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Complexes of Polystyrene Ionomers with Mono- and Bifunctional Styrene Oligomers (Homografts)

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ABSTRACT: Lightly sulfonated polystyrene (7 mol %) (PS−SSA) that is ionically complexed with monodisperse tertiary amine-terminated oligomers of styrene, both mono- and bifunctional, were investigated by dynamic mechanical thermal analysis (DMA). The chain lengths of the oligomers are significantly greater than the average segmental length between the functional groups in PS−SSA. The monofunctional oligomer plasticizes PS−SSA as expected but considerably less than do alkyl chains, attributed to the greater bulkiness and stiffness of the styrene segments. The bifunctional oligomer, twice as long as the monofunctional oligomer, has very little plasticizing action and, at high concentrations, phase separates from the PS−SSA, despite extensive intercomponent interactions. This is related to a copolymer effect, suggested to be all the more pronounced because no cluster phase is apparent.

Introduction

In two previous papers,[1,2] we analyzed ionomer/oligomer blends where both the nonionic moieties and the ionic moieties are chemically identical and the oligomers are monodisperse. In the first,[1] the length of the (monofunctional) oligomer chains is much less than that of the average segmental length between ionic groups in the (biphasic) ionomers, and preferential plasticization of the cluster phase was observed. In fact, in comparison with another study,[3] where the nonionic part of the short oligomer (a soap) used is not, in principle, miscible with the nonionic part of the ionomer and yet similar results were obtained, it was concluded that, when significant ionic interactions take place, the nature of the nonpolar tail is of minor importance to the plasticization effects observed. The nature and strength of the ionic interactions, on the other hand, are of critical importance.

In the second paper,[2] the oligomer length was much greater than the inter-ionic segmental length. Plasticization effects in the blends, for both mono- and bifunctional oligomers, are very much attenuated. Furthermore, for the bifunctional oligomers, an antiplasticization effect was observed at low ion contents, whereas, in the blends involving an ionomer with a majority cluster phase, phase separation was observed. The latter phenomenon was attributed to insufficiently large ion-poor regions in the ionomer to accommodate the long nonionic portion of the oligomer chains at higher oligomer contents. A parallel was drawn between blends of block copolymers and homopolymers of the same chemical composition as one of the blocks but of too high a molecular weight to be accommodated in the phase formed by that block, provoking phase separation.[2,4−6]

Now, it has previously been observed that miscibility is considerably enhanced when the ionic groups in the two components are forced to interact (because one forms the counterion to the other) compared to a blend system where the ionic groups in the two components are similar (or identical) and so do not necessarily have to be in contact.[7,8] For example, blends of poly(styrene-*co*-sulfonic acid) and poly(ethyl acrylate-*co*-vinyl pyridine), where proton transfer from the acid to the base occurs, leading to direct ion−ion interactions (ionic complexes), are largely miscible at about 5 mol % ion content, whereas blends of poly(styrene-*co*-sodium methacrylate) and poly(ethyl acrylate-*co*-sodium acrylate) show only a small enhancement in miscibility at similar ion content.[7]

From this point of view, it is of interest to investigate ionomer/oligomer blends where the ionic groups of the two components are forced to interact via complexation and compare their behavior with the blends mentioned above where the ionic groups of the two components are identical. This is the subject of this paper and the next. In order to promote strong ionic complexation, recourse was made to lightly sulfonated polystyrene copolymers (PS−SSA) and monodisperse dimethyl amine-functionalized oligomers. Ion−ion complexes are expected to be formed as a result of proton transfer from the acid to the amine.[7,9] These blends can be viewed also as ionomers possessing counterions with long organic tails when using monofunctional oligomers or with long organic bridges when using bifunctional oligomers or as graft copolymer-like materials. When the nonionic parts of the two components are identical, the blends can be referred to as “homografts”; these are dealt with in the present paper. When the nonionic parts are not identical, the blends can be considered as “heterografts”, to be dealt with in the next paper.

In the present paper, the oligomers are styrene-based like the ionomer and are similar in length and identical in functionality number (mono- and bi-) to the long oligomers of the system mentioned above[2] and with which they will be compared. In other words, the oligomers are significantly longer than the average segmental length between functional groups in the copolymer. The bifunctional oligomer is about twice the length of the monofunctional oligomer in order to maintain a comparable functional group content. Of particular interest is the extent of plasticization that is observed in these systems and whether or not phase separation occurs despite complexation.

Experimental Section

1. Synthesis. The sulfonated polystyrene copolymer was obtained by chemical modification of polystyrene, according

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Table 1. Characteristics of the Oligomers Synthesized (*n* = Average Number of Styrene Units per Chain; *f* = Functionality)

oligomer	n	M_n	M_w/M_n	f	T_g (°C)
S21−NMe$_2$	21	2200	1.2	0.9	88
S39−α,ωNMe$_2$	39	4100	1.2	1.8	95

to the usual procedure first described in ref 10. For this purpose, polystyrene was synthesized by classical free radical techniques and determined to have a molecular weight (M_n) of 70 000 (M_w = 140 000) and a polydispersity of 2.0. Following the sulfonation procedure and purification in boiling water, the copolymer was dried at 50 °C under reduced pressure for three weeks. The sulfonic acid content was determined by titration using phenolphthalein to be 7.0 mol %.

The styrene oligomers were synthesized in THF by living anionic techniques,[11] using *sec*-butyllithium and sodium naphthalene as initiators for the mono- and bifunctional oligomers, respectively. They were deactivated by addition of a 20 molar excess of 1,3-bis(dimethylamino)propyl chloride, prepared as described in ref 12. The reactor was maintained at −78 °C for 1 h during this step and then allowed to warm to ambient temperature, where stirring was continued for another few hours. Finally, the solution was concentrated and the oligomers purified by precipitating three times in a 0 °C solution of 90/10 (v/v) methanol/H$_2$O. They were dried for 1 week under reduced pressure at ambient temperature.

The molecular characteristics and the glass transition temperatures of the oligomers are given in Table 1. The molecular weights, M_n, and the polydispersities, M_w/M_n, were determined in THF by size exclusion chromatography (Waters) and a refractive index detector (Wyatt), using polystyrene standards. The chromatograph was fitted with a Shodex column for molecular weights below 10 000 in addition to the (Waters) ultralinear μ-styragel column (molecular weights 1500 to 10^6). The functionalities were determined by potentiometric titration of the amine end groups of the oligomer dissolved in benzene/methanol (90/10 v/v), using a standardized solution of 0.02 M perchloric acid. The glass transition temperatures, T_g, were determined by differential scanning calorimetry (DSC) (Perkin-Elmer DSC-4) at 20 °C/min, taken at the midpoint of the transition.

The monofunctional oligomer is designated by the acronym, S21−NMe$_2$; the bifunctional one, by S39−α,ωNMe$_2$. S refers to the styrene repeat unit, and is followed by a figure indicating the average number of styrene units per chain.

2. Blend Preparation and Methods of Analysis. The blends were prepared by dissolving calculated amounts of the components in benzene/methanol (90/10 v/v) to give about 1% (w/v) solutions. These solutions were stirred for about 12 h at ambient temperature and then freeze-dried and further dried under reduced pressure at ambient temperature for 4 weeks. They were subsequently compression-molded (10 MPa maximum pressure) at about 180 °C into rectangular bars (35 × 10 × 2 mm^3) for dynamic mechanical experiments and into thin films (about 20 μm thick) for infrared analysis, after which they were placed in a vacuum oven at about 100 °C overnight and then stored in a desiccator until used. The molded samples were all transparent; this is expected whether or not phase separation occurs, since the refractive indexes of both components are necessarily similar.

The infrared spectra were obtained from 100 interferograms at a resolution of 2 cm^{-1}, using a Mattson Sirius 100 FTIR, equipped with a MCT detector. Dynamic mechanical thermal analysis (DMA) was performed using the Polymer Laboratories DMTA, Mk II, in dual cantilever bending mode. The measurements were made at five frequencies (0.3, 1, 3, 10, and 30 Hz) and a nominal deflection of 64 μm, at a heating rate of 1 °C/min. The sample chamber was constantly flushed with a light flow of dry nitrogen. The "free length" of the samples, when clamped, was 5 mm. All of the data reported are for a frequency of 1 Hz (except activation energies, calculated using all five frequencies).

Results

Infrared analysis was first applied to the blends in order to verify that proton transfer leading to ionic grafting indeed occurs and to what extent (since it is not necessarily complete[13]). Several studies involving proton transfer from styrene sulfonic acid to amine or pyridine units for other blend systems have already been reported in the literature,[13,14] and so the expected changes in the spectra, especially as related to the sulfonic acid group, are well-documented. One of the most telltale features is the shoulder on the low-wavenumber side of the polystyrene band at 906 cm^{-1}, assigned to the stretching vibration of the SO bond with single-bond character.[15] Other characteristic bands related to the acid group are found at 1172 and 1350 cm^{-1} (symmetric and antisymmetric stretching vibrations of the two SO bonds with double-bond character) and near 1100 cm^{-1} (in-plane skeleton vibrations of the benzene ring with strong participation of the substituents). When the acid group is ionized, the shoulder at 900 cm^{-1} disappears, as do the other three bands mentioned, to be replaced by new bands related to the sulfonate group.[13,15] The latter include intense bands at 1009 cm^{-1} (assigned to in-plane bending vibrations of the benzene ring substituted by the sulfonate group in the para position) and 1120 cm^{-1} (in-plane skeleton vibration of the benzene ring with strong participation of the sulfonate groups).

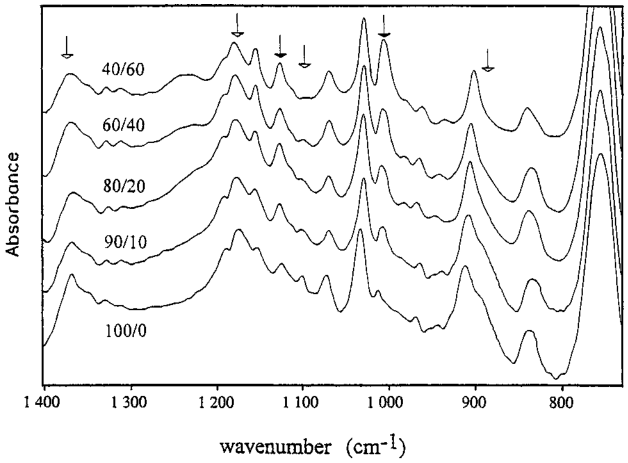

Figure 1. Infrared spectra for the homografts with S39−α,ωNMe$_2$ at the ionomer/oligomer weight ratios indicated.

Table 2. Amine/Acid Molar Ratios (*R*) and Fraction of Proton Transfer (PT) in the Homografts of Various Ionomer/Oligomer Weight Ratios (w/w)

blend	w/w	R	PT
PS−SSA/S21-NMe$_2$	90/10	0.08	0.15
	80/20	0.19	0.31
	60/40	0.51	0.46
	40/60	1.14	0.85
PS−SSA/S39−α,ωNMe$_2$	90/10	0.09	0.15
	80/20	0.20	0.38
	60/40	0.53	0.46
	40/60	1.19	0.92

As shown in Figure 1, the bands associated with the sulfonate group (marked with filled arrows) become progressively apparent with increasing oligomer content in the homografts, whereas those associated with the acid group (marked with open arrows) progressively disappear. For the blend containing 60% styrene oligomer, in particular, the shoulder near 900 cm^{-1} has essentially disappeared. Since the amine and acid groups are approximately equimolar in this blend (Table 2), this indicates that proton transfer is complete or nearly so.

The extent of proton transfer can actually be quantified by determining the area under the 906−900 cm^{-1}

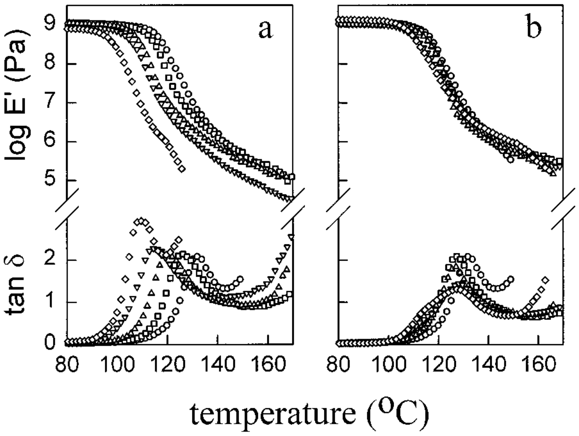

Figure 2. Young's storage modulus and loss tangent at 1 Hz as a function of temperature for the (a) PS−SSA/S21−NMe$_2$ and (b) PS−SSA/S39−α,ωNMe$_2$ homografts. Ionomer/oligomer weight ratios: ○, 100/0; □, 90/10; △, 80/20; ▽, 60/40; ◇, 40/60.

Table 3. Dynamic Mechanical Thermal Analysis Data for the Homografts

blend	w/w	T_g (°C)	T_g(Fox) (°C)	activation energy (kJ/mol)
PS−SSA		132		480
PS−SSA/S21-NMe$_2$	90/10	126	129	400
	80/20	120	126	450
	60/40	115	120	490
	40/60	111	114	470
PS−SSA/S39−α,ωNMe$_2$	90/10	127	130	510
	80/20	127	128	570
	60/40	128	123	560
	40/60	127	118	600

bands and normalizing it to the area of the 759 cm^{-1} (or 1945 or 1875 cm^{-1}) polystyrene band, assuming 0% proton transfer for PS−SSA and assigning 100% proton transfer for homopolystyrene (for which there is no shoulder to the 906 cm^{-1} band). This operation has been effected previously for blends of PS−SSA with ethyl acrylate/vinylpyridine copolymers[14] and for PS−SSA neutralized (partially or completely) by amine- and pyridine-containing small molecules.[13] As shown in Table 2, the spectroscopically determined extents of proton transfer generally correspond to within 10% of the value expected considering the amine/acid stoichiometry in question. We can conclude that we indeed have ionically grafted materials, with the amount of grafts corresponding approximately to the lesser of the number of acid or amine groups present.

We can now investigate the dynamic mechanical properties and what they tell us about the materials with confidence regarding the state of complexation. The Young's storage modulus and loss tangent curves at 1 Hz as a function of temperature for the blends with the mono- and bifunctional oligomers are shown in Figure 2. Various parameters associated with these curves, as well as the T_g's calculated according to the Fox equation,[16] are listed in Table 3. For the latter calculation, the oligomer DMA T_g's are considered to be 15 °C above their DSC-determined T_g's (which is approximately the difference we generally observe between the two techniques under the conditions of analysis used[8,9]); moreover, the possible effects of ionization and of changes in hydrogen-bonding interactions among acid groups are ignored. Thus, the choice of the Fox equation is based on its simplicity, and it is only to be considered as a guide for comparing the behavior in the two sets of blends.

The monofunctional oligomer clearly plasticizes the polymer (Figure 2a): the curves are essentially displaced to lower temperatures as oligomer is added, with the T_g's, as determined by the maximum in the loss tangent peak, being fairly similar to those calculated by the Fox equation. The apparent Arrhenius activation energy of the transition undergoes relatively little change with added oligomer or, at most, increases a little (the experimental error being estimated at about ±30 kJ/mol). The intensity and half widths of the peaks remain approximately constant. The seemingly greater intensity of the peak for the 40/60 blend can be explained by the flow region which sets in within the transition zone (judging from the sharp upturn in the loss tangent curves at the upper temperature end), thus adding to its intensity. For the other compositions, the flow zone sets in at much higher temperatures (even higher than that for PS−SSA), this temperature decreasing moderately with increase in oligomer content.

The rate of plasticization by the monofunctional oligomer resembles that observed for the matrix T_g of the previously studied blends of chemically identical ionomer (10 mol %) and monofunctional oligomer.[2] Furthermore, the plasticization behavior is similar to that reported for the same copolymers complexed with linear alkylamines,[17,18] and is, therefore, not very surprising. It is of interest, however, to note that the degree of plasticization depends on the nature of the chain. For stoichiometric blends of linear alkylamines with an 8.1 mol % sulfonated polystyrene, a decrease in T_g of 2.5 °C per methylene unit in the alkyl chain was observed (or 5.0 °C per ethylene unit, which is a more accurate comparison for the styrene unit).[17] A similar decrease of 2.4 °C per methylene unit was noted for copolymers of styrene and 7 mol % 4-vinylpyridine quaternized with iodoalkanes.[19] The stoichiometric blend in our case shows a T_g decrease of about 1.0 °C per styrene unit in the oligomer chain. This comparatively smaller decrease in T_g no doubt reflects the greater bulkiness and stiffness of the styrene chains compared to the alkyl chains.

In contrast to the monofunctional oligomer, the bifunctional oligomer has very little plasticizing action (Figure 2b and Table 3). Indeed, the T_g of PS−SSA is decreased by only a few degrees with the addition of 10% oligomer and thereafter remains essentially unchanged; the T_g's are clearly much greater than those calculated by the Fox equation. The apparent Arrhenius activation energy again undergoes relatively little change (or at most increases a little) with added oligomer, although it is notable that the values for the bifunctional oligomer are about 100 kJ/mol higher than those for the monofunctional oligomer. The intensity of the loss tangent maximum decreases significantly from that of PS−SSA (and the blend with 10% oligomer) as 20% and more oligomer is added. Simultaneously, the transition widens and a shoulder develops on its low-temperature side (110−115 °C), clearly visible for the blends with 40 and 60% oligomer. Evidently, increased concentration of oligomer gives rise to a second phase, this despite the fact that the nonionic segments of both ionomer and oligomer are chemically identical and that the two components are chemically grafted. The observation that the shoulder is at about 15−20 °C above the DSC T_g of the oligomer suggests that this phase is a pure, or almost pure, oligomer phase (although there is some uncertainty as to the effect of the quaternization of the oligomer extremities on the oligomer T_g in the blends, compared to the unquaternized form for the unblended oligomer).

It is also noteworthy that the flow zone is substantially elevated in temperature by the presence of the bifunctional oligomer, setting in somewhere beyond 170 °C for oligomer contents of 10 and 20%; even with 60% bifunctional oligomer present (in contrast to the monofunctional oligomer), the loss tangent begins to increase rapidly only at about 160 °C. This effect is evident also from the storage modulus curves in the rubbery region: for example, a storage modulus of 10^6 Pa is achieved in the vicinity of 145−150 °C for all of the blends with the bifunctional oligomer (about 10 °C above the same point for PS−SSA), in contrast to a decrease in temperature of this point from 140 to 120 °C as monofunctional oligomer is added to the polymer.

Finally, it is to be noted that no cluster transition is apparent in the curves for any of the blends. This is not unexpected for the blends with the monofunctional oligomer, where significant plasticization occurs. However, it could not have been ruled out a priori for the blends with the bifunctional oligomers, especially in view of the analogous system involving two PS-based ionomers, notably the blends of sulfonated polystyrene with styrene/vinylpyridine copolymers, where a cluster phase was detected.[20] This may indicate that any potential cluster phase present in the homografts of this study is too small in volume fraction and/or that any multiplets (ionic aggregates) present are insufficiently rigid to give rise to a detectable phase.

Discussion

The complexed blends with the monofunctional oligomer appear to be completely miscible and result in an ionically grafted material where the oligomer chains act as long side chains to the parent polymer. As such, plasticization effects are normal, and it is primarily of interest that the greater bulkiness and stiffness of the styrene side chains result in a concomitant reduction in their plasticizing efficiency compared to that of alkyl side chains.

The results for the blends with the bifunctional oligomer are more complex and merit further discussion. The most important points are the small effect of the oligomer on the T_g of the parent polymer and the appearance of a separate, essentially pure, oligomer phase despite the fact that both components are styrene-based and, furthermore, complexed via the ion pairs formed from proton transfer.

The minimal amount of plasticization, or reduction in T_g, can be related both to the limited solubility of the bifunctional oligomer in PS−SSA, giving rise to phase separation at higher oligomer contents, and to the fact that both ends of the oligomer chains are ionically “pinned” to ionomer chains, thus eliminating the free volume added by tail ends. The latter effect probably accounts also for the extension of the rubbery zone (retardation of the flow zone), this through the double effect of ionizing the polymer and forming effective bridges among polymer chains.

The phase separation phenomenon can be compared to what was observed in the previously studied, chemically identical ionomer/oligomer blends. There, phase separation into an ionomer, or ionomer-rich, phase and an essentially pure oligomer phase was observed to take place for blends of polystyrene ionomers possessing 10 mol % Cs and Ba carboxylate units (PS−0.10SCA−Cs and PS−0.10SCA−Ba) with bifunctional styrene oligomers of similar length to S39−α,ωNMe$_2$, but end-functionalized by Cs and Ba carboxylate (S42−α,ωCACs and S42−α,ωCABa).[2] This is shown in Figure 3, where the loss tangent curves for the 40/60 (w/w) PS−SSA/S39−α,ωNMe$_2$ blend are compared to those for the 40/60 (w/w) Cs and Ba blends. It can be observed that the loss peak reflecting the oligomer phase occurs in the same temperature region for all three blends (the T_g's of the three pure oligomers are also almost identical).

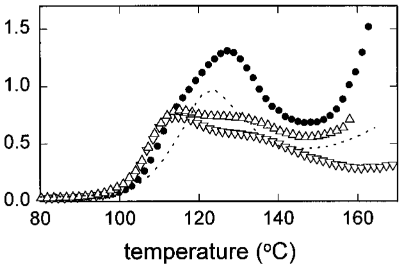

Figure 3. Loss tangent at 1 Hz as a function of temperature for the 40/60 (w/w) ionomer/oligomer blends: ●, PS−SSA/S39−α,ωNMe$_2$; △, PS−0.10SCA−Cs/S42−α,ωCACs;[2] ▽, PS−0.10SCA−Ba/S42−α,ωCABa;[2] dashed line, PS−0.07SCA−Ba/S42−α,ωCABa.[2]

It is to be recalled that the Cs and Ba ionomers are biphasic, with a majority cluster phase that remains present in the blends. Furthermore, for blends involving 7 mol % Cs and Ba ionomers (the latter shown as a dashed line in Figure 3), which are also biphasic but where the matrix phase dominates, phase separation of the bifunctional oligomers was not observed. In the present homografts, a cluster phase is not apparent; nevertheless, there is phase separation, and this at an ion content (the PS−SSA contains 7 mol % SSA) similar to that of the Cs and Ba system for which no detectable phase separation appears. Evidently, the existence or not of a cluster phase is not critical to the miscibility of ionomer/oligomer blends. This reinforces the explanation given in ref 2 that phase separation in the Cs and Ba blends is due to insufficiently large ion-poor styrene domains in the ionomer to accommodate the long nonionic portion of the oligomer chains. We can now add that this effect may be operative whether or not a cluster phase is present.

With this viewpoint, it is conceivable that the lack of a clear cluster phase may even contribute to the extent of phase separation observed and thus account, at least in part, for why phase separation occurs in the (bifunctional) homografts of the present study but not in the (bifunctional) oligomer/ionomer blends of ref 2 having similar ion content. For, according to the Eisenberg−Hird−Moore model,[21] the cluster phase arises from the aggregation of ionic groups into rigid multiplets. This aggregation favors the existence of ion-poor, or ion-depleted, domains. When no cluster phase is apparent, the ionic groups are presumably less aggregated; that is, they must be more dispersed throughout the polymer matrix, and there will be fewer or smaller ion-poor domains. This creates an unfavorable copolymer effect for the long oligomer molecules that provokes their phase separation at a lower ion content for unclustered ionomers than for clustered ionomers. In other words, there is greater miscibility of the oligomers with a biphasic ionomer than with a monophasic ionomer of the same ion content. A similar explanation has been evoked to explain the greater miscibility of some ionomers compared to others with poly(2,6-dimethyl-1,4-phenylene oxide).[4,5]

In the PS−SSA/styrene oligomer blends of this study, various factors may contribute to a greater dispersion of the ionic groups and therefore lack of cluster phase, among them, the fact that the ionic groups of both components are forced to interact through complexation,

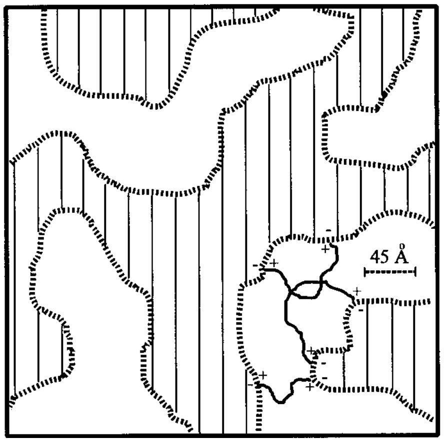

Figure 4. Schematic of the biphasic morphology in a homograft of similar ionomer and oligomer fractions. The ionomer, or ionomer-rich, phase is hatched. Representative oligomer chains are shown, and the approximate end-to-end distance is indicated. The ion pairs are preferentially located at the hatched interface (and are not necessarily uniformly distributed). Some chains or segments of one component may be located within the phase of the other component.

the relatively large size of the ammonium moieties that can weaken the strength of the ionic interactions as well as result in steric hindrance to significant aggregation,[17,18] the presence of the acid groups (for the blends for which the acid groups are in excess), and the lower molecular weight of the oligomer chains compared to polymer chains. An additional factor which may be considered is the distribution of counits, which is not necessarily the same in the sulfonated and the carboxylated polystyrene copolymers used.

A final point to address briefly is how to reconcile the simultaneous appearance of a detectable oligomer phase and the existence of extensive interactions through ion−ion bonds between the two components. If there is little mutual solubility of one component in the other, as indicated by the above results, the majority of the intercomponent ionic interactions must be interfacial. A possible explanation is related to the length of the bifunctional oligomer chains. The end-to-end distance of a chain containing about 40 styrene units, in its most probable configuration, is about 45 Å. As illustrated schematically in Figure 4 for a hypothetical homograft possessing similar ionomer and oligomer fractions, this may well allow the formation of oligomer regions that are detectable by DMA, for which a minimum size of the order of 50−100 Å is thought to be necessary.[21] The image is one of a highly irregular (and probably not very well-defined) interface between the ionomer and oligomer domains where most of the ionic interactions take place. In future work, it is of interest to verify this suggested morphology by other methods.

Conclusions

The homografts, where ionic complexation necessarily forces the ionic groups of the two components to be in proximity, behave qualitatively similarly to the previously studied blends of chemically identical ionomers and long-chain oligomers, where the ionic groups do not necessarily interact intimately.[2] The monofunctional oligomers in both cases appear to be completely miscible with the ionomer and have the expected plasticization effects; the extent of plasticization is modulated by the greater stiffness and bulkiness of the styrene segments compared to similar blends involving alkyl chains. When the oligomer is very long compared to the average segmental length between ionic (or functional) groups of the ionomer, phase separation occurs at high oligomer contents, illustrating its limited solubility in, or miscibility with, the ionomer. This can be attributed to the copolymer effect, in that the nonionic portion of the oligomers is miscible only with the nonionic portion of the ionomer. For oligomers beyond some critical length, there are insufficiently large ion-poor regions in the ionomer matrix to accommodate the nonionic portion of the oligomer, and it thus phase separates. One of the significant points of the present study is that this can occur even while maintaining extensive intercomponent ion-ion interactions. Furthermore, we suggest that the lack of a cluster phase, which may reflect a greater dispersion of the ionic groups throughout the ionomer matrix, may intensify the copolymer effect, hence provoking phase separation at lower ion contents than for a biphasic ionomer.

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