Small-Angle X-ray Scattering and Pulsed NMR Studies of Polyurethane Interpenetrating Polymer Networks

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ABSTRACT: Pulsed NMR and small-angle X-ray scattering studies were performed on simple mixtures, semi-interpenetrating polymer networks (semi-IPN), and interpenetrating polymer networks (IPN) of polystyrene and polyurethane which were synthesized at different high pressures. It was found that, with increasing pressure, mixing of the components was enhanced. This was evidenced by the reduction in the size scale of the phases and/or the extent of mixing within the phases. In general, it was found that increasing the amount of cross-linking enhanced the mixing. Temperature-dependent small-angle X-ray scattering studies showed that the enhanced mixing of the linear chains could be reversed at elevated temperatures. For the semi-IPN's and IPN's, however, the cross-linking of the components either retarded the amount of coarsening that could occur or fully arrested the coarsening. However, for both the semi-IPN's and IPN's local coarsening processes were evident.

Introduction

Interpenetrating polymer networks, IPN's, ideally are a mixture of two or more cross-linked polymers which are dispersed or mixed on the segmental level. In general, due to the low entropy of mixing, polymers are immiscible and, hence, achieving ideal, segmentally dispersed networks is difficult. The extent to which IPN's undergo phase separation can be controlled by the cross-link density, the interactions between unlike segments, and the route used to prepare the IPN. It is easy to see that dramatically different degrees of phase separation, i.e., the size scale of the phase separation, will be markedly different in the cases where polymers and monomers are mixed and then cross-linked (sequential polymerization method) or when a simultaneous polymerization and cross-linking is performed.[1]

It is possible to take two immiscible polymers and by variation of the conditions of the synthesis, i.e., pressure and temperature, control the rate of phase separation and, consequently, the size scale over which phase separation occurs.[2,3] For example, in the cases of polyurethane/poly(methyl methacrylate) or polyurethane/polystyrene IPN's, two cases where the constituent homopolymers are highly immiscible, by use of the simultaneous polymerization process under high pressure a transparent, nearly segmentally dispersed mixture of the IPN could be obtained. Alternatively, similar results could be obtained by performing the polymerization at low temperatures where the viscosity of the medium is dramatically increased, hence reducing the rate at which phase separation occurs. Consequently, without altering the chemical composition of the constituents, means are available to control the heterogeneity of an IPN.

Herein, a study of IPN's prepared under high pressure by small-angle X-ray scattering, SAXS, and NMR spin relaxation is presented. This study deals with IPN's formed from polyurethane and polystyrene as a function of the synthesis pressure and molecular weight between cross-link points. It is shown that, with increasing pressure or cross-link density, the extent of phase separation is reduced and that the extent of mixing decreases, in the order of IPN's, to semi-IPN's to linear mixtures. Real time SAXS as a function of temperature shows that the enhanced mixing can be partially reversed once the system has sufficient mobility. However, the coarsening of the phase separation depended upon the pressure of the reaction and the molecular weight between cross-link points.

Experimental Section

Poly(tetramethylene ether) glycol (PTMG) and 4,4′-diphenylmethane diisocyanate (MDI) were used for preparing polyurethane (PU) prepolymers. The molecular weight PTMG was 986. Mixtures of 1,4-butanediol (1,4-BD) and trimethylolpropane (TMP), the chain-extending and cross-linking agent for the PU network, in 1:4 and 1:1 equivalent ratios, were used to obtain two different levels of cross-link density. The resulting theoretical molecular weights between cross-links ($\bar{M}_c$) were 2000 and 3200, respectively. Styrene monomer and divinylbenzene (DVB) were used for the polystyrene (PS) network. The composition of DVB was 4% and 2.5% by weight in styrene monomers for $\bar{M}_c$'s of 2000 and 3200. The thoroughly degassed mixtures of PU prepolymer, 1,4-BD/TMP mixture, dibutyltin dilaurate catalyst (0.03% by weight of PU), styrene monomer, DVB, and benzoyl peroxide (one part per 100 styrene units by weight) were charged into a reaction capsule and kept at room temperature for approximately 24 h. The PU component was allowed to react partially at room temperature to reach the gel point with the intent of increasing the viscosity at high-temperature molding of PU. The capsule was inserted into a reaction mold as described in a previous paper[2] and polymerized at 80 °C for 24 h and 100 °C for 4 h. The reaction was carried out with varying pressures

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Table I
Spin–Spin Relaxations[a]

synthesis pressure (10^3 kg/cm^2)	UC50SC50 $\bar{M}_c$ = 2K A_i (%)	UC50SC50 $\bar{M}_c$ = 2K $T_{2,i}$ (μs)	UC50SC50 $\bar{M}_c$ = 3.2K A_i (%)	UC50SC50 $\bar{M}_c$ = 3.2K $T_{2,i}$ (μs)	UC50SL50 A_i (%)	UC50SL50 $T_{2,i}$ (μs)	UL50SC50 A_i (%)	UL50SC50 $T_{2,i}$ (μs)	UL50SL50 A_i (%)	UL50SL50 $T_{2,i}$ (μs)
atm	33	9.3	28	10	34	11	26	10	37	11
	29	18	31	17	30	29	33	15	22	20
	38	89	41	97	36	220	41	210	41	210
1.25					32	10				
					30	23				
					38	150				
2.5	28	12	40	11	26	11	29	10		
	42	18	30	24	35	17	36	16		
	30	72	30	80	39	95	35	120		
5.0	49	13	48	12	30	11	28	11	45	12
					34	20	39	16	30	31
	51	35	52	44	36	93	33	100	25	140
7.5	44	12	57	13	28	11	28	10	47	12
					40	18	37	16	45	37
	56	34	43	44	32	64	35	84	8	122
10.0	44	13	51	13	39	12	24	10	43	12
							47	17	41	30
	56	30	49	34	61	29	29	79	16	120

[a] In the table A_i is the fraction of the NMR signal arising from the spin–spin relaxation, $T_{2,i}$.

up to 10^4 kg/cm^2. The detailed methods of sample preparation and characterization have been discussed previously.[2,3]

The samples used in this experiment are listed in Table I. The samples have been coded as follows. U and S denote polyurethane and polystyrene, respectively. C or L immediately following the U or S denote which component is cross-linked or linear, respectively. The composition of PU and PS were kept fixed at 50%, hence, the use of 50 in the code. For example, UC50SL50 designates a 50/50 mixture of cross-linked polyurethane with linear polystyrene. The reaction pressure and $\bar{M}_c$ are indicated separately.

SAXS experiments were performed on Beam line I-4 at the Stanford Synchrotron Radiation Laboratory which is described in detail elsewhere.[4] The white radiation emanating from the storage ring was focused by a platinum-coated float glass mirror bent to approximate an ellipse and by a bent, asymmetrically cut Si(111) crystal to a position coincident with the detector plane. The Si monochromator was adjusted to deliver X-rays with a wavelength, λ, of 1.429 Å with $\Delta\lambda/\lambda \approx 0.001$. Two sets of slits between the monochromator and the specimen were used to reduce the parasitic scattering. At the detector the incident beam had dimensions of 125 μm in the vertical by 1 mm in the horizontal. The detector, a 1024-pixel EG&G Reaction photodiode array cooled to ~190 K, was interfaced to a DEC 1134 computer via CAMAC electronics. Scintillation detectors placed before and after the sample cell continuously monitored the incident and transmitted beam intensities by the scattering from a 25-μm-thick Kapton window inclined at 45° with respect to the incident radiation. Changes in the specimen attenuation factor are consequently monitored continuously. The data were placed on an absolute level by means of a polyethylene secondary standard.[5,6]

NMR measurements were performed at 20 MHz using a Bruker PC20 proton pulsed NMR spectrometer. The temperature of the samples was controlled at 40 °C. Pulsed sequences for T_2 measurement used in this experiment are the solid-echo method[7] ($90°_x\tau 90°_y$) and spin-echo method[8] [$90°_x\tau(180°_y 2\tau)_n$]. $T_{1\rho}$ was measured by the solid-echo-train method[9] [$90°_x\tau(90°_y 2\tau)_n$]. T_1 was measured by the modified inversion-recovery method ($180°_x\tau 90°_x\tau 90°_y$). A detailed description of the NMR experiments has been reported previously.[10,11]

Results and Discussion

It has been shown previously[2,3] that increasing the reaction pressure tended to promote mixing between the components. For example, shown in Figure 1 is the temperature dependence of the dynamic mechanical loss tangent of UC50SC50 as a function of different reaction pressures. At atmospheric pressure, two distinct maxima in tan δ are seen which is characteristic of a phase-separated system having essentially pure polyurethane and polystyrene phases. As the reaction pressure increases, the two loss maxima are seen to merge into a single relaxation occurring at 55 °C, characteristic of a T_g for a segmentally dispersed mixture of the two components. From the value of T_g the composition of the phases can be estimated and the relatively simple picture of enhanced mixing emerges. Shown in Figure 2 is the mass fraction of polyurethane in the polystyrene phase as a function of reaction pressure for the IPN (UC50SC50 with $\bar{M}_c$ = 2000 and 3200), the semi-IPN's (UC50SL50 and UL50SC50) and the simple mixtures (UL50SL50). In all cases, the concentration of polyurethane in the PS phase increases with increasing pressure, indicative of an enhanced mixing. For UC50SC50 ($\bar{M}_c$ = 2000) at the highest reaction pressures the mass fraction is equal to that charged in the reaction and, consequently, complete mixing appears to have been achieved. In all other cases, the reduced mass fraction of polyurethane suggests that demixing has occurred. However, cross-linking the urethane component seems to be

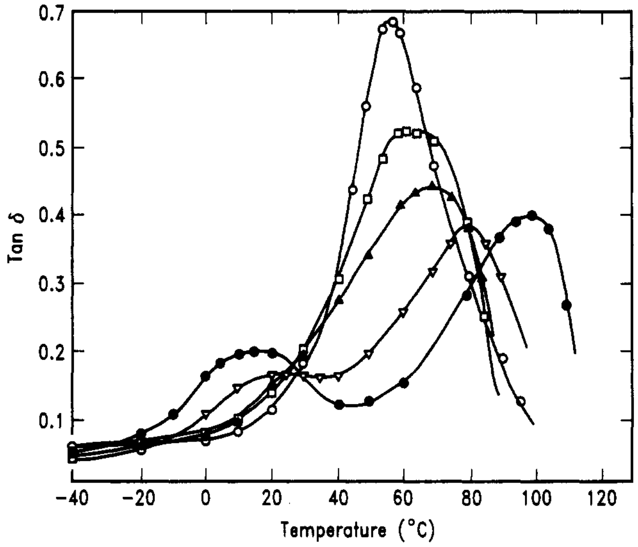

Figure 1. Dissipation factor (tan δ) as a function of temperature for the full IPN where both the urethane and styrene are cross-linked and where $\bar{M}_c$ = 3200. The pressure used during the synthesis was (●) atmospheric; (▽) 2.5 × 10^3 kg/cm^2, (▲) 5 × 10^3 kg/cm^2, (□) 7.5 × 10^3 kg/cm^2, and (○) 10^4 kg/cm^2.

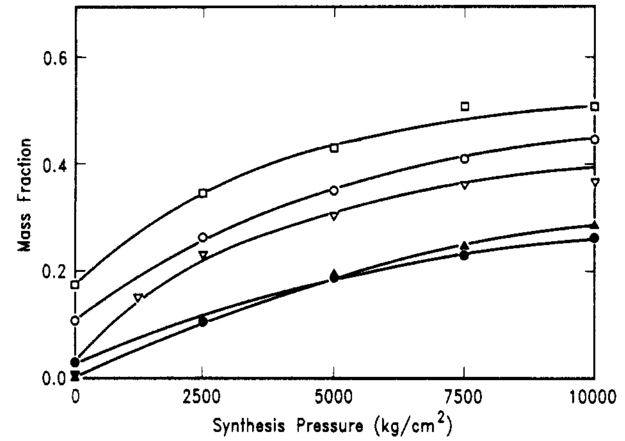

Figure 2. Calculated mass fraction of polyurethane in the polystyrene phase as a function of the synthesis pressure for (□) UC50SC50 ($\bar{M}_c$ = 2000), (○) UC50SC50 ($\bar{M}_c$ = 3200), (▽) UC50SL50, (●) UL50SC50, and (▲) UL50SL50.

more efficient in promoting mixing. In fact, UL50SC50 behaves similarly to the linear mixture UL50SL50 where the largest amount of demixing occurs.

For a multiphase system the relaxation time observed in the NMR experiments results from the different environments of the nuclei. Provided the relaxation times of the components are sufficiently different, the transverse magnetization, $M(t)$, can be approximated by

$$M(t) = A_1 e^{-(1/2)(t/T_{2,1})^2} + A_2 e^{-t/T_{2,2}} + A_3 e^{-t/T_{2,3}} \quad (1)$$

where A_i is the fraction of the signal arising from $T_{2,i}$ relaxations. This approximation and the minimization of the number of terms in eq 1 have been discussed in detail elsewhere.[10,12-15] In general, for a two-phase system one can assign contributions to the relaxations from the environments of the two phases. In our case, the fast relaxation $T_{2,1}$ is attributed to the hard segment component (PS) whereas the slower relaxation $T_{2,3}$ is attributed to the soft segment component (PU). For cases where the interfaces between the domains are sharp, these are the only contributions. However, for the studies of interest here, two relaxation times were not sufficient to produce a suitable fit to $M(t)$. In such cases, the use of an intermediate relaxation time, $T_{2,2}$ was used which can be assigned to an interface between the phases. This coarsely approximates the composition gradient in the interface by an average composition having intermediate dynamics.

$T_{2,i}$ for the IPN's, semi-IPN's, and linear mixtures are shown in Table I as a function of the synthesis pressure. Also shown are the weighting fractions of each component. For all specimens the relaxation time of PS, the fast component, is relatively constant in the range from 9.3 to 13 μs. Slight differences are observed if the PS is cross-linked or linear, but quantitatively assessing differences from the data is not possible. The invariance of this relaxation time, $T_{2,1}$, suggests that the PU segments are not substantially altering the relaxation of the PS component. However, the situation is markedly different for the PU relaxation, i.e., $T_{2,3}$. At atmospheric pressure $T_{2,3}$ for the linear mixture, UL50SL50, was found to be 210 μs. As the extent of cross-linking increases, i.e., for the UC50SL50 and UL50SC50 semi-IPN's, $T_{2,3}$ is not altered significantly, which suggests that distinct phases of both components are present. Further increasing the cross-linking to the IPN case results in a reduction of $T_{2,3}$ by nearly a factor of 2, indicating a mixing of the PS and PU components in the PU-rich phase. This general trend is seen for all reaction pressures, which means that increasing the extent of cross-linking results in an enhanced mixing of the components and a reduction in the T_2 relaxation time of the PU segments. A similar trend is seen as the reaction pressure is increased; i.e., increasing the reaction pressure reduces $T_{2,3}$, the relaxation of the PU segments. For example, for the UC50SC50 ($\bar{M}_c$ = 2000) increasing the reaction pressure from atmospheric to 10^4 kg/cm^2 results in a reduction in the $T_{2,3}$ from 89 to 30 μs and for the UL50SL50 a reduction from 210 to 120 μs is seen. Consequently, increasing the pressure forces the components into a more highly mixed state.

It should be noted that the size of the phases can alter the relaxation times measured by NMR. In particular, Tanaka and Nishi[11] discussed the dependence of T_2 on the domain size for the model system of styrene–isoprene–styrene triblock copolymers having the same styrene content with varying molecular weights. As the size of the PS microdomains increases, T_2 decreases and approaches the bulk value of T_2 for PS. Specifically, the PS microdomain size from 23 to 100 Å yielded a reduction in T_2 from 12.6 to 9.3 μs. Since the interface between the two components is not infinitely sharp, then, as the size of the microdomain decreases, the motions of the segments of this microphase are increasingly influenced by the alternate component. This influence is enhanced by the connectivity of the blocks of the copolymer. Therefore, for the $T_{2,3}$ data reported herein, an increase in $T_{2,3}$ does not necessarily mean that segmental mixing is increased and could result from a reduction in the phase size.

The intermediate relaxation time, $T_{2,2}$, is assumed to arise from the interface between PS-rich and PU-rich phases. In this interfacial region the composition of the components varies continuously and the NMR measurements reflect only an average relaxation time between PS and PU. $T_{2,2}$ ranges from 16 to 30 μs, exhibiting no systematic variations with pressure or cross-linking conditions. However, it is important to note that the weighting fraction of $T_{2,2}$ is seen to increase with increasing reaction pressure. This suggests that the fraction of the system occupied by the interface increases as the reaction pressure is increased. This is consistent with an enhanced mixing of the components at higher pressures. This behavior was found for all the systems studied.

For cases where $T_{2,2}$ is not listed, it cannot be assumed that the interface between the PS-rich and PU-rich domains is infinitely sharp. In fact, just the opposite is true. For example, for UCSC ($\bar{M}_c$ = 2000 or 3200) where the reaction pressure exceeds 2.5 × 10^3 kg/cm^2, $T_{2,3}$ has decreased from 210 μs, i.e., for the PU-rich phase for ULSL. This low value of $T_{2,3}$ suggests either an enhancement in the mixing of the two components or a reduction in the size of the PU phase. This would result in either a shallow concentration gradient in the interface between the phases or a substantial increase in the fraction of the specimen occupied by the interface. In either case, a distinct relaxation attributable to the interface would not be found.

In a multiphase system, T_2 provides no information on the size scale of the phases. However, as shown by Tanaka and Nishi[10,11] one can use spin–lattice relaxation times, T_1, or spin–lattice relaxation times in a rotating frame, $T_{1\rho}$, where the distance over which spin diffusion occurs comes into play. T_1 samples the spin–lattice relaxation times in the megahertz region whereas as $T_{1\rho}$ samples the kilohertz frequency range. The utility of this approach for determining phase sizes depends critically upon the spin dynamics and the differences in the distribution of spin–lattice relaxation times. The maximum spin diffusive path length, L, can be estimated as $L \sim (6Dt)^{1/2}$ where

Table II
Spin–Lattice Relaxations[a]

synthesis pressure (10^3 kg/cm^2)	UC50SC50 $\bar{M}_c$ = 2K		UC50SC50 $\bar{M}_c$ = 3.2K		UC50SL50		UL50SC50		UL50SL50	
	A_i (%)	$T_{1,i}$ (ms)	A_i (%)	$T_{1,i}$ (ms)	A_i (%)	$T_{1,i}$ (ms)	A_i (%)	$T_{1,i}$ (ms)	A_i (%)	$T_{1,i}$ (ms)
atm			57	73	42	55	69	86	55	67
			43	210	58	220	31	380	45	330
1.25					18	28				
					82	150				
2.5	100	110	100	120	100	120	100	120		
5.0	100	120	100	110	100	110	100	120	100	120
7.5	100	110	100	110	100	110	100	120	100	120
10.0	100	110	100	120	100	130	100	120	100	120

[a] A_i is the fraction of the NMR signal arising from a spin–lattice relaxation time $T_{1,i}$.

Table III
Spin–Lattice Relaxation Times in the Rotating Frame[a]

synthesis pressure (10^3 kg/cm^2)	UC50SC50 $\bar{M}_c$ = 2K		UC50SC50 $\bar{M}_c$ = 3.2K		UC50SL50		UL50SC50		UL50SL50	
	A_i (%)	$T_{1\rho,i}$ (ms)	A_i (%)	$T_{1\rho,i}$ (ms)	A_i (%)	$T_{1\rho,i}$ (ms)	A_i (%)	$T_{1\rho,i}$ (ms)	A_i (%)	$T_{1\rho,i}$ (ms)
atm			24	0.15	11	0.36	20	0.99	9	0.41
			76	1.1	89	1.4	80	2.7	91	2.2
1.25					13	0.38				
					87	1.7				
2.5	100	1.1	100	1.3	100	1.2	100	1.6		
5.0	100	1.1	100	1.1	100	1.0	100	1.9	100	1.4
7.5	100	1.1	100	1.5	100	0.91	100	1.4	100	1.2
10.0	100	1.4	100	0.8	100	1.0	100	1.1	100	1.0

[a] A_i is the fraction of the NMR signal arising from the spin–lattice relaxation time in the rotating form, $T_{1\rho,i}$, of component i.

the spin diffusion coefficient, D, is $\sim 10^{-12}$ cm^2/s and t is the characteristic time for diffusion. For T_1 measurements, as will be shown, $t \sim 120$ ms which results in $L \sim 85$ Å whereas, for $T_{1\rho}$, $t \sim 1.5$ ms and $L \sim 9$ Å. Provided the domains in a multiphased system are larger than L, the compositions of the domains are distinctly different, and the distribution of relaxation times are sufficiently different at the frequency of the measurements, the systems with phase sizes larger than L will give rise to multiple relaxation times.

With the exception of UC50SC50 ($\bar{M}_c$ = 2000), the results for both T_1 and $T_{1\rho}$ in Tables II and III, respectively, are similar ($\bar{M}_c$ = 2000). For the T_1 measurements, the near-equal weightings of the fast and slow relaxations at atmospheric pressure suggests that there are domains of at least 85 Å for both components. The slow relaxations decrease as the extent of cross-linking of the urethane component is increased, which suggests that this is a more effective means of either reducing the phase size or enhancing mixing. With $T_{1\rho}$ the slower relaxation comprises ~80% of the signal. For T_1, a marked decrease in the relaxation of the slower component is seen as the urethane component is cross-linked. With increasing pressure, only one relaxation is observed which suggests either that the sizes of the domains have decreased significantly or that the concentration of the components within the phases are such that distinctly different domains are not observable. In either case, both T_1 and $T_{1\rho}$ measurements show an enhanced miscibility with increasing pressure.

Small-angle X-ray scattering results for the linear mixture, semi-IPN's, and IPN's investigated in this study are shown in Figures 3–7 as a function of the reaction pressure. The intensity, normalized according to the film thickness, attenuation coefficient, and incident beam monitor intensity, is plotted as a function of the scattering vector $\mathbf{q} = (4\pi/\lambda)\sin(\theta/2)$ where λ is the wavelength and θ is the scattering angle. In all cases, there is a shift of the scattering to higher $\mathbf{q}$ or smaller distances with increasing reaction pressure, indicating an enhancement of miscibility and/or a reduction in phase size. However, as will be discussed, complete miscibility is not achieved, as evidenced by the appearance of interferences resulting from the multiphased nature of the morphology.

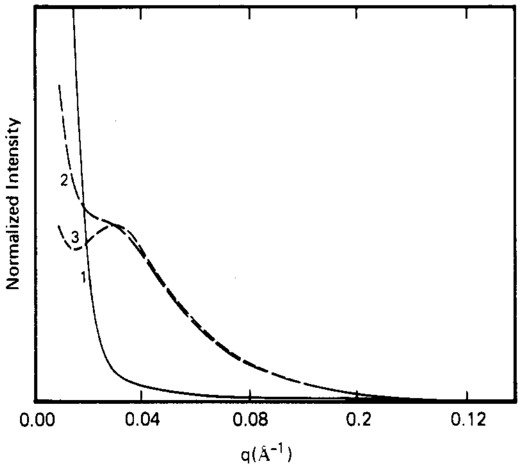

Figure 3. SAXS profiles for UL50SL50 as a function of the scattering vector $\mathbf{q}$ for synthesis pressures of (1) atmospheric, (2) 5×10^3 kg/cm^2, and (3) 7.5×10^3 kg/cm^2.

For simple, linear mixtures of the two components, the data in Figure 3 show that at atmospheric pressures the scattering monotonically decreases with increasing $\mathbf{q}$. For a coarsely phase separated two-component system with domains randomly arranged in space, such a result is expected. However, owing to the macroscopic phase sizes, most of the scattering occurs at angles beyond the resolution limit of the instrument. Consequently, extracting a domain size from the data is not possible. One can only say that the sizes of the domains are in excess of many hundreds of angstroms. The application of pressure during the synthesis, however, produces quite dramatic changes. At 5×10^3 kg/cm^2 (curve 2) a distinct shoulder in the scattering is observed at $\mathbf{q} \sim 0.025$ Å^{-1}, which sharpens into a well-resolved reflection at $\mathbf{q} \sim 0.029$ Å^{-1} at a pressure of 7.5×10^{-3} kg/cm^2 (curve 3). These

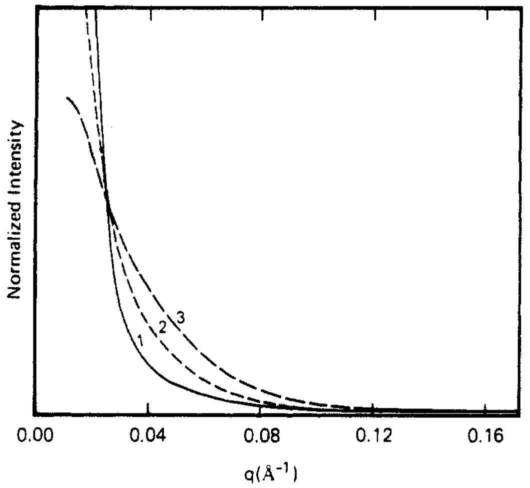

Figure 4. SAXS profiles for UC50SL50 as a function of the scattering vector **q** for synthesis pressures of (1) atmospheric, (2) 7.5 × 10^3 kg/cm^2, and (3) 1 × 10^4 kg/cm^2.

correspond to Bragg spacings of 251 and 216 Å, respectively. From the volume fractions of the components, average domain sizes of 125 and 108 Å, respectively, are obtained. Consequently, the average size of the domains is decreasing with the application of pressure.

One important aspect of these results is that the linear mixtures are still phase separated and that the spatial distribution of the domains is not random. Otherwise, a scattering maximum would not be evident. From equation of state arguments,[16] increasing the pressure produces an elevation of the LCST; i.e., mixing is enhanced. The appearance of a SAXS maximum demonstrates that phase separation has occurred. However, it is important to note that the size scale of the phase separation is quite small in comparison to that usually seen in polymer mixtures (typically on the micron size scale). Consequently, a coarsening of the domains has not occurred and the phase separation has been arrested. The observation of a scattering maximum clearly demonstrates that phase separation is occurring via a spinodal mechanism. Nucleation and growth would produce only a monotonically decreasing scattering profile. The periodic composition fluctuations established during spinodal decomposition and the rate at which these fluctuations grow depend upon a balance between the diffusive processes and thermodynamics. Thus, perturbing the thermodynamics by the use of pressure will decrease the size scale of the fluctuations and retard their growth. Consequently, while phase separation occurs, enhanced mixing is still evident.

For the semi-IPN's investigated cross-linking the urethane or styrene component produces markedly different results. In Figure 4 the scattering data for the urethane cross-linked semi-IPN are shown as a function of pressure. In all cases, monotonically decreasing scattering profiles are seen. However, with increasing pressure, the rate at which the scattering decays as a function of **q** decreases with increasing pressure. Thus, as with the linear mixtures, the enhancement of the scattering at higher **q** translates into enhanced interferences over shorter distances, or in other words, an enhanced miscibility. In fact, in the data shown for the UC50SL50 synthesized at 7.5 × 10^3 kg/cm^2, a shoulder in the scattering at the smallest **q** values, corresponding to a distance of ~600 Å, is seen. From the shape of the scattering profiles it appears that the linear mixtures (Figure 3) are more miscible than the semi-IPN (Figure 4). This is an unexpected result since the intent in producing a semi-IPN is physically to force a miscibility between the components. However, as will be discussed later, the total integrated scattering demonstrates that, while the phases may be larger, the extent of mixing within the phases is greater in the semi-IPN case.

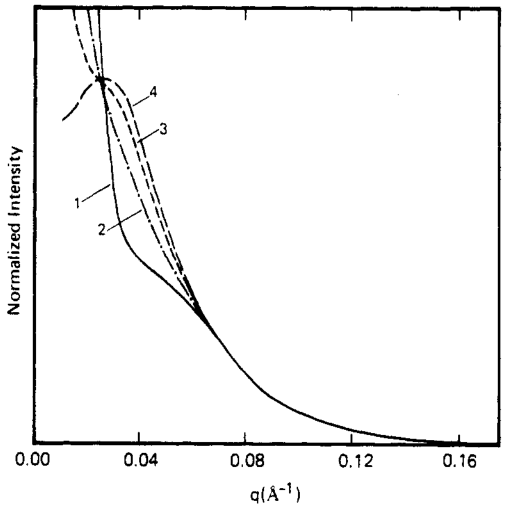

Figure 5. SAXS profiles for UL50SC50 as a function of the scattering vector **q** for synthesis pressures of (1) atmospheric, (2) 5 × 10^3 kg/cm^2, (3) 7.5 × 10^3 kg/cm^2, and (4) 1 × 10^4 kg/cm^2.

For the semi-IPN where the styrene component is cross-linked, i.e., UL50SC50, discrete interferences are seen for nearly all pressures, as shown in Figure 5. At atmospheric pressures a shoulder is observed at **q** ~ 0.05 Å^{-1}, corresponding to a Bragg spacing of 126 Å. From the manner in which the intensity increases with decreasing **q**, it is evident that this shoulder represents a higher order reflection and cannot be taken as the first-order reflection. Consequently, when the styrene component is cross-linked, the extent to which the phase separation occurs is restricted to the several hundreds of angstrom size scale. Increasing the pressure to 2.5 × 10^3 kg/cm^2 eliminates any vestiges of a shoulder or scattering maximum. This indicates that the spatial ordering of the phase-separated domains is disrupted which could be associated with the enhancement of smaller wavelength fluctuations in the concentration or at least a broadening of the distribution of the spatial fluctuations in the concentration over that seen at lower pressures. In keeping with this, as the reaction pressure is increased further, a distinct maximum in the scattering develops at **q** ~ 0.027 Å^{-1}, corresponding to a Bragg spacing of 230 Å. Consequently, the enhanced reaction pressure forces a smaller size scale of the phases which can be viewed as enhancing the mixing. As will be discussed later, in addition to the limitation or restriction of the size scale of the domain, the mixing of the components is also enhanced.

The scattering data for the two full IPN's, i.e., where both the urethane and styrene components are cross-linked, are shown in Figures 6 and 7. Figure 6 corresponds to the case where $\bar{M}_c$ = 3200 and Figure 7 where $\bar{M}_c$ = 2000. The trends in the data as a function of pressure are similar in both cases. At atmospheric pressure a monotonically decreasing scattering profile is observed, and as the reaction pressure is increased, a maximum is observed which progressively shifts to higher **q** or smaller spacing with increasing reaction pressure. For the case where $\bar{M}_c$ = 3200, at the highest pressure of 10^4 kg/cm^2 a maximum is observed at **q** ~ 0.035 Å^{-1}, corresponding to a Bragg spacing of 180 Å, and for $\bar{M}_c$ = 2000 a very broad, weak reflection is observed at **q** ~ 0.045 Å^{-1}, corresponding to 140 Å. Thus, while the enhanced pressure reduces the spatial extent of phase separation, increasing the cross-link density of the component further reduces the size

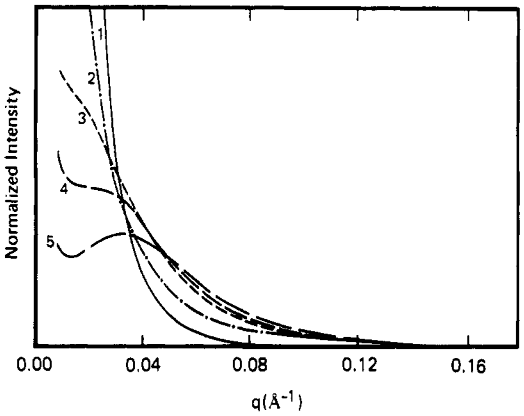

Figure 6. SAXS profiles for UC50SC50 ($\bar{M}_c = 3200$) as a function of the scattering vector for the synthesis pressures of (1) atmospheric, (2) 2.5 × 10^3 kg/cm^2, (3) 5 × 10^3 kg/cm^2, (4) 7.5 × 10^3 kg/cm^2, and (5) 1 × 10^4 kg/cm^2.

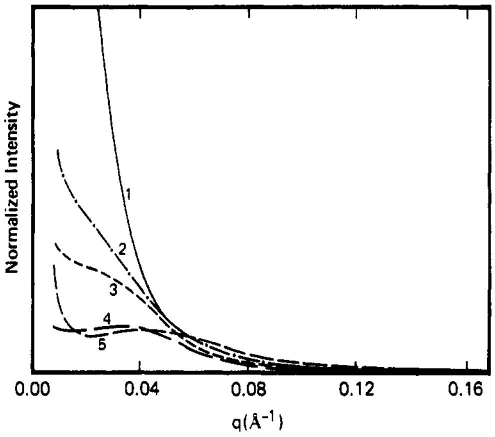

Figure 7. SAXS profiles for UC50Sc50 ($\bar{M}_c = 2000$) as a function of the scattering vector **q** for synthesis pressures of (1) atmospheric, (2) 2.5 × 10^3 kg/cm^2, (3) 5.0 × 10^3 kg/cm^2, (4) 7.5 × 10^3 kg/cm^2, and (5) 1 × 10^4 kg/cm^2.

scale of the phase separation. On the basis of a volume fraction of 0.5, the size scale of the individual phases will be ~90 Å for $\bar{M}_c \simeq 3200$ and ~70 Å for $\bar{M}_c = 2000$. It should be recalled that only one T_1 and $T_{1\rho}$ relaxation were observed for this specimen. While this result appears at first to stand in contradiction to the phase separation observed by SAXS, it should be noted that the sizes of the domains are less than or comparable to the spin diffusion distance. Therefore, even if the domains were pure styrene and urethane, the small size scale would limit the effectiveness of the NMR.

From the angular dependence of the scattering, it is evident that increasing the reaction pressure retards the phase separation. Cross-linking the components promotes mixing by limiting the size scale of the phase separation. Unlike linear mixtures, cross-linking should lock in the morphology and the coarsening of the phases should be restricted by the presence of the cross-links. This point will be discussed further in the temperature-dependent studies presented later in this article.

To evaluate the extent of mixing within the phases, the total integrated scattering or invariant Q was determined. By definition

$$Q = \kappa \int_0^\infty \mathbf{q}^2 I(\mathbf{q})\, d\mathbf{q} \qquad (2)$$

where κ is a calibration constant which has been determined by use of a secondary polyethylene standard calibrated against a set of silica sols.[5] Experimentally, the invariant is composed of three separate components since the data are limited to a finite set of scattering vectors. Integraton from 0 to $\mathbf{q}_{\min}$, where $\mathbf{q}_{\min}$ is the smallest measurable value of $\mathbf{q}$, is performed by a linear extrapolation of $I\mathbf{q}^2$ to zero, thus the first component of Q is given by $I^3\mathbf{q}_{\min}/2$. Extrapolation to $\mathbf{q} \rightarrow \infty$ is performed by use of Porod's law. After correction of the data for deviations due to diffuse phase boundaries, the intensity varies as $\mathbf{q}_p^{-4}$ where $\mathbf{q}_p$ is the value of $\mathbf{q}$ above which Porod's law holds. Thus, the extrapolated portion of $\mathbf{Q}$ is given by $k_p/3\mathbf{q}_p^3$ where k_p is the Porod constant. A simple numeric integration of $I\mathbf{q}^2$ over the range from $\mathbf{q}_{\min}$ to $\mathbf{q}_p$ is then performed. Summation of these three yields Q.

For a two-phase system the invariant is given by

$$Q = \phi_1\phi_2(\rho_1 - \rho_2)^2 \qquad (3)$$

where ϕ_i is the volume fraction of phase i with electron density ρ_i. Assuming that the volume fraction of the phases is 0.5, then the electron density difference between the phases is simply given by

$$\rho_1 - \rho_2 = 2Q^{1/2} \qquad (4)$$

The electron density of the phases will depend on the extent of mixing of the components, and hence, the more pure the phases, the greater the difference in the electron density. From the scattering data alone, it is not possible to determine the electron density of each phase, only the difference. From this difference, in comparison to the calculated value of the electron density difference of the pure components, one can obtain a measure of the extent of mixing.

For polystyrene, with a mass density of 1.05 g/cm^3, an electron density of 0.565 mol e/cm^3 is calculated. For the polyurethane component (using 14 tetramethylene oxide units) with a mass density of 1.105 g/cm^3, an electron density of 0.602 mol e/cm^3 is found. Thus, if the components were fully demixed, then an electron density difference of 0.0372 mol e/cm^3 would result. It is against this value to which the experimental data will be compared.

Shown in Table IV are the electron density differences determined for the linear mixtures, semi-IPN's, and IPN's. For the linear mixtures, the invariant at atmospheric pressure is seen to be quite small. This, however, cannot be interpreted as an indication of a thorough mixing of the components. It will be recalled that the scattering data for this system were seen only at small **q** and rapidly decreased with increasing **q**. Most of the scattering, due to the large size of the phases, occurred at angles too small to be resolved experimentally, thereby producing an artificially low value of the electron density difference. At higher pressures, phase sizes are reduced and scattering occurs at higher **q**. The values of the electron density difference are seen to be very close to the calculated difference for the pure components and suggest that the components are fully demixed. For the semi-IPN's and full IPN's, there is a general trend for the electron density difference to decrease with increasing pressure. However, there is no indication that this difference decreases with increasing amounts of cross-linking in the system. It is apparent from the data in Table IV, with the exception of the linear mixtures, that a significant amount of phase mixing is evident. This explains the limited number of relaxations observed by NMR since the mixing within the phases will tend to homogenize the system and, hence, cause the relaxations of the different phases to be similar.

The evaluation of the scattering invariant requires, as mentioned, the determination of the diffuse phase boundary.[17-19] For all the specimens studied, a sigmoidal concentration profile between the phases was assumed.

Table IV
Electron Density Differences ($\rho_1 - \rho_2$) (mol of e/cm^3)[a]

pressure (10^3 kg/cm^2)	UC50SC50 $\bar{M}_c = 2000$	UC50SC50 $\bar{M}_c = 3200$	UC50SL50 $\bar{M}_c = 3200$	UL50SC50 $\bar{M}_c = 3200$	UL50SL50
atm	0.013 ± 0.002 (13)	0.015 ± 0.002 (5)	0.017 ± 0.003 (27)	0.013 ± 0.002 (20)	0.008 ± 0.002 (25)
1.25			0.016 ± 0.002 (18)		
2.5	0.014 ± 0.002 (15)		0.017 ± 0.002 (22)	0.032 ± 0.002 (19)	
5.0	0.014 ± 0.002 (13)	0.028 ± 0.002 (12)	0.013 ± 0.002 (26)	0.010 ± 0.003 (18)	0.033 ± 0.003 (18)
7.5	0.013 ± 0.002 (14)	0.022 ± 0.003 (6)	0.013 ± 0.002 (25)	0.009 ± 0.003 (17)	0.033 ± 0.003 (20)
10.0	0.014 ± 0.004 (8)	0.019 ± 0.003 (5)	0.013 ± 0.003 (22)		0.033 ± 0.008 (18)

[a] Values in parentheses are the widths of the diffuse phase boundaries in angstroms, assuming a sigmoidal concentration profile at the interface. The maximum electron density difference between the two pure phases is 0.037 mol of e/cm^3.

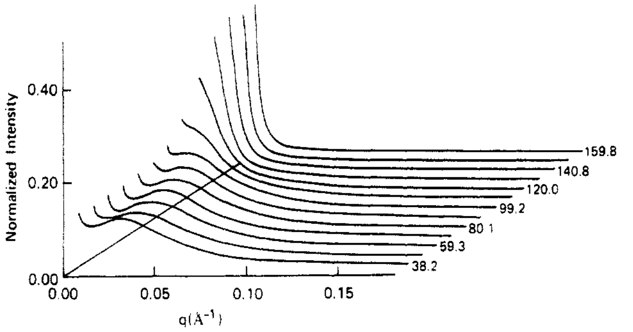

Figure 8. Temperature dependence of the SAXS as a function of the scattering vector **q** for UL50SL50 at a heating rate of 10 °C/min.

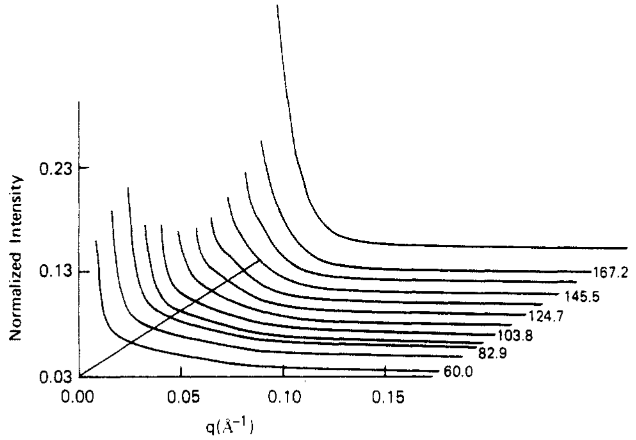

Figure 9. SAXS for UC50SL50 as a function of a temperature at a heating rate of 10 °C/min.

Consequently, ln(I(**q**)**q**^{4}) was plotted as a function of **q**^{2}, which at high values of **q** yielded a linear region from which the diffuse phase boundary could be estimated. Due to the weak scattering at high angles and large contribution to the scattering from thermal density fluctuations, the interfacial widths can be in error by as much as 40%. Shown in Table IV in the parentheses are the values of the diffuse phase boundary determined for the specimens investigated. With the exception of a few cases, the diffuse phase boundary ranges from ~12 to 30 Å. In those cases where exceptions are found, the values are less than this. What is surprising with these values is that they are so small. It was expected that the transition zone widths would be much larger since any factors that would compatibilize components would also produce an increase in the interfacial widths. Since this was not found, the data suggest that while pressure tends to promote compatibility, phase separation still occurs. In fact, coarsening of the phases must have occurred so as to reduce the width of the interface. The linear mixtures, semi-IPN's, and full IPN's prepared at a pressure of 10^4 kg/cm^2 were placed in a heating stage through which the incident X-ray beam could pass unhindered. Kapton windows were used to prevent flow of the specimen. The specimens were heated at a rate of 10 °C/min while the small-angle X-ray scattering was simultaneously recorded. Thus, changes in the degree of mixing could be monitored as a function of temperature at atmospheric pressure. The temperature dependence of the scattering for the linear mixture is shown in Figure 8. Initially, a maximum in the scattering is seen at $\mathbf{q} \simeq 0.032$ Å^{-1}. As the temperature is increased, a gradual shift in the reflection to smaller values of **q** is observed. This occurs at temperatures well below the glass transition temperature of PS and indicates a significant mobility of the components. Consequently, the two phases cannot be composed of pure components since, if this were the case, such mobility at temperatures less than ~100 °C, the T_g of PS, would not be expected. From the invariant and electron density difference, however, the extent of mixing cannot be substantial. Near 100 °C, dramatic changes in the scattering are observed where the maximum is seen to shift to angles beyond the resolution of the instrument, indicating that a coarse phase separation is occurring. Such behavior is quite typical of a linear mixture undergoing a coarsening process. These results, it should be noted, dramatically emphasize the effect of pressure on mixing. Without the use of pressure, only a coarsely phase separated morphology would have been produced. With the application of pressure the mixture can be forced into a state where the size scales of the phases are quite small and can be trapped in a state where the extent of phase separation is limited. Although experiments were not performed at higher pressures, it can be envisioned that even a homogeneous mixture of the components could have been achieved.

One would expect that by cross-linking one or both of the components at elevated pressures, the enhanced mixing could be locked in. However, for the semi-IPN's where one component is cross-linked, this is not the case. Shown in Figure 9 are the temperature-dependent scattering profiles for the UC50SL50 semi-IPN where the urethane component is cross-linked. The scattering remains relatively constant as a function of temperature up to ~105 °C whereupon a distinct shoulder in the scattering begins to appear. Increasing the temperature causes a marked increase in the scattering at small **q**, and at the highest temperatures, scattering profiles quite similar to the linear mixtures are seen. These results suggest that, in comparison to the linear mixtures, the rate at which the phase separation occurs is reduced but a coarse phase separation can still occur. Cross-linking is seen to limit the maximum size scale of the phase separation in that domains of several hundreds of angstroms (as determined by a Debye–Beuche analysis of the scattering at the highest temperatures) are still seen at the elevated temperatures. Consequently, while the network formation enhances the extent of mixing, the nonfavorable interactions between the components are sufficiently strong to force the phase separation. Time-dependent studies on the semi-IPN's were not performed.

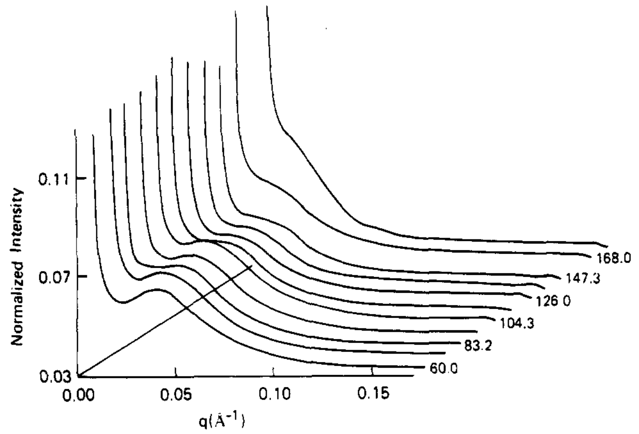

Figure 10. SAXS for UC50SC50 ($\bar{M}_c$ = 3200) as a function of temperature at a heating rate of 10 °C/min.

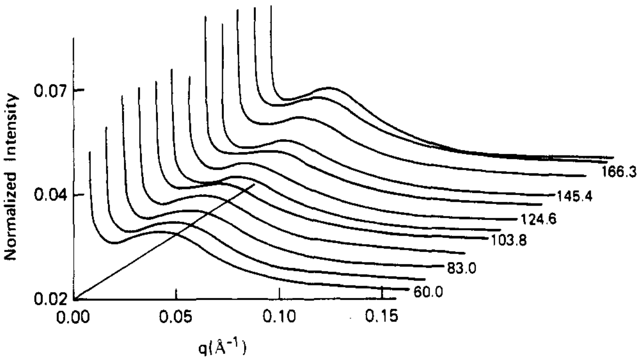

Figure 11. SAXS for UC50SC50 ($\bar{M}_c$ = 2000) as a function of temperature at a heating rate of 10 °C/min.

However, it would be expected that further phase separation or coarsening of the morphology would occur as the linear chains aggregated after diffusing through the surrounding network.

The results on the full IPN's were found to depend upon the extent of cross-linking. For UC50SC50 where $\bar{M}_c \simeq$ 3200 the SAXS shown in Figure 10 remains constant up to ~105 °C. At higher temperatures the maximum is seen to become somewhat more diffuse and diminish slightly in intensity. However, for temperatures in excess of 150 °C a strong increase in the scattered intensity is seen at smaller angles. Thus, even for the case where one has two interdispersed networks, a local coarsening of the morphology can occur where, over a distance of a few hundred angstroms, the components can separate, and on a local level the IPN appears to be quite heterogeneous. Nonetheless, due to limited molecular mobility, the distances over which separation can occur are quite limited.

Finally, the data for UC50SC50 where $\bar{M}_c \simeq$ 2000 are shown in Figure 11. For this IPN the cross-link density is much higher. In keeping with this, regardless of the temperature, the shape of the scattering profile remains virtually unchanged. Consequently, any long-range motions of the molecules has been fully suppressed. However, it should be noted that the total amount of scattering has increased somewhat. This would suggest that some coarsening has occurred on a very local level, i.e., over distances comparable to the distance between cross-links. Thus, even for this case where the cross-link density is high, on the tens of angstrom size scale the full IPN's are heterogeneous. A similar conclusion was drawn from the dynamic mechanical behavior in a previous paper.[2]

In conclusion, it has been shown by a combination of pulsed NMR and small-angle X-ray scattering that the synthesis of IPN's and semi-IPN's under high pressure can yield relatively homogeneous dispersions of two highly incompatible polymers. The extent of mixing of the components can be enhanced and the size scale of heterogeneities in the system can be reduced by the application of pressure during the synthesis. In general, it has been found that increasing the amount of cross-linking of the components and the density of cross-links will tend to promote mixing of the components. Temperature-dependent SAXS studies have shown that even full IPN's can undergo a coarsening process. Unlike the linear or semi-IPN counterparts, however, the size scale of the phase separation and coarsening is dramatically reduced.

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