

Blends of Polyurethane Carboxylates with Styrene Vinylpyridinium Copolymers

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SYNOPSIS

This is a continuation of an ongoing investigation of miscibility enhancement via ionic interactions in urethane-styrene blends. The present study deals with a polyurethane which contains in the hard segments pendant carboxylate groups neutralized by ammonium ions while the polystyrene contains pendant vinyl pyridinium methyl iodide groups. Miscibility of the styrene is seen with the hard segments of the urethane because of ion pair/ion pair interactions. Methanol extraction raises the T_g because it eliminates low molecular weight components, without removing the microions.

INTRODUCTION

Polymer blends have been the subject of considerable interest in recent years. One of the areas of interest has been the compatibilization of otherwise immiscible systems, and a wide range of techniques has been employed to improve miscibility.¹⁻⁷ In this laboratory, ionic interactions have been explored systematically in their role as miscibility enhancers. A range of studies have been devoted to ion-ion, ion pair-ion pair, and ion-dipole interactions in this context.⁸⁻¹⁶

One aspect of the blend research was a study of systems involving segmental polyurethanes as one of the components. The first study in that area concerned blending of a polystyrene containing sulfonic acid groups with a polyurethane containing amines.^{11,12,15} It was shown that proton transfer from the sulfonic acid on the styrene to the polyurethane yielded polyanionic and polycationic charges, respectively, and that miscibility could, indeed, be achieved between the polystyrene and the polyurethane hard segment. This was accompanied by the exclusion of the soft segment of the polyurethane into a separate phase. The subsequent aspect of the work explored ion pair-ion pair interactions in similar systems.¹³ Specifically, a polyurethane was pre-

pared which contained a quarternary ammonium salt, which then was mixed with a polystyrene chain containing sodium methacrylate. It was shown that ion pair-ion pair interactions were, indeed, strong enough to achieve miscibility in this system also.

In the present work, we also wish to explore the effect on miscibility of ion pair-ion pair interactions. In the present work, however, the polyurethane carries the pendant anion, which is a carboxylate, the counterion being an ammonium ion, while the polystyrene carries a cation, i.e., a vinylpyridinium group, the counterion being the iodide ion. An added feature involves methanol extraction of the blend, which was performed to eliminate small nonionic molecules. It was established that the microions remain in the system.

EXPERIMENTAL

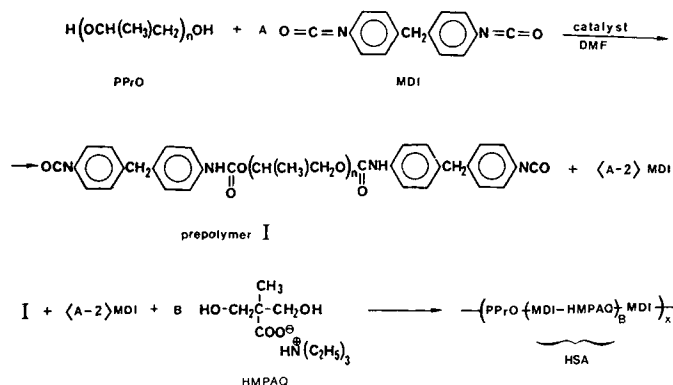
4,4'-Methylene bis(phenyl isocyanate) (MDI, Eastman Kodak Co.) was purified by filtration of the liquid at 70°C. Polypropylene glycol (PPG, average MW = 1000, Aldrich Chemical Co.) was dried under vacuum at 60°C for 5 h. 2,2-Bis(hydroxymethyl) propionic acid (Aldrich Chemical Co.), triethyl-amine (Aldrich Chemical Co.), stannous octoate catalyst (Research Organic/Inorganic Chemical Corp.) and anhydrous *N,N'*-dimethylformamide (DMF) were used as received.

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The salt (HMPAQ) of 2,2-bis hydroxymethyl propionic acid (HMPA) and triethylamine (TEA) was obtained in DMF by mixing an equimolar ratio of the components at room temperature after stirring

for 3 h. The quaternization was confirmed by IR studies. The salt was used as a chain extender for the urethane prepolymer.

The hard segment of polyurethane (HSA) was made as shown in Scheme 1:



SYNTHETIC SCHEME FOR POLYETHER POLYURETHANE ANIONOMER

Scheme 1

The MDI was dissolved in DMF at a concentration of about 40% by weight and stannous octoate was added (0.1% by weight). Then the salt, HMPAQ, was added in an appropriate quantity to maintain a NCO : OH ratio of 1 : 1, and the synthesis was carried out at 65°C for 2 h under vacuum. The HSA was dried initially by evaporation of the DMF with a rotary evaporator and then dried further under vacuum at 80°C for 2 weeks.

The polyurethane (PUA) was prepared by a two-step condensation reaction, also shown in Scheme 1. The prepolymer (I) was made as follows: MDI was dissolved in DMF at a concentration of about 30% by weight. This solution was added to a solution of PPrO (30% 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 was added in an appropriate quantity to maintain a NCO : OH ratio of 1 : 1 and the reaction was continued for an additional 2 h. The polyurethane was dried initially by evaporation of DMF with rotating pump and then dried further under vacuum at 80°C for 2 weeks.

The styrene-2-methyl-5-vinylpyridine copolymer (PS-VP) was prepared by free radical copolymerization in bulk.¹⁷ The content of vinylpyridine in the copolymer was 8.5 mol %. The copolymer was quaternized with methyl iodide in a THF/ethanol mixture. A sevenfold excess of methyl iodide was

used and the mixture was refluxed for 4 h to insure that the extent of the reaction was close to 100%. The ionomer was recovered by precipitation into methanol and dried in a vacuum oven at 80°C for 24 h.

Blending

The neutralized HSA or PUA was dissolved in a DMF-dimethyl sulfoxide (Me₂SO) [90/10 (v/v)] mixture. The quaternized PS-VP (PS-VP-Q) was dissolved in DMF and this solution was added dropwise to the vigorously stirred PUA solution. The mixture was stirred for 5 h and subsequently dried for a few days by evaporation of the solvent at progressively higher temperature up to 120°C under vacuum; subsequently, it was kept at 120°C for 48 h. Since the components of the blends were mixed in solution and the solvent evaporated, it is clear that the microions, (C₂H₅)₃NH⁺I⁻, must have remained in the system. A Soxhlet extraction in boiling methanol was carried out for 24 h to remove low molecular weight components, after which the blend was dried *in vacuo* at 80°C for several days.

Elemental Analysis

The elemental analysis for iodide was made on extracted and unextracted samples of the 50% blends PUA/PS-VP-Q, by Guelph Chemical Laboratories Ltd. (Guelph, ON, Canada).

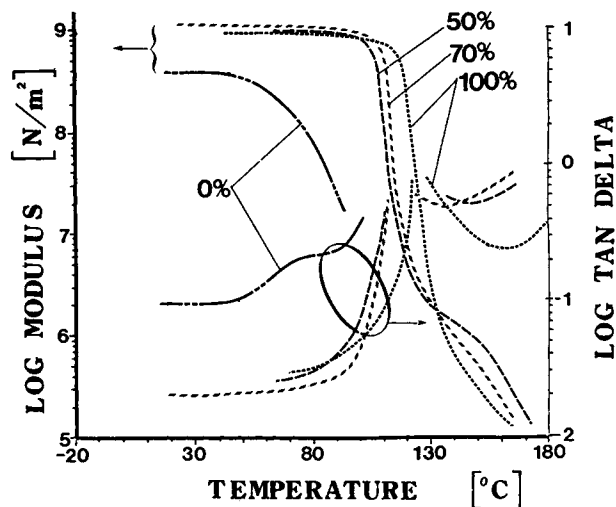


Figure 1 Variation of the shear storage modulus (G') and the loss tangent with temperature for the blends of HSA/PS-VPQ with varying contents of PS-VPQ. The numbers indicate the wt % of the PS-VPQ in the blends.

Sample Preparation for Dynamic Mechanical Studies

Samples used for the torsion pendulum measurements were prepared by compression molding 1.0 g of the blend. The polymer was heated in the mold to a temperature slightly above 100°C for about 1 h at 45 MPa. The sample was removed from the mold after it had cooled to room temperature. 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 -10 and $+180^\circ\text{C}$ using a computerized torsional pendulum partly described elsewhere.¹⁸ The frequencies varied from ca. 4 to 0.1 Hz, depending on the temperature. The heating or cooling rates were always less than $1^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Figure 1 shows plots of the shear storage modulus (G') and the loss tangent for the individual components as well as two blends of the anionic hard segment polyurethane (HSA) and the styrene-2-methyl-5-vinylpyridine copolymer quaternized with methyl iodide (PS-VPQ). All the plots show behavior of a one phase system. A one-step descent in the modulus is seen and only one peak in the loss tangent is present. The glass transition temperature of PS-VPQ drops in the blends, showing that compatibilization had been achieved between the styrene ionomers and the HSA, even in the presence of microions. This parallels the observations in the previous paper.¹³ In a parallel series of studies, the same samples were run after methanol extraction. No significant changes were observed.

Figure 2 shows a plot of the shear storage modulus (G') as a function of temperature and Figure 3 a plot of the loss tangent for the pure anionic polyurethane (PUA), curve 1, the styrene-2-methyl-5-

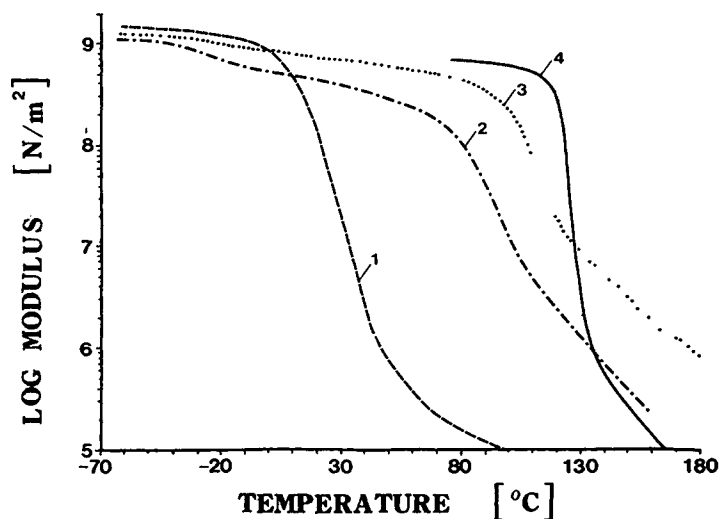


Figure 2 Variation of the shear storage modulus (G') with temperature for pure PUA (1), PS-VPQ (4), and blends of PUA/PS-VPQ (50/50) before extraction (2) and after extraction (3). Experimental points are shown only for one sample (3); they are omitted in the other plots for the sake of clarity.

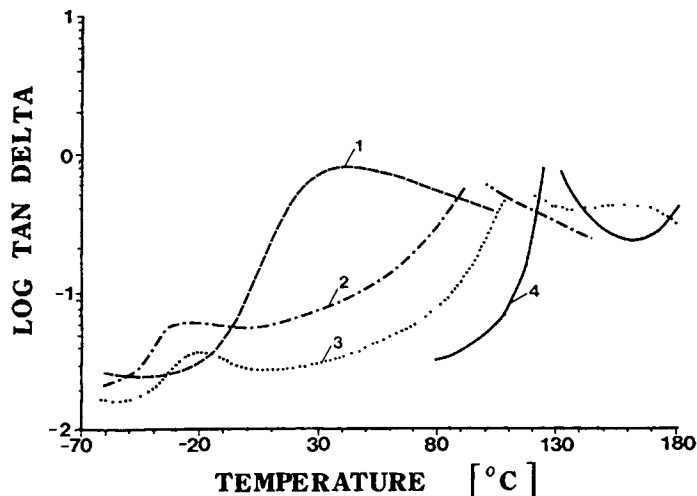


Figure 3 Variation of the loss tangent with temperature for PUA (1), PS-VPQ (4), and blends of PUA/PS-VPQ (50/50) before extraction (2) and after extraction (3).

vinylpyridine copolymer quaternized with methyl iodide (PS-VPQ), curve 4, and the 50% blends: curve 2 for the unextracted sample, and curve 3 for the sample after methanol extraction.

The plots for the PUA containing the salt HMPAQ and the PS-VPQ show behavior characteristic of a one-phase system. The samples thus do not seem to be clustered. As in other unclustered ionomers, the multiplets, act as thermolabile cross-links and increase the glass transition temperature of the polyurethane PUA by about 45°C (to = +35°C) in comparison with nonionic PU ($T_g \sim -10^\circ\text{C}$).¹² By contrast, in the ionized form of a polyurethane containing a tertiary amine, two glass transitions were observed.¹³ The process of ionization of the polyurethane by the reaction of the ethyl iodide with the tertiary amine leads to phase separation and thus to the exclusion of the hard segment form from the soft segment.¹³

This is not the case in the present system. The blends 50% PUA/PS-VPQ show clear evidence of two-phase behavior in that a two-step descent in the modulus is seen and two peaks in the loss tangent are present. The glass transition temperature of the polystyrene drops significantly in the blends, showing that here also compatibilization has been achieved between the styrene ionomers and the hard segment of the polyurethane.

The upper T_g is much lower for the unextracted sample than for the blend after extraction. The elemental analysis for iodide indicates that the microions remain in the system after extraction with methanol, because the sample before extraction contains 3.42% of iodide (4% calcd) while after ex-

traction the content is 3.28%. This suggests that some of the short chain material in the polyurethane (for example, chain extender with MDI), which plasticize the system, are extracted with methanol.

It is also seen that blending of PUA with PS-VPQ leads to phase separation, and thus to the separation of the hard segment form from the soft segment, as was found before in other ionomer blends involving PU.¹³ The T_g of the soft segment phase in the unextracted blend is almost the same as in the other blends.¹³ After extraction of the low molecular components, the lower T_g also shifts to a higher temperature ($T_g = -20^\circ\text{C}$).

CONCLUSIONS

Ion pair-ion pair interactions are sufficient to achieve miscibility in blends of a polyurethane which carries a pendant carboxylate groups neutralized by an ammonium ion with polystyrene with a pendant cation (i.e., a vinylpyridinium group) the counterion being the iodide ion. Methanol extraction removes only the low molecular components of polyurethane, but microions remain in the system.

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