

# Ion Pair-Ion Pair and Ion-Dipole Interactions in Polyurethane-Styrene Blends

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## Synopsis

It is shown that ion pair-ion pair interactions can be utilized to achieve miscibility in blends of urethanes with styrene ionomers. The urethanes contain quaternary ammonium salts in the hard segments, while the styrenes contain sodium methacrylate groups (~9.6 mol %). By contrast, ion-dipole interactions are not strong enough to achieve miscibility enhancement; a polyurethane containing short (ethylene oxide) sequences in the hard segment did not exhibit miscibility with a styrene-lithium methacrylate copolymer.

## INTRODUCTION

Recently, the morphology and mechanical properties of polyether and polyester-based polyurethane block copolymers have been of considerable academic and technological interest.<sup>1-5</sup> Advantageous mechanical properties are observed as a result of partial or complete phase separation, which is characteristic of these systems above a certain block length.<sup>6,7</sup>

Ionomers have also been the subject of many recent investigations.<sup>8-11</sup> The incorporation of ions into polymeric materials provides a very useful and versatile technique for major modifications of polymer properties. For example, changes in the modulus or the viscosity of these materials of several orders of magnitude are routinely observed with changes in ion content.

Ionic interactions have been utilized recently as miscibility enhancers.<sup>12-14</sup> For example, it was shown that lightly sulfonated polystyrene can be mixed with ethyl acrylate-vinyl pyridine copolymers at a functional group level of 4% or more to achieve a homogeneous system with a single glass transition temperature.<sup>12</sup> Several other systems have shown similar behavior. Ion-dipole interactions have also been explored as miscibility enhancers. It was shown that poly(ethylene oxide) or poly(propylene oxide) could be mixed over wide concentration ranges with styrene lithium methacrylate copolymers to achieve one phase blends<sup>15</sup> which demix reversibly at elevated temperatures. In these systems, the poly(alkylene oxide) chain is believed to interact strongly with the lithium cation yielding a polycationic chain, which remains in close association with the polystyrene chain carrying the anionic charges. These are only a few examples of a range of recent studies.

In our previous study, ion-ion interactions were utilized to enhance the miscibility of polystyrene with polyurethanes.<sup>16,17</sup> In one publication<sup>16</sup> it was shown that the proton from the pendant sulfonic acid group on the styrene

chain transfers to a tertiary amine in the hard segment of the polyurethane, giving a blend of the polyurethane hard segment and the styrene. This results in the phase separation of the hard segment containing the polystyrene from the soft segment of the polyurethane. In a subsequent study<sup>17</sup> it was shown that proton transfer from the sulfonic acid could also occur to the nitrogen of the urethane or urea groups; the tertiary amine groups are thus not essential to achieve this effect.

The polyurethane studies mentioned above involved in all cases the use of sulfonic acid as proton donors. The advantage of this approach is that proton transfer yields an ionic pair whose components are on different chains—the cation being located on the polyurethane chain and the anion on the styrene chain; Coulombic interactions force the two chains to remain in each other's vicinity. The disadvantage of the approach is that sulfonic acid (or another strong acid) is a necessary ingredient and the use of strong acids may present difficulties in some systems, since they may lead to hydrolytic reactions on the polyurethanes. For this reason it would be advantageous to achieve miscibility enhancement involving Coulombic interactions of some type without the presence of sulfonic acid on the polymer chain.

The present report describes a project in which ion pair–ion pair and ion–dipole interactions are explored as miscibility enhancers. In all cases the ion pairs or the dipolar groups are located on the hard segment on the polyurethane; ion pairs are also located on the polystyrene chains with which the polyurethane is to be mixed.

It is worth noting that ion pair–ion pair interactions have been utilized in the formation of polysalts, i.e., adducts of, for example, poly(sodium acrylate) with poly(vinyl pyridinium methyl iodide).<sup>18</sup> In most of these cases the microions can remain in the system.

## EXPERIMENTAL

### Materials

The polyether–polyurethanes used in this study were prepared by a two-step condensation reaction.<sup>16</sup> Polyoxytetramethylene diol (PTMO, average MW = 930) 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. *N*-methyldiethanolamine (MDEA) 2-dihydroxyethyl ether (DEO), stannous octoate catalyst, and anhydrous *N,N'*-dimethylformamide 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, PTMO (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 (MDEA for PU-1 or DEA for PU-2) 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 polyurethanes PU-1 and PU-2 were precipitated with warm water and dried under vacuum at 80°C for 2 weeks.

Reaction of the ethyl iodide ( $C_2H_5I$ ) with the tertiary amine on the backbone of the extender converts the polyurethane PU-1 to ionomer PU-I. Synthesis was carried out in DMF solution at room temperature for 5 h, and the polymer was then dried by evaporation of solvent.

The styrene methacrylic acid copolymers used in this work were synthesized in connection with another project using previously described methods.<sup>19</sup> To obtain sodium or lithium neutralized samples, a standard solution of NaOH or LiOH in methanol (ca. 1*N*) was added to solution of less than 3% of the styrene methacrylic acid copolymers in a mixture of benzene and methanol (90:10 v/v) until the phenolphthalein end point was reached. The solution was then freeze-dried.<sup>20</sup> Polymers containing 9.6% sodium methacrylate (PS-NaMA) or 10.4% lithium methacrylate (PS-LiMA) were employed in this work.

### Blending

The polyurethane PU-I was dissolved in a benzene-DMF (90:10 v/v) mixture. The polymer PS-NaMA was dissolved in a mixture of benzene and methanol (90:10 v/v), and this solution was added dropwise to the vigorously stirred PU-I solution. The dissolved PS-LiMA was added in the same way to the PU-2 solution. The mixtures were stirred for 5 h and subsequently dried by evaporation of the solvent at progressively higher temperature (up to 70°C) under vacuum.

### Sample Preparation

The samples used for the torsion pendulum measurement were prepared by compression molding 1.0 g of the blend. The polymers were heated in the mold to a temperature ca. 20°C above  $T_g$  for about 1 h at 45 MPa. The sample was removed from the mold after it had cooled to room temperature and was then maintained at 25°C under vacuum. Typical dimensions of the specimens were  $2.5 \times 6 \times 50$  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.<sup>21</sup> The frequencies varied from ca. 4-0.1 Hz depending on the temperature. The heating or cooling rates were always less than 1°C/min.

## RESULTS AND DISCUSSION

### Ion Pair-Ion Pair Interactions

Figure 1 shows a plot of the shear storage modulus ( $G'$ ) as a function of temperature for pure nonionic parent polyurethane (PU-1), the same polyurethane in the ionized form (PU-I), as well the styrene ionomer and two blends containing, respectively, 30% and 70% of the polystyrene ionomer based on sodium methacrylate. The corresponding loss tangent plots are shown in Figure 2. Looking at the curves for the ionomers and the ionomer blend samples, it is clear that glass transition temperature ( $T_g$ ) of

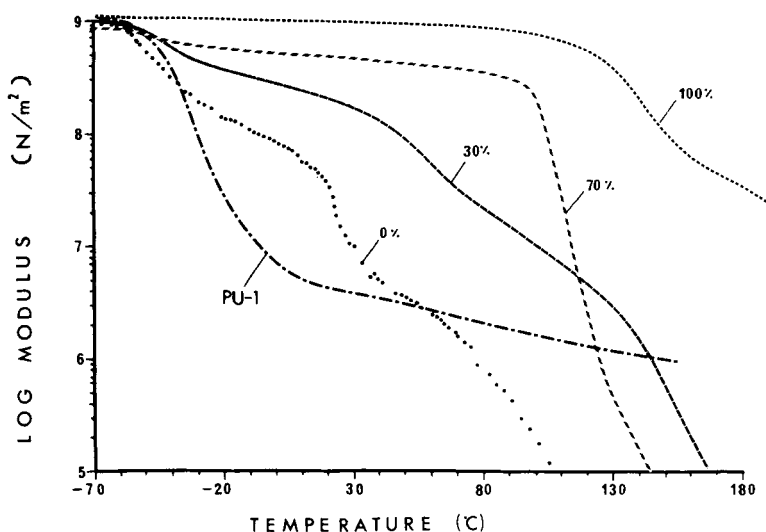


Fig. 1. Variation of the shear storage modulus with temperature for PU-1 and blends of PU-1/PS-NaMA with varying contents of PS-NaMA. The numbers indicate the wt % of the styrene copolymer in the blends. Experimental points are shown for one sample only for simplicity.

the polystyrene drops dramatically as the content of the polyurethane increases, showing that the compatibilization had, indeed, been achieved between the styrene ionomers and the hard segment of the polyurethane. For the nonionic system, only one glass transition temperature is observed at approximately  $-22^{\circ}\text{C}$ , while for the ionic urethane two glass transitions are observed. This suggests that the process of ionization of the polyurethane

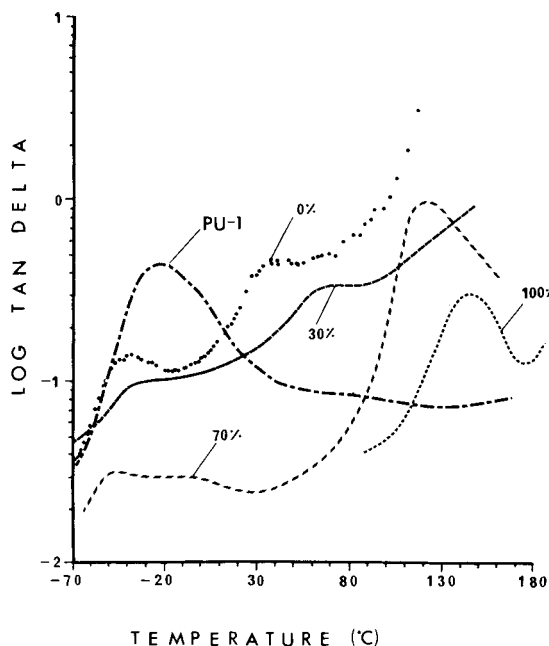


Fig. 2. Variation of the loss tangent with temperature for PU-1 and blends of PU-1/PS-NaMA with varying contents of S-NaMA.

leads to phase separation and thus to the exclusion of the hard segment form from the soft segment. It is also clear that the glass transition temperature of the soft segment of polyurethane remains constant in all the ionic systems. The high value of the modulus of the pure nonionic polyurethane above room temperature is due to the presence of allophanate crosslinks, which apparently are not present in the ionic systems.

Since the components of the blends were mixed in solution and the solvent evaporated, it is clear that the microions ( $\text{Na}^{\oplus}\text{I}^{\ominus}$ ) must have remained in the system. At this time it is not known whether they are incorporated in the ionic domains along with the macroions or whether they are excluded from the ionic domains and are present as individual crystals. This will be the subject of the future study.

The positions of the glass transition temperature peaks are shown in Figure 3. It is clearly seen that the glass transition temperature of the samples varies continuously from 145°C for the styrene ionomer down to 35°C for the pure ionic polyurethane. It is further clear that the  $T_g$  of the low temperature phase (soft segment of the polyurethane) remains unchanged at about  $-40^\circ\text{C}$  provided that the system is ionized. We can thus conclude that ion pair-ion pair interactions of the type utilized here are sufficient to achieve miscibility in the present system.

### Ion-Dipole Interaction

Since the poly(ethylene oxide) (which has previously been shown to be miscible with the ionic groups in styrene ionomers<sup>15</sup>) is present only in the

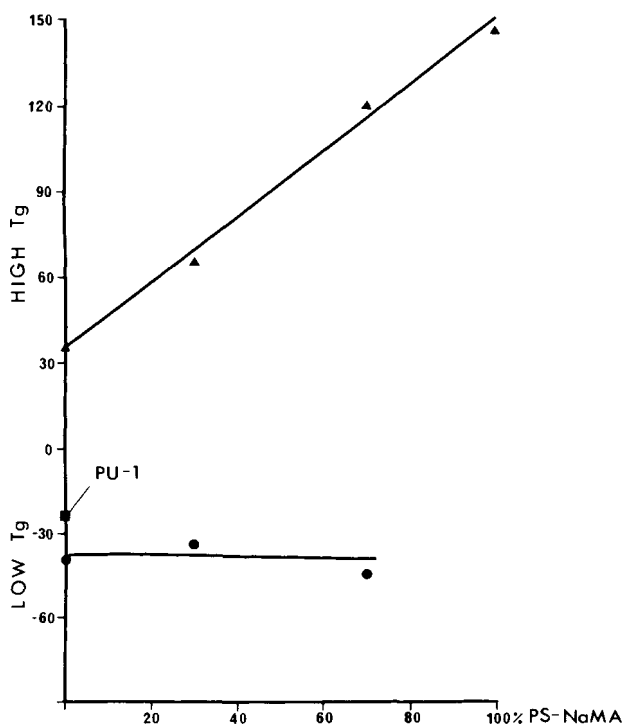


Fig. 3. Positions of the maxima in the loss tangent-temperature plots for PU-1 and for blends of PU-I/PS-NaMA with varying contents of PS-NaMA.

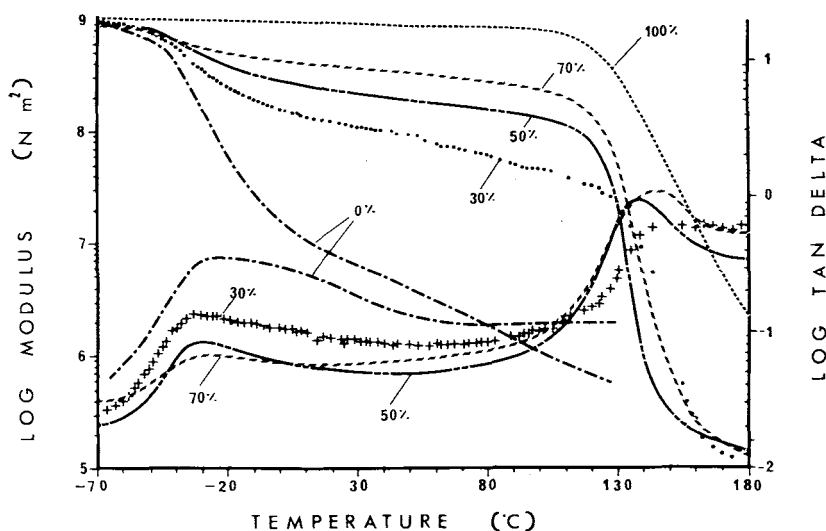


Fig. 4. Variation of the shear storage modulus and the loss tangent with temperature for blends of PU-2/PS-LiMA with varying contents of PS-LiMA.

hard segments of the polyurethanes, it is to be anticipated (if miscibility enhancement via ion-dipole interaction is operative) that the glass transition temperature of the polystyrene should be lowered as a result of the inclusion of the polyurethane. Modulus ( $G'$ ) and loss tangent vs. temperature plots are shown in Figure 4 for the pure styrene ionomer containing lithium methacrylate groups, the pure polyurethane, and the 30%, 50%, and 70% styrene ionomer blends. It is clear that the glass transition temperature of the polystyrene does not change (or at most only marginally) as the polyurethane content increases. It is, furthermore, seen that the glass transition temperature of the soft segment also remains constant. This suggests strongly that ion-dipole interactions in these systems are not sufficient to achieve miscibility.

It is worth pointing out that poly(tetramethylene oxide) groups are present in the soft segment. These, however, were not expected to interact with the ionomer because it has been shown by James et al.<sup>22</sup> that sequences of four methylene groups make that type of ion-dipole interactions impossible. It should be recalled that ion-dipole interactions are much weaker than ion pair-ion pair interactions; it is thus not surprising that the small number of ions and dipoles present in this system does not lead to significant miscibility enhancement. Conceivably, a much higher content of ethylene oxide groups might be successful. This will be the subject of a future study.

One of us (A. E.) is indebted to the U.S. Army Research Office for partial funding of this research.

### References

1. T. K. Kwei, *J. Appl. Polym. Sci.*, **27**, 289 (1982).
2. C. B. Wang and L. S. Cooper, *Macromolecules*, **16**, 775 (1983).
3. K. K. S. Hwang, D. Y. Hemker, and S. L. Cooper, *Macromolecules*, **17**, 307 (1984).

4. M. Rutkowska and P. Tekely, *Polym. Bull.*, **7**, 481 (1982).
5. Y. Camberlin, Y. P. Pascault, M. Letoffe, and P. Claudy, *Polymer*, **22**, 1428 (1982).
6. G. M. Estes, R. W. Seymour, and S. L. Cooper, *Macromolecules*, **4**, 452 (1971).
7. R. W. Seymour and S. L. Cooper, *J. Polym. Sci., Polym. Symp.*, **46**, 69 (1974).
8. J. A. Miller, K. K. S. Hwang, and S. L. Cooper, *J. Macromol. Sci. Phys.*, **22**, 321 (1983).
9. A. D. Wilson and H. J. Prosser, *Developments in Ionic Polymers—I*, Applied Science, London, 1983.
10. C. G. Bazuin and A. Eisenberg, *Ind. Chem. Prod. Res. Dev.*, **20**, 271 (1981).
11. A. Eisenberg *Ions in Polymers*, ACS 187, Am. Chem. Soc., Washington, DC, 1980.
12. A. Eisenberg, P. Smith, and Z. L. Zhou, *Polym. Eng. Sci.*, **22**, 1117 (1982).
13. A. Eisenberg, Proceedings of 28th Macromolecular Symposium, Amherst, MA, 1982, p. 877.
14. P. Smith and A. Eisenberg, *J. Polym. Sci., Polym. Lett. Ed.*, **21**, 223 (1983).
15. M. Hara and A. Eisenberg, *Macromolecules*, **17**, 1335 (1984).
16. M. Rutkowska and A. Eisenberg, *Macromolecules*, **17**, 821 (1984).
17. M. Rutkowska and A. Eisenberg, *J. Appl. Polym. Sci.*, **29**, 755 (1984).
18. A. S. Michaels, *Ind. Eng. Chem.*, **57**, 32 (1965).
19. A. Eisenberg and M. Navratil, *Macromolecules*, **6**, 604 (1973).
20. N. Z. Erdi and H. Morawetz, *J. Colloid Sci.*, **19**, 708 (1964).
21. B. Cayrol, Ph.D. thesis, McGill University, 1972.
22. D. B. James, R. E. Wetton, and D. S. Brown, *Polymer*, **20**, 187 (1979).

Received November 8, 1984

Accepted November 16, 1984