Macromolecules **1984,** *17,* 2222–2227

chain lengths, by the initiation of polymerization of epoxide from the propagating end of living poly(β-lactone).[9]

The attempted synthesis of polyether–polyester block copolymer by the polymerization of β-lactone from the living propagating end of poly(epoxide) initiated by (5,10,15,20-tetraphenylporphinato)aluminum chloride was not successful. This fact indicates that (porphinato)aluminum alkoxide is not a good initiator for the polymerization of β-lactone[10] and corresponds to the fact that the structure of the living propagating end in the polymerization of β-lactone catalyzed by (5,10,15,20-tetraphenylporphinato)aluminum chloride is a (porphinato)aluminum carboxylate but not an alkoxide.[5]

Registry No. (TPP)H_2, 917-23-7; Et_2AlCl, 96-10-6; (TPP)AlCl, 71102-37-9; β-propiolactone (homopolymer), 25037-58-5; β-propiolactone (SRU), 24938-43-0; β-butyrolactone (homopolymer), 36486-76-7; β-butyrolactone (SRU), 26744-04-7; (β-butyrolactone)·(β-propiolactone) (copolymer), 92078-52-9; (β-butyrolactone)·(ethylene oxide) (copolymer), 92078-53-0; (β-butyrolactone)·(propylene oxide) (copolymer), 52237-89-5.

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(9) (Tetraphenylporphinato)aluminum carboxylate ((TPP)AlO_2CR), prepared by the equimolar reaction between (tetraphenylporphinato)aluminum ethyl and carboxylic acid, was found to initiate the living polymerization of epoxide and β-lactone to give the corresponding polymer with narrow molecular weight distribution carrying a RCO_2 end group.[5,11]
(10) The ring-opening reaction of β-lactone by (tetraphenylporphinato)aluminum alkoxide, prepared by the reaction between (TPP)AlCl and epoxide,[3] was found to proceed slowly, while ϵ-lactone reacts much faster to form an aluminum alkoxide. The polymerization of ϵ-caprolactone initiated by the living prepolymer of propylene oxide, a (porphinato)aluminum alkoxide, proceeds to give the corresponding block copolymer (unpublished data). The polymerization of ϵ-caprolactone initiated by bimetallic (μ-oxo)alkoxide as the catalyst proceeding with alkoxide as the propagating end was reported: Hamitou, A.; Jerome, R.; Hubert, A. J.; Teyssie, Ph. *Macromolecules* **1973,** *6,* 651.
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Polyurethane Interpenetrating Polymer Networks (IPN's) Synthesized under High Pressure. 3. Morphology and T_g Behavior of Polyurethane–Polystyrene Semi-IPN's and Linear Blends

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ABSTRACT: Semiinterpenetrating polymer networks (semi-IPN's) and linear blends of polyurethane and polystyrene were prepared under high pressure to compare with full IPN's and to evaluate the effect of interpenetration in IPN synthesis. The morphology, dynamic mechanical properties, and density behavior were analyzed to determine the effect of synthesis pressure and the effect of interlocking on the degree of intermixing of the component polymers. The degree of intermixing increased with increasing synthesis pressure, and the relative degree of intermixing among IPN, semi-IPN, and linear blend was in the following order: IPN > semi-I IPN (PU cross-linked/PS linear) > semi-II IPN (PU linear/PS cross-linked) = linear blend. The morphology also showed a similar trend in the electron microscopy study. The relative degree of intermixing depended on the mobility of the polymer component having linear structure. Thus when PU component was made linear, the resulting semi-II IPN showed a higher degree of phase separation compared to semi-I IPN in which the relatively immobile PS component was linear.

Introduction

In previous papers,[1,2] the phase separation mechanism of the interpenetrating polymer network (IPN) synthesized under high pressure was illustrated with relation to the Gibb's free energy of mixing,[3,4] ΔG_m, conversion (molecular weight), mobility of polymer segment (polymer diffusion rate), and cross-link density[5] (gelation point and molecular weight between cross-links, $\bar{M}_c$). Particularly important factors in determining the morphology were the onset point of phase separation, the rate of phase separation, and the time of physical interlocking. The onset point of phase separation was the time when the molecular weight of the component polymers exceeded a certain critical value so that the ΔG_m of the mixture became positive as the polymerization proceeded. The rate of phase separation was related to the mobility of the polymer chain and thus was indirectly related to the synthesis temperature and pressure. The time of physical interlocking was the time when both component polymers reached the gel point and thus the phase domain size could not increase much further beyond this point.

The existence of the physical interlocking (interlocked macrocycles of the two component networks) had been the major factor in determining the characteristic properties

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Table I
Sample Preparation

desig	code	TMP/1,4-BD equiv ratio in PU formulation	DVB (wt %) in PS monomer mixture
semi-I IPN	UC50SL50	1	0
semi-II IPN	UL50SC50	0[a]	2.5
linear blend	UL50SL50	0[a]	0

[a] 1,4-Butanediol alone was used.

of IPN materials such as the density increase,[6,7] synergistic effect in mechanical properties,[6,8-10] finer dispersed domain structure,[6,11] and increased thermal stability.[12,13]

If we prepare semi-IPN's (one of the component polymers has a linear structure) or a linear blend, we will be removing the effect of physical interlocking in determining the morphology of IPN's synthesized under high pressure. The phase separation process will continue to proceed until the polymerization is completed. If the phase separation has not reached the equilibrium state because of the low rate of phase separation at low temperature and high pressure, we can increase the rate by thermal treatment afterward to have the mixture reach the equilibrium state.

In this study, semi-IPN's and a linear blend of PU and PS were prepared to study the effect of synthesis pressure, synthesis temperature, and the cross-linked state. The morphology, dynamic mechanical properties, and density behavior were measured to observe the degree of enhancement of polymer miscibility with increasing synthesis pressure in comparison with the cases of IPN's.[2]

Experimental Section

Synthesis. The method of PU prepolymer preparation and the materials used were the same as described in the previous paper.[2] The PU component was formed by reacting isocyanate-terminated poly(tetramethylene ether) glycol (molecular weight 986)–MDI prepolymer with chain extender. 1,4-Butanediol (1,4-BD) was used as the chain extender for the linear PU component and a mixture of 1,4-BD and trimethylolpropane (TMP) with 1:1 equivalent ratio was used for the cross-linked network.

The PS cross-linked network was formed by copolymerizing styrene–divinylbenzene monomer mixture using benzoyl peroxide as the initiator. Divinylbenzene was omitted from the mixture when the linear PS component was formed. The cross-link density was set at $\bar{M}_c = 3200$.

Two types of semi-IPN and linear blend were prepared (Table I). The semi-I IPN had PU component cross-linked and PS component linear (50/50 ratio; coded as UC50SL50). The semi-II IPN had PU component linear and PS component cross-linked (coded as UL50SC50). The linear blend was formed by excluding the cross-linking agents in both component polymer formulations (coded as UL50SL50).

The first letter in the sample code denotes polymer component (U for PU and S for PS), the second letters C and L denote polymer network (C = crosslinked, L = linear), and the third numeral denotes the weight percentage.

The method of preparing the semi-IPN and linear blend was the same as IPN preparation described before.[2] The PU component was reacted at room temperature for 24 h for partial polymerization before the high-pressure reaction. This could be considered to be a SIN (simultaneous interpenetrating network) with a different polymerization rate. To see the effect of the physical interlocking characteristics of the IPN, an annealing experiment was done at 100 °C for 13 h and also at 120 °C for 13 h.

Measurements. An electron microscope, dynamic mechanical analyzer, and density gradient column were used to observe the morphology, glass transition behavior, and densities of the samples prepared. The testing methods were described in the previous paper.[2]

Results and Discussion

Glass Transition Behavior. The dynamic mechanical behavior of the PU–PS semi-IPN's and linear blends synthesized under varying pressures is shown in Figures 1–3.

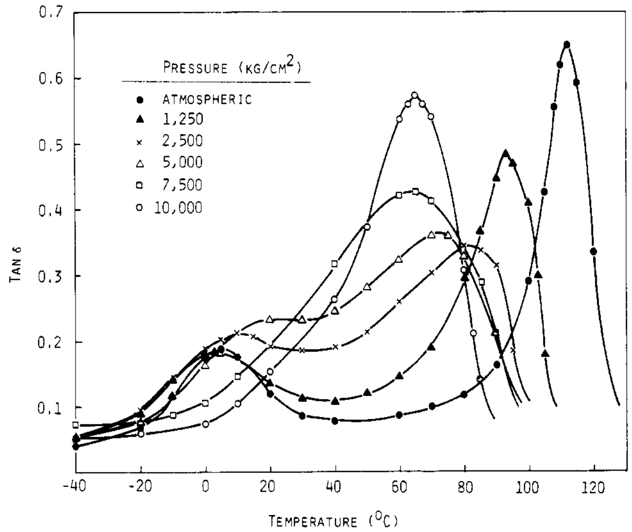

Figure 1. Dissipation factor (tan δ) vs. temperature of UC50SL50 semi-I IPN's synthesized at varying pressures.

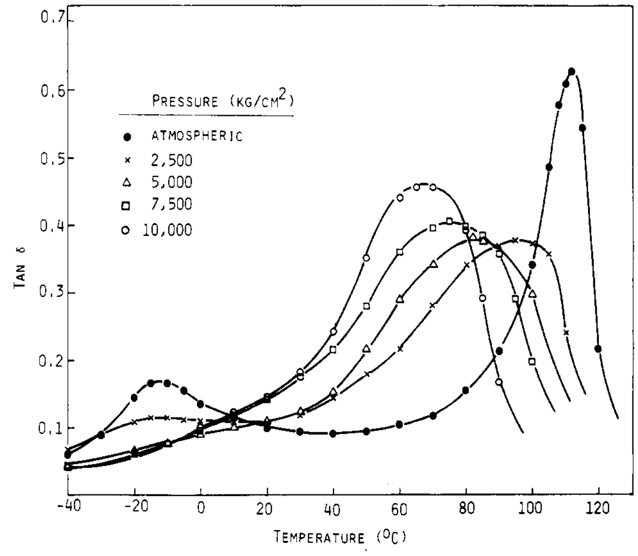

Figure 2. Dissipation factor (tan δ) vs. temperature of UL50SC50 semi-II IPN's synthesized at varying pressures.

Figure 1 shows the tan δ change of UC50SL50 semi-I IPN. There is a gradual shift of the two transition temperatures of the PU and PS component polymers. They finally merge to form a broad transition when the synthesis pressure reaches 7500 kg/cm², and the merged transition becomes sharper when the synthesis pressure is 10 000 kg/cm².

The tan δ curve for the UL50SC50 semi-II IPN (Figure 2) shows a similar trend as the UC50SL50 semi-I IPN but the PU damping magnitude is much lower in UL50SC50 semi-II IPN's. The degree of phase separation seems to be higher as noted by the broad transition even at the high synthesis pressure of 10 000 kg/cm². The reason for the

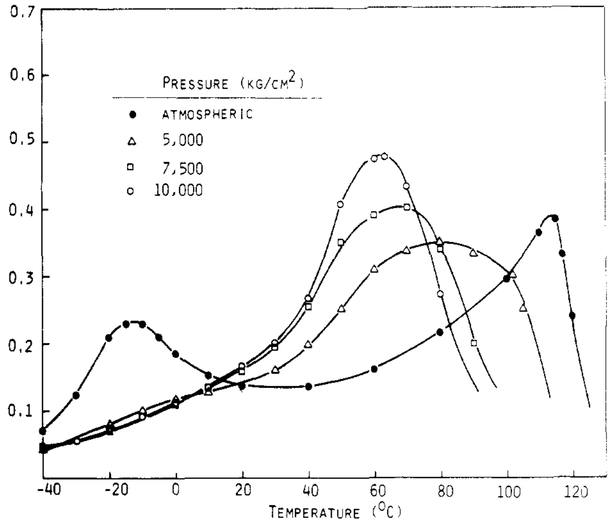

Figure 3. Dissipation factor (tan δ) vs. temperature of UL50SL50 linear blends synthesized at varying pressures.

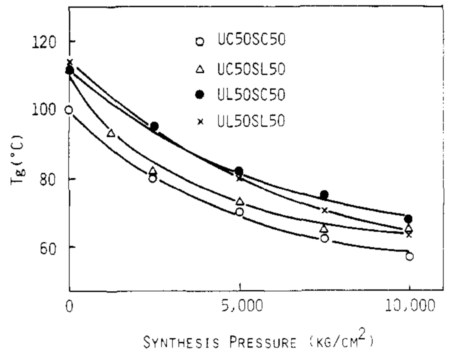

Figure 4. Glass transition temperature (T_g) of the PS-dominant phase in IPN's,[2] semi-IPN's, and linear blends.

low damping near the PU transition is related to the morphology of the semi-IPN. It is believed that in UC50SL50 semi-I IPN's, the PU phase forms a continuous matrix because of the cross-linked nature of the PU component, while in UL50SC50 semi-II IPN's, the linear PU chain phase-separates as the polymerization proceeds and forms a dispersed phase. The tan δ curve for the linear blends (UL50SL50) also shows low damping near the PU transition (Figure 3). The differences in the degree of phase separation lie in the mobility of the polymer component having the linear structure (no physical interlocking and free to phase-separate). Thus when the PU component is made linear, the resulting semi-II IPN and linear blend have a higher degree of phase separation, while the semi-I IPN with linear PS component shows increased intermixing due to the low mobility of the PS chain (or low rate of phase separation under high pressure). The synthesis temperature of 80 °C under high pressure is below the T_g of the PS component, and thus the PS chain is relatively immobile during the synthesis.

The shifted T_g's of the predominantly PS phase show an exponential decrease with increasing synthesis pressure (Figure 4, Table II). The degree of shift is highest in the UC50SC50 full IPN,[2] UC50SL50 semi-I IPN is second, and UL50SC50 semi-II IPN and UL50SL50 linear blend show a lower degree of shift. The PU mass fraction in the PS-dominant phase calculated by assuming the Fox equation is shown in Table II and Figure 5. The PU mass fraction increases as the synthesis pressure is increased. The UL50SC50 semi-II IPN and UL50SL50 linear blend show the lowest degree of mixing, again due to the mobility of the linear PU chain.

Table II
T_g and Composition in the PS-Dominant Phase[a]

code	synth press, kg/cm²	T_g, K	mass fraction PU	mass fraction PS
UC50SL50	atmos	385	0.01	0.99
	1250	366	0.15	0.85
	2500	355	0.23	0.77
	5000	346	0.30	0.70
	7500	338	0.37	0.63
	10000	338	0.37	0.63
UL50SC50	atmos	385	0.03	0.97
	2500	368	0.11	0.89
	5000	355	0.19	0.81
	7500	348	0.23	0.77
	10000	341	0.27	0.73
UL50SL50	atmos	387	0	1
	5000	353	0.19	0.81
	7500	343	0.25	0.75
	10000	336	0.29	0.71

[a] T_g of the linear homopolymer synthesized at atmospheric pressure: UL100, 255 K; SL100, 387 K; UC100, 278 K; SC100, 390 K.

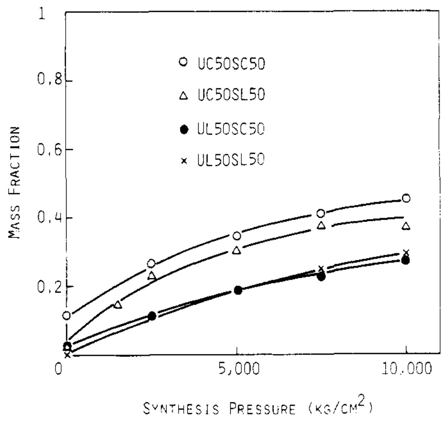

Figure 5. Calculated mass fraction of PU in the PS-dominant phase in IPN's,[2] semi-IPN's, and linear blends.

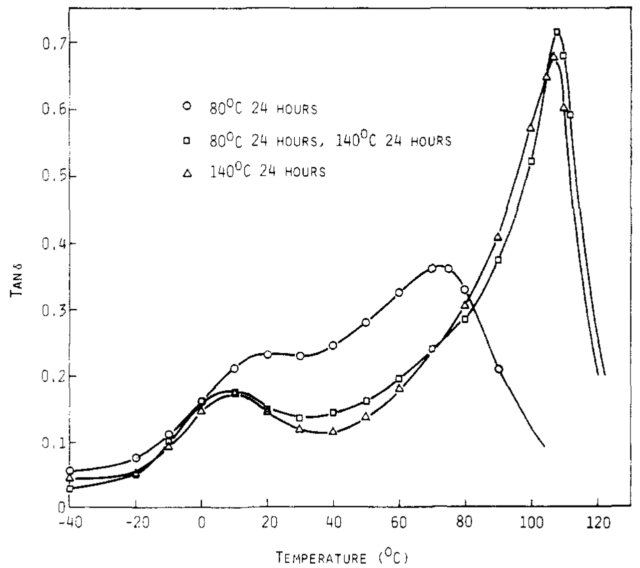

Figure 6. Effect of synthesis temperature on the tan δ curve of UC50SL50 semi-I IPN synthesized at 5000 kg/cm².

The effect of the synthesis temperature of the UC50SL50 semi-I IPN is shown in Figure 6. As reported for the IPN cases,[2] the rate of phase separation is increased at high temperature due to the increased mobility of the linear PS chain, and the resulting IPN shows an increased degree of phase separation as evidenced by the two sepa-

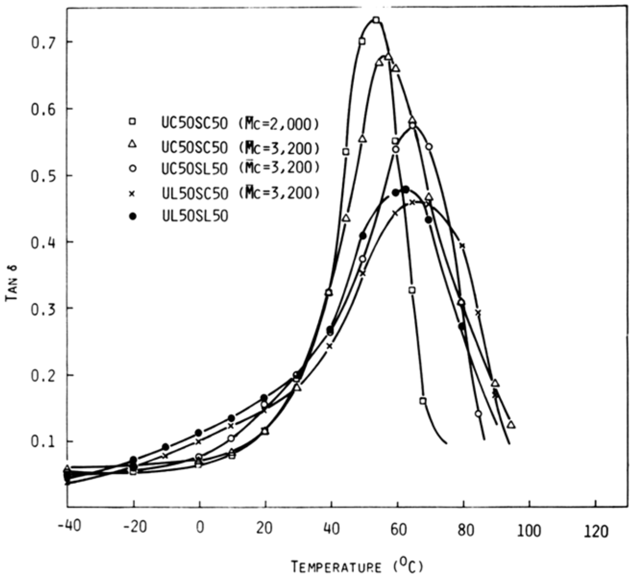

Figure 7. Comparison of the degree of intermixing of PU and PS in IPN's,[2] semi-IPN's, and linear blend synthesized at 10 000 kg/cm^2.

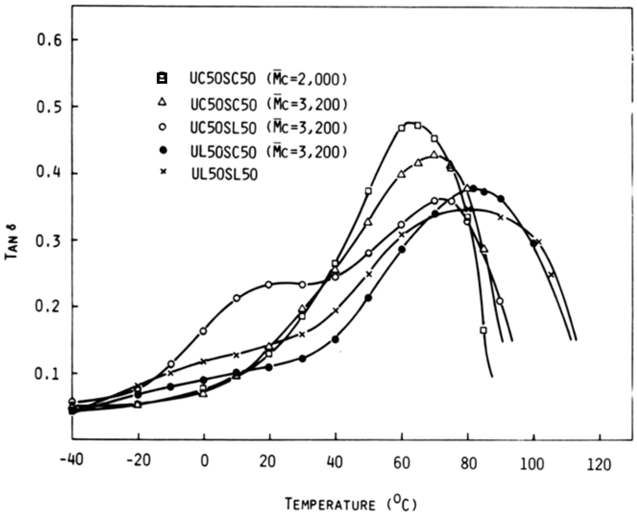

Figure 8. Comparison of the degree of intermixing of PU and PS in IPN's,[2] semi-IPN's, and linear blend synthesized at 5000 kg/cm^2.

rated transitions. The differences in synthesis conditions of two-step heating at 80 °C for 24 h followed by 140 °C for 24 h and one-step heating at 140 °C for 24 h are not detectable due to the fact that the semi-IPN mixture seems to reach equilibrium at 140 °C.

The comparison of the degree of intermixing of the IPN, semi-IPN, and the linear blend synthesized at 10 000 kg/cm^2 is shown by the shape of the tan δ curve in Figure 7. The IPN with higher cross-link density has the highest degree of intermixing with a high probability of physical interlocking, which prohibits further phase separation from occurring. Those synthesized at 5000 kg/cm^2 (Figure 8) also show a similar trend as in Figure 7.

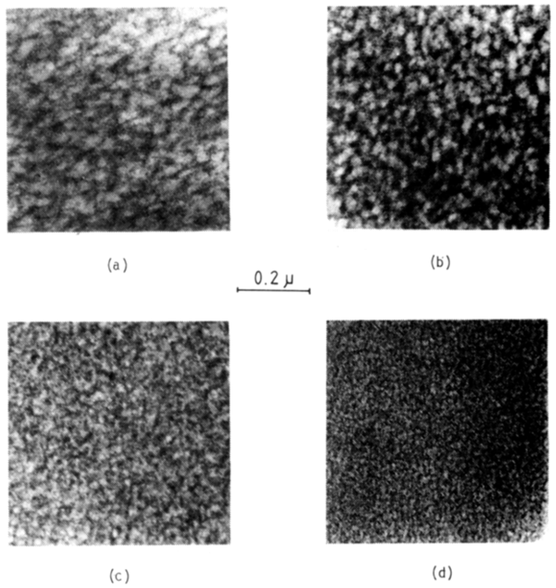

Figure 9. Electron micrographs of UC50SL50 semi-I IPN synthesized at (a) atmospheric pressure, (b) 1250 kg/cm^2, (c) 5000 kg/cm^2, and (d) 10 000 kg/cm^2.

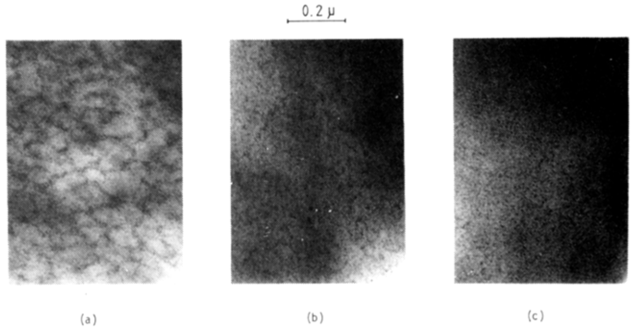

Figure 10. Electron micrographs of UL50SC50 semi-II IPN synthesized at (a) atmospheric pressure, (b) 5000 kg/cm^2, and (c) 10 000 kg/cm^2.

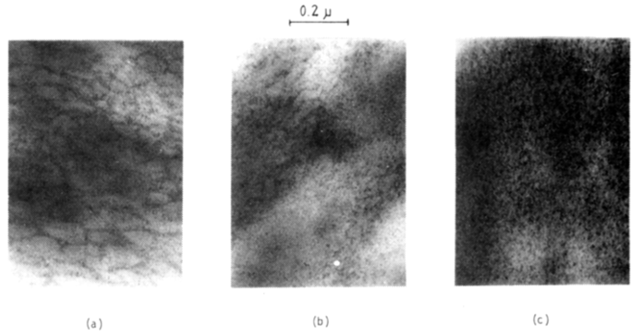

Figure 11. Electron micrographs of UL50SL50 linear blend synthesized at (a) atmospheric pressure, (b) 5000 kg/cm^2, and (c) 10 000 kg/cm^2.

Morphology. The morphology via transmission electron microscopy also shows the synthesis pressure effects on the polymer miscibility and phase structure (Figures 9–11). In the case of UC50SL50 semi-I IPN (Figure 9), the domain sizes of the PS-dominant phase decrease from about 500 to 70 Å with increasing synthesis pressure. Close examination of the morphology of semi-I IPN synthesized at atmospheric pressure (Figure 9a) reveals that it has undergone secondary phase separation in the PU-rich matrix phase. A similar morphology was also observed in the poly(ethyl acrylate)–polystyrene sequential IPN system.[3] The secondary phase separation in the PU-rich matrix phase is more evident in the UL50SC50 semi-II IPN and UL50SL50 linear blend (Figures 10a and 11a). The PU phase forms the matrix when synthesized at low pressure, but when the synthesis pressure is increased it tends to become a dispersed state. The morphology of semi-I IPN synthesized at 10 000 kg/cm^2 shows a somewhat cocontinuous nature in both phases (Figure 9c), but in semi-II IPN and linear blend in which the PU component has linear structure (Figures 10c and 11c), the linear

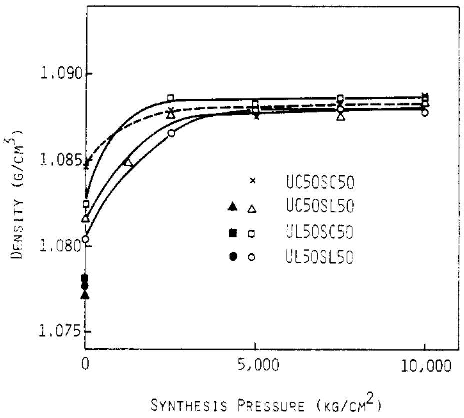

Figure 12. Density vs. synthesis pressure of IPN,[2] semi-IPN's, and linear blend ((●), (■), (▲): calculated values based on volume additivity rule).

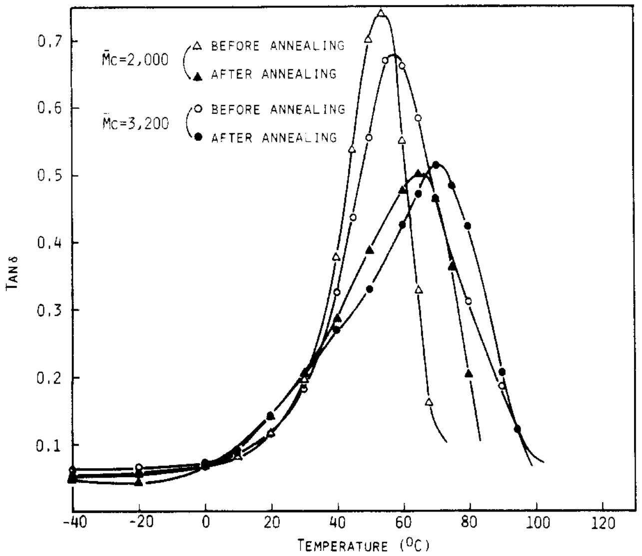

Figure 13. Dissipation factor (tan δ) vs. temperature of UC50SC50 IPN's synthesized at 10 000 kg/cm^2 before and after annealing at 100 °C for 13 h.

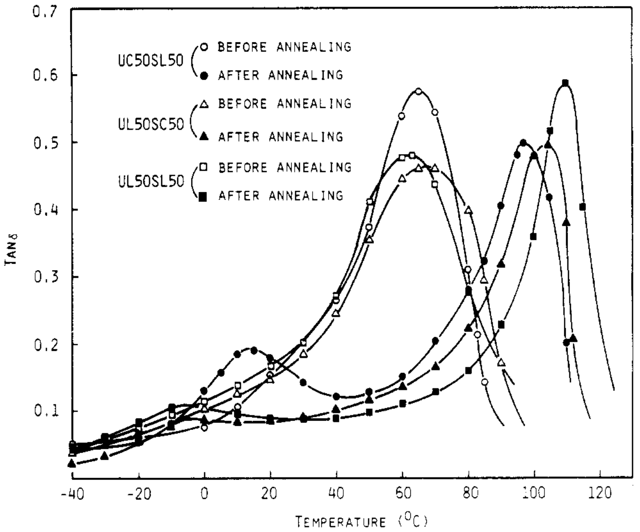

Figure 14. Dissipation factor (tan δ) vs. temperature of semi-IPN's and linear blend synthesized at 10 000 kg/cm^2 before and after annealing at 100 °C for 13 h.

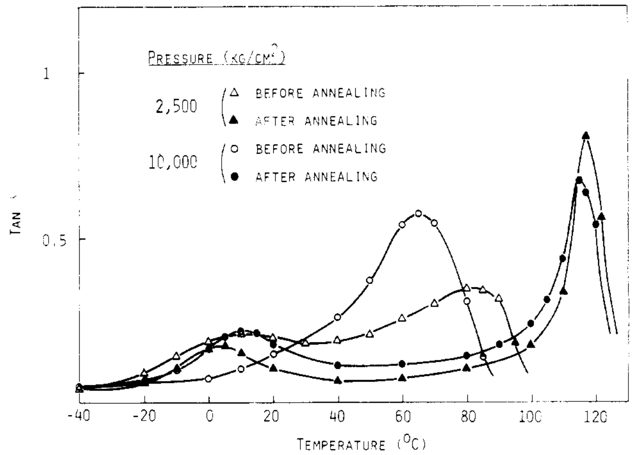

Figure 15. Dissipation factor (tan δ) vs. temperature of UC50SL50 semi-I IPN synthesized at 2500 and 10 000 kg/cm^2 before and after annealing at 120 °C for 13 h.

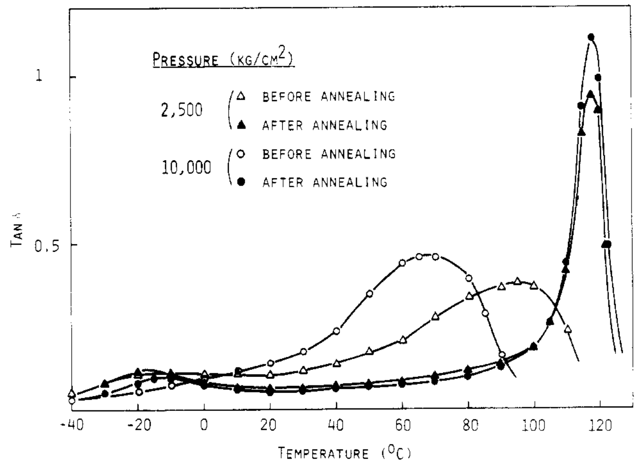

Figure 16. Dissipation factor (tan δ) vs. temperature of UL50SC50 semi-II IPN synthesized at 2500 and 10 000 kg/cm^2 before and after annealing at 120 °C for 13 h.

PU phase clearly forms a dispersion in the PS matrix.

Density. The densities of the semi-IPN's and linear blends are shown in Figure 12. There is an abrupt change in density when the synthesis pressure is changed from atmospheric to 2500 kg/cm^2. The increase amounts to 0.006–0.007 g/cm^3. The densities of semi-IPN and linear blend synthesized above 2500 kg/cm^2 were almost equal and showed no further change with pressure. Similar behavior was also observed in the cases of IPN.[2] Semi-IPN's and linear blend synthesized at atmospheric pressure have lower density values compared to the IPN, presumably due to the lower degree of intermixing of the PU and PS component polymers. The calculated density averages of semi-IPN's and linear blend based on volume additivity at atmospheric pressure are 1.077–1.078 g/cm^3.

Annealing Effect. The effect of physical interlocking characteristics of the IPN's is demonstrated by the annealing test at 100 °C for 13 h at atmospheric pressure. The tan δ vs. temperature plot of UC50SC50 full IPN's synthesized at 10 000 kg/cm^2 with varying theoretical $\bar{M}_c$ of 2000 and 3200 (Figure 13) shows some degree of phase separation (shown by the upward shift of the PS-dominant-phase T_g) after the thermal treatment. This phase separation is considered to be a local separation within the cross-linked network and the degree of T_g shift is small, indicating that the complete phase separation is restricted by the presence of the physical interlocking of the PU and PS cross-linked networks.

In semi-IPN's and linear blend (Figure 14) synthesized at 10 000 kg/cm^2 pressure, there is a large phase separation observed after the thermal treatment at 100 °C 13 h. This indicates that although the mixture remains in a partially

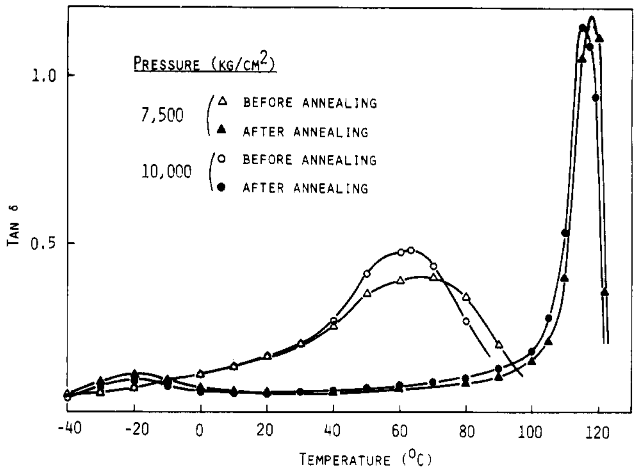

Figure 17. Dissipation factor (tan δ) vs. temperature of UL50SL50 linear blend synthesized at 7500 and 10 000 kg/cm^2 before and after annealing at 120 °C for 13 h.

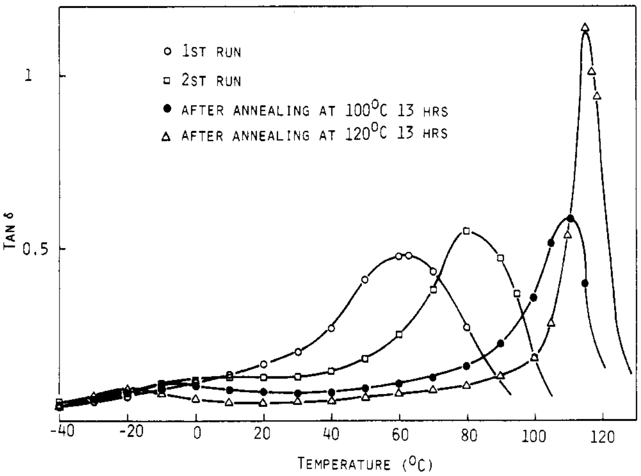

Figure 18. DMA thermograms of UL50SL50 linear blend synthesized at 10 000 kg/cm^2 showing the gradual progress of the phase separation.

intermixed state after the removal of the pressure due to the reduced mobility of the linear polymer chain at room temperature, it undergoes further phase separation at elevated temperature because there is no physical interlocking between the two polymer components. The semi-II IPN and linear blend in which the mobile PU component is linear show a larger degree of phase separation when treated at 100 °C for 13 h. The phase separation is not completed under this thermal treatment condition. When treated at 120 °C for 13 h (Figure 15–17), the semi-IPN's and linear blends show almost complete phase separation, and the two separated T_g's of the annealed samples are very close to the homopolymer T_g's of PU and PS. The difference observed in the degree of intermixing when synthesized at 2500 and 10 000 kg/cm^2 before annealing disappears after the thermal treatment at 120 °C for 13 h.

The gradual progress of the phase separation is clearly shown in Figure 18. The DMA thermograms show the course of phase separation of UL50SL50 linear blend synthesized at 10 000 kg/cm^2 when it is heated continuously at 5 °C/min in the first run, heated again at same rate after quenching in the second run, isothermally annealed at 100 °C for 13 h, and isothermally annealed at 120 °C for 13 h.

Acknowledgment. This work was supported by the Korea Science and Engineering Foundation. We thank Dr. J. K. Yeo and Mr. C. M. Oh of Lucky Ltd. for their help in the electron microscopy work.

Registry No. Polystyrene, 9003-53-6; (divinylbenzene)·(styrene) (copolymer), 9003-70-7; (1,4-butanediol)·(MDI)·(poly(tetramethylene glycol)) (copolymer), 9018-04-6; (1,4-butanediol)·(MDI)·(poly(tetramethylene glycol))·(trimethylolpropane) (copolymer), 39281-41-9.

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