Graft Copolymers of Polystyrene and Polyisoprene Prepared by Complexation of Functionalized Homopolymers

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ABSTRACT: Physical graft copolymers were prepared from intermolecular interactions between functionalized polystyrene and polyisoprene. The polystyrene was modified with up to 8 mol % sulfonic acid or zinc sulfonate groups, and the polyisoprene was capped at one end of the chain with a dimethylamino group. Hydrogen bonding or transition-metal complexation between the functional groups yielded a *graft copolymer* molecular architecture that led to stabilization of the scale of phase separation in blends of the two polymers. Intermolecular aggregation also persisted in solution in relatively nonpolar solvents, which also perturbed the solution viscosity.

Introduction

The compatibility of the components of a polymer blend can be improved by incorporating specific interacting functional groups into the two polymers. For example, intermolecular hydrogen bonding reduces the enthalpy of mixing, ΔH_m, and when ΔH_m becomes exothermic, a miscible, i.e., one-phase, mixture results.[1] Interactions other than hydrogen bonding, e.g., ionic interactions and complexes involving transition-metal salts can also improve blend compatibility. The subject of the compatibilization of polymer blends using ionic interactions was recently reviewed by Smith et al. (2).

The objective of the present work was to employ specific intermolecular interactions to develop in a polymer blend a molecular architecture similar to that of a graft copolymer. It was anticipated that by doing so, one might obtain a finer two-phase texture than normally achievable in noninteracting blends, as well as improved mechanical properties.

Previous work[3-6] in our laboratories has involved the preparation of block and graft copolymers in which the different polymer segments were coupled by functional group interactions. Sen et al.[3] prepared graft copolymer networks derived from acid–base interactions and transition-metal complexation between poly(styrene-*co*-4-vinylpyridine) and α,ω-dicarboxylpolybutadiene or its Cu(II) salt. The blends based on the transition-metal complex exhibited improved dimensional stability at elevated temperature, and the microstructure of these blends was discussed by Register et al.[4] Horrion and co-workers[5] used ion-pair formation between telechelic polystyrene and polybutadiene with carboxylic acid and tertiary amine end groups, respectively, to prepare multiblock copolymers. Similar work was reported by Russell et al.[6]

In this article we describe the formation of graft copolymers of polyisoprene onto polystyrene formed by blending lightly sulfonated polystyrene (SPS) and ω-(dimethylamino)polyisoprene. Complexes were prepared from the free acid and Zn(II) salts of SPS.

Experimental Details

Materials. Polystyrene (PS) (M_n = 35 000, M_w/M_n = 1.1) was prepared by anionic polymerization. Two different sulfonated polystyrenes (SPS), 2.5 and 8 mol % substitution, were prepared by sulfonation of the PS in 1,2-dichloroethane (DCE) at 50 °C following the procedure of Makowski et al.[7] Acetyl sulfate was prepared by the reaction of concentrated sulfuric acid and acetic anhydride in DCE at 0 °C. The freshly prepared acetyl sulfate was added to a well-stirred solution of PS in DCE, and the reaction was allowed to proceed for 2 h before termination by the addition of 2-propanol. The H-SPS product (i.e., the free acid form) was isolated by steam stripping, washed several times with ethanol, and vacuum dried for several days. The Zn(II) salt, ZnSPS, was formed by neutralization of the H-SPS in a 90/10 (v/v) mixture of toluene and methanol with a 10% excess of zinc acetate dihydrate. ZnSPS was recovered by steam stripping, washed with methanol, and dried for several days under vacuum.

ω-(Dimethylamino)polyisoprene (DAPI) was synthesized by anionic polymerization. Isoprene was dried first over CaH_2 and then over *n*-BuLi prior to use. (Dimethylamino)propyl chloride was purified by following the procedure of Yen et al.[8] The initiator, *sec*-BuLi, and sufficient THF to make a 4% solution of the final polymer were added to a dried flask under nitrogen. The system was cooled to −78 °C and the isoprene monomer was added. Polymerization was allowed to proceed for at least 1 h and was then terminated by the addition of DMAPC (at least a 3-fold excess based on the initiator concentration). The polymer was precipitated in methanol and 1% (wt) Irganox 1010 antioxidant was added. M_n and M_w/M_n were 4100 and 1.2, respectively, as determined by gel permeation chromatography calibrated with polystyrene standards. The polyisoprene microstructure was determined by ^{1}H NMR spectroscopy to be 34% 1,2-addition and 66% 3,4-addition. The amine functionality was determined by titration to be 0.98, i.e., one per polymer chain.

Polymer blends were prepared by combining 10% solutions of the polymers in toluene, stirring for 2 h at room temperature, and evaporating off the solvent in air. Final drying was done under vacuum. The blends are summarized in Table I. The nomenclature used was a.bMSPS/DAPI(c.d), where a.b is the sulfonate concentration expressed as mole percent of styrene repeat units sulfonated, M is the counterion for the SPS, and c.d is the nominal ratio of amine groups/sulfonate groups in the blend. Thus, 2.5ZnSPS/DAPI(1.0) designates a blend of a 2.5 mol % ZnSPS and DAPI with a 1:1 ratio of zinc sulfonate and amine groups. A nominally 50/50 blend of unfunctionalized PS with DAPI, denoted PS/DAPI was also prepared for comparison. A 50/50 composition of the functionalized polymers corresponded to a 1:1 ratio of functional groups for the 2.5SPS/DAPI blends, and a sulfonate/amine ratio of 3:1 for the blends based on 8.0SPS.

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Table I
Materials

sample designation	starting polymer composition, wt %								mol ratio (amine/sulfonate)	T_g,[a] °C
	PS	DAPI	2.5HSPS	2.5ZnSPS	3.6HSPS	3.6ZnSPS	8.0HSPS	8.0ZnSPS		
DAPI		100								-5
PS	100									83
2.5HSPS			100							107
8.0HSPS							100			114
2.5ZnSPS				100						103
8.0ZnSPS								100		112
2.5HSPS/DAPI(1.0)		48.5	51.5						0.97	1/99
2.5HSPS/DAPI(2.0)		65.4	34.6						1.96	2/94
2.5ZnSPS/DAPI(1.0)		48.5		51.5					0.98	1/99
2.5ZnSPS/DAPI(2.0)		65.4		34.6					1.96	1/96
3.6HSPS/DAPI(1.0)		57.3			42.7				0.97	
3.6HSPS/DAPI(2.0)		72.8			27.2				1.92	
3.6ZnSPS/DAPI(1.0)		57.3				42.7			0.98	
3.6ZnSPS/DAPI(2.0)		72.8				27.2			1.96	
8.0HSPS/DAPI(0.33)		48.5					51.5		0.32	10/95
8.0ZnSPS/DAPI(0.33)		48.5						51.5	0.33	8/94
PS/DAPI	51.5	48.5							0	-4/82

[a] Determined by DSC; details given in text.

Infrared Spectroscopy. Infrared spectra were obtained with a Nicolet 60SX Fourier-transform infrared (FTIR) spectrometer. One hundred scans were taken, corresponding to a resolution of 2 cm^{-1}. The samples were thin films cast from tetrahydrofuran onto NaCl plates and vacuum dried.

Thermal Analysis. Glass transition temperatures (T_g's) were measured with a Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) using a heating rate of 20 °C/min and a dry nitrogen atmosphere. The specimens were conditioned by heating to 125 °C in the DSC and quenching to -15 °C before the measurements.

Thermomechanical analyses (TMA) were made with a Perkin-Elmer TMA-7 thermomechanical analyzer using a 1-mm-diameter, flat-tip penetration probe and a force of 100 mN. The softening behavior of 1-mm-thick compression-molded specimens was determined by using a heating rate of 10 °C/min and a dry helium atmosphere.

Dilute Solution Viscosity. Reduced viscosities of the individual components and the blends were determined with a Cannon-Ubbelohde 9722-M53 dilution viscometer at 25 ± 0.05 °C. Polymer concentrations ranged from 0.1 to 4.0 g/dL in xylene.

Transition Electron Microscopy (TEM). Electron micrographs of the blends were obtained with a Philips EM-300 transmission electron microscope. Thin films were cast from tetrahydrofuran onto 200-mesh carbon-coated grids. The DAPI was preferentially stained by suspending the sample over osmium tetraoxide, which complexes with the diene double bond much more readily than with the aromatic groups of the SPS.

Results and Discussion

FTIR. Figure 1 shows the FTIR spectra of PS, DAPI, and their blend. The latter spectrum is simply the weighted sum of those of the individual components, which was expected since PS and polyisoprene are well-known to be immiscible. In this case, the dimethylamine functionality of the DAPI has no corresponding functional group with which to interact on the PS.

The effect of sulfonating PS is shown in Figures 2 and 3. Figure 2 shows the spectral region from 800 to 1400 cm^{-1} for 2.5 HSPS, 8.0 HSPS, DAPI, and their blends and Figure 3 shows the region from 2000 to 4000 cm^{-1} for the same materials. The absorption peak at 1101 cm^{-1} in the HSPS samples is due to the sulfonic acid group.[9] This band disappeared in the blends and four new absorbances were observed at 1009, 1125, 1228, and 1280 cm^{-1}. The first three of these are due to the sulfonate anion, which indicated that blending resulted in the formation of a sulfonate salt. The moderately broad band centered at ~1280 cm^{-1} in the blends is believed to be due to the C–N stretch,

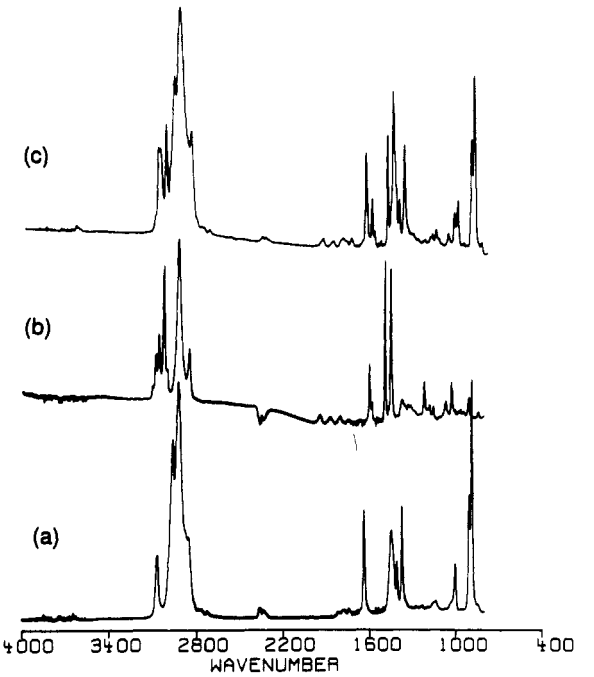

Figure 1. FTIR spectra of (a) DAPI, (b) polystyrene, and (c) a blend of 51.5% PS and 48.5% DAPI (PS/DAPI).

which occurred at 1234 cm^{-1} in the neat DAPI. The shift to higher frequency of this absorbance band was presumably a result of interaction of the amine group with the sulfonic acid group or, more specifically, the formation of an ammonium salt. This conclusion is supported by the broad absorption between 2250 and 2700 cm^{-1}, which was observed only in the blends and is due to the formation of a tertiary aliphatic ammonium salt due to proton transfer from the sulfonic acid group to the amine.[9] It should be noted that the disappearance of the 1101-cm^{-1} band in the blend is not proof that all the sulfonic acid has complexed with amine groups. The level of sulfonic acid in the SPS polymers was low to begin with and the resolution of the 1101-cm^{-1} absorption was not adequate for any quantitative conclusions. In fact, the microscopy experiments discussed later in this paper revealed a phase size for the DAPI that would preclude complete complexation.

For the blends containing ZnSPS, Figure 4, the sulfonate absorbances were already present in the spectra of the ZnSPS and, therefore, were expected. Blending

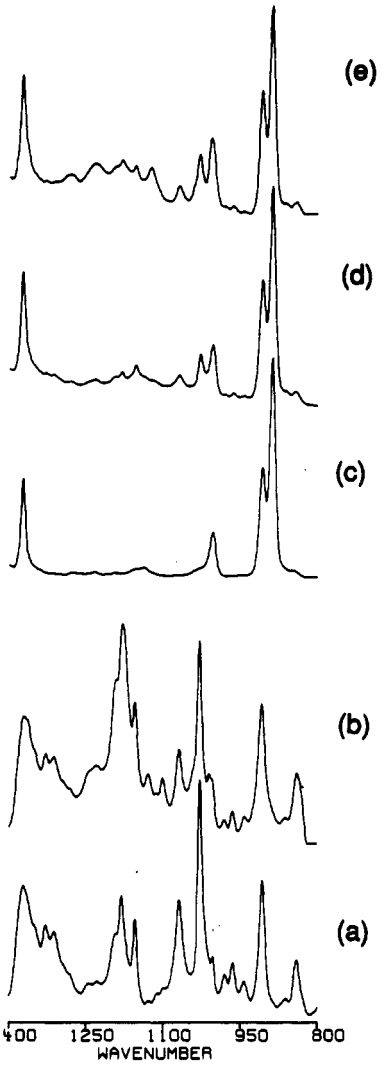

Figure 2. FTIR spectra (800–1400 cm^{-1}) of (a) 2.5HSPS, (b) 8.0HSPS, (c) DAPI, (d) 2.5HSPS/DAPI(1.0), and (e) 8.0HSPS/DAPI(0.32).

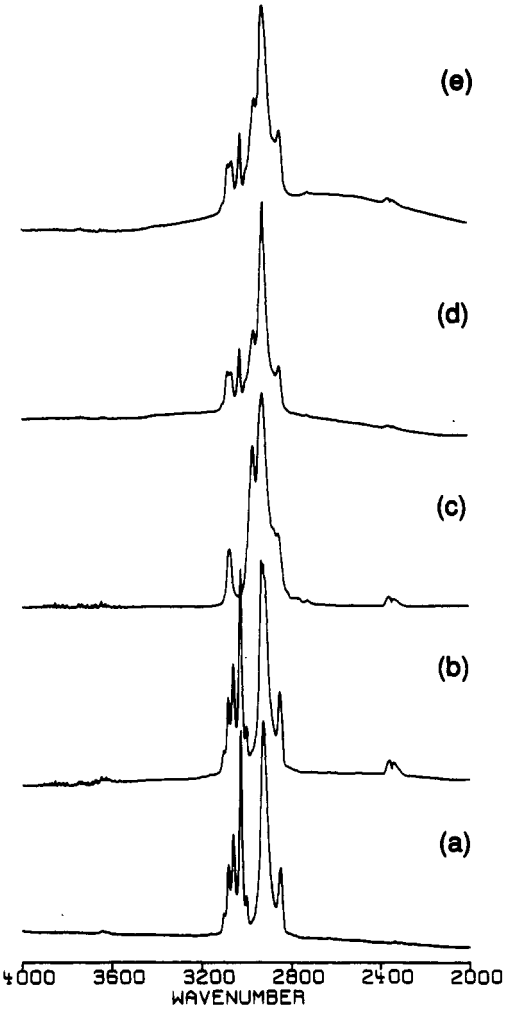

Figure 3. FTIR spectra (2000–4000 cm^{-1}) of the same materials as in Figure 2.

produced a new absorbance centered at ~1290 cm^{-1}, which by analogy with the results discussed above was assigned to the C–N stretch that was perturbed by complexation of the amine with the zinc sulfonate group. For these blends no evidence of the formation of an ammonium salt was observed in the spectra between 2200 and 2700 cm^{-1}, Figure 5. Thus, in this case, the interaction is transition-metal complexation. No obvious effects of varying the ratio of sulfonate to amine groups were observed.

Thermal Analyses. A single T_g was observed in the DSC thermograms of the individual component polymers and these are listed in Table I. The increase of T_g with increasing sulfonation is a consequence of intermolecular associations of the sulfonic acid or metal sulfonate groups, which inhibit the chain mobility. The T_g's measured for the ZnSPS were slightly lower than for the corresponding HSPS, but this was not considered to be significant and may be due to minute amounts of water.[10]

The DSC thermograms of the blends are shown in Figure 6 and the transition temperatures are summarized in Table I. The arrows correspond to the T_g's of the component polymers. In all cases, the blends exhibited two T_g's, indicating that phase separation of a polyisoprene-rich phase and a polystyrene-rich phase occurred. For the PS/DAPI blend, the two T_g's closely corresponded to those of PS and DAPI, which indicates that essentially no phase mixing occurred in this blend. In contrast, for the functionalized blends, both T_g's were shifted relative to those for the pure components. T_g of the polyisoprene-rich phase increased from −5 °C for DAPI to 1–2 °C for the blends with the 2.5SPSs and to 8–10 °C for blends with the 8.0SPSs. Similarly, the T_g of the polystyrene-rich phase decreased ~10 °C for the 2.5SPS blends and ~18 °C for the 8.0SPS blends. Phase separation still occurred, which is expected since the only part of the polyisoprene chain in which favorable interactions with the SPS can occur is at the amino end group. Because of the isolation of the amine group on the end of the polyisoprene chain, it would appear unlikely that the changes in the T_g's were due to extensive phase mixing. The increase in the T_g of the polyisoprene phase may be explained by the salt formation or complex between the terminal amine and the sulfonate groups of the SPS. This will decrease the mobility of the polyisoprene, thus increasing its T_g. The decrease in the SPS T_g was also a consequence of the amine–sulfonate interactions. In this case, however, the primary result is to break up the conventional ionomeric associations between the sulfonate groups, and by doing so move the T_g toward that of the unfunctionalized PS. This is similar to the effects observed by Weiss et al.[11] of using bulky alkylamine groups for the cation of SPS. Steric hindrance associated with the large cation effectively shields the sulfonate from ion–dipole interactions with another sulfonate group, which diminishes the ionomeric nature of the material.

TMA thermograms of the PS/DAPI blend and 8.0HSPS, 8.0ZnSPS, and their blends with DAPI are

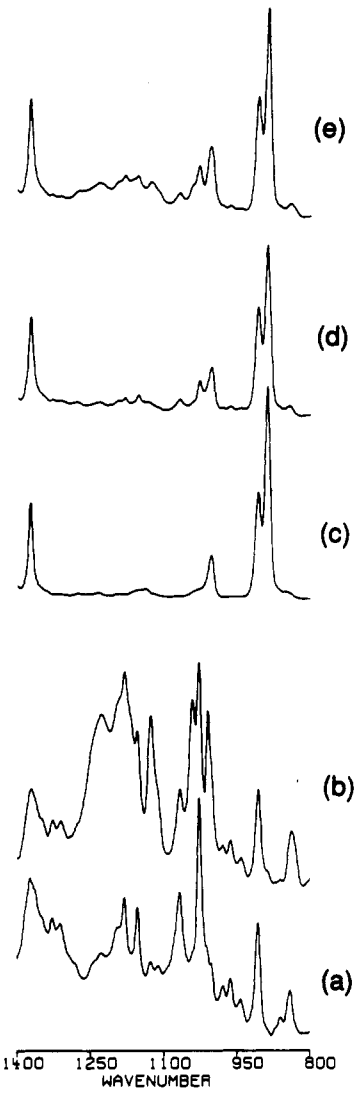

Figure 4. FTIR spectra (800–1400 cm^{-1}) of (a) 2.5ZnSPS, (b) 8.0ZnSPS, (c) DAPI, (d) 2.5ZnSPS/DAPI(1.0), and (e) 8.0ZnSPS/DAPI(0.32).

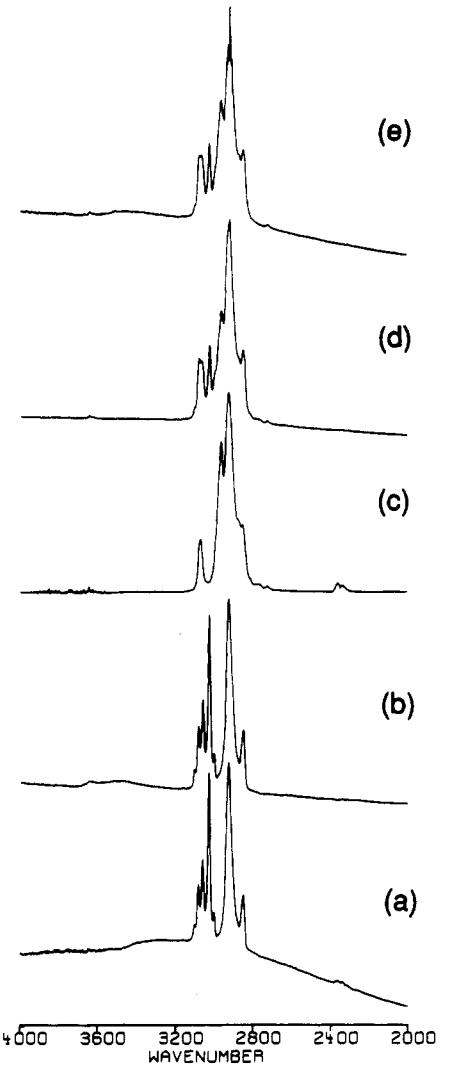

Figure 5. FTIR spectra (2000–4000 cm^{-1}) of the same materials as in Figure 4.

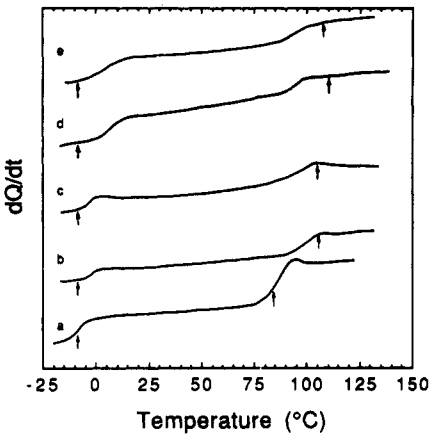

Figure 6. DSC thermograms for (a) PS/DAPI, (b) 2.5HSPS/DAPI(1.0), (c) 2.5ZnSPS/DAPI(1.0), (d) 8.0HSPS/DAPI(0.32), and (e) 8.0ZnSPS/DAPI(0.33). Arrows correspond to T_g's of pure components used for each blend.

shown in Figure 7. The PS/DAPI blend exhibits two distinct softening transitions that coincide with the softening points of the component polymers. This behavior is expected in the absence of any interaction between phases. For the SPS/DAPI blends, the softening transition associated with the polyisoprene-phase T_g is absent. Furthermore, the pseudorubbery plateau above T_g that is visible in the TMA thermograms of 8.0HSPS and 8.0ZnSPS, which results from intermolecular ionic associations, was not observed in these blends. Both of these observations, i.e., the absences of the DAPI softening and the SPS rubbery network, are consistent with the formation of an intermolecular complex between the amine and sulfonate groups. In the functionalized blend, the polyisoprene phase is intimately connected to the polystyrene phase through interaction of the respective functional groups. Therefore, even after the polyisoprene phase undergoes T_g, a rigid polystyrene network exists, which dominates the mechanical response. The softening of the polystrene-rich phase occurred at higher temperatures in the functionalized blend than in PS/DAPI blend, which was primarily a consequence of the higher T_g of the sulfonated polystyrene. In addition, the interactions between the phases may slow the relaxation behavior of the polystyrene phase by essentially increasing the apparent molecular weight. The major effect, however, of the interaction of the DAPI with the SPS was a major *reduction* in the softening behavior of the polystyrene phase compared with the ionomers. This decrease can be attributed to solvation of intermolecular ionic or hydrogen bond associations by the amine group. As a result, the relaxation behavior of that phase is expected to be similar to that of unfunctionalized polystyrene. Similar results

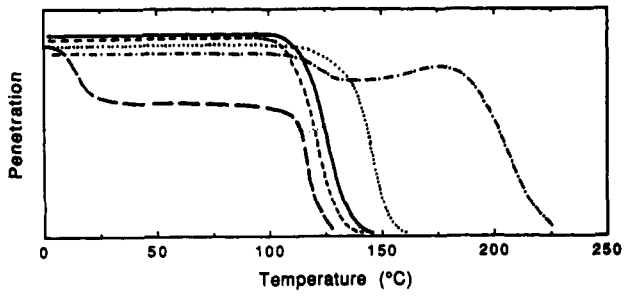

Figure 7. TMA thermograms for (···) 8.0HSPS, (–·–) 8.0ZnSPS, (– –) PS/DAPI, (—) 8.0HSPS/DAPI(0.33), and (– · –) 8.0ZnSPS/DAPI(0.33).

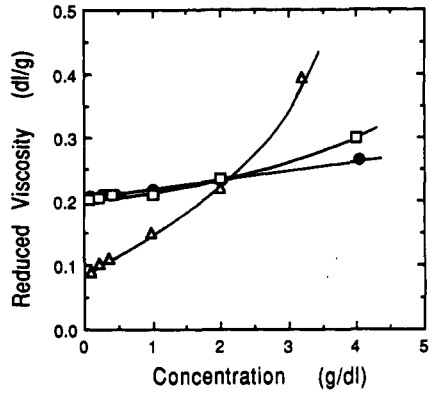

Figure 8. Reduced viscosity in xylene vs concentration for (●) PS, (□) 2.5HSPS, and (△) 8.0HSPS (T = 25 °C).

on alkylamine-neutralized SPS were reported by Weiss et al.[11] It will also be shown later in this paper that the characteristic domain size of the PI phase was significantly reduced by these interactions, which further minimizes the influence of that phase on the mechanical behavior. As for the absence of a rubbery plateau above the T_g of the SPS phase, the explanation is the same as that given above for the reduction of the T_g in the blends. The bulky cation or ligand, in this case the polymeric amine, restricts the ionomer associations, and because the relatively low molar mass of the PS does not yield a large number of entanglements per chain, viscous flow of the SPS phase occurs immediately following T_g.

Solution Behavior. The dilute solution viscosities of the blends in xylene provide further evidence for complex formation. The reduced viscosity vs concentration curves for PS and the HSPS ionomers are shown in Figure 8. Similar results were obtained for the ZnSPS ionomers (not shown). The results of sulfonation, which are consistent with those described in previous studies,[12] were to decrease the viscosity relative to PS at low concentrations and increase it at high concentrations. Both effects became more pronounced with increasing sulfonation. The viscosity increase at the higher polymer concentrations was due to *inter*molecular associations, in this case hydrogen bonding, of the sulfonic acid groups that effectively increased the hydrodynamic volume of the flow unit, i.e., the associated chains. One explanation for the viscosity decrease and lower concentrations is that *intra*molecular associations predominated and the hydrodynamic volume decreased as the chain collapsed.[12]

The viscosity behaviors of the 2.5HSPS blends and the 8.0HSPS blend are shown in Figures 9 and 10, respectively. Also included in these figures are the data for DAPI and the curves of the HSPS used in the blends and the PS taken from Figure 8. In all cases, the viscosity behavior of the HSPS at low and high concentrations was moderated

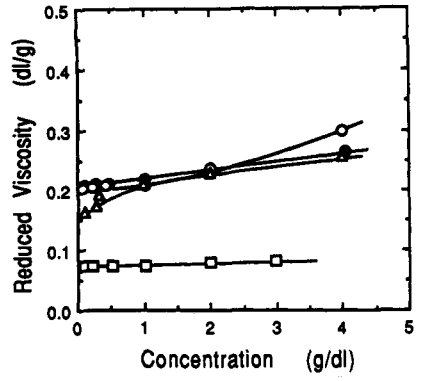

Figure 9. Reduced viscosity in xylene vs concentration for (○) 2.5HSPS, (□) DAPI, (△) 2.5HSPS/DAPI(1.0), and (●) PS (T = 25 °C).

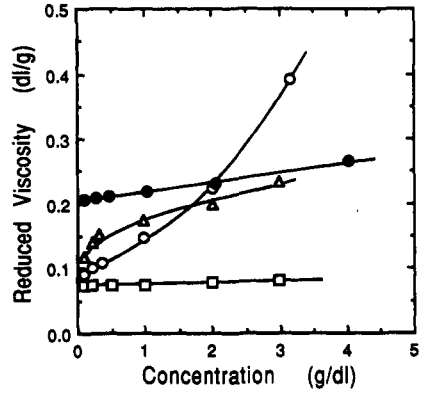

Figure 10. Reduced viscosity in xylene vs concentration for (○) 8.0HSPS, (□) DAPI, (△) 8.0HSPS/DAPI(0.32), and (▲) PS (T = 25 °C).

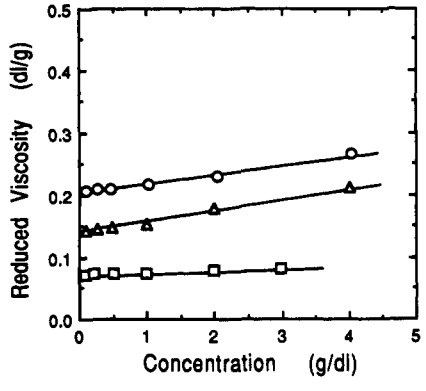

Figure 11. Reduced viscosity in xylene vs concentration for (○) PS, (□) DAPI, and (△) PS/DAPI (T = 25 °C).

by the addition of DAPI. That is, compared with the viscosity of the HSPS, the viscosity of the blends at low concentrations increased and at high concentrations decreased, in both regimes approaching the viscosity of the PS solutions. These results are fully consistent with the formation of a complex between the two polymers that solvates the ionic or hydrogen-bonding interactions. Thus, at low polymer concentrations, the addition of the DAPI either dissociates intramolecular interactions for the SPS and expands the coil or it breaks up the intermolecular aggregates. At higher concentration, the DAPI reduces the intermolecular interactions. Figure 11 shows the solution behavior of PS, DAPI, and the PS/DAPI blend. In stark contrast to the data for the blends shown in Figures 9 and 10, the viscosity of the PS/DAPI blend was essentially a weighted average of the viscosities of the individual components, which is expected for a solution

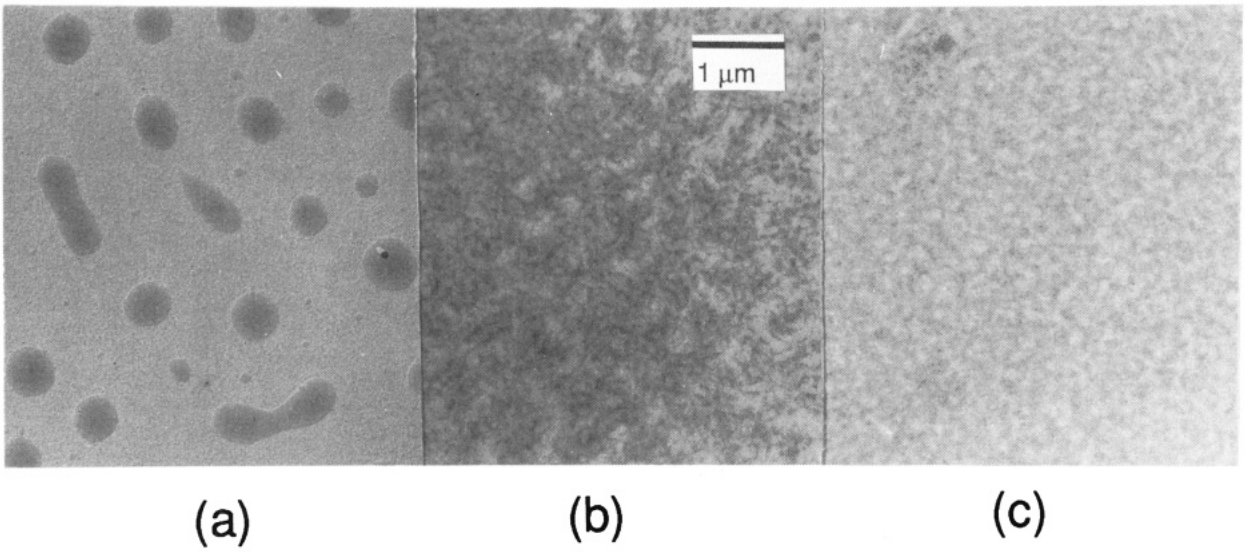

Figure 12. Transmission electron micrographs of (a) PS/DAPI, (b) 8.0HSPS/DAPI(0.32), and (c) 8.0ZnSPS/DAPI(0.33). All blends were stained with OsO_4.

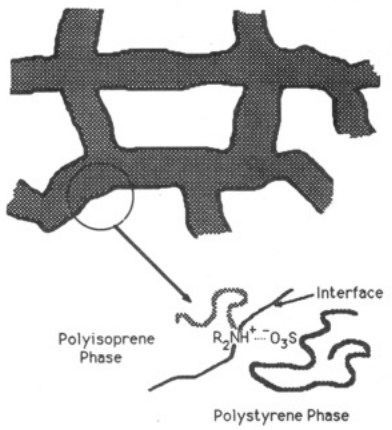

Figure 13. Schematic of SPS/DAPI microstructure showing the functional groups interacting at the interface between phases.

of two polymers in the absence of specific interactions.

Morphology. The most striking difference between the SPS/DAPI and PS/DAPI blends was the morphology observed by TEM, Figure 12. All three blends were phase separated; in Figure 12 the dark regions correspond to the PI phase. For the PS/DAPI blend, the phase separation was coarse with the domain size corresponding to ca. 0.5 μm. The morphology of the 8.0HSPS/DAPI(0.32) blend was much finer with a characteristic size smaller than 0.1 μm, and for the 8.0ZnSPS/DAPI(0.33) the dispersion was even finer. Given that the composition of the blend was about 50/50, it is very likely that the microphotographs in Figure 12b and c show cocontinuous phases. Thus, the SPS appears to act as an interfacial agent to stabilize a dispersed PI phase in these blends. This is entirely consistent with the formation of a graft copolymer complex such as shown schematically in Figure 13.

Conclusions

It was demonstrated that specific interactions between immiscible polymers can be used to stabilize the scale of phase separation. That is, for polystyrene/polyisoprene blends, an acid–base interaction or transition-metal complexation between randomly placed sulfonate groups on the PS and an amine terminal group on the PI yielded a smaller and more uniform dispersed phase in blends compared with similar compositions of unfunctionalized polymers. Complexation was confirmed by FTIR spectroscopy and the improved compatibility of the two polymers was also manifest by changes in the two T_g's as a result of specific interactions. Complexation increased the T_g of DAPI as a consequence of restricting its mobility and decreased the T_g of SPS by breaking the sulfonate associations. Dilute solution viscosity behavior provided further evidence for complexation in that the addition of the amine-terminated PI to sulfonated polystyrene solvated the *inter*molecular interactions of the SPS at higher polymer concentrations and *intra*molecular interactions at lower concentrations.

A number of unanswered questions remain from this research. For example, circumstantial evidence suggests that the sulfonate and amine groups should be located at the interface between the two phases. Direct confirmation of this is desirable. Also, although the sulfonate/amine ratio was varied from 1:2 to 3:1 in this study, no real differences were observed. This raises the question of how quantitative were the interactions and what is the functionality of the complex (i.e., amines per sulfonate). Previous results of other workers[13] suggest that a stoichiometry of 1:1 is expected for the complex, but the data presented herein do not confirm that.

One might also argue that the PI-phase sizes observed by TEM are too large to allow all amine groups to be at the phase interface. This implies that some amine groups must be trapped within the phase and are, therefore, not available for complexation. Thus, one wants to know the efficiency of the complexation and whether that is limited by kinetic or thermodynamic factors. In regard to the first point, some intriguing time effects were recently observed in our laboratory for intermolecular complexes between SPS and an amine-terminated rigid rod polymer. That is, when the two polymers were mixed in dilute nonpolar solutions, polymer precipitation occurred, but was time dependent, occurring over a period of weeks.[14] Answers to these questions, as well as further control of the microstructure by varying the component polymer molar masses will be the subject of further studies on these systems.

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