Complexes of Polystyrene Ionomers with Butyl Acrylate Oligomers (Heterografts)

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ABSTRACT: Monodisperse *tert*-butyl acrylate (*t*BA) oligomers of several lengths, functionalized at one end by a tertiary amine, were ionically grafted to lightly sulfonated polystyrene. Despite the oligomers being immiscible with the polystyrene matrix, dynamic mechanical analysis of the blends indicates only a weak phase separation effect, and the polymer is plasticized moderately. However, the blends (studied up to 30 wt %) are translucent, suggesting phase separation on a larger scale. A possible explanation is given in terms of nonspherical *t*BA domains subject to a hard-wall effect coupled with interfacial ionic interactions as well as ester−acid interactions. Evidence for the latter was noted in the infrared spectra.

Introduction

Graftlike polymer complexes can be prepared by ionic bonding of side chains to a polymer backbone. Blends of ionomers with oligomers functionalized by groups which specifically interact with those of the ionomer are materials of choice for such complexes. With these materials, the density of the grafted side chains is low. It is expected that the properties of the complexes will depend not only on the strength of the ionic interaction but also on the nature and length of the side chain for a given polymer backbone.

In the previous paper,[1] we investigated complexes involving components with chemically identical (nonionic) segments, or what we called homografts. It was observed that the monofunctional oligomers plasticize the materials to an extent which depends on the length and stiffness of the side chains. Especially noteworthy was that blends with longer bifunctional oligomers give a biphasic material despite the ionic contacts between, and segmental identity of, the two components.

The complexes of the present paper involve components whose segments are intrinsically immiscible, that is, chemically dissimilar. These give what we will call heterografts. The polymer used, lightly sulfonated polystyrene (PS−SSA), is the same as that used in the previous paper. The oligomers are based on *tert*-butyl acrylate (*t*BA), monofunctionalized by a tertiary amine, with three different degrees of polymerization, ranging from about 20 to 85.

It will be shown that dynamic mechanical analysis shows only marginal phase separation, whereas the visible appearance of the molded materials suggests that phase separation occurs at a much larger scale. This will be discussed and rationalized. The results presented, which are for blends with relatively low amine-to-acid molar ratios, are complementary to those published by Weiss et al.[2] for similar complexes, but at higher amine-to-acid molar ratios, involving monofunctional isoprene oligomers and PS−SSA.

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

oligomer	n	M_n	M_w/M_n	f	$T_g{}^a$ (°C)
tBA2−NMe$_2$	24	3100	1.2	1.0	20
tBA4−NMe$_2$	43	5600	1.1	1.0	35
tBA8−NMe$_2$	82	10600	1.1	1.0	40

[a] Poly(*t*BA) = 43−107 °C.[4]

Experimental Section

The same sulfonated polystyrene copolymer as described in the previous paper[1] was used for the blends of this paper. The *tert*-butyl acrylate (*t*BA) oligomers were anionically polymerized in the presence of LiCl as described in ref 3. The dried salt, dissolved in dry THF, was first introduced into the reactor, followed by the initiator, *sec*-butyllithium (in a molar ratio LiCl/initiator of 10/1) in suspension in cyclohexane. The monomer, previously dried over CaH_2, was purified by diluting with dry toluene and adding a cyclohexane solution of triethylaluminum until a persistent yellow-green color was obtained, followed by distillation under vacuum just prior to polymerization. The diluted monomer was then added to the initiator solution (cooled at −78 °C), and the polymerization was completed in about 10 min. Finally, the oligomers were deactivated by addition of a 20 molar excess of 1,3-bis(dimethylamino)propyl chloride, as described in the previous paper.[1] After concentration of the solution, they were purified by precipitation in a 0 °C solution of 50/50 (v/v) methanol/H_2O, drying, redissolution in toluene, and then filtering (Millipore) in order to remove the Li salt. Finally, they were freeze-dried and further dried for a week under reduced pressure at ambient temperature.

The molecular characteristics and the glass transition temperatures of the oligomers are given in Table 1. For comparison, the glass transition temperatures reported in ref 4 for poly(*tert*-butyl acrylate) are also given. 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 (recognizing that the use of these standards implies that the values obtained for the *t*BA oligomers are nominal). 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.

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Table 2. Dynamic Mechanical Thermal Analysis Data for the Heterografts

blend	w/w	R^a	T_g (°C)	T_g(Fox) (°C)	activation energy (kJ/mol)
PS−SSA/*t*BA2−NMe$_2$	90/10	0.06	122	120	460
	80/20	0.13	119	108	450
	70/30	0.23	116	97	490
PS−SSA/*t*BA4−NMe$_2$	90/10	0.03	123	122	450
	80/20	0.09	120	112	470
	70/30	0.13	113	103	420
PS−SSA/*t*BA8−NMe$_2$	90/10	0.02	122	123	520
	80/20	0.04	119	114	460
	70/30	0.07	113	105	420
PS/*t*BA2−NMe$_2$	90/10		42, 105		

[a] Amine/acid molar ratio.

The blends were prepared and analyzed exactly in the same way as described in the Experimental Section of the previous paper,[1] to which the reader is referred. The molded bars of blends with PS−SSA were translucent, whereas a 90/10 (w/w) blend of homopolystyrene (PS) with one of the butyl acrylate oligomers was opaque.

The oligomers are given the acronym, *t*BA*x*−NMe$_2$, where *x* denotes to the nearest decade the average number of *t*BA repeat units per chain.

Results

From studies of other blend systems involving the same or similar interacting groups,[2,5−8] as well as that in the previous paper,[1] extensive and perhaps virtually complete proton transfer from SSA to the amine moiety, leading to ionic grafting, is expected. This is normally verified by infrared analysis. In the present system, the amine content is low compared to the acid content, the maximum amine/acid stoichiometry being 0.23 (see Table 2). This means that the acid bands in the infrared spectra remain strongly present. Therefore, the extent of proton transfer, which may be determined by normalizing the area under the 906 cm^{-1} band (which contains a 900 cm^{-1} band attributed to the acid moiety) to a polystyrene band,[7,8] generally falls within the experimental error involved. Some confidence can be given to the calculation only for the 70/30 PS−SSA/tBA2-NMe$_2$ blend. In this case, the value calculated (using the 1945 and 1875 cm^{-1} bands as references, since an oligomer band overlaps the 759 cm^{-1} PS band) is 35% compared to the expected value of 23%.

Qualitatively, the calculation assures us that proton transfer indeed occurs. Moreover, a broad, weak band at about 2600 cm^{-1}, characteristic of the protonated tertiary amine and absent in the pure components, and a band at 1009 cm^{-1}, associated with the styrene sulfonate group, are also apparent in the spectra of all of the blends. Because the acid groups are well in excess of the amine groups, it is likely that virtually all of the amine groups are protonated and hence ionically grafted to PS−SSA.

The remaining acid groups may specifically interact with the ester moieties in the *t*BA chains. Such interactions, in the form of hydrogen bonding, have been shown by infrared spectroscopy to take place between lightly sulfonated polystyrene and poly(ethyl acrylate) (PEA).[9] Indeed, evidence for acid−ester interactions can also be observed in the infrared spectra of our own blends. As shown in Figure 1, the carbonyl band in neat *t*BA*x*−NMe$_2$ (shown for $x = 2$) is located at 1729 cm^{-1}; in the blends with PS−SSA, another C═O band is present at lower wavenumbers, indicating that some proportion of the C═O in neat *t*BA*x*−NMe$_2$ is hydrogen-bonded in the blends. This can only involve the sulfonic acid group. In the blends with 20 and 30 wt % *t*BA*x*−NMe$_2$, the bonded C═O band appears as a shoulder to the free C═O band, whereas in the 10% blend the bonded C═O band is predominant, with a maximum at 1712 cm^{-1}. Significantly, a blend of 8% *t*BA2−NMe$_2$ is required in order that the sulfonic acid moieties and the ester moieties be in (nominal) equimolar ratio, thereby permitting all of the C═O groups to be H-bonded with sulfonic acid groups. Beyond 8% *t*BA2−NMe$_2$, a decreasing fraction of C═O groups can be H-bonded. This is entirely consistent with what is observed in the infrared spectra.

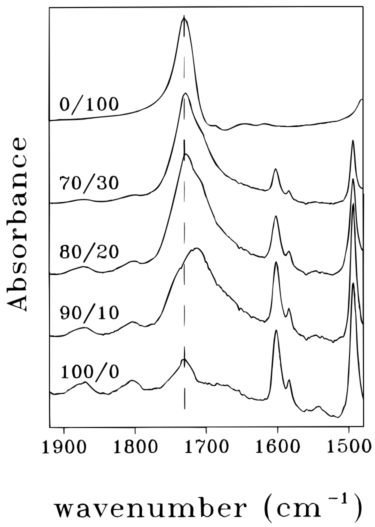

Figure 1. Infrared spectra for the heterografts with *t*BA2−NMe$_2$ at the ionomer/oligomer weight ratios indicated.

The storage moduli and loss tangent curves as a function of temperature for the heteroblends are shown in Figure 2, with associated parameters listed in Table 2. A sharp transition corresponding to the T_g of the material takes place at a temperature which decreases moderately from that of pure PS−SSA (at 132 °C) with increasing oligomer content. Thus, the oligomer has a mild plasticizing effect on the polymer, although less than would be predicted, for example, by the Fox equation[10] (an equation often used to describe the T_g variation of plasticized polymers).

There is no evidence in these curves of a transition at low temperatures corresponding to phase-separated oligomer—not even at 30 wt % concentration, the highest oligomer concentration studied. This is confirmed in DSC measurements, where only a single T_g corresponding to the DMA loss tangent peak is present, with no hint of a lower temperature T_g. On the other hand, Figure 3, where enlarged portions of the loss modulus curves in the vicinity of T_g are drawn for the 90/10 and 70/30 blends for the different oligomer lengths, shows that a shoulder on the low-temperature side of the primary loss modulus peak is apparent, even slightly visible for some of the 90/10 blends. This shoulder, around 75 °C, tends to become more pronounced with an increase in concentration and in the chain length of the oligomer. In some cases, a slight shoulder can also be seen in the expanded forms of the loss tangent curves (as shown in the insets in Figure 2), but much less clearly than in the loss modulus curves.

The weakness of the lower temperature relaxation indicates that whatever phase separation occurs in the heterografts is near the limit of detection by dynamic mechanical thermal analyses (DMA), suggesting domain

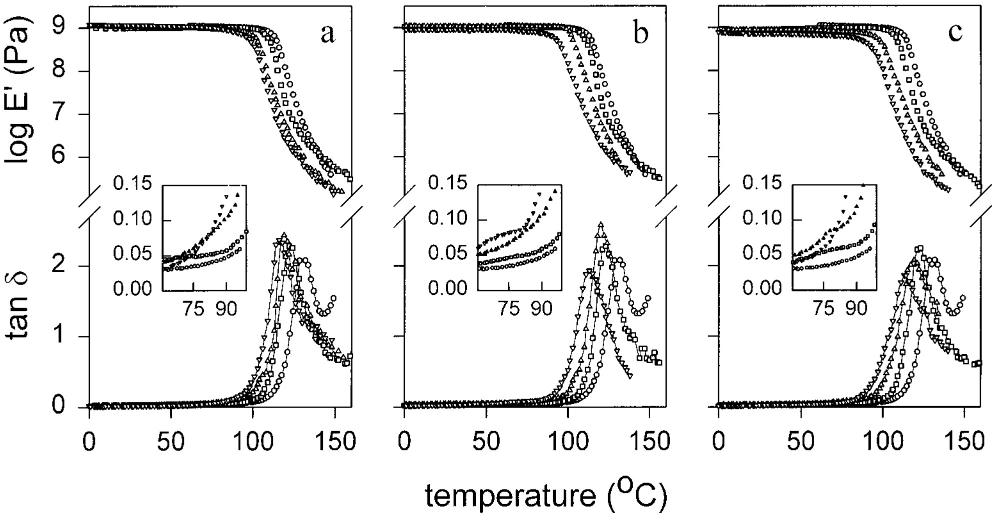

Figure 2. Young's storage modulus and loss tangent at 1 Hz as a function of temperature for the heterografts of PS−SSA and (a) *t*BA2−NMe$_2$, (b) *t*BA4−NMe$_2$, and (c) *t*BA8−NMe$_2$. Ionomer/oligomer weight ratios: ○, 100/0; □, 90/10; △, 80/20; ▽, 70/30. The insets show an enlarged portion of the tan δ curves.

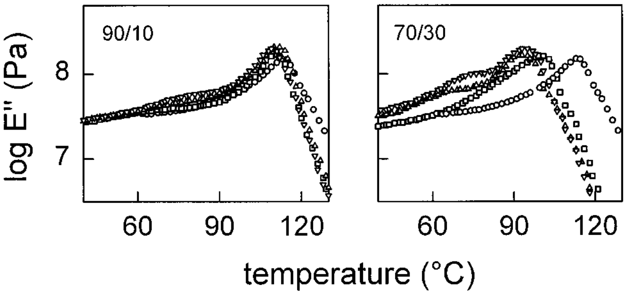

Figure 3. Young's loss modulus at 1 Hz as a function of temperature for the heterografts of PS−SSA (○) with *t*BA2−NMe$_2$ (□), *t*BA4−NMe$_2$ (△), and *t*BA8−NMe$_2$ (▽). Ionomer/oligomer weight ratios are indicated.

sizes for the incipient phase of the order of 100 Å.[11] This, and the high temperature of the minor phase relaxation, may be explained by the occurrence of considerable phase mixing, possibly driven by the SSA−ether interactions. On the other hand, the molded materials are optically translucent, indicating domain sizes that are near the limit of that detectable by the wavelength of light, namely of the order of 1000 Å, for which one might have expected a more intense DMA relaxation. This will be commented upon in the Discussion.

In contrast to the heterografts, a blend of the oligomer *t*BA2−NMe$_2$ with homopolystyrene, where neither ionic nor hydrogen-bonding interactions are present, clearly possesses two T_g's (Figure 4), which correspond approximately to those of the two components separately (the maximum at 40 °C for the lower temperature loss tangent peak is 20 °C higher than the T_g measured by DSC for the neat oligomer, which is consistent with the difference we usually observe between DMA- and DSC-measured T_g's under the conditions used[1]). This is consistent with the visible appearance of the blend, namely that it is opaque. The intensity of the loss tangent peak corresponding to the oligomer T_g and the significant drop in the storage modulus curve at that transition, with only 10% oligomer present, is noteworthy. The phase separation is clearly on a much larger scale than that for the blends with PS−SSA, even with 30% oligomer present, for which there is no telltale manifestation of a separate phase in the storage modulus curves and only faint evidence in the loss tangent curves.

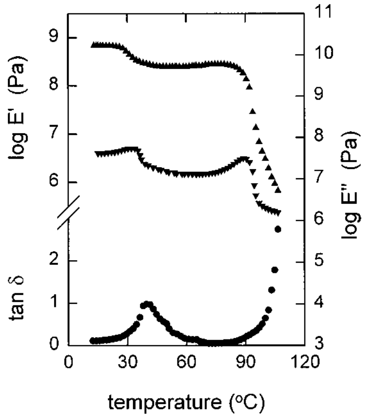

Figure 4. Young's storage and loss moduli and loss tangent at 1 Hz as a function of temperature for a 90/10 blend of polystyrene and *t*BA2−NMe$_2$.

Similar ionic graftlike copolymers, composed of PS−SSA and monofunctional, amine-terminated isoprene oligomers (of about 60 isoprene units per chain), were studied by Weiss et al.[2] In contrast to our results, they were able to detect two T_g's (through DSC) for all blend compositions investigated (both being shifted somewhat towards each other compared to the T_g's of the pure components). However, two important differences between our blends and theirs must be considered. First, the oligomer contents investigated by Weiss et al. were significantly higher than those in our blends. The lowest amine/sulfonate molar ratio they studied was 0.32 for a PS−SSA containing 8 mol % SSA, which corresponds to 2.6 mol % ion content supposing complete proton transfer. The highest molar ratio we studied was 0.23, which corresponds to 1.6 mol % ion content given complete proton transfer. The butyl acrylate oligomer with the most similar degree of polymerization to that of the isoprene oligomer is *t*BA4−NMe$_2$, for which the highest molar ratio we studied was only 0.13. This highlights the observation that our heterografts are in the composition range where phase separation is barely detectable, in contrast to those of Weiss et al., which, with a much higher oligomer content, show clear phase separation. Second, the ionic interactions between SSA and the terminal amine moieties are the only specific intercomponent interactions present in the

PS−SSA/isoprene blends, whereas, as shown above, the SSA also interacts with the carbonyl groups along the *t*BA chains in the PS−SSA/*t*BA blends.

It is useful to point out that, despite those differences, there are also similarities in the two systems. First, no softening transition corresponding to the oligomer T_g is observed in thermomechanical thermograms of either series of ionomer/oligomer blends. Evidently, the ionic grafting results in a mechanical response dominated by the polystyrene matrix, probably related to a decrease in the domain sizes of the oligomer phase.[2] Second, in both systems, the plasticization effect of the oligomers on the T_g of PS−SSA is mild. That some plasticization occurs suggests that a certain amount of oligomer may be solubilized in the PS−SSA matrix; this effect, if present, should be more pronounced for the *t*BA chains than the isoprene chains, given the acid−ester interactions in the former. Another explanation is also possible. The bulkiness of the groups attached to the quaternized amine may reduce the strength of the ion pair association[2] compared to the strong hydrogen-bonding association among SSA groups and thereby decrease the T_g of PS−SSA in the blends relative to that of its acid form. In either case, the significant point is that in both series of blends the decrease in T_g is limited (i.e., less than what is observed for usual plasticizers, as predicted by the Fox equation). This can be related to the tendency of the oligomer to form a separate phase, even if only at the microphase level.

It should be emphasized that it has been shown in ref 2 that the presence of ionic interactions in the heterografts reduces the domain sizes of the phases significantly compared to those of a blend without those interactions. A significant reduction in domain sizes was also observed in the PS−SSA/PEA blends of ref 9, characterized by hydrogen-bonding interactions as mentioned above. The latter blends were observed to be optically clear and display a dominant loss tangent peak, intermediate to the T_g's of the two components, for SSA contents near 5 mol % and greater.

Discussion

At first sight, the optical appearance of the heterografts suggests that there are *t*BA or *t*BA-rich domains of the order of 1000 Å, whereas the DMA data imply that the domains are of the order of 100 Å at most. The elevated T_g of these domains compared to that of pure oligomer suggests that PS−SSA is dissolved in the oligomer phase. The presence of acid−carbonyl interactions may well enhance phase mixing, as was observed for the PS−SSA/PEA blends. From this point of view, it is possible that the optical haziness of the samples may be a result, at least in part, of the reduced refractive index contrast between the majority copolymer (or copolymer-rich) phase and the minority phase which also contains copolymer. In addition, the distribution of phase sizes of the minority domains may be such that only a small proportion are able to scatter light and, furthermore (to rationalize the weakness of the corresponding DMA transition), that a significant fraction are below the limit of detection by DMA. On the other hand, one might have expected a greater reduction in the T_g of the majority phase than observed if this were true.

Another possible explanation for both the weakness of phase detection in DMA and the translucency involves postulating that the minority (oligomer) phase forms rodlike or platelike domains having only one or two dimensions of sufficient size to scatter light. Variable degrees of haziness or opacity have been observed, for example, for dilute solutions of ionic diblock copolymers that form randomly dispersed cylindrical aggregates of diameters significantly less than the wavelength of light (1 wt % solutions of rods of about 300 Å in diameter and 10−20 times that in length are hazy; moreover, the turbidity of the solutions increases with increasing average rod length).[12,13] Under these circumstances, it is also reasonable that the rigid polystyrene phase, which is clearly the dominant phase in our blends, may exercise a "hard-wall" effect on the minority phase that is transmitted through the ionic bonds.

This allows a phenomenon analogous to that evoked to explain the cluster phase in ionomers to be operative. In ionomers, the rigidity of ionic aggregates (cores) is said to cause a reduction in mobility of the matrix segments in its vicinity, and when a sufficient amount of the regions of reduced mobility are contiguous, it gives rise to a second phase with a higher T_g than that of the matrix.[11] A soft phase that is surrounded by a hard phase and rigidly connected to it through ionic bonds may similarly experience decreased mobility to within a certain distance from the interface with the hard matrix (creating what is often called an interphase[11]); moreover, this decrease may be more or less progressive. A consequence of the decreased mobility may be an increase in the T_g of the soft phase. In this case, it is not necessary to evoke the presence of PS−SSA in the oligomer phase (although it is not excluded either) to explain why the temperature of the weak DMA transition is higher than the T_g of the oligomer.

Another consequence of the reduced mobility may be a reduction in the effective size of the minority phase as detected by DMA. If the domains have a nonspherical morphology (platelike, rodlike), this effect will be all the more pronounced, since a greater proportion of the minority phase will be found within the interphase. The scattering of light, on the other hand, which depends only on the difference in chemical composition between phases and is therefore sensitive to the true size of the phase, reflects a larger phase than does DMA (as well as its largest dimensions).

A nonspherical morphology may be all the more favored given the interactions between excess sulfonic acid groups in the polymer and ester moieties in the oligomers, which may, in turn, favor alignment of the oligomer chains parallel to the surrounding PS walls. This possible driving force for forming flattened domains is not present either in the homograft system of the previous paper[1] or in the PS−SSA/isoprene heterografts of ref 2. It will be useful, in future studies, to distinguish between the possible morphologies by other techniques.

Summary

In the heterografts of this study, some (micro-) phase separation, as would have been expected, appears to be present according to the optical appearance of the materials; on the other hand, a separate phase is barely detectable by DMA. It was suggested that this apparent contradiction can be rationalized by a hard-wall effect of the high-T_g matrix on the low-T_g oligomer phase, the latter being in the form of relatively thin (or flat) domains. Reduction of mobility of oligomer segments near the hard matrix, due to the strong ionic interactions, results in reduction of the effective size of the

oligomer domains as detected by DMA, particularly effective when the domains are nonspherical, whereas light scattering is sensitive to the true size of the phases (as determined by the chemical composition) as well as their greatest dimensions.

Flattened domains may be all the more favored by the existence of hydrogen-bonding interactions between excess sulfonic acid and the ester groups in the oligomer. Evidence for such interactions was found in the infrared spectra of the heterografts. The latter demonstrates that favorable "cross" interactions between the ionic or functional groups of one component and the organic segments of the other component can also contribute to the characteristics of ionomer/oligomer blends. A related situation was reported previously for an amine-terminated surfactant blended with a poly(ethyl acrylate) ionomer, where the polar end groups of the surfactant preferentially interact with the ester rather than carboxylate groups of the ionomer.[14]

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