

Ion-Dipole Interactions in Polyether Polyurethane-Styrene Ionomers Blends

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Synopsis

It is shown that polyurethanes containing polyether segments of MW = 1000 or 2000 are miscible with styrene ionomers. The soft segment interacts with the ionomer via ion-dipole interactions, but some of the hard segments containing ether moieties are also incorporated into the polystyrene.

INTRODUCTION

Several recent publications have been devoted to the area of miscibility enhancement in blends of polyurethanes and polystyrene utilizing ion-ion interactions.¹⁻⁴ In those studies, the polystyrene contained small concentrations of pendant sulfonic acid groups, while the polyurethane had, as a part of the hard segment, tertiary amine groups.

It was shown in these studies that miscibility was, indeed, achieved between the polystyrene and the hard segment of the polyurethane.¹⁻³ The miscibility enhancement mechanisms consisted of ionic interaction which resulted from proton transfer from the sulfonic acid to the tertiary amine.^{1,3} In a subsequent study, it was also shown that the sulfonic acid is a strong enough proton donor to transfer the hydrogen even to the nitrogen on the urethane or urea groups.² These mechanistic interpretations are now the subject of IR and NMR studies.^{5,6}

In a parallel investigation, miscibility enhancement via ion-dipole interactions was explored utilizing styrene ionomers and poly(alkylene oxide)s.^{7,8} In those studies, it was shown that poly(ethylene oxide) or poly(propylene oxide) were, indeed, miscible with the styrene ionomers. The miscibility improved as the size of the cation decreased or as the concentration of the ions increased.

In view of these studies, it was of interest to see whether miscibility enhancement could also be achieved in the polyurethane-styrene blends using ion-dipole interactions. This attempt had already been made in a recent study, but the use of only a short polyether segment (2-dihydroxyethyl ether as a chain extender) in the hard segment of the polyurethane was shown to be insufficient to induce miscibility.⁴

The present study is devoted to a more detailed exploration of ion-dipole interactions as miscibility enhancers between polyurethanes and polystyrene ionomers. Specifically, it involves styrene-lithium methacrylate copolymers on the one hand and polyurethanes containing polypropylene diol of MW =

1000 or 2000 as the soft segment. These molecular weights are much higher than those employed in the previous study, and thus the possibility of miscibility enhancement is much greater.

EXPERIMENTAL

Materials

The polyether-polyurethane (PU1) used in this study was prepared by a two-step condensation reaction.¹ Polypropylene diol (PPrO, average MW = 1000) was dried under vacuum at 60°C for 5 h. 4,4'-Methylene bis(phenyl isocyanate) (MDI) was purified by filtration of the liquid at 70°C. 2-Dihydroxyethyl ether (DEO), stannous octoate catalyst, and anhydrous *N,N'*-dimethylformamide (DMF) were used as received. The prepolymer was made as follows: MDI was dissolved in DMF at a concentration of about 40% by weight. This solution was added to a solution of DMF, PPrO (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. DEO as chain extender was added in an appropriate quantity to maintain a NCO:OH ratio of 1:1, and the reaction was continued for an additional 1 h. The polyurethane was precipitated with warm water and dried under vacuum at 80°C for 2 weeks.

The elastomer PU2 was synthesized in bulk by a two-step condensation reaction. The prepolymer was prepared from polypropylene diol (PPrO, average MW = 2000), 4,4'-Diphenylmethane diisocyanate (MDI) at molar ratio NCO:OH = 4:1 (by heating the mixture for 1 h at 80°C). The final stage of the synthesis, i.e., the last 15 min, was carried out under vacuum. A chain extender (glycol-1,4-butanediol) in an appropriate quantity to maintain a steady NCO:OH ratio of 1:1 was added to the prepolymer with intensive mixing at a temperature of 80°C. After 30 s of mixing, the reaction mixture was poured into a mold which had been preheated to a temperature of 110°C. The mold was placed in an oven and maintained at the same temperature for 24 h.

The styrene-methacrylic acid copolymer was synthesized by a procedure described elsewhere.⁹ To obtain the lithium neutralized samples, a standard solution of LiOH in methanol (ca. 1*N*) was added to solution of less than 3% of styrene methacrylic acid copolymers in a mixture of benzene and methanol (90:10 v/v) to the phenolphthalein end point. The solution was then freeze-dried. Polymer containing 10.5% lithium methacrylate (PS-MAALi) was employed in this work.

Blending

The polyurethanes were dissolved in DMF (at a concentration of ca. 10%). PS-MAALi was also dissolved in the same solvent at the same concentration, and this solution was added to the former solution slowly with stirring. The mixtures of varying contents of PS-MAALi were stirred for 5 h and subsequently dried by evaporation of the solvent at progressively higher temperatures (up to 70°C) under vacuum. Subsequently all samples (except sample B in Fig. 1) were annealed at 120°C under vacuum for 24 h.

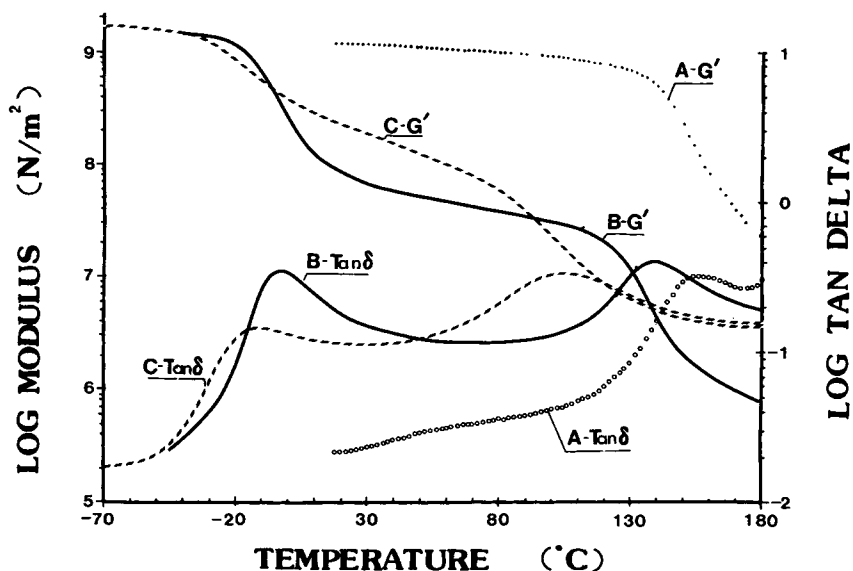


Fig. 1. Variation of the shear storage modulus and the loss tangent with temperature for PS-MAALi (curves A) and blend of PU1/PS-MAALi (70/30) (curves B for sample annealed at 70°C and curves C for sample annealed at 120°C). Experimental points are shown for PS-MAALi only for simplicity.

Sample Preparation

The samples used for the torsion pendulum measurements were prepared by compression molding 0.8–1.0 g of the blend. The polymers were heated in the mold to a temperature slightly higher than the highest T_g for about 1 h at 45 MPa, before being cooled slowly down to room temperature and removed from the mold. Typical dimensions of the rectangular specimens were $2.5 \times 6 \times 50$ mm.

Dynamic Mechanical Measurements

Dynamic mechanical studies were performed under dry helium between -70 and $+180^\circ\text{C}$ using a computerized torsion pendulum, an early version of which is described elsewhere.¹⁰ The frequencies varied from ca. 4 to 0.1 Hz, depending on the temperature. The heating rate was always less than $1^\circ\text{C}/\text{min}$ with a temperature control of $\pm 1^\circ\text{C}$.

RESULTS AND DISCUSSION

Figure 1 shows a plot of the shear storage modulus (G') and the loss tangent ($\tan \delta$) as a function of temperature for the blend of PU1/PS-MAALi containing 30% of PS-MAALi copolymer. The curve A- G' shows the variation of the G' and A- $\tan \delta$ that of the loss tangent with temperature for the styrene ionomer itself, while curves B and C show the plots for the blends.

Curves B are the plots for the sample which has been prepared according to the technique described in the Blending subsection except that it was dried only at 70°C , while curves C show the results for the same sample annealed at

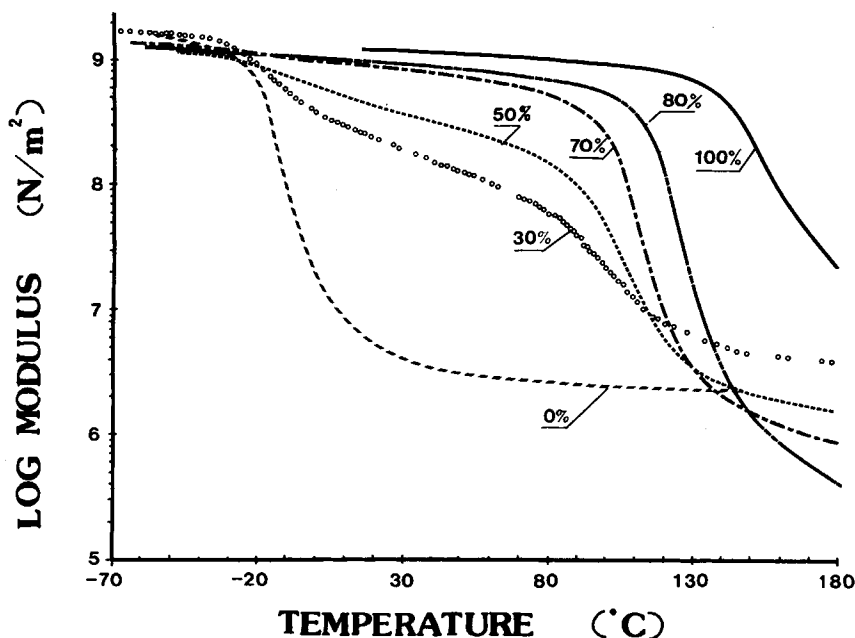


Fig. 2. Variation of the shear storage modulus with temperature for blends of PU1/PS-MAALi with varying contents of PS-MAALi. The number indicates the weight percent of the styrene copolymer in the blend.

120°C for 24 h. It is clearly seen that the annealing improves the miscibility considerably because the high temperature glass transition is depressed. A parallel NMR investigation has revealed that the unannealed sample contains traces of DMF. This DMF undoubtedly is associated with the ionic groups and therefore prevents interactions with the polyether from taking place. Annealing drives off the DMF as shown by NMR and allows the interactions between the PS ionomer and the soft segment of PU to be achieved. This is the reason for the dramatic depression of the high glass transition temperature following annealing.

Figure 2 shows the effect of the changes in the relative amount of the PU1 vs. PS-MAALi copolymers in the plots G' and Figure 3 in the plots for the loss tangent. The plots for the 0% (pure PU1) and 100% (pure PS-ionomer) samples show behavior typical of a one-phase system. The three intermediate curves are plots for the blends containing 30, 50, 70, and 80% of the PS-MAALi ionomer. They show clear evidence of two-phase behavior in that a two-step descent in the modulus is seen in Figure 2; in Figure 3, as before, two loss tangent peaks are seen. The high temperature peak shows considerable lowering below that of the loss tangent peak of pure PS ionomer.

As in the previous study, the upper $\tan \delta$ peak moves to progressively lower temperatures with increasing PU content and reflects the glass transition temperature of the blend containing the PS. In this case, however, it is possible that the soft segment which contains a considerable polyester component, should interact with the PS. If it were only that material, however, which gets incorporated into the PS, then the T_g of the remaining material

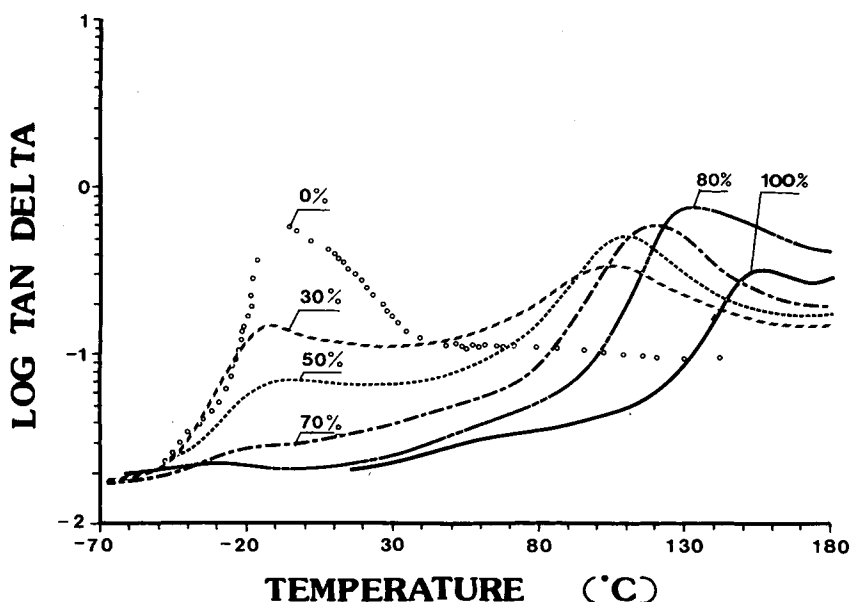


Fig. 3. Variation of the loss tangent with temperature for PU1/PS-MAALi with varying contents of PS-MAALi.

(reflected in the low T_g) should move to progressively higher temperatures as the styrene content increases. However, the position of the low T_g peak also drops with increasing styrene content. It seems, therefore, that both the soft segment as well as the hard segment are included in the styrene-rich phase, possibly even more of the latter than the former. This is not unreasonable, because each of the polyester segments can be accompanied by two hard segments which are capable of reacting with PS-MAALi.

Figure 4 shows plots of G' and $\tan \delta$ as a function of temperature for the pure components PU2 and PS-MAALi, as well as the blend containing 50% of each component. The curve shows two features which are noteworthy. First, it is clear that the T_g of the polystyrene ionomer is very close to that of the hard segment of PU2. Second, the PU2 shows very clear evidence of two-phase behavior, in that two loss tangent peaks are observed, as well as a two-step descent in the modulus. The blend also shows evidence of two-phase behavior. However, in this case, the T_g of the soft segments is lowered only very slightly from the position of T_g of soft segments of PU2, while the intensity of the loss-tangent peak is dramatically lower from what it was in the pure PU2. Simultaneously, the T_g of the blend (the high T_g peak) shifts to lower temperatures by approximately 50°C, which can be explained only by the participation of the soft segments in the blend. This shows conclusively that it is the soft segments of the PU2 which interact with the polystyrene.

In conclusion, it can be seen that ion-dipole interactions can lead to miscibility enhancement between polyether-urethanes and polystyrene ionomers, in which predominantly the soft segments are incorporated in the styrene. It should be recalled that in the previous study involving ion-ion interactions,¹⁻³ it was predominantly the hard segments which were incorpo-

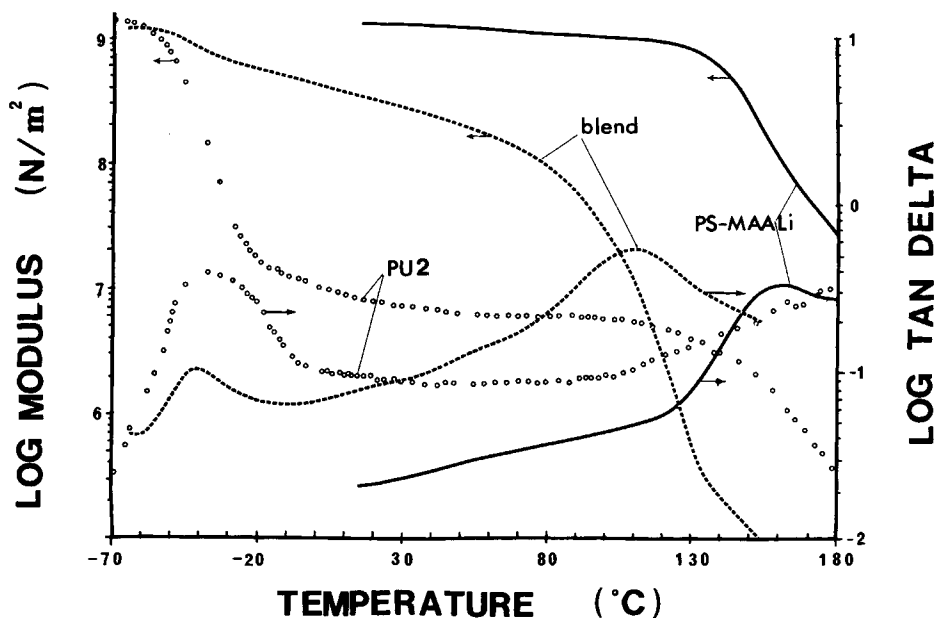


Fig. 4. Variation of the shear storage modulus and the loss tangent with temperature for PU2, PS-MAALi, and the blend containing 50% of each.

rated in the styrene-rich phase. Coulombic interactions are thus seen to be a very versatile tool for miscibility enhancement in polyurethanes.

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