# Ionomeric Blends. 3. Miscibility Enhancement via Ionic Interactions in Polyurethane–Styrene Blends

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ABSTRACT: Blends of lightly sulfonated polystyrenes with polyurethanes containing a tertiary amine in the chain extender were prepared. In the absence of polystyrene, the polyurethanes are not phase separated. Addition of the sulfonated polystyrene leads to a blend of the latter with the hard segments in one phase with the exclusion of the soft segments into a separate phase. The degree of phase purity of the soft segments increases with increasing sulfonate content at a constant styrene concentration or with increasing styrene content at a constant sulfonate concentration in the styrene. Blend formation is confirmed in a study involving the mixing of a polyurethane containing hard segments without any soft segments, which leads to a one-phase system at a high enough sulfonated polystyrene content.

## Introduction

Heterophase polymer systems have been of considerable academic and technological interest in recent years.[1–7] Systems such as the ABA block copolymers,[1–3,8,9] the segmented polyurethanes,[10–16] and other partially compatible blends[17–20] or interpenetrating networks[21–23] have received extensive attention both because of the wide range of mechanical properties which can be observed as a result of this partial or complete phase separation and because of the intriguing scientific aspects of the general problem of heterogeneity in polymers.

Perhaps the most interesting systems among the various materials mentioned above are those in which a substantial glass transition temperature difference exists between the two phases but in which interphase adhesion is high, so that the materials do not suffer from failure at the interphase. One example of this latter family comprises the segmented polyurethanes, which have been studied in a number of laboratories recently.[10–16]

Compatibility or miscibility of polymers has also been the subject of many recent investigations.[4–7,23–31] As is well-known, most polymer pairs are not miscible. However, if specific interactions are present, such as hydrogen bonding,[25] polymer pairs may be compatible. Furthermore, by incorporating specifically interacting species, otherwise incompatible pairs may be made compatible.[26–31]

One example of utilizing specific interactions is the recent work[29] on Coulombic interactions as miscibility enhancers. For example, in one study, a copolymer of styrene and styrenesulfonic acid was shown to be compatible with a copolymer of ethyl acrylate and vinylpyridine at a functional group level of 5% or less. This type of miscibility enhancement via Coulombic interactions has been applied to several systems and is now under extensive investigation.[28–31]

In the segmented polyurethanes, phase separation is very much a function of the length of the segments of different composition.[32,33] If the soft segments are long enough (MW = 2000), then phase separation can be expected. Alternately, if the soft segments are too short, then phase separation is not found, and the materials are believed to be relatively homogeneous and to exhibit only one glass transition temperature. It has recently been shown that the incorporation of ionic groups into polyurethanes causes dramatic changes in their physical properties,[34–40] such as increases in the moduli and the glass transitions, as well as improvements in hard-domain cohesiveness by the aggregation of ionic groups or enhanced phase separation in materials lacking soft-segment crystallinity.

The purpose of the present study is to explore whether a polymer which is incompatible with the usual polyurethanes can be blended with the latter, or at least with one of the components, if specifically interacting ionic or ionizable groups are present. Furthermore, it is of interest to see whether this preferential blending of a non-urethane polymer such as polystyrene with one of the components of the polyurethane can enhance phase separation in an otherwise apparently non-phase-separated system. Specifically, this study is devoted to a blending of a copolymer of styrene (S) and styrenesulfonic acid (SSA) with a polyurethane consisting of poly(caprolactone) $\alpha,\omega$-diol (MW = 830), 4,4′-methylenebis[phenyl isocyanate], and *N*-methyldiethanolamine as a chain extender. It is anticipated, on the basis of previous miscibility enhancement studies, that the polystyrene will preferentially interact with the hard segment of the polyurethane via proton transfer from the sulfonic acid to the tertiary nitrogen. This proton transfer should yield anions on one chain and cations on the others and thus enhance the phase separation of the hard segments plus polystyrene blend, which contains all the ionic groups, from the soft segments of the polyurethane.

## Experimental Section

**Materials.** One of the polyurethanes used in this study was prepared by a two-step condensation reaction shown in Figure 1. Poly(caprolactone) diol (PCLD, average MW = 830, Aldrich Chemical Co., Inc.) was dried under vacuum at 60 °C for 5 h. 4,4′-Methylene bis[phenyl isocyanate] (MDI, Eastman Kodak Co.) was purified by filtration of the liquid at 70 °C. *N*-Methyldiethanolamine (MDEA, Aldrich Chemical Co.), stannous octoate catalyst (Research Organic/Inorganic Chemical Corp.), and anhydrous *N,N′*-dimethylformamide (DMF) were used as received.

The prepolymer was made as follows: 4,4′-methylenebis[phenyl isocyanate] was dissolved in DMF at a concentration of about 40% by weight. This solution was added to a solution of DMF, poly(caprolactone) diol (40% by weight), and stannous octoate (0.1% by weight). The synthesis of the urethane prepolymer was carried out at 65 °C for 2 h, under vacuum, maintaining a NCO:OH molar ratio of 3:1. The chain extender, *N*-methyldiethanolamine, in an appropriate quantity to maintain a NCO:OH ratio of 1:1 was added, and the reaction continued for an additional 1 h.

The hard-segment (HS) polyurethane was synthesized in DMF solution by reacting MDI with MDEA, maintaining a NCO:OH molar ratio of 1:1. This synthesis was carried out at 65 °C for 3 h under vacuum. The polyurethanes were precipitated with warm water and were dried under vacuum at 80 °C for 2 weeks.

The polystyrene (PS) (MW = 125 000–250 000) was obtained from Polysciences and sulfonated by the procedure developed by Makowski et al.[41] The sulfonation was carried out at 50 °C in 1,2-dichloroethane solution, using a mixed anhydride of acetic acid and sulfuric acid as the sulfonating agent. Polymers containing 3.8, 6.0, 7.9, 8.7, and 9.9 mol % styrenesulfonic acid were employed in this work.

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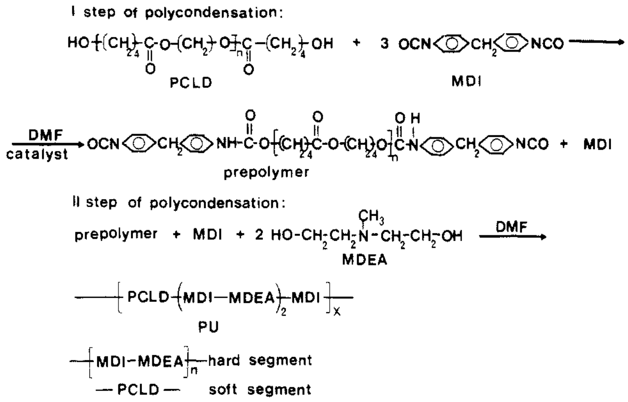

**Figure 1.** Synthesis of polyurethanes (PU). MDI:MDEA:PCLD molar ratio is 3:2:1.

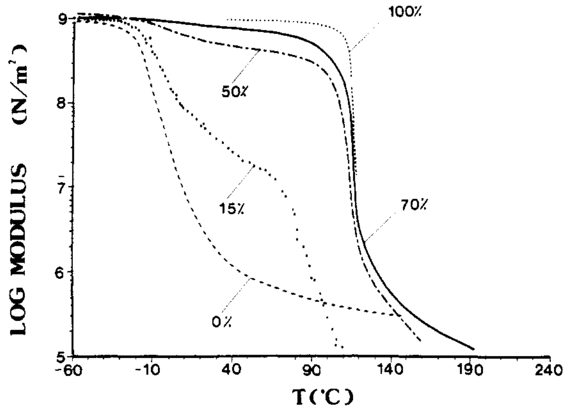

**Figure 2.** Variation of the shear storage modulus with temperature for blends of PU/PS-SSA with varying contents of PS-SSA. Experimental points are shown only for the 15% sample; they are omitted in the other plots for the sake of clarity. The numbers indicate the weight percent of the styrene copolymer in the blend.

**Blending.** The polyurethanes were dissolved in a tetrahydrofuran (THF)-dimethyl sulfoxide ($Me_2SO$) (90/10 (v/v)) mixture. The sulfonated polystyrenes (PS-SSA) were dissolved in THF, and these solutions were added dropwise to the vigorously stirred polyurethane solutions. For the polyurethanes containing both hard and soft segments, the mixtures were gellike precipitates, if the PS-SSA copolymer content exceeded 30% by weight. If a precipitate was not obtained, the mixture was stirred for 5 h and subsequently dried by evaporation of the solvent at progressively higher temperatures (up to 80 °C). The blends containing only hard segments precipitated immediately on mixing with the polystyrene solution. Finally, the blends were dried in vacuo for 1 week at 70 °C.

**Sample Preparation.** The samples used for the measurement were prepared by compression molding 0.8–1.0 g of the blend. The polymers were heated in the mold to a temperature ca. 20 °C above $T_g$ (depending on the sample) for about 1 h at 45 MPa. The samples were removed from the mold after it had cooled to room temperature and were then maintained at 25 °C under vacuum. Typical dimensions of the specimens were 2.5 × 6 × 50 mm.

**Dynamic Mechanical Studies.** Dynamic mechanical studies were performed under dry helium between −60 and +200 °C using a computerized torsional pendulum partly described elsewhere.[42] The frequencies varied from ca. 4 to 0.1 Hz, depending on the temperature. The heating or cooling rates were always less than 1 °C/min.

## Results and Discussion

Figure 2 shows a plot of $G'$ vs. temperature for the polyurethane blended with varying amounts of a polystyrene–styrenesulfonic acid copolymer containing 7.9 ± 0.1 mol % of styrenesulfonic acid. The plots for the 15% and 50% samples show clear evidence of two-phase behavior in that a two-step descent in the modulus is seen. The 0%, 70%, and 100% systems, by contrast, show behavior very strongly reminiscent of a one-phase system. Figure 3 shows a plot of the loss tangent as a function of temperature for the 0%, 15%, 70%, and 100% samples. Here it is seen very clearly that, even in the 70% sample, two peaks are present. The peak positions themselves are shown in Figure 4 for both the high-temperature peaks and the low-temperature peaks. It is seen very distinctly that the peak positions are strongly composition dependent.

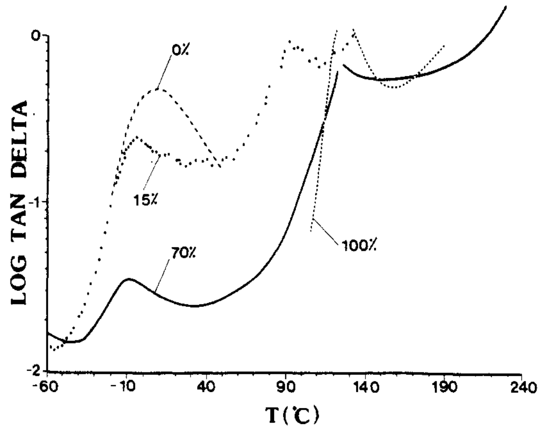

**Figure 3.** Variation of the loss tangent with temperature for blends of PU/PS-SSA with varying contents of PS-SSA.

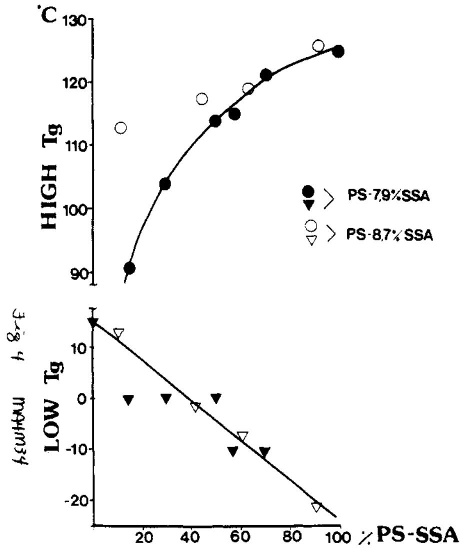

**Figure 4.** Positions of the maxima in the loss tangent-temperature plots for blends of PU/PS-SSA with varying contents of PS-SSA.

This is the case both for the 7.9% SSA samples discussed above and for 8.7% SSA samples, which were also investigated in some detail. It is seen here also that the position of the upper glass transition peak increases with increasing styrenesulfonic acid content, while that of the lower glass transition peak decreases. For the high-temperature peaks, the peak positions are somewhat composition dependent, especially at the low PS-SSA contents. This is not the case for the low-temperature peak. No explanation can be offered at this time for that observation.

These phenomena can be understood on the following basis. As can be seen from the curve for pure polyurethane in Figure 3, the material is not phase separated. This is in accord with previous observations of Estes[32] and Seymour,[33] who suggested that only systems which contain more than 38% by weight of MDI (like the present system) exhibit an interconnected hard-domain morphology. In the present case, as the PS-SSA is added, proton transfer

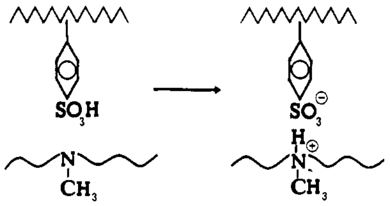

**Figure 5.** General scheme for the interaction of pendant sulfonic acid and amine groups on polyurethane chains.

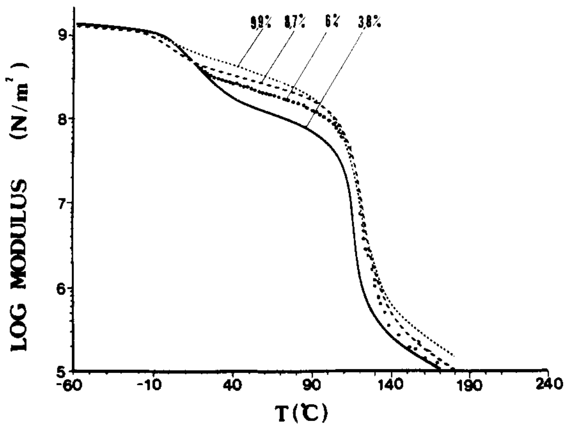

**Figure 6.** Variation of the shear storage modulus with temperature for blends of PU/PS-SSA (70/30) with varying sulfonate ion concentration.

from PS-SSA to the tertiary nitrogen can be expected[28] (Figure 5). This would lead to strong Coulombic interactions between the sulfonate anion ($SO_3^-$) on the polystyrene chain and the quaternary ammonium cation on the hard segment of the PU, which would result in very intimate mixing of the PS-SSA copolymer with the hard segment. Proton transfer has, indeed, been confirmed spectroscopically in blends in which one component carried a sulfonic acid and the other a vinylpyridine group, a weaker base than the tertiary amine used here.[43]

A consequence of this would also, most likely, be the preferential exclusion of the soft segment from the blend of the hard segment and the PS-SSA copolymer. Thus, with increasing PS-SSA content, the glass transition temperature of the hard segment-styrene blend should increase while the glass transition temperature of the soft-segment phase should decrease because of increasing phase purity. If the polystyrene had not been incorporated into the hard segment, the glass transition temperatures would be independent of composition, which they clearly are not, thus confirming the formation of the blend.

A 58% sample corresponds to a stoichiometric ratio of sulfonic acid to tertiary amine. It is noteworthy that samples containing a higher sulfonate content also seem to form excellent blends. This might suggest that the sulfonic acid can interact with other groups in the polyurethane chain, the most reasonable possibility being the urethane group. A model study has, indeed, confirmed that possibility. This will be the subject of a future publication.[44]

The suggestion that the polystyrene is intimately mixed with the hard segment of the PU is further confirmed in a parallel investigation of the same PU containing 30% PS-SSA of varying SSA contents. Figure 6 shows a plot $G'$ vs. temperature for this blend system containing, respectively, 3.9, 6.0, 8.7 and 9.9 mol % SSA in the polystyrene. These blends are strongly reminiscent of two-phase systems showing a two-step descent in $G'$. The intermediate plateau modulus increases with increasing ion content, again suggesting strong mixing between the PS-SSA copolymer and the hard segment of PU. If this mixing had not occurred, the value of the modulus at that point would be far less dependent on the ion content of the PS-SSA. Figure 7 shows plots of the loss tangent in the low-$T_g$ region. Again, a maximum corresponding to the transition is seen, the position of which clearly decreases with increasing ion content. The peak positions for the upper and lower $T_g$'s are shown in Figure 8. As before, this behavior suggests that the purity of the soft segment increases with increasing ion content, again confirming the strong interaction between PS-SSA and the hard segment of the PU.

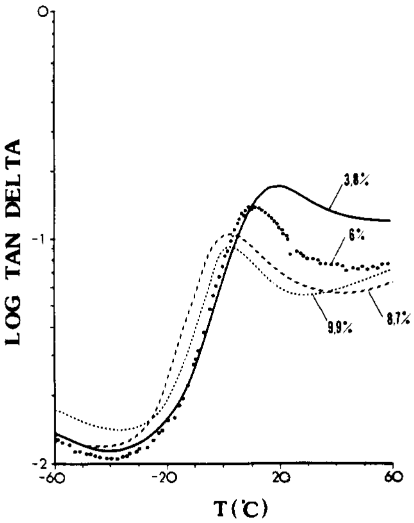

**Figure 7.** Variation of the loss tangent with temperature for blends of PU/PS-SSA (70/30) with varying sulfonate ion concentration.

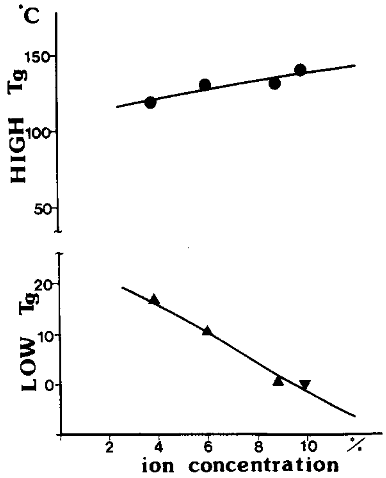

**Figure 8.** Positions of the maxima in the loss tangent-temperature plots for blends of PU/PS-SSA (70/30) with varying sulfonate ion concentration.

Finally, in order to confirm in still another way that the PS-SSA is reacting with the hard segments of the PU, samples of a PU were prepared containing only hard segments. On mixing of this material with PS-SSA (containing 7.9 ± 0.1 or 9.7 ± 0.1 mol % SSA) in solution, a precipitate was formed immediately. On drying, the blends were completely clear and transparent. Figure 9 shows a plot of $G'$ vs. temperature for one of these blend systems utilizing PS-SSA containing 7.9 ± 0.1 mol % SSA. It can be observed that the blends containing more than 30% PS-SSA show clear evidence of one-phase behavior, while the 21% and 30% systems show some indication of a two-phase behavior. This observation suggests that the upper $T_g$ is connected with the glass transition of the

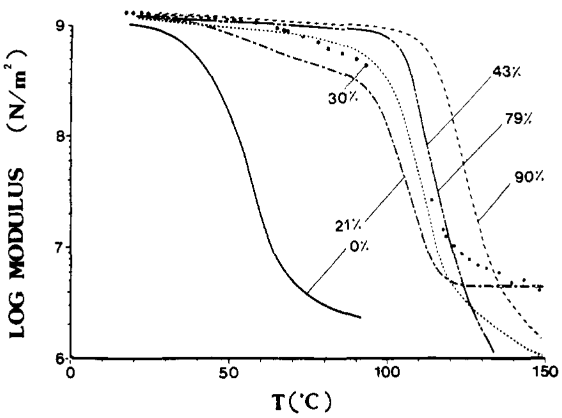

**Figure 9.** Variation of the shear storage modulus with temperature for blends of HS/PS-SSA with varying contents of PS-SSA.

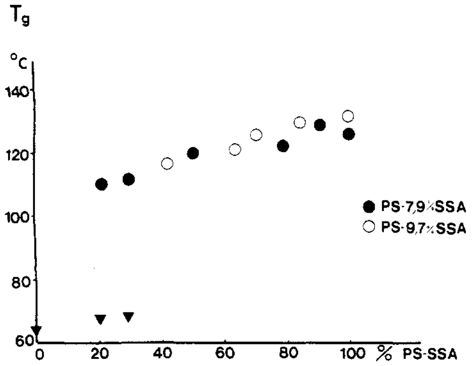

**Figure 10.** Positions of the maxima in the loss tangent-temperature plots for blends of HS/PS-SSA with varying contents of PS-SSA.

blends of the hard segment with PS-SSA, while the low-$T_g$ peak is due to the pure hard segment which remains at low PS-SSA contents. The composition dependence of the peak positions, shown in Figure 10, confirms the strong interaction resulting from proton transfer from SSA to the hard segment.

## Conclusion

It is shown that styrene-styrenesulfonic acid copolymers are miscible with amine-containing hard segments of polyurethanes. Strong interactions resulting from proton transfer from the sulfonic acid to the urethane lead to miscibility, which in turn leads to the exclusion of the soft segment into a separate phase.

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**Registry No.** (MDI)·(MDEA)·(PCLD) (polymer), 89106-01-4; (MDI)·(MDEA) (copolymer), 62503-70-2; (MDI-MDEA)$_n$, 89106-00-3.

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