconia rotors using magic-angle spinning (typically 5 kHz) and high-power proton decoupling. To achieve uniform excitation and to permit quantitative analysis of peak areas, the samples were run with a pulse width of 1.5–2.0 μs (corresponding to a 12.7° tip angle). A pulse delay of 10 s was necessary to obtain fully relaxed spectra, and a total of ca. 17 000 scans were ensemble averaged. ^{23}Na spectra were obtained from samples containing varying contents of DBSNa, BSNa, and DB. For QCC calculations, data were also collected using a Bruker MSL-200 spectrometer running at 52.5 MHz. The spinning speed used for samples run in this spectrometer was 4 kHz.

Results and Discussion

Effect of Preferential Plasticizers on the Crystallization of SsPS Ionomers. Previous DSC investigations of SsPS ionomers[50] have shown that crystallization is greatly inhibited for ion contents greater than 2.0 mol %. In addition, the ability of these systems to crystallize decreases with a decrease in counterion size.[51] For example, isothermally crystallized 2.4 mol % SsPS in the Cs$^+$ form displays significant crystallinity, while the Na$^+$-neutralized SsPS ionomer does not crystallize under identical thermal conditions.[53]

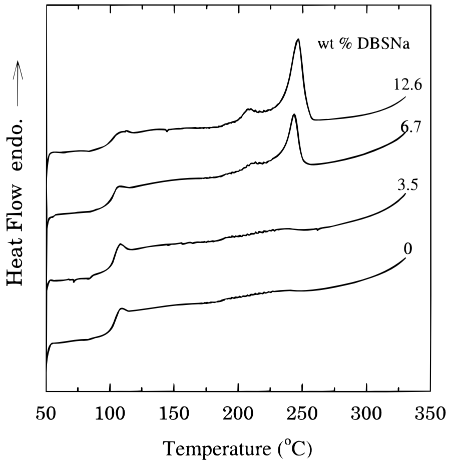

Figure 1. Effect of the sodium salt of dodecylbenzenesulfonic acid concentration on isothermally crystallized Na$^+$-neutralized sulfonated syndiotactic polystyrene ionomers containing 2.2 mol % sulfonation. Samples were isothermally crystallized from the melt at 190 °C for 1 h.

In attempt to enhance the crystallization of SsPS ionomers containing greater than 2.0 mol % ionic groups, we have recently initiated studies of the effect of preferential plasticization by surfactant molecules on the crystallization of SsPS ionomers. Preliminary studies of these plasticized ionomers[54] have shown that melt-quenched SsPS-2.2Na samples containing as much as 12.6 wt % DBSNa do not crystallize during heating scans (e.g., at 20 °C/min) and display only a slight depression (less than 3 °C) in the matrix T_g. This reduction in the T_g was attributed to a slight plasticization of the SsPS matrix. In addition, no evidence of plasticizer phase separation was observed during thermal treatment.

In contrast to the melt-quenched samples, isothermal crystallization yields a significant increase in the degree of crystallinity. Figure 1 shows the effect that added DBSNa plasticizer has on the thermal behavior of SsPS-2.2Na$^+$ samples that had been isothermally crystallized at 190 °C for 1 h. While the pure SsPS-2.2Na$^+$ displays a slight melting endotherm in the range 180−240 °C, the addition of 3.5 wt % DBSNa only moderately increases the magnitude of the melting endotherm. However, significant increases in the melting endotherms are obtained with the addition of 6.7 and 12.6 wt % DBSNa. The increased crystallinity of the DBSNa plasticized SsPS-2.2Na$^+$ samples, in agreement with the results of Kim et al.,[33] suggests that preferential plasticization of the ionic domains increases segmental mobility and thus enhances the ability of these ionomers to crystallize. Moreover, these data yield indirect evidence that increasing the surfactant content increases the overall rate of crystallization.

Isothermal crystallization experiments were performed to evaluate the effect of DBSNa surfactant on the overall rate of crystallization of the Na$^+$-neutralized SsPS ionomers. Figure 2 compares the isothermal crystallization kinetics of a Cs$^+$-neutralized SsPS with

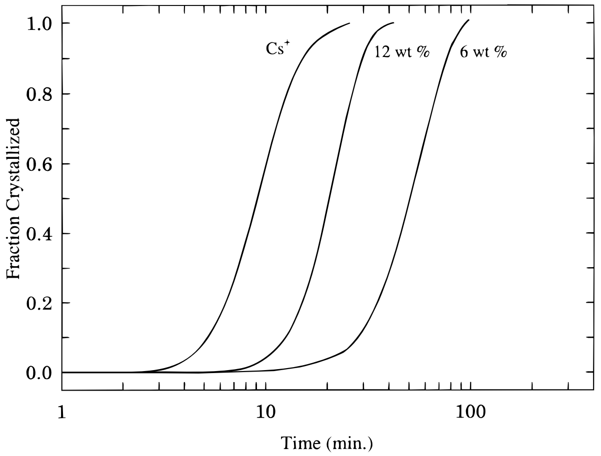

Figure 2. Effect of DBSNa concentration on the crystallization kinetics of SsPS-2.2Na$^+$. The samples were quenched from the melt and isothermally crystallized at 190 °C.

the crystallization kinetics of Na$^+$-neutralized SsPS containing 6.7 and 12.6 wt % DBSNa. For the Na$^+$-neutralized SsPS and the ionomer containing 0 and 3.5 wt % DBSNa, the rate of crystallization at 190 °C was too slow to be monitored using this DSC method. However, for the Na$^+$-neutralized SsPS containing 6.7 and 12.6 wt % DBSNa, the rate of crystallization increases with increasing levels of surfactant. Comparison of the rates of crystallization for the Na$^+$-neutralized SsPS containing 12.6 wt % DBSNa with unplasticized Cs$^+$-neutralized SsPS shows that, even with this level of surfactant, the ionomer neutralized with the larger Cs$^+$ counterions still crystallizes faster. Upon complete crystallization, the level of crystallinity for the Cs$^+$-neutralized SsPS and the SsPS-2.2Na containing 6.7 and 12.6 wt % DBSNa were all comparable; the ΔH_f values were in the range of ca. 20 J/g, corresponding to a degree of crystallinity of ca. 36 wt %.[50]

The crystallization kinetics data in Figure 2 suggest that the Na$^+$−sulfonate groups do not disrupt crystallization of the SsPS but that the strong electrostatic interactions simply retard the rate of crystallization.[51] The addition of DBSNa disrupts the kinetic stability of the multiplets and weakens the electrostatic cross-links of the ionomer. This disruption of the ionic cross-links by the DBSNa apparently increases the mobility of the polymer backbone and subsequently increases the rate of crystallization.

To understand better the mechanism of plasticization for the DBSNa molecule, analogous samples were prepared by mixing SsPS-2.2Na$^+$ with DB and BSNa. Note that these molecular analogues have similar structures to the ionic headgroup (BSNa) and the hydrocarbon tail (DB) of the DBSNa surfactant. On the basis of the study by Kim et al.,[33] the sodium benzenesulfonate headgroups of the surfactant molecules are expected to preferentially reside in the multiplets along with the sodium styrenesulfonate groups of the ionomer. The hydrocarbon tails of the surfactants are consequently expected to plasticize primarily the PS chains within the regions of restricted mobility in the multiplet-rich cluster phase. In contrast, the DB molecules are certainly not expected to associate with the polar multiplets and should simply act as organic plasticizers of the PS chains in both the cluster and matrix phases. Conversely, the BSNa molecules should associate strongly with the multiplets; however, the lack of sufficient organic character is expected to yield little or no PS plasticization.

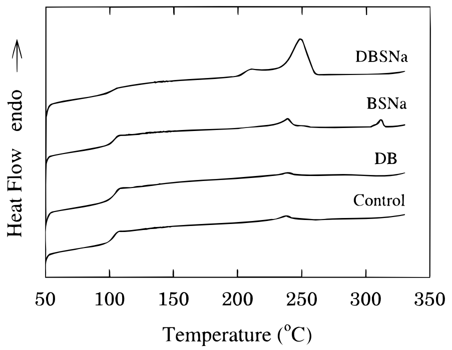

Figure 3. Influence of plasticizer type on the thermal behavior of isothermally crystallized SsPS ionomers. The samples were crystallized at 190 °C from the melt for 1 h.

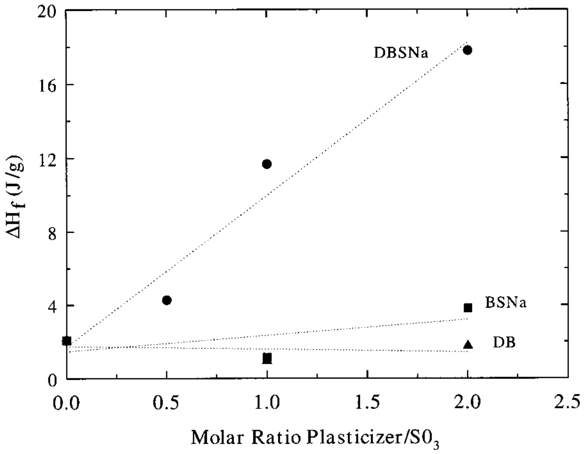

Figure 4. Effect of plasticizer concentration and type on the heat of fusion of isothermally crystallized Na$^+$-neutralized sulfonated syndiotactic polystyrene ionomers containing 2.2 mol % sulfonation. Samples were isothermally crystallized form the melt at 190 °C for 1 h.

Figure 3 shows DSC thermograms of isothermally crystallized (1 h at 190 °C) SsPS ionomers containing a 2:1 molar ratio of the various additives to ionomer SO_3^- groups. While the T_g's are similar for all the samples, only the ionomer plasticized with DBSNa yields significant crystallinity. The sample containing the hydrocarbon DB plasticizer shows no enhancement in crystallinity compared with the pure SsPS ionomer, while the ionic BSNa additive yields only a slight increase in crystallinity. Figure 4 compares the melting behavior of isothermally crystallized SsPS-2.2Na$^+$ containing different amounts of the three types of additives. The ΔH_f associated with the melting endotherm for samples containing either DB or BSNa does not significantly increase relative to the pure ionomer. In contrast to the low ΔH_f's obtained for the DB and BSNa additives, the level of crystallinity dramatically increases with addition of DBSNa surfactant.

It is interesting to note that the ionomer containing BSNa displays an additional endotherm at 315 °C (Figure 3). On the basis of the melting point of pure BSNa, this new endotherm is attributed to melting of "phase-separated" BSNa crystallites. Comparison of the melting endotherm of pure BSNa with the BSNa containing samples suggests that greater than 50% of the ionic additive is in a separate crystalline phase. The remainder of the BSNa is likely to be finely dispersed within the ionic domains of the ionomer.[55,56] Note that

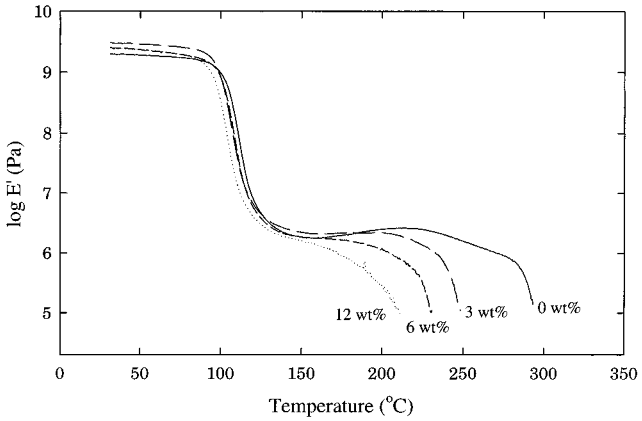

Figure 5. Effect of the sodium salt of dodecylbenzenesulfonic acid concentration on the dynamic mechanical properties (storage moduli) of sulfonated atactic polystyrene containing 2.1 mol % sodium sulfonate groups.

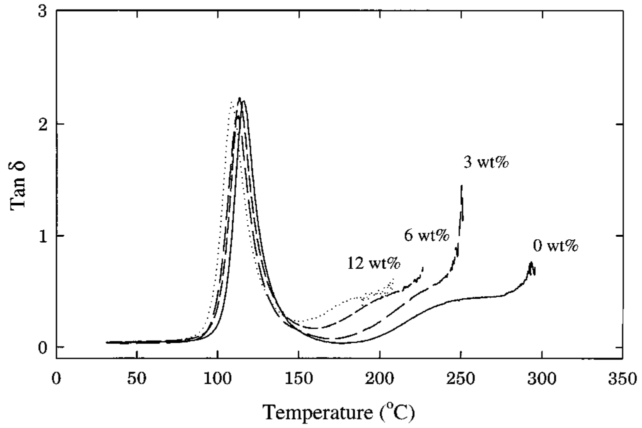

Figure 6. Effect of the sodium salt of dodecylbenzenesulfonic acid concentration on the dynamic mechanical properties (tan δ) of sulfonated atactic polystyrene containing 2.1 mol % sodium sulfonate groups.

this salt crystallite, phase-separation behavior is similar to that observed for ionomers containing excess neutralizing agent.[55,57]

Effect of Preferential Plasticizers on the Electrostatic Network in Sulfonated Polystyrene Ionomers. *Dynamic Mechanical Properties of SaPS Ionomers Containing Preferential Plasticizers.* Dynamic mechanical analysis was utilized to probe the influence of the preferential plasticizer molecules on the strength of the electrostatic network in the PS-based ionomers.[6,13,30,51,58] To avoid the complications of crystallinity in SsPS, sulfonated *atactic* polystyrene ionomers (SaPS) were utilized to isolate the influence of the additives on the dynamic mechanical properties. The primary focus of this mechanical investigation was to evaluate the viscoelastic behavior of SaPS/additive mixtures in the rubbery and terminal flow regimes between 125 and 300 °C. By understanding the effect of the additive structure on the network stability, this information will be correlated to the crystallization behavior of SsPS/additive systems in the same temperature range.

Figures 5 and 6 show the storage modulus, E', and the loss tangent, tan δ, versus temperature profiles for SaPS-2.1Na$^+$ ionomers containing various levels of DBSNa surfactant. The storage modulus for the pure SaPS ionomer (containing no surfactant) shows a dramatic decrease at ca. 100 °C, which is attributed to the T_g of the matrix. Above the matrix T_g, there is an extended rubbery plateau that is commonly observed in ionomers and is attributed to the electrostatic network formed by ionic aggregation.[2,13,30,59] At temperatures near 300 °C, the SaPS-2.1Na$^+$ sample begins to exhibit the onset of flow.[58] Note that the strength of the electrostatic interactions is believed to govern the terminal flow behavior, and this process has been postulated to occur by ion hopping (i.e., the dynamic behavior of ion pairs transferring from multiplet to multiplet in an attempt to satisfy the local balance between electrostatic and elastic forces).[58,60,61] As the temperature approaches the flow regime (ca. 290 °C), the elastic forces on the polymer segments increase and become comparable in strength to the electrostatic forces within the multiplet.[51] Above 290 °C, the rate of ion hopping is accelerated which enables the ionomer to flow.[58]

In agreement with the DSC results for the semicrystalline ionomer (Figure 1), the matrix T_g for SaPS-2.1Na$^+$ ionomers containing the DBSNa surfactant (taken as the peak maximum in Figure 6) decreases only slightly with increasing levels of surfactant. In contrast, however, the breadth of the rubbery plateau decreases remarkably with increasing DBSNa concentration, and the onset of flow begins at significantly lower temperatures relative to the unplasticized ionomer. Moreover, at temperatures above the matrix T_g, each of the profiles shows a weak maximum or broad shoulder just before the final upward curvature (i.e., the onset of flow). For polystyrene-based ionomers, this high-temperature relaxation has been attributed to the glass transition of the cluster phase.[2,13,30,32] By comparison with the behavior of the matrix T_g, the cluster phase relaxation shifts profoundly to lower temperatures with increasing levels of surfactant. These data suggest that the DBSNa preferentially plasticizes the ionic domains and disrupts the thermomechanical stability of the electrostatic network.[58] Similar selective plasticization behavior was observed by Kim et al.,[33] for SaPS ionomers with ion contents greater than 4.7 mol %. Since the DBSNa preferentially incorporates into the multiplets and disrupts the regions of restricted mobility,[2] the electrostatic cross-links are weakened, which promotes ion hopping at lower temperatures relative to the pure ionomer.

The effect of the type of additive on the dynamic mechanical properties of SaPS-2.1Na$^+$ ionomers containing a 2:1 molar ratio of additive to ionomer SO_3^- groups is shown in Figures 7 and 8. The E' vs temperature profiles (Figure 7) of the unplasticized sample and those of the DBSNa and BSNa mixed ionomers are similar below 150 °C, although the T_g of the DBSNa plasticized SaPS-2.1Na$^+$ is slightly lower than that of the BSNa mixed ionomer. This difference may be attributed to a more efficient plasticization of the matrix phase by the hydrocarbon tails of DBSNa molecules associated with lone ion pairs or isolated multiplets, relative to the ionic BSNa additive. In contrast to the polar additives, the nonpolar DB additive is quite soluble in the matrix phase and significantly reduces the matrix T_g.

At temperatures greater than the matrix T_g, it is interesting to note that the BSNa mixed sample yields a relatively high rubbery modulus. Moreover, the magnitude of this elevated rubbery plateau exceeds that of the pure ionomer over a 100 °C temperature range. In agreement with previous studies of ionomers containing

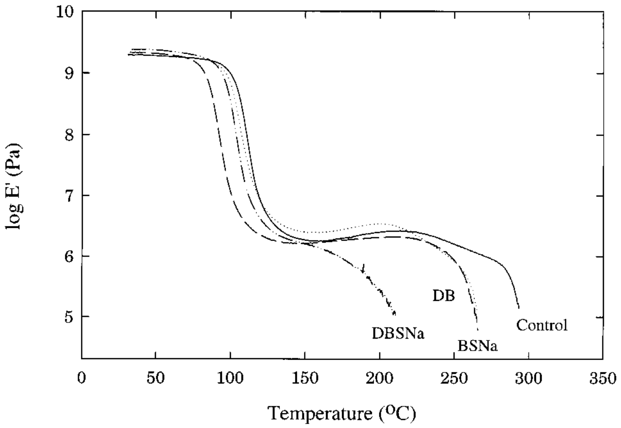

Figure 7. Effect of plasticizer type on the dynamic mechanical properties (storage moduli) of sulfonated atactic polystyrene ionomers.

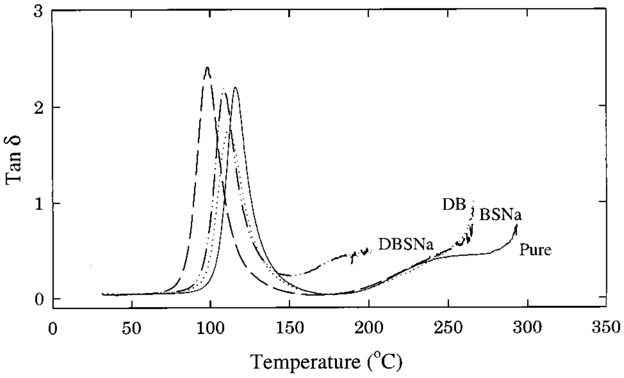

Figure 8. Effect of plasticizer type on the dynamic mechanical properties (tan δ) of sulfonated atactic polystyrene ionomers.

excess neutralizing agent[55,57] and filled polymers,[62] this elevated storage modulus in the rubbery plateau region of the BSNa mixed sample may be attributed to BSNa crystallites acting as solid filler particles.

Above 150 °C, there is a significant effect of the additive type on the dynamic mechanical behavior of SaPS. Despite the profound differences in polarity between the BSNa and DB molecules, it is surprising to see that these two additives yield virtually identical flow behavior. In comparison to the very large drop in flow temperature of the DBSNa-containing sample (ca. 100 °C), the BSNa and DB additives only lower the onset of flow by ca. 40 °C, relative to the pure ionomer. Thus, the DB and BSNa additives are apparently much less efficient at disrupting the electrostatic network, relative to DBSNa.

To understand the flow behavior of the plasticized ionomers, it is useful to evaluate the loss tangent (tan δ) vs temperature profiles. Figure 8 shows the tan δ vs temperature plots for the SaPS-2.1Na$^+$ ionomer samples corresponding to the data in Figure 7. Over the temperature range 200−250 °C, the broad relaxation attributed to the cluster T_g for the DB and BSNa mixed samples appears to be similar to that of the pure, unplasticized ionomer. In contrast to the BSNa and DB additives, the DBSNa molecules possess polar and nonpolar character and thus reside preferentially within the ionic domains. The preferential plasticization apparently increases the mobility of the chains surrounding the multiplets which reduces the cluster T_g[33] and subsequently causes a profound reduction in the terminal flow temperature. This behavior may be attributed to a decrease in the thermal stability of the electrostatic network, which increases the rate of ion hopping.[58] Thus, these data yield further evidence that, at temperatures less than ca. 250 °C, the DB and BSNa additives are less efficient at disrupting the stability of the ionic domains, relative to the DBSNa plasticizer.

While the samples containing the DB or BSNa additives appear to have cluster T_g's similar to that of the unplasticized ionomer and virtually identical depressions in the terminal flow temperature, it is noted that precise interpretation of the high-temperature relaxation in ionomers is difficult. With these ionomers, the uncertainty stems from the fact that the relaxations of the cluster phase and the flow processes (involving ion hopping) are convoluted within the same temperature region. Nevertheless, since these ionomers behave as multiphase materials (consisting of ionic and matrix domains), it is reasonable to expect that the long-range molecular motions associated with flow will be limited by the mobility of the most rigid phase.[63] Clearly, the cluster-phase relaxations shown in Figure 8 occur at significantly higher temperatures than the matrix T_g. Therefore, significant ion hopping associated with bulk flow should only occur as the segmental motions of the cluster-phase chains become thermally activated.[58]

Due to the polar and nonpolar nature of the BSNa and DB additives, respectively, it is likely that the origins of the enhanced flow behavior (Figure 7) may be attributed to two distinctly different mechanisms. Since a significant portion of the BSNa molecules apparently reside within phase-separated, microcrystalline domains, the surfaces of the BSNa crystallites or particles may act as additional sites for ion hopping,[55] thereby increasing the long-range chain mobility and diffusion. For the nonpolar plasticizer, the DB molecules may act to lower the local viscosity of the system and facilitate difffusion/migration of the ion pairs through the PS matrix.[35] While a study aimed specifically at the ion-hopping process in ionomers is required to fully elucidate the precise mechanism of flow with these polar and nonpolar plasticizers, additional insight into the effect of these additives on the state of the electrostatic cross-links may be obtained through spectroscopic analysis.

^{23}Na SSNMR of SsPS-2.1Na$^+$ Ionomers Containing Plasticizers. Recent ^{23}Na SSNMR investigations by Cooper and co-workers[20−23] have shown that sodium ions in dry, lightly sulfonated polystyrene ionomers may exist in two distinctly different environments: (1) isolated sodium nuclei in lone sodium−sulfonate ion pairs and (2) sodium nuclei in close proximity to other sodium nuclei (i.e., in ionic aggregates). The sodium nuclei existing in lone ion pairs yield a sharp peak centered at 7 ppm, while the sodium nuclei in the ionic aggregates (i.e., doublets, triplets, ..., multiplets) yield a broad peak centered in the range −8 to −12 ppm, depending on the state of ionic aggregation. Due to quadrupolar coupling interactions of the ^{23}Na nuclei, these specific ionic environments yield different electric field gradients surrounding the nuclei, resulting in distinctly different quadrupolar coupling constants (QCC).[20] Note that the QCC is a measure of the strength of interactions between the quadrupolar sodium nuclei and electric field gradients in their surrounding environment.[20]

For lightly sulfonated PS, the peak corresponding to aggregated ions was found to broaden and shift upfield

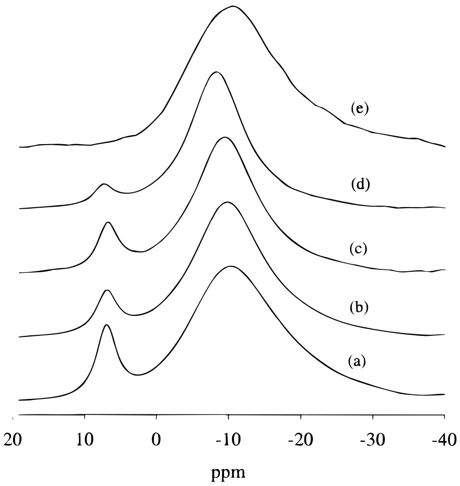

Figure 9. Effect of the sodium salt of dodecylbenzenesulfonic acid on ^{23}Na SSNMR spectra of SsPS-2.2Na^{+}: (a) without DBSNa; (b) with 1:2 molar ratio of DBSNa to sodium sulfonate along the polymer backbone; (c) with 1:1 molar ratio of DBSNa to sodium sulfonate along the polymer backbone; (d) with 2:1 molar ratio of DBSNa to sodium sulfonate along the polymer backbone; and (e) surfactant DBSNa.

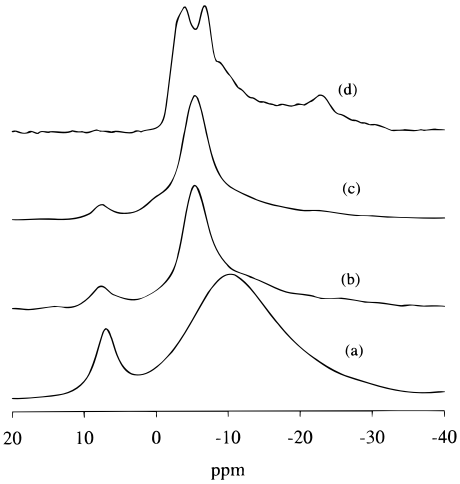

Figure 10. Effect of the benzene sodium sulfonate on ^{23}Na SSNMR spectra of SsPS-2.2Na^{+}: (a) without BSNa; (b) with 1:1 molar ratio of BSNa to sodium sulfonate along the polymer backbone; (c) with 2:1 molar ratio of BSNa to sodium sulfonate along the polymer backbone; and (d) BSNa salt.

(toward more negative ppm values) with increasing ion contents;[20] this spectral behavior indicated an increase in the QCC value. On the basis of the factors that influence quadrupolar coupling, the increase in QCC was attributed to stronger interactions between the ion pairs arising from a possible combination of a greater number of ions held in aggregates, a closer packing between the ions, and/or a less symmetrical packing of the ion pairs.[20]

^{23}Na SSNMR spectra of SsPS-2.2Na^{+} containing DBSNa (Figure 9) show a downfield shift of the aggregate peak maximum from ca. −11 to ca. −8 ppm as the DBSNa content is increased. In addition, the width of the aggregate peak decreases with increasing DBSNa. It is of interest to note that this behavior is opposite to that observed by simply increasing the ionic content along the PS backbone.[20] The downfield shift coupled with the decrease in peak width is attributed to a decrease in the QCC, reflecting weaker quadrupolar interactions within the ionic aggregates.

To confirm that the observed downfield shifts of the aggregate peaks in Figure 9 correspond to a quantitative change in the QCC value with added DBSNa, the pure SsPS-2.2Na^{+} sample and the SsPS-2.2Na^{+} sample containing a 2:1 molar ratio of DBSNa were run at 52.5 MHz on a Bruker MSL-200 spectrometer and compared to the results obtained at 105 MHz. Following the analysis of Samoson,[64] and assuming that the asymmetry factor is equal to zero,[20] the QCC values for the pure SsPS-2.2Na^{+} and the ionomer sample containing DBSNa were calculated to be 1.63 and 1.46 MHz, respectively. In addition to the confirmation of a decreased QCC with increasing DBSNa content, it is of interest to note that the QCC value calculated for the pure SsPS-2.2Na^{+} ionomer is equivalent to that found for sulfonated, *atactic* polystyrene ionomers.[20] This observation suggests that, for sulfonated polystyrene, the local organization of the ionic aggregates is virtually independent of backbone tacticity.

The change in quadrupolar interactions with added DBSNa may be rationalized by considering the relative mobility of ion pairs on the DBSNa molecule to those attached to the polymer chains. As multiplets are formed, the very mobile surfactant molecules are likely to facilitate more symmetrical packing within the aggregates (i.e., yielding a decrease in QCC). Furthermore, the typical surfactant character of the DBSNa molecules is likely to create a better dispersion of polymer-bound ion pairs (i.e., by micellar stabilization[65]) and may decrease the average number of ion pairs per aggregate (i.e., a decrease in QCC). Since the surfactant and polymer-bound ion pairs are both attached to phenyl rings, the closeness of packing of ion pairs in the multiplet (and thus the contribution to QCC) should not be affected by the presence of surfactant. To confirm this qualitative interpretation, however, further morphological investigations of these systems are warranted.

The data in Figure 9 also show that, with increasing DBSNa content, the area of the peak attributed to the isolated ions (at ca. 7 ppm) decreases relative to the area of the aggregate peak. This change indicates a decrease in the relative population of isolated ion pairs as DBSNa is added to the ionomer. It should be noted, however, that this behavior does not necessarily suggest that the surfactant molecules enhance the driving force for aggregation of polymer bound ion pairs. On the basis of the decrease in the rubbery modulus of SaPS with increasing DBSNa (Figure 5), it is more likely that a fraction of the surfactant molecules simply associate with a portion of the previously isolated ion pairs. This association is analogous to that observed with surfactant/ionomer interactions in nonpolar solutions[65] and does not contribute to an increase in the density or functionality of electrostatic cross-links (i.e., with a corresponding increase in the rubbery modulus).

Figure 10 compares the ^{23}Na SSNMR spectrum of SsPS-2.2Na^{+} to those of SsPS-2.2Na^{+}/BSNa mixtures and pure BSNa. With the addition of BSNa to the ionomer, a relatively sharp peak is observed at ca. −5 ppm. In agreement with the DSC results shown in Figure 4, this new, sharp peak occurs at the same chemical shift as that of pure (crystalline) BSNa (Figure 10d)[66] and further confirms the existence of a distinct phase of BSNa within the ionomer matrix. As the BSNa content is increased, the aggregate peak (detected as a shoulder at ca. −10 ppm) and the peak attributed to isolated ions (at ca. 7 ppm) diminish in intensity relative to the pure BSNa peak. This behavior is consistent with

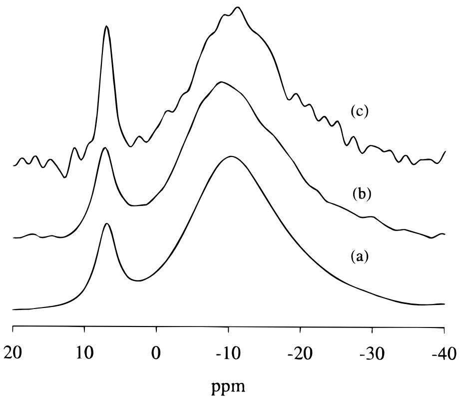

Figure 11. Effect of the dodecylbenzene on ^{23}Na SSNMR spectra of SsPS-2.2Na$^+$: (a) without DB; (b) with 1:1 molar ratio of DB to sodium sulfonate along the polymer backbone; and (c) with 2:1 molar ratio of DB to sodium sulfonate along the polymer backbone.

the tendency of added BSNa to phase separate instead of significantly contributing to the fractions of isolated or aggregated ion pairs.[55] Furthermore, peak deconvolution indicates that the position of the aggregate peak remains constant with the addition of BSNa. Therefore, these data suggest that BSNa does not appreciably affect the electrostatic (quadrupolar) interactions within the ionic aggregates.

^{23}Na SSNMR spectra of SsPS-2.2Na$^+$ containing DB are compared to that of the pure ionomer in Figure 11. With the addition of DB, no significant change in the position and width of the peak corresponding to the ionic aggregates is observed. This invariance of the QCC value upon addition of DB indicates that the DB molecules do not perturb the electrostatic environment within the ionic aggregates. With high DB content, there is, however, an increase in the intensity of the sharp peak corresponding to the isolated ions. On the basis of previous studies of SaPS ionomers, this behavior may be attributed to the effect of a nonpolar additive during the solution-casting procedure.[21] With a solvent mixture of low polarity, less ion pair rearrangement occurs during the final stages of solvent evaporation, resulting in a greater fraction of lone ion pairs trapped in the matrix. Thus, in accordance with the DSC and DMA results for this system, the nonpolar DB additive simply acts as an organic plasticizer and does not have a significant effect on the interactions within the electrostatic cross-links.

Relationship between the Stability of the Electrostatic Network and Crystallization in SsPS Ionomers. Due to the ionic nature of the aggregates, the interactions between the sodium nuclei and their local environments are principally electrostatic. Thus, the QCC generally reflects the strength of ionic interactions within the electrostatic network.[20] The ^{23}Na SSNMR data indicate that the added DBSNa molecules effectively disrupt interactions within the ionic aggregates and consequently weaken the electrostatic network in SsPS. In addition, these surfactant molecules may redistribute the ion pairs by effectively displacing a portion of the polymer-bound ions in the multiplets. This conceivable decrease in the average fraction of polymer-bound ion pairs per multiplet lowers the cross-link functionality (i.e., cross-link efficiency) of the aggregates, which further diminishes the ability of the resulting network to restrict the mobility of crystallizable segments.

The dynamic mechanical behavior of SaPS containing DBSNa demonstrates that the polar/nonpolar character of the surfactant is quite effective in weakening the electrostatic network within these ionomers. The decrease in the strength of electrostatic interactions, as indicated by ^{23}Na SSNMR, and the decrease in the cluster T_g, observed in DMA experiments, suggests that these weak multiplets are easily destabilized at elevated temperatures.[58] During isothermal crystallization of SsPS, the mobile surfactant molecules weaken the electrostatic network, increase the rate of ion hopping, and consequently increase the mobility of crystallizable chain segments. In a fashion that is consistent with our previous investigations of SsPS ionomers,[50,54] this destabilization of the dynamic, electrostatic network enhances the crystallization kinetics of SsPS containing DBSNa.

In contrast to the desirable effects of preferential plasticization, the partial molecular analogues of DBSNa (i.e., the polar and nonpolar parts, respectively), by themselves, are not effective at significantly lowering the electrostatic barrier to crystallization. DMA results of SaPS ionomers, with BSNa and DB, indicate an enhancement of flow in the mixtures relative to the control; however, the onset to flow occurs at a temperature higher than that of the isothermal crystallization temperature and close to the T_m of pure sPS. Moreover, the ^{23}Na SSNMR results from SsPS containing BSNa or DB suggest that these additives do not significantly affect the interactive forces that govern the stability of the electrostatic network. Therefore, at these concentrations of DB or BSNa, the electrostatic network is kinetically stable during the isothermal crystallization process, and the modest lowering of the terminal flow temperature is insufficient to induce significant crystallization of SsPS ionomers.

Conclusions

The strong electrostatic interactions within SsPS containing 2.2 mol % sodium sulfonate ionic groups impose a formidable barrier to crystallization from the melt. Isothermal crystallization studies have demonstrated that the incorporation of small amounts of the sodium salt of dodecylbenzenesulfonic acid dramatically increases the crystallizability of the ionomer. Furthermore, crystallization kinetics studies of these ionomers show that the rate of crystallization increases with increasing surfactant concentration. This behavior is attributed to a preferential plasticization of the ionic domains, which enhances the molecular mobility of the crystallizable chain segments.

The influence of preferential plasticization on the stability of the electrostatic network and the resulting enhancement of crystallization in SsPS ionomers was evaluated by correlating the dynamic mechanical behavior of Na$^+$-neutralized sulfonated atactic polystyrene to the specific ionic interactions of the sodium sulfonate groups in SsPS, as probed by ^{23}Na solid-state NMR spectroscopy. DMA data from the ionomers containing DBSNa showed that the surfactant molecules selectively plasticize the ionic domains. This preferential plasticization weakens the electrostatic network by apparently increasing the rate of ion hopping. With enhanced ion hopping, a large decrease in the temperature of bulk flow was observed. For the crystallizable SsPS ionomers, preferential plasticization with DBSNa is likely to provide greater mobility of the crystallizable polymer backbone at the chosen isothermal crystallization temperature.

^{23}Na SSNMR investigations of the ionic interactions in SsPS containing DBSNa showed a significant decrease in the QCC value with increasing contents of the surfactant. This behavior may be attributed to a weakening of electrostatic interactions within ionic aggregates. On the basis of the factors that govern the magnitude of the QCC, the surfactant molecules are postulated to redistribute the polymer-bound ions by creating smaller, symmetrically packed multiplets composed of both surfactant and polymer-bound ion pairs. Since the ionic interactions within these "mixed" multiplets are weakened, and the mobile surfactant molecules are not covalently attached to the cross-linked network, the kinetic stability of the electrostatic network (at elevated temperatures) is severely compromised. Therefore, during isothermal crystallization of SsPS, the surfactant molecules increase the dynamics of the electrostatic network, enhance the mobility of crystallizable chain segments, and consequently increase the rate of crystallization.

The role of the polar/nonpolar character of the surfactant in affecting the stability of the electrostatic network may be evaluated further by bracketing the behavior of the SaPS/DBSNa system between that of the ionomers containing polar and nonpolar molecular analogues of the surfactant. The onset of flow observed in the dynamic mechanical data of the ionomers containing BSNa (i.e., the polar component of the surfactant) and DB (i.e., the nonpolar component of the surfactant) was found to be intermediate to that of the SsPS/DBSNa system and the pure ionomer. These changes in the dynamic mechanical behavior were attributed to simple organic plasticization and to an increase in the quantity of sites for ion hopping for the DB and BSNa additives, respectively. Nevertheless, the modest enhancement in flow observed with DB and BSNa was found to be insignificant at the chosen isothermal crystallization temperature of SsPS. In addition, ^{23}Na SSNMR analysis suggested that the electrostatic interactions within the aggregates of SsPS containing these molecular analogues are strong and virtually identical to that of the pure SsPS. Thus, these additives have little influence on the stability of the electrostatic network and do not provide a means of enhancing the crystallization of SsPS. Clearly, the dual polar/nonpolar character of the DBSNa surfactant is required to effectively invade the complex multiplet structure in order to influence the stability of the electrostatic network and enhance SsPS crystallization.

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(66) The line shape of the spectrum in Figure 10d reflects quadrupolar features characteristic of the ordered environment surrounding the sodium nuclei within the crystalline BSNa salt.

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