

Dynamic Mechanical Properties of Polyurethane Grafted onto Styrene–Styrene Sulfonic Acid Copolymers

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SYNOPSIS

The object of this study was the exploration of the dynamic mechanical properties and thereby also of the phase behavior of partly sulfonated polystyrenes containing polyurethane grafts. The synthesis was accomplished by stepwise grafting onto the partly sulfonated polystyrene of *N*-methyldiethanolamine, via ionic interactions resulting from proton transfer followed by chain growth on the hydroxyl sites of the polyurethane structures. NMR spectra confirmed that the protons of the sulfonic acid groups had been transferred exclusively to the tertiary nitrogen of the *N*-methyldiethanolamine. If the grafts consist of only hard segments, then a single glass-transition temperature is observed that depends on the length of attached hard segment. If, on the other hand, soft segments are also included in the grafts, then these phase-separate and yield a new glass-transition temperature. For the phase-separated systems, the grafts yield a low T_g phase of higher purity than blending of sulfonated polystyrene with the preformed polyurethane of the same composition. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

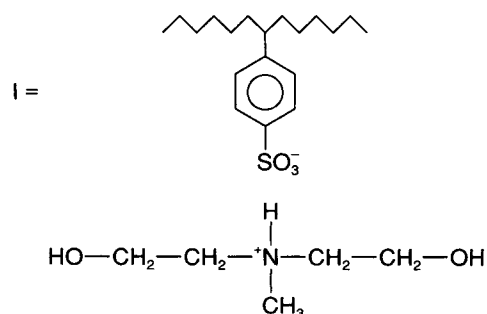
Miscibility of polyurethanes (PU) with lightly sulfonated polystyrene (PSSSA) has been the subject of several recent investigations.^{1–5} In the early studies, a proton-transfer mechanism from the PSSSA to the hard segment of the PU (which contained a tertiary amine as part of the chain extender) was postulated by analogy with other polymer mixtures employing similar miscibility enhancement techniques.^{6–8} The ionic interaction between the sulfonate anions on the styrene and the cations on the PU enhanced the miscibility of the system.

More recently, NMR spectra of blends of the same PU with PSSSA as well as model compounds in DMSO solutions, along with two-dimensional COSY spectra, showed that the labile protons of the SSA groups were transferred preferentially to the secondary structures (allophanates), followed by the

urethane nitrogens, and finally by the tertiary nitrogens of the *N*-methyldiethanolamine (MDEA).⁵

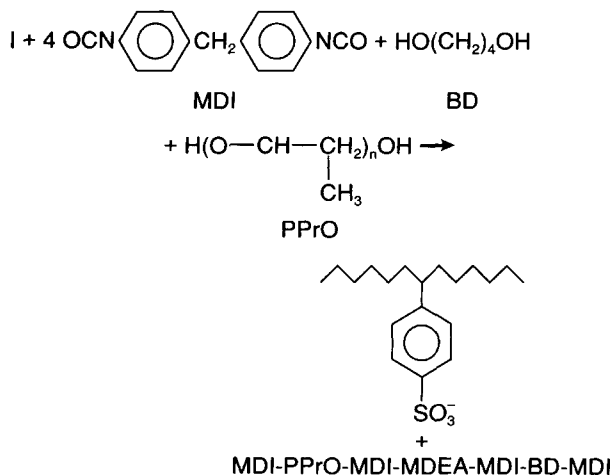
Since the miscibility enhancement mechanism in these blends is based on interactions between sulfonate anions and several different cations, it was thought advisable to study a system in which the cation was located only on the tertiary amine, rather than the secondary structures. To do this, a procedure was employed that involves stepwise grafting onto sulfonated polystyrene (PS) chains of MDEA, followed by chain growth on the hydroxyl sites of any polyurethane structures of interest. An example of the approach is shown in Scheme 1 below.

1st Step: PSSSA + MDEA \rightarrow I



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2nd Step:



Since this is a condensation polymerization, statistics will dictate the specific nature of the final product, and only the most probable structure is shown here. Further growth is obviously possible. This approach is of interest also because it allows the synthesis of a very wide range of grafts of PU on PS. The extension to networks is obvious, but is not the

major aim of the present study. In the limit of very high molecular weight of the PU, structures similar to those of the earlier blends will be approached except for the specific location of the cation. It should be added that interpenetrating networks based on ionic polyurethanes have also been prepared.^{9,10}

EXPERIMENTAL

Synthesis of PU Grafted onto PSSSA

The PS ($M_w = 39,000$) was made by radical polymerization and sulfonated by the procedure developed by Makowski et al.¹¹ 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 4.0, 4.8, 9.9, and 12.0 mol % of styrene sulfonic acid (SSA) were employed in this work.

The PU grafts on PSSSA were prepared by a condensation reaction shown in Scheme 1. 4,4'-methylene bis(phenylisocyanate) (MDI, Eastman Kodak Co.) was purified by filtration of the liquid at 70°C. Poly(propylene glycol) (PPrO, $M_w = 400$,

Table I Polyurethanes Grafted Onto Sulfonated Polystyrene

Designation	Molecular Ratio of Chemical Components	Glass Transition Temperature, T_g (°C)	
		Low	High
PS-4.8SSA ^a			125
PS-4.8SSA-MDEA	SSA/MDEA = 1/1		86
PS-4.8SSA-HS1 ^b	SSA/MDEA/MDI = 1/1/2		92
PS-4.8SSA-HS2	SSA/MDEA/MDI/BD = 1/1/3/1		105
PS-4.8SSA-HS2a	SSA/MDEA/MDI = 1/2/3		103
PS-4.8SSA-HS3	SSA/MDEA/MDI/BD = 1/1/4/2		113
PS-4.0SSA-PU1 ^c	SSA/MDEA/MDI/BP/PPrO ₄₀₀ = 1/1/4/1/1		98
PS-4.0SSA-PU2	SSA/MDEA/MDI/BD/PPrO ₇₂₅ = 1/1/4/1/1	~ -20 (very weak)	100
PS-4.0SSA-PU3	SSA/MDEA/MDI/BP/PPrO ₁₀₀₀ = 1/1/4/1/1	-38	100
PS-4.0SSA-PU4	SSA/MDEA/MDI/BD/PPrO ₂₀₀₀ = 1/1/4/1/1	-43	105
PS-12.0SSA-PU1	SSA/MDEA/MDI/BD/PPrO ₄₀₀ = 1/1/4/1/1		102
PS-12.0SSA-PU4	SSA/MDEA/MDI/BD/PPrO ₂₀₀₀ = 1/1/4/1/1	-32	120
PS-4.0SSA-PU5	SSA/MDEA/MDI/BD/PPrO ₄₂₅ = 1/1/3/1/1		90
PS-4.0SSA-PU6	SSA/MDEA/MDI/BD/PPrO ₇₂₅ = 1/1/3/1/1	~ -30 (very weak)	92
PS-4.0SSA-PU7	SSA/MDEA/MDI/BD/PPrO ₁₀₀₀ = 1/1/3/1/1	-45	95
PS-9.9SSA-PU7	SSA/MDEA/MDI/BD/PPrO ₁₀₀₀ = 1/1/3/1/1	-38	110
BLEND PS-9.9SSA/PU _n	SSA/MDEA/MDI/PPrO ₁₀₀₀ = 1/2/3/1	-8	115

^a PS-4.8SSA refers to polystyrene containing 4.8 mol % styrenesulfonic acid.

^b HS refers to structures containing only hard segments.

^c PU refers to structures containing both hard and soft segments.

425, 725, 1000, 2000, Aldrich Chemical Co. Inc.) was dried under vacuum at 60°C for 5 h. *N*-Methyldiethanolamine (MDEA), and 1,4-butanediol (BD, Aldrich Chemical Co. Inc.), stannous octoate (Research Organic/Inorganic Chemical Corp.) and anhydrous *N,N*-dimethylformamide (DMF) were used as received.

To obtain hard segment (HS) grafts onto PSSSA, the PSSSA was dissolved in DMF at a concentration of about 40% by weight. Then the MDEA was added in an amount needed to maintain an equimolar ratio with that of the SSA groups. The reaction was carried out at room temperature for 2 h. Then the MDI and BD in DMF (40% by weight) along with the stannous octoate (0.1% by weight) were added in an appropriate quantity to maintain a NCO:OH molar ratio as shown in Table I. The reaction was carried out at 70°C for 2 h. The solution was subsequently dried by evaporation of the solvent at

progressively higher temperatures up to 80°C and kept under vacuum at that temperature for 1 week.

To obtain a PU with both hard and soft segments grafted onto PSSSA, in the first step of the reaction the prepolymer was made as follows: MDI was dissolved in DMF at a concentration of 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 70°C for 2 h maintaining a NCO:OH molar ratio of 3 : 1 or 4 : 1. Simultaneously, the PSSSA was dissolved in DMF at a concentration of about 40% by weight, and the MDEA was added at an equimolar ratio to that of the SSA groups. The reaction was carried out at room temperature for 2 h to obtain the ammonium salt. In the last step of the reaction, the solution of the ammonium salt (PSSSA-MDEA) and the BD were added to the PU prepolymer solution maintaining the NCO : OH

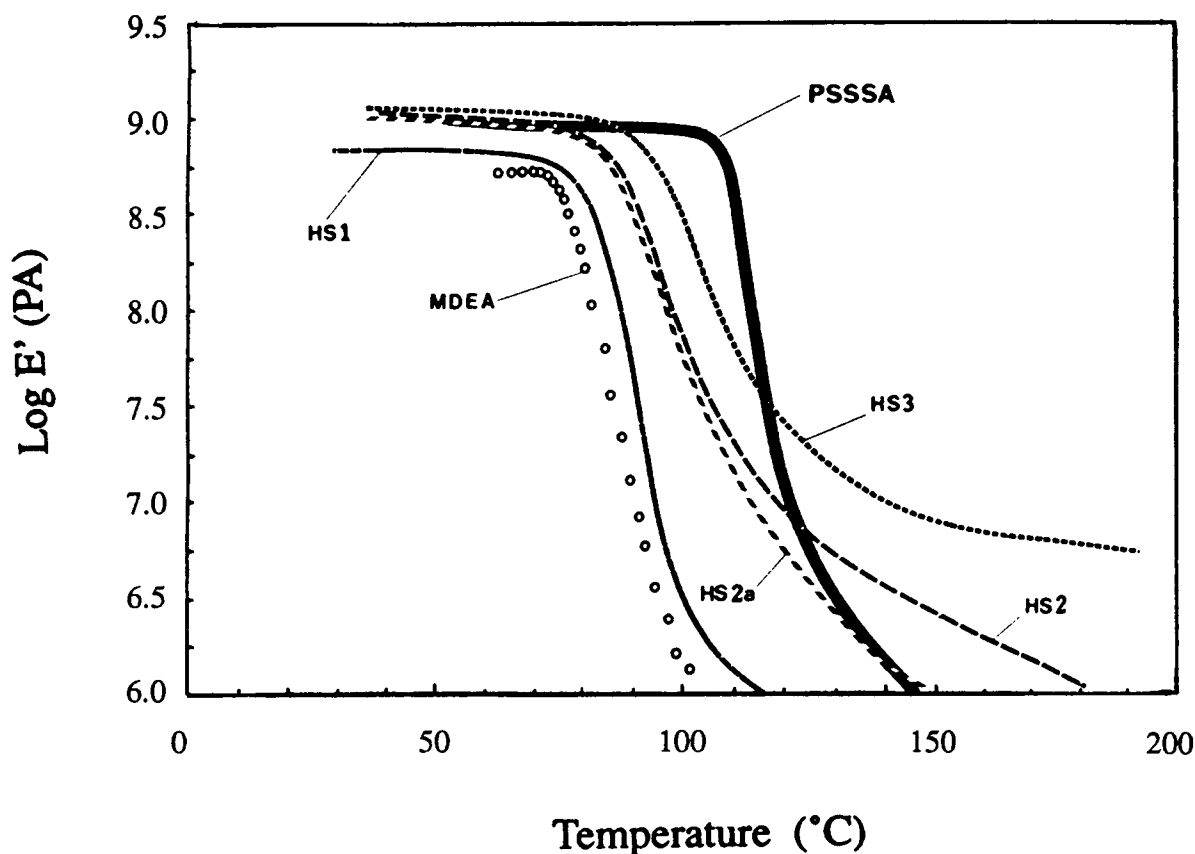


Figure 1 Variation of the shear storage modulus E' with temperature for PSSSA containing grafted polyurethane hard segments (HS) of different lengths. Designations refer to Table I (with PSSSA omitted). Experimental points are shown only for the MDEA sample; they are omitted in the other plots for the sake of clarity.

molar ratio shown in Table I. The reaction was carried out at 70°C for 2 h. The solution was dried by evaporation of the solvent at progressively higher temperatures up to 80°C and kept under vacuum at that temperature for 1 week.

Dynamic Mechanical Studies

The samples used for DMTA measurements were prepared by compression molding of 1.0 g of the styrene/PU grafts. The polymers were heated in the mold to a temperature above 110°C for 0.5 h at 45 MPa. The sample was removed from the mold after it had cooled to room temperature. Typical dimensions of the specimens were $2.5 \times 10 \times 50$ mm. Dynamic mechanical studies were performed between -100°C and +200°C at 1 Hz using the Polymer Laboratories dynamic mechanical thermal analyser (DMTA) at a heating rate of 1°C/min.

NMR Studies

Proton NMR spectra were taken in DMSO- d_6 (100% deuterated, MSD ISOTOPES) solutions on a Varian

XL-200 spectrometer. The concentration of the solution was approximately 5% (w/w). The assignments and methods used in the present study follow those of the previous publication.⁵ The NMR spectra confirmed that the protons of the SSA groups had been transferred to the tertiary nitrogen of the MDEA, as was expected.

RESULTS AND DISCUSSION

The designation of the investigated polyurethane grafts and their chemical composition and glass-transition temperatures are shown in Table I. Figure 1 shows plots of E' vs. temperature for the HS grafts (see Table I) with different lengths of attached hard segments. The plots show clear evidence of one-phase behavior as detected by mechanical techniques in that a one-step descent in the modulus is seen. It should be recalled that mechanical tests are sensitive to minimum dimensions of the order of 50–100 Å. The glass-transition temperatures (T_g) of the grafts are estimated from the loss tangent peak positions. Looking at the T_g column in Table I for the

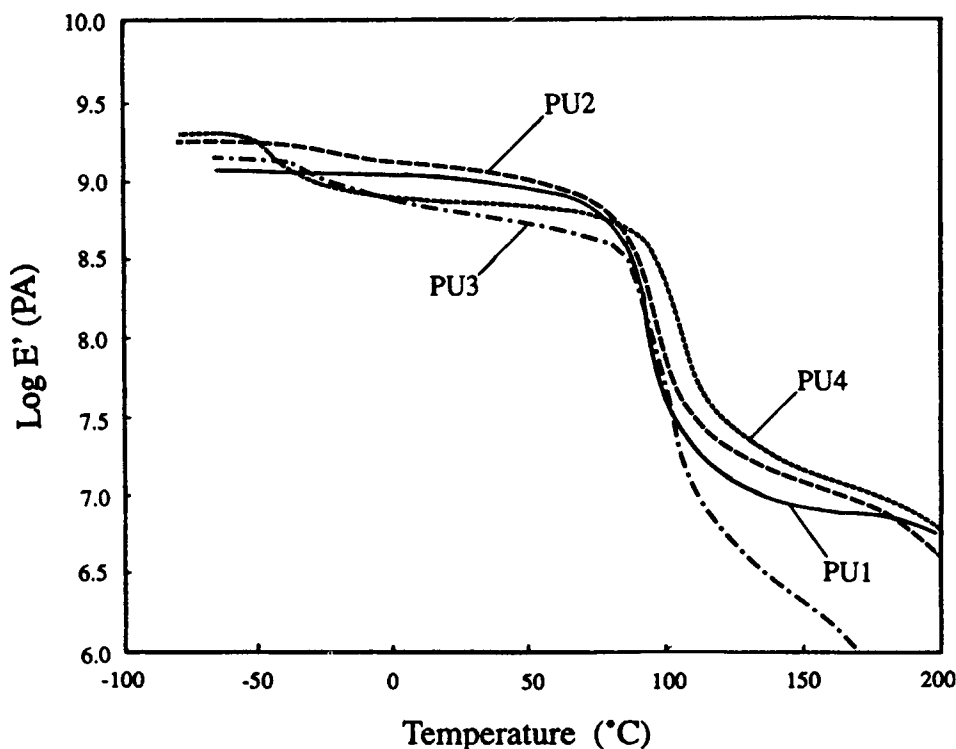


Figure 2 Variations of the shear storage modulus E' with temperature for the PSSSA with grafted PU segments. Sample designations follow Table I (with PSSSA omitted).

MDEA and HS grafts, it is seen very clearly that glass-transition temperatures are strongly dependent on the length of attached hard segment. The PSSSA with only MDEA grafted onto it has the lowest T_g , which increases with increasing length of the hard segment. For samples PSSSA-HS2 and PSSSA-HS2a in which the hard segments have the same lengths but a slightly different chemical structure, the glass-transition temperatures are almost the same. These phenomena are not unexpected.

Figures 2 and 3 show the plots of E' and $\tan \delta$ for PU grafts with different lengths of the PPrO soft segment. For the grafts with the shortest soft segment ($M_w = 400$) only one glass-transition temperature is observed.

From Table I, it is seen that the (high) glass-transition temperature for the one-phase system increases with increasing SSA content of the PSSSA (compare PS-4.0SSA-PU1 and PS-12.0SSA-PU1) as well as with increasing length of the hard segment (compare PS-4.0SSA-PU1 and PS-4.0SSA-PU5).

However, if a somewhat longer soft segment is used ($M_w = 725$), one begins to see the appearance of a second glass-transition (see PS-4.0SSA-PU2 and PS-4.0SSA-PU6). When the soft segment length reaches $M_w = 1000$, the second T_g is seen very clearly in mechanical tests (Figs. 2, 3).

In regular PU, phase separation occurs when the soft segments exceed a certain length ($M_w = 2000$).¹² In case of PU grafts, the soft segments of the PU already exhibit phase separation for soft-segment lengths > 725 . This shows that phase separation in the PU grafts is achieved more easily, presumably because of the single point of attachment. The positions of the low temperature peaks are dependent on the length of the soft segment. With increasing soft-segment length the low temperature peaks move to a lower temperature. The same phenomena were observed for regular PUs¹³ and their blends.¹

The higher the sulfonate ion concentration in the PSSSA, the higher the T_g (compare PS-4.0SSA-PU4

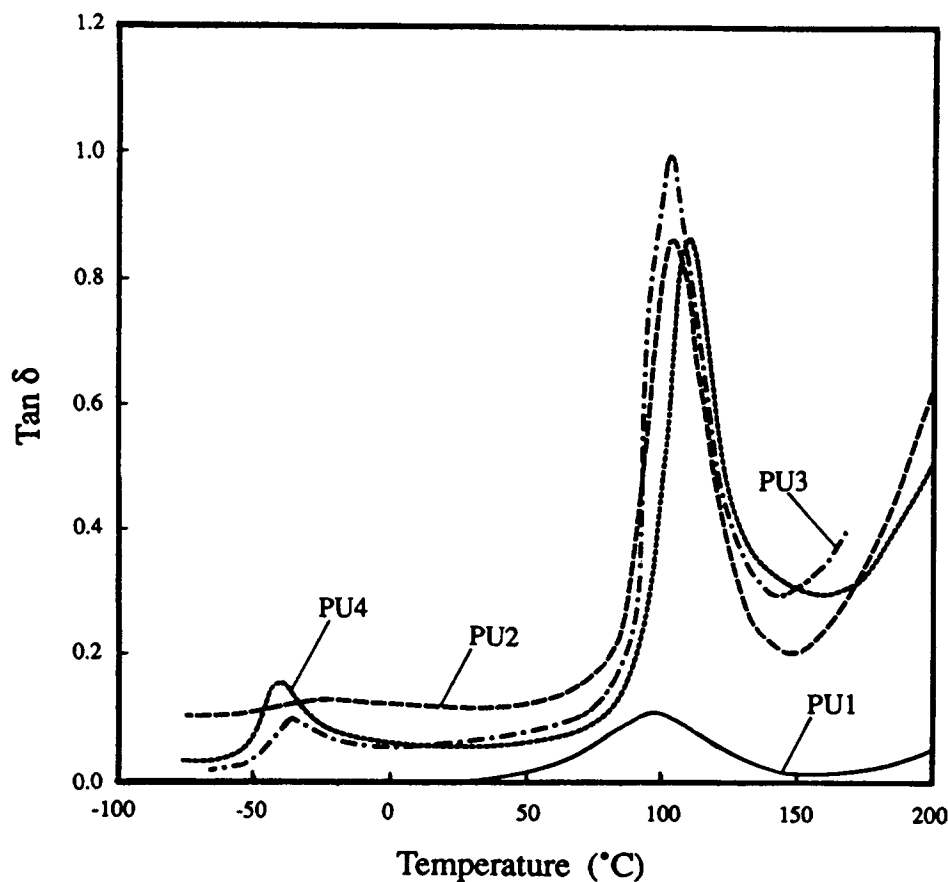


Figure 3 Loss tangent ($\tan \delta$) plots for the same samples as Figure 2.

with PS-12.0SSA-PU4 in Table I). This further confirms the strong interactions between the PSSSA and hard segments of the PU. Surprisingly, however, the low T_g of these systems is higher for higher SSA contents even if the length of the soft segment is the same (compare PS-4.0SSA-PU4 with PS-12.0SSA-PU4). It suggests that in these syntheses either some of the hard segments that interact with SSA are incorporated into the soft phase, or that domain sizes are smaller. Other possible reasons might also be operative.

We also investigated the PU grafts prepared to yield a high molecular weight material with multiple points of attachment per PU chain, via the MDEA units. Ratios of 1/1/3/1/1 of SSA/MDEA/MDI/BD/PPrO yield, in principle, PUs of very high molecular weight that are attached at multiple sites to the PSSSA chains. As before, soft-segment lengths as low as 725 yield systems that are heterogenous. An increase in the ion concentration of the PSSSA increases both the high and the low T_g (compare PS-4.0SSA-PU7 with PS-9.9SSA-PU7 in Table I).

Finally we compared the T_g of the PS-9.9SSA-

PU7 graft with that of the blend of PU_n and PSSSA containing 9.9 mol % sulfonate ions (see the last position in Table I and Fig. 4). In the PU_n all the BD is replaced by MDEA. PU_n was obtained by a two step condensation reaction.¹ The blending at a stoichiometric ratio of SSA to tertiary amine was performed by mixing solutions of the high molecular weight materials.¹

It appears that the upper T_g is very similar for both materials, while the low T_g is much lower for the graft than for the blend, suggesting that the phase separated (low T_g) regions are more pure. This is not unreasonable.

The PU_n used for blending consists of a mixture of soft and hard segments. After blending with the PSSSA, ion interactions occur between the NH groups of secondary structures, as well as the urethanes and tertiary nitrogens of the MDEA.⁵ These strong coulombic interactions result in a very intimate mixing of the PSSSA copolymer with the hard segments, which in turn leads to the exclusion of the soft segments into a separate phase (Fig. 4). This exclusion, however, is not complete because of

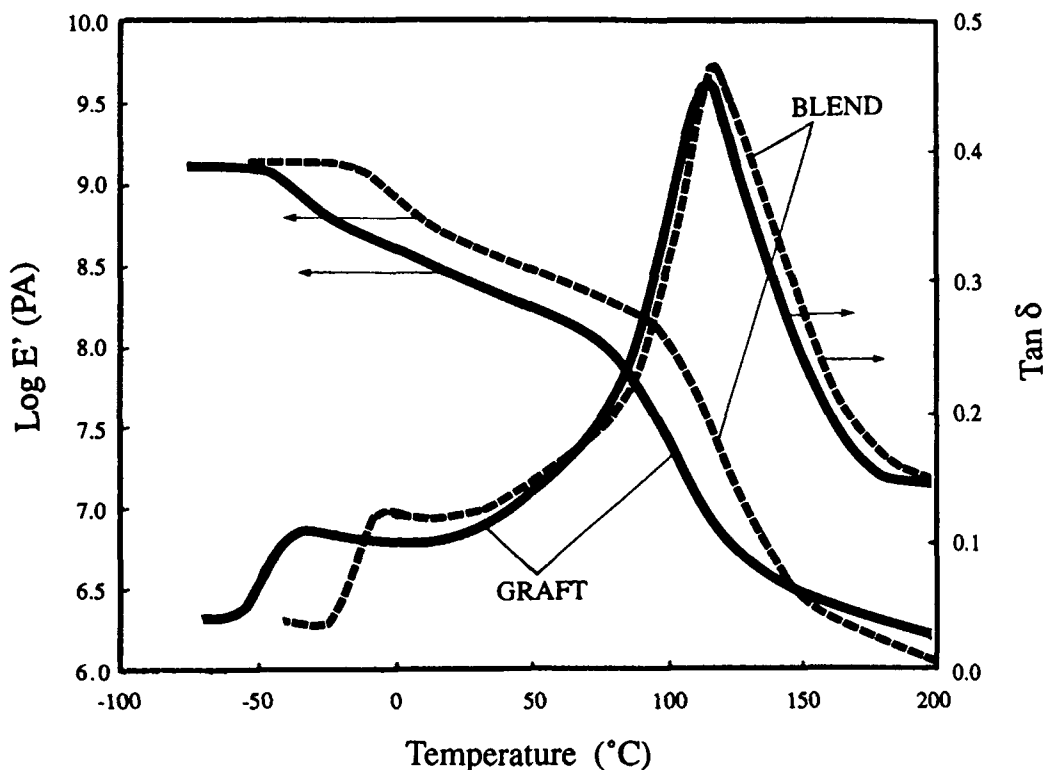


Figure 4 Variations of the shear storage modulus E' and the loss tangent ($\tan \delta$) with temperature for PS-9.9SSA-PU7 graft, and blend of preformed polymers of a similar composition.

the strong coulombic interactions with multiple sites and the statistical nature of the PU. In the grafts, on the other hand, the interactions occur only with the tertiary amine of the MDEA, and since the PU is formed after these interactions have occurred, a higher degree of phase purity can be expected. Obviously, this will yield a lower T_g of the low T_g phase.

CONCLUSIONS

Polyurethane grafts on PSSSA were obtained by the stepwise grafting onto PSSSA chains of MDEA followed by chain growth on the hydroxyl sites of a wide range of polyurethane structures. NMR spectra confirmed that the protons of the SSA groups had been transferred exclusively to the tertiary nitrogens of the MDEA. The single glass-transition temperature of the grafts consisting only of hard segments is strongly dependent on the length of attached hard segment and increases with increasing length. If long soft segments are added to the grafts, then these phase-separate and yield a new glass-transition temperature. The high and low glass-transition temperatures depend on the lengths of the soft segments and the sulfonate ion concentrations in the styrene copolymers. The alloys of PU and PSSSA obtained by the grafting method yield materials in which the phase purity in phase-separated systems seems to be better than in the regular blends of similar composition.

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