

Ionomeric Blends. IV. Miscibility of Urethane Elastomers With Styrene–Styrene Sulfonic Acid Copolymer

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Synopsis

Blends were prepared from two kinds of urethane elastomers, containing 1,4-butanediol or 3,3'-dichloro-4,4'-diamino-diphenyl-methane as chain extenders, with lightly sulfonated polystyrenes. Dynamic mechanical studies show that strong interactions occur between the sulfonic acid and the urethane or urea moieties on the polyurethane chains. These strong interactions are clearly seen in the composition dependence of the loss tangent peaks (due to the glass transitions) for both the high temperature and the low temperature glass transitions of the blends. They are further confirmed by model studies.

INTRODUCTION

Polyurethane elastomers are segmented copolymer systems that find extensive industrial applications. They possess mechanical properties similar to those of crosslinked rubbers, but are thermoplastic, and can therefore be processed by conventional molding and extrusion techniques. The unusual elastomeric properties of these materials have been attributed to the formation of a micro-phase-separated domain structure consisting of hard-segment-rich and soft-segment-rich domains. At use temperature, one component is viscous or rubbery (soft segment), while the second component is glassy or semicrystalline in nature (hard segment), the mobility of which is therefore low. The hard segment domains are thought to act as thermally labile physical crosslinks or filler particles for the flexible soft segment matrix.

It is well known that the relative compatibility of the two dissimilar blocks, and therewith the degree of phase separation, is a function of the thermodynamics of the system. This includes the block length, number of blocks, chemical structure, presence of hydrogen bonds, and other factors.^{1–12}

Materials with a 2000 MW soft segment exhibit incompatible behavior, whereas those containing soft segments with an 830 MW generally exhibit compatible behaviour.^{8,11–12} Recent studies have elucidated^{9,13,14} the size and relative volume fraction of the domains and the width of the domain boundaries as well as the presence of possible disordered regions, i.e., hard segments which are dissolved in the matrix as well as soft segments which are incorporated in the domains. The hard blocks are rigid, and their presence among the soft segments imposes restrictions on the motion of the soft segment and increases the soft segment T_g .¹⁰

Polymer blends are, at this time, also receiving extensive attention.^{15–17} In

the development of these materials, much effort was devoted to multicomponent systems, leading to a heterophase structure.^{18,19} Blends of miscible polymers frequently exhibit desirable mechanical properties, and many attempts have been made to enhance the miscibility of otherwise immiscible systems. These include the use of coulombic interactions.²⁰⁻²³

In a previous study²⁴ of the blending of polyurethanes containing tertiary amine groups with polystyrene-styrene sulfonic acid copolymers, evidence was found of strong interactions resulting from proton transfer from the sulfonic acid on the polystyrene to the amine on the hard segment. The resulting formation of ionic groups on the different chains led to considerable miscibility enhancement, which in turn resulted in a blend of the hard segment domains with the polystyrene, with the exclusion of the soft segment into another phase.

Several studies have been performed which suggest that the urethane or urea nitrogens in polyurethane chains are capable of undergoing quaternization.²⁵⁻²⁹ In an investigation of the crosslinking of urethane elastomers containing 3,3'-dichloro-4,4'-diaminodiphenylmethane using dibromohexane as the crosslinking agent, it was found that it was not only the presence of tertiary nitrogen atoms in the backbone of the elastomer macrochains, but also the NH groups in the urea (or urethane) moieties which are capable of the formation of crosslinks in the presence of dibromohexane. It is likely that a reaction leading to the formation of chemical crosslinks with simultaneous appearance of ionic centers takes place in these systems.²⁵⁻²⁷

In the study of the ion enhancement of miscibility in the polyurethanes with styrene-styrene sulfonic acid copolymers which was mentioned above,²⁴ it was found that miscibility enhancement could be achieved even under conditions where the amount of sulfonic acid greatly exceeded the amount of tertiary nitrogen groups.²⁴ This suggested that proton transfer from the sulfonic acid could occur to the urethane or urea nitrogen in these systems.

In view of the above findings, it was thought advisable to explore whether quaternization of the urethane or urea nitrogens could be used to enhance miscibility of styrene-styrene sulfonic acid copolymers with normal urethanes, in a manner analogous to the work of the previous study in which a tertiary amine was used as the proton acceptor.²⁴ This investigation is described in the present publication.

Finally, to confirm the feasibility of strong interactions between the sulfonic acid and the urea or urethane linkages on the polyurethane chains, a brief study involving low molecular weight model compounds was undertaken. This will also be described.

EXPERIMENTAL

Materials. The two urethane elastomers studied in this work were synthesized in bulk by a two-step condensation reaction. The prepolymer was prepared from poly(caprolactone) diol (CAPA 220, MW 2000, Interlox Chemicals, Ltd., Great Britain) and 4,4'-diphenylmethane diisocyanate (MDI, Farben Fabriken Bayer AG) at a molar ratio NCO:OH = 4:1 (by heating the mixture for 30 min at 120°C). The final stage of the synthesis, i.e., the last 15 minutes, was carried out under a reduced pressure of ~150 Pa. The prepolymer was characterized by deter-

mining the concentration of free isocyanate groups using the amine equilibrium method.³⁰

A chain extender [glycol-1,4-butanediol (BASF) or diamine-3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA, Gee Lawson Chemicals)], 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 50–80°C. After 15–90 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 polystyrene (PS MW = 125,000–250,000) was obtained from Polysciences and sulfonated by Makowski's method³¹ at 50°C in a 1,2-dichloroethane solution using a mixed anhydride of acetic acid and sulfuric acid as the sulfonating agent. Polymers containing 7.9 ± 0.1 mol % styrene sulfonic acid (SSA) were employed in this work.

For the low molecular weight model study, urethane (ethyl carbonate, $\text{H}_2\text{NCO}_2\text{C}_2\text{H}_5$, Aldrich Co., mp 48.5–50°C) was dissolved in tetrahydrofuran (THF), 30 wt %, and added to a solution of 30 wt % of *p*-toluene sulfonic acid ($\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$, Eastman Organic Chemicals, mp 103–106°C) in THF; the solutions were mixed for 5 h and stored at room temperature. After a few days the salt (mp 170°C) precipitated out. In another experiment, 1,3-dimethyl urea (J.T. Baker Chemical Co., mp 104–106°C) was dissolved in THF, 30 wt %, and added to a solution of 30 wt % of *p*-toluene sulfonic acid, also in THF. The two solutions were mixed for 5 h. After standing for few days at room temperature, the salt precipitated out. The melting point of this salt was 118°C.

Blending. The polyurethanes were dissolved in dimethyl sulfoxide (DMSO), while the sulfonated polystyrene (PS-SSA) was dissolved in THF; this solution was added dropwise to the vigorously stirred polyurethane solution. The mixture was stirred for 5 h and, subsequently, dried by evaporation of the solvent at progressively higher temperatures (up to 80°C). Finally, the blends were dried in vacuo for 1 week at 70°C.

Sample Preparation. The samples used for the torsion pendulum measurements were prepared by compression molding of 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 down to room temperature and were then kept at room temperature 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°C and 200°C using a computerized torsion pendulum described in part elsewhere.³² 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

Figure 1 shows a plot of the shear storage modulus (G') vs. temperature for the polyurethane PU-BU (chain extender, 1,4-butanediol) blended with varying amounts of a polystyrene-styrene sulfonic acid copolymer (PS-SSA) containing

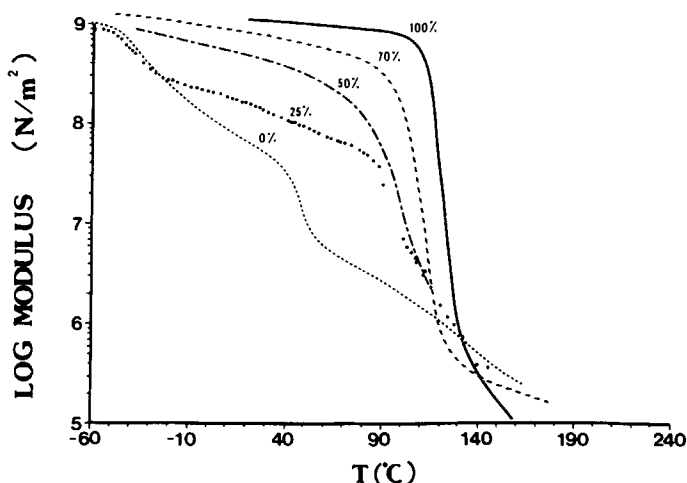


Fig. 1. Variation of the shear storage modulus with temperature for blends of PU-BU/PS-SSA with varying contents of PS-SSA. Experimental points are shown only for the 25% sample. They are omitted in the other plots for the sake of clarity. The numbers indicate the wt % of the styrene copolymer in the blend.

7.9 ± 0.1 mol % of styrene sulfonic acid. The pure PU-BU and the 25% system exhibit two phase behavior in that a two-step descent in the modulus is seen. The PU-BU has a soft segment which is long enough (MW 2000) for phase separation to occur.^{8,11,12} Usually the glass transition temperature of this kind of soft segment is about -50°C .⁸ However, as can be seen in Figure 1, the glass transition for this system is found at -30°C . It has been suggested that this value can be expected for a "homogeneous mixture" of hard and soft segments.¹⁰

The step at ca. 50°C for the pure PU-BU sample has been ascribed to disordering of the hard segment domains⁷ with relatively short range order. At about 100°C , hard domain softening begins. It is generally attributed to the glass transition of the hard segments.³³

The 100% PS-SSA shows a behavior very strongly reminiscent of a one-phase system in the region studied here. This is true of the 50% and 70% samples as well. The steep descent of G' at high temperatures for the 70%, 50%, and 25% systems is very clearly shifted to progressively lower temperatures, but the temperatures are still higher than the disordering temperatures of the hard segment domains.

Figure 2 shows a plot of the loss tangent as a function of temperature for the 0%, 25%, 50%, 70%, and 100% samples. Here it is seen that, even in the 50% and 70% samples, two peaks are present, and that the high temperature peak positions are strongly composition-dependent. The upper glass transition peak shifts to higher temperature with increasing PS-SSA content. The low glass transition temperatures for the 0%, 25%, and 50% samples seem to be independent of composition; by contrast, the peak for the 70% sample is shifted to a higher temperature. At low PS-SSA concentrations, the phase purity of soft segments most probably does not change with the compositions; however, once a higher content of PS-SSA has been incorporated into the blend, it seems likely that some of SSA will react with some of the NH groups in the urethane linkages of

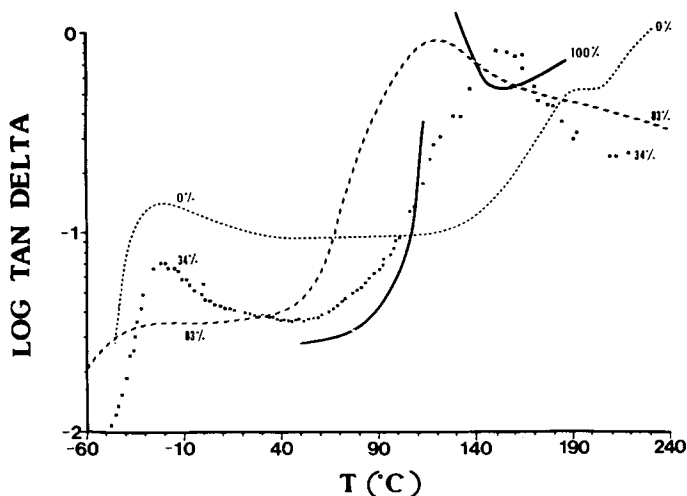


Fig. 2. Variation of the loss tangent with temperature for blends of PU-BU/PS-SSA with varying contents of PS-SSA.

the hard segments present in the soft phase. Phase separation is thus partially disrupted by ionic crosslinks. This mechanism raises the glass transition temperature of the soft regions.

To confirm this explanation, 50% blends were prepared of the PU-BU with pure PS on the one hand and the PU-BU with PS-SSA on the other. The results of mechanical studies are shown in Figure 3. It is seen very clearly that the high temperature glass transition is decreased appreciably for the sample containing PS-SSA while at the same time the low temperature glass transition is increased. This confirms that extensive interactions are taking place between the sulfonic acid and the NH groups in the hard segment of PU-BU. It should be stressed that the T_g of the PS-SSA copolymer is higher than that of the pure PS.³⁴

To test the generality of these observations, blending of PU-MOCA (chain extender 3,3'-dichloro-4,4'-diaminodiphenylmethane) with PS-SSA was attempted. This system contains —NH groups in urethane and urea moieties in the polymer chains. Figure 4 shows a plot of the loss tangent as a function of temperature for these blends with varying amounts of PS-SSA containing 7.9 ± 0.1 mol % SSA. It can be seen very clearly that the samples show two-phase behaviour. For pure PU-MOCA the glass transition temperature of the soft segments occurs at about -25°C which, incidentally, is about 5°C higher than that found in PU-BU. The T_g does not seem to vary with blend composition for low styrene contents (34%). However, at high styrene contents (83%), the low temperature T_g peak is lowered appreciably. This suggests that the phase purity of the low T_g phase has improved, presumably because some of the hard segments which had been incorporated into the soft phase have reacted with the styrene sulfonic acid and have become incorporated into the hard phase.

The upper glass transition temperature for PU-MOCA occurs about 200°C . This temperature is much higher than that found in PU-BU; this high value is due not only to the presence of urea linkages, but also to dipole-dipole interactions between groups containing chlorine atoms, and also to the presence of two aromatic rings per molecule of chain extender.³⁵

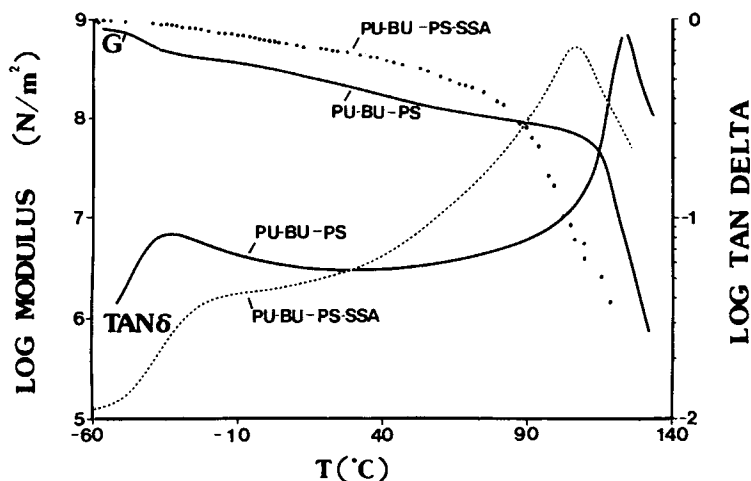


Fig. 3. Variation of the shear storage modulus and the loss tangent with temperature for blends of PU-BU/PS-SSA (50/50) and PU-BU/PS (50/50).

It was found that for the sample containing 34% of PS-SSA the high temperature glass transition is lower than for the pure PU-MOCA, while for the 83% sample the T_g occurs at about the same point as for pure PS-SSA. There, again, the composition dependence of the glass transition peak confirms the existence of strong interactions between the urethane and the sulfonic acid leading to the formation of a miscible blend.

The model study, which shows that high melting salts are produced upon mixing of toluene sulfonic acid with either urea or urethane, further confirms the postulate of strong interactions between these species.

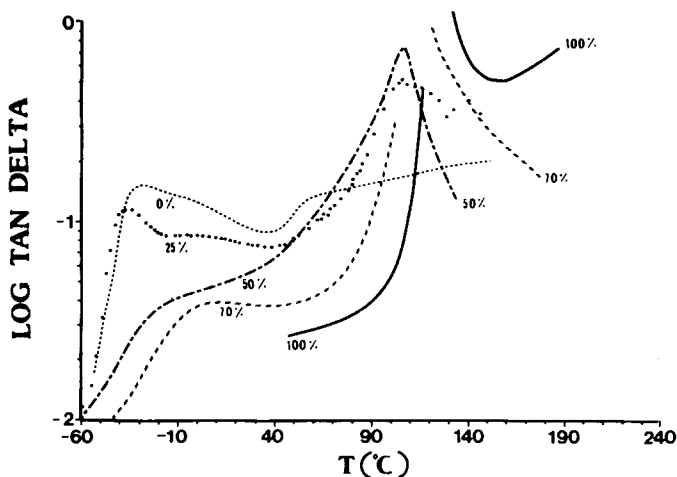


Fig. 4. Variation of the loss tangent with temperature for blends of PU-MOCA/PS-SSA with varying contents of PS-SSA.

CONCLUSION

It has been demonstrated that strong interactions occur between sulfonic acid on the styrene chains and the urethane or urea moieties on the polyurethane chains. These strong interactions are clearly seen in the composition dependence of the glass transition peaks for both the high temperature and low temperature glass transition.

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References

1. *Multiphase Polymers*, S. L. Cooper and G. M. Estes, Eds., Advances in Chemistry Series No. 176, American Chemical Society, Washington, D.C., 1979.
2. C. S. Paik Sung, C. B. Hu, and C. S. Wu, *Macromolecules*, **13**, 111 (1980).
3. R. W. Seymour and S. L. Cooper, *Macromolecules*, **6**, 48 (1973).
4. R. A. Assink and G. L. Wilkes, *Polym. Eng. Sci.*, **17**, 606 (1977).
5. A. Lilaonitkul and S. L. Cooper, *Rubber Chem. Technol.*, **50**, 1 (1977).
6. R. Bonart, L. Morbitzen, and G. Henze, *Macromol. Sci. Phys.*, **B3**, 337 (1969).
7. T. K. Kwei, *J. Appl. Polym. Sci.*, **27**, 2891 (1982).
8. J. W. C. Van Bogart, A. Lilaonitkul, L. E. Lerner, and S. L. Cooper *J. Macromol. Sci. Phys.*, **B17**(2), 267 (1980).
9. W. Neumüller and R. Bonart, *J. Macromol. Sci. Phys.*, **B12**(2), 203 (1982).
10. S. Abouzahr and G. L. Wilkes, *Polymer*, **23**, 1077 (1982).
11. G. M. Estes, R. W. Seymour and S. L. Cooper, *Macromolecules*, **4**, 452 (1971).
12. R. W. Seymour and S. L. Cooper, *J. Polym. Sci. Symp.*, **46**, 69 (1974).
13. Z. Ophir and G. L. Wilkes, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 1469 (1980).
14. J. T. Koberstein, B. Morra, and R. S. Stein, *J. Appl. Crystallogr.*, **13**, 34 (1980).
15. *Polymer Alloys*, D. Klempner and K. C. Frisch, Eds., Polymer Science and Technology, Vol. 10, Plenum, New York, 1977.
16. *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic, New York, 1978.
17. *Polymer-Polymer Miscibility*, O. Olabisi, L. M. Robeson, and M. T. Shaw, Eds., Academic, New York, 1978.
18. G. Riess, M. Schlienger, and S. Marti, *Macromol. Sci. Phys.*, **B17**(2), 355 (1980).
19. G. Riess, Proceedings of 28th Macromolecular Symposium, Amherst, Mass., 1982.
20. A. Eisenberg, P. Smith, and Z. L. Zhou, *Polym. Eng. Sci.*, **22**, 17, 1117 (1982).
21. A. Eisenberg, Proceedings of 28th Macromolecular Symposium Amherst, Mass., 1982, p. 877.
22. P. Smith and A. Eisenberg, *J. Polym. Sci., Polym. Lett. Ed.*, **21**, 223 (1983).
23. Z. L. Zhou and A. Eisenberg, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 595 (1983).
24. M. Rutkowska and A. Eisenberg, to appear.
25. M. Rutkowska and R. Zeilinski, Proceedings of the International Rubber Conference, Paris, 1982.
26. M. Rutkowska and R. Zielinski, Proceedings of the Symposium on Molecular Mobility in Polymer Systems, Leipzig, 1981.
27. M. Rutkowska, Proceedings of the 27th International Symposium on Macromolecules, Strasbourg, 1981.
28. D. Acierno, F. P. La Mantia, and G. Polizzotti, *J. Polym. Sci., Polym. Phys. Ed.*, **17**, 1903 (1979).
29. R. Benson, S. Yoshikawa, K. Knutson, and D. J. Lyman, in *Biomaterials: Interfacial Phenomena and Applications*, S. L. Cooper and N. A. Peppas, Eds., Advances in Chemistry Series No. 199, 1982, p. 133.

30. H. Roth, *Mikrochim. Acta*, **6**, 766 (1958).
31. H. S. Makowski, R. D. Lundberg, and G. H. Singhal, U.S. Pat. 3, 870, 841 (1975).
32. B. Cayrol, Ph.D. thesis, McGill University, 1972.
33. R. Bonart, *Polymer*, **20**, 1389 (1979).
34. M. Rigdahl and A. Eisenberg, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 1641 (1981).
35. Y. Camberlin, J. P. Pascault, J. M. Letoffe, and P. Claudy, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 1445 (1982).

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