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William MacKnight, *University of Massachusetts Amherst*

Gaetano Guerra

Soonja Choe

David J. Williams

F. E. Karasz



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Fourier Transform Infrared Spectroscopy of Some Miscible Polybenzimidazole/Polyimide Blends

Gaetano Guerra,[†] Soonja Choe, David J. Williams, Frank E. Karasz,* and William J. MacKnight

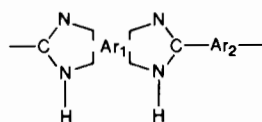
*Polymer Science & Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003. Received April 17, 1987;
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ABSTRACT: The IR spectra of representative miscible aromatic polybenzimidazole/aromatic polyimide (PBI/PI) blends have been studied. Composition-dependent frequency shifts of up to 55 cm⁻¹ in the N-H stretching band of PBI and up to 6 cm⁻¹ in the carbonyl stretching bands of PI were observed. These shifts were removed by thermally induced phase separation. The results suggest that the miscibility of these blends derives from specific intermolecular interactions involving the >NH and carbonyl groups.

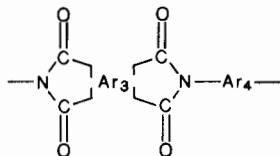
Introduction

The discovery of novel miscible polymer blends based on an aromatic polybenzimidazole (PBI) and a range of aromatic polyimides (PI) has recently been reported.¹ These polymers have the following generic structures

aromatic polybenzimidazoles



aromatic polyimides



where Ar_i represents a number of aromatic moieties. Polymers of these generic types are believed to be miscible for a comparatively wide range of compositions, and structural variations though these variations significantly affect the phase separation temperatures. This assertion is based on results obtained with the materials listed in Chart I and several other available PIs.¹

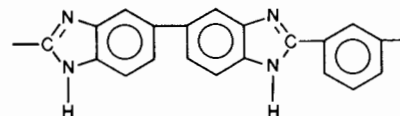
PBI and the PIs Ultem 1000, XU 218, and PI 2080 are soluble in *N,N*-dimethylacetamide (DMAc) so it was found that blends of these materials could be prepared by solution mixing followed either by precipitation into a non-solvent or by casting a film.¹⁻³ Blends with LaRC TPI, which is insoluble in its fully imidized form, were prepared by blending either the polyamic acid form or a 95% imidized form of LaRC TPI, both of which are soluble in DMAc, with PBI in DMAc solution, recovered as a powder or film and then fully imidized.³ Blend miscibility was confirmed by the presence of single composition dependent *T_g*'s lying between those of the constituent polymers, by well-defined composition dependent tan δ dynamic mechanical relaxation peaks associated with the glass transitions, by the formation of clear films and, in one case, by enhanced solvent resistance.^{1,3}

Miscibility in binary homopolymer blends is often attributed to the existence of specific interactions between the blend components. Consequently, an FTIR study of the PBI/PI system was undertaken by using PBI/XU 218 and PBI/Ultem 1000 as representative blends. The objectives were to obtain evidence for the existence of specific interactions in this system and to elucidate the nature of these interactions. In this study, the composition dependent changes in the spectral properties of the N-H stretching bands, which arise solely from the PBI component, and the carbonyl stretching bands, which arise solely from the PI component, were followed.

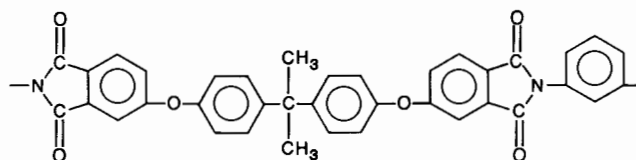
[†] Present address: Dipartimento di Chimica, Università di Napoli, Napoli, Itali 80134.

Chart I

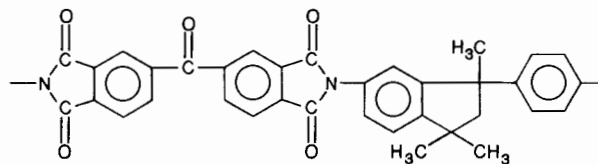
poly(2,2'-(*m*-phenylene)-5,5'-bibenzimidazole)
[(PBI: Celanese Corp.) (*T_g* = 420 °C)]



poly[2,2'-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane-*m*-phenylenediimine]
[(Ultem 1000: General Electric Co.)
(*T_g* = 220 °C)]



condensation product of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 5(6)-amino-1-(4'-aminophenyl)-1,3,3-trimethylindan
[(XU 218: Ciba-Geigy Corp.)
(*T_g* = 320 °C)]



FTIR has been widely used in characterizing miscible polymer systems. Composition-dependent frequency shifts and band broadenings for many such blends have been ascribed to specific intermolecular interactions and to changes in polymer chain conformations. Many of these studies involve blends of polymers containing a carbonyl group,⁴⁻⁸ which appears to be particularly sensitive to the presence of intermolecular interactions.

Experimental Section

PBI powder (Celanese) was dissolved in *N,N*-dimethylacetamide (DMAc) at 225 °C for 30 min under nitrogen in a high-pressure vessel, leaving an undissolved residue of about 0.25 wt % which was removed by filtration. The Ultem 1000 (General Electric) sample had a reported molecular weight of *M_w* = 30 000 ± 10 000 and *M_n* = 12 000 ± 4 000. The XU 218 sample (Ciba-Geigy) had an inherent viscosity of 0.65 dL/g (0.5% in *N*-methylpyrrolidone, 25 °C).

In this study thin films were prepared by casting from 0.5 to 3% (w/v) DMAc solutions of the respective polymer mixtures on glass plates in a nitrogen atmosphere at 80 °C for 24 h. The films were then washed in water at 50 °C for 24 h and dried under vacuum at 200 °C for at least 3 days. Infrared spectra were

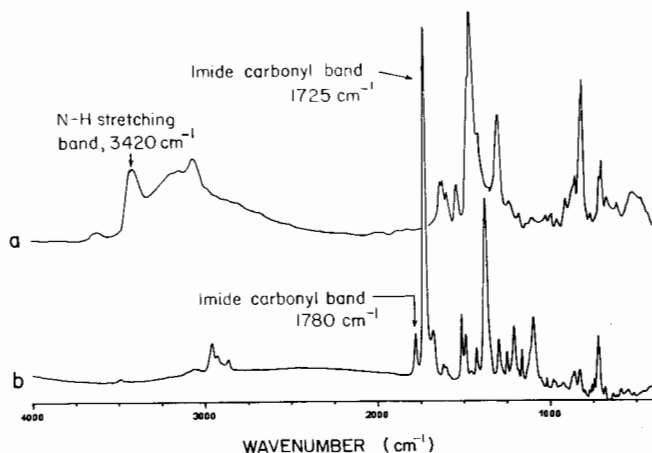


Figure 1. IR spectra of polybenzimidazole and XU 218 polyimide films.

measured at room temperature under nitrogen on an IBM IR/30 FTIR spectrometer at a resolution of 2 cm^{-1} and were signal-averaged over a minimum of 30 scans. The thickness of the samples was in the range of $4\text{--}20\ \mu\text{m}$, but $4\text{--}8\ \mu\text{m}$ thick films were preferred because these provided higher resolution spectra. The efficacy of the solvent removal procedure was confirmed from the measured spectrum of a PBI film using the DMAc methyl group stretching band near 2940 cm^{-1} as an assay peak.

The thermal treatments of the films described below were conducted in a nitrogen atmosphere by heating at a rate of $5\text{ }^{\circ}\text{C}/\text{min}$ to the annealing temperature and then immediately cooling to room temperature, also at a rate of $5\text{ }^{\circ}\text{C}/\text{min}$.

Results and Discussion

Figure 1 shows the spectra of films of PBI and of the polyimide XU 218 in the range of $4000\text{--}400\text{ cm}^{-1}$. Evidence for the existence of specific interactions should be found primarily in the regions of the N-H and carbonyl stretching bands which occur in the vicinity of 3400 and 1700 cm^{-1} , respectively.⁹

The spectrum of PBI shows a series of stretching bands in the $3600\text{--}3000\text{ cm}^{-1}$ range. The peaks at about 3420 and 3065 cm^{-1} can be assigned to N-H and aromatic C-H stretching bands, respectively.⁹ The nature and properties of other bands found in this region are discussed below.

Figure 1 also shows the spectrum of a representative PI, XU 218. Polyimides typically display two sharp bands near 1780 and 1725 cm^{-1} ; the former is always lower in intensity. This pattern is characteristic of cyclic imides,¹⁰ and it has been ascribed to symmetric and asymmetric imide carbonyl vibrations.¹¹ Mixed-mode assignments, analogous to those seen in polyamides, have also been proposed.¹² The low absorbances of polyimides in the N-H stretching region of PBI, and of PBI in the carbonyl region of the PIs, means that a computer subtraction of the pure polymer spectra from that of the blends was not needed in this study to define the locations or shapes of these bands.

Figure 2 shows the IR spectra of PBI and of some representative blends of PBI with XU 218 in the $3500\text{--}3000\text{ cm}^{-1}$ region. The N-H stretching band of PBI at about 3420 cm^{-1} displays a substantial broadening and a displacement to lower frequencies with increasing XU 218 content in the blends, while there is no change in the position of other bands, such as the C-H stretching band near 3065 cm^{-1} . Figure 4A shows that the locations of the N-H stretching band maxima are displaced to lower wavenumbers up to a maximum of about 55 cm^{-1} at about $50\text{ wt } \%$ XU 218, where a plateau value is reached.

Figure 3 shows the spectra in the region of the principal (1725 cm^{-1}) phthalimide carbonyl band for XU 218 and

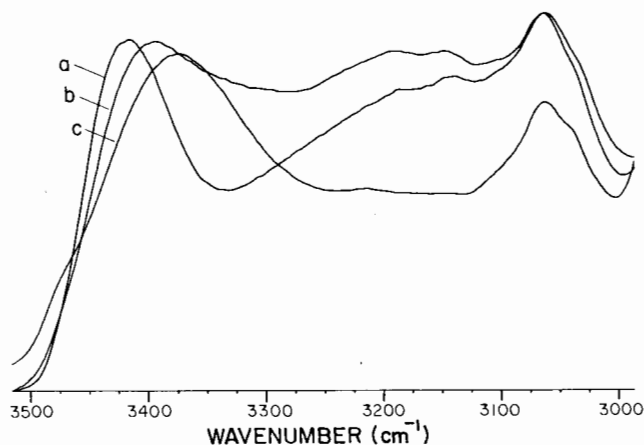


Figure 2. IR spectra of the N-H and C-H stretching region for (a) pure PBI, (b) PBI/XU 218, 70/30 wt % blend, and (c) PBI/XU 218, 30/70 wt % blend.

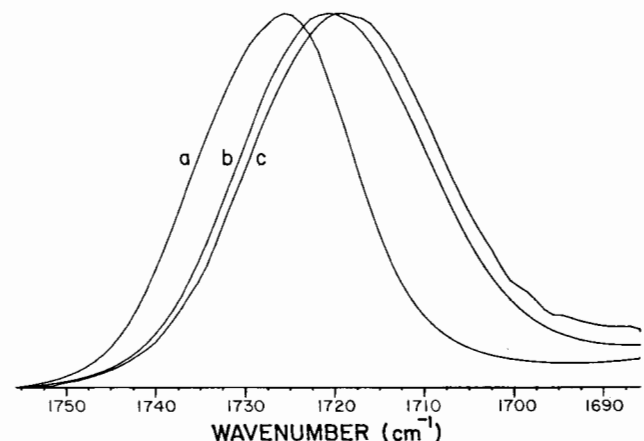


Figure 3. IR spectra of the principal phthalimide carbonyl band for (a) pure XU 218, (b) PBI/XU 218, 70/30 wt % blend, and (c) PBI/XU 218, 90/10 wt % blend.

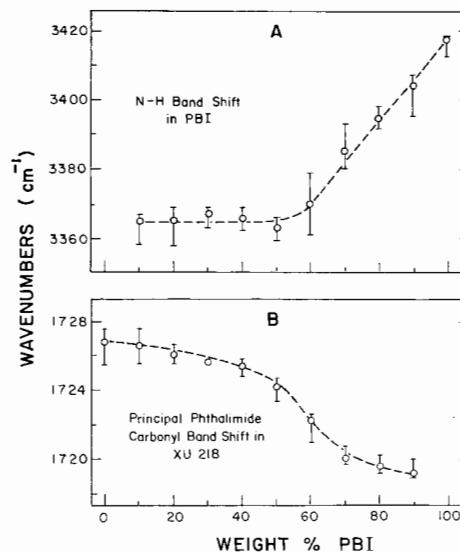


Figure 4. Location of the maxima as a function of blend composition for (a) the N-H stretching band of PBI and (b) the principal phthalimide carbonyl stretching band of XU 218.

for two representative blends of XU 218 with PBI. Figure 4B shows that the maxima of this band are displaced to lower frequencies with increasing PBI content up to a maximum of 6 cm^{-1} . In addition, the width at half-height of the principal phthalimide carbonyl peak increases with

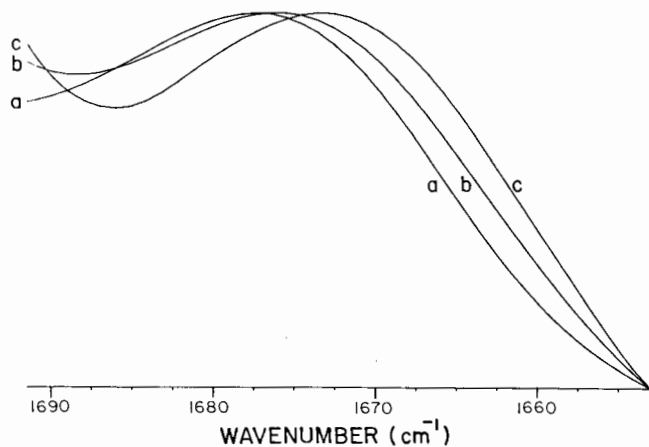


Figure 5. IR spectra of the benzophenone carbonyl band for (a) pure XU 218, (b) PBI/XU 218, 30/70 wt % blend, and (c) PBI/XU 218, 70/30 wt % blend.

increasing PBI content from about 22 to 26 cm^{-1} at about 70 wt % PBI where a plateau value is reached. Well-defined, but smaller, frequency displacements of up to 3–4 cm^{-1} were also observed in the minor (1780 cm^{-1}) phthalimide carbonyl band, as also previously reported for a PBI/Ultem 1000 blend.¹ The carbonyl group in the benzophenone moiety in XU 218 generates an additional band near 1680 cm^{-1} that is close to typical reported values for carbonyls in similar environments.¹³ As shown in Figure 5, blending with PBI also displaces this carbonyl band up to 6 cm^{-1} . The far smaller frequency carbonyl group shifts, compared to those observed in the N–H group, are however of the same order of magnitude as other reported carbonyl shifts in miscible blends.⁴ It may be noted that the carbonyl bands are much sharper than the N–H bands and the error in the evaluation of the position of the maxima is correspondingly smaller (about 1 vs 3 cm^{-1}).

The irreversible phase separation of PBI/Ultem 1000 blends at temperatures above their glass transitions has been described.^{1,2} If the frequency shifts in the spectra of the blends arise as a result of specific interactions between the polyimide and PBI, the displaced bands should return to the positions observed for the pure polymers after phase separation.^{14,15} The presence of well-defined band shifts in both components thus makes it possible to study phase separation over the whole composition range of the system. Measurement of the location of the N–H band of PBI was preferred because of greater sensitivity, but for blends rich in PBI the locations of the carbonyl bands of the polyimide were also measured. For example, Figure 6A shows the spectra of PBI and of a 50/50 wt % PBI/Ultem 1000 blend in the N–H stretching region, and Figure 7A shows the spectra of Ultem 1000 and of a 75/25 wt % PBI/Ultem 1000 blend in the principal phthalimide carbonyl stretching region. The blends display displacements in the positions of the maxima for the N–H and the principal phthalimide carbonyl bands of 30 and 5 cm^{-1} , respectively. These values are similar to those observed for PBI/XU 218 blends of the same composition.

Figures 6B and 7B show the spectra of these blends after annealing at temperatures approaching their T_g 's. The shift for the N–H band in the 50/50 wt % ($T_g \approx 350^\circ\text{C}$) blend was essentially eliminated by heating to 350 $^\circ\text{C}$, and the shift for the carbonyl group in the 75/25 wt % blend ($T_g \approx 390^\circ\text{C}$) was eliminated by heating to 400 $^\circ\text{C}$. These temperatures correspond to the approximate phase separation temperatures and T_g 's of these compositions as determined by DSC measurements.^{1,2}

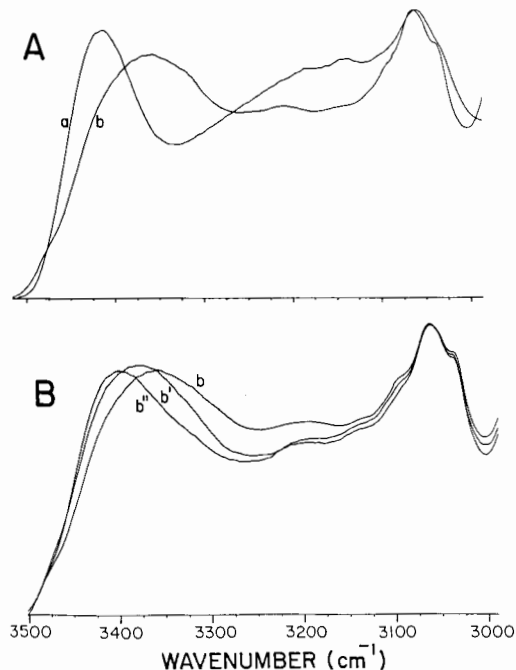


Figure 6. IR spectra of the N–H and C–H stretching bands for (a) pure PBI, (b) PBI/Ultem 1000, 50/50 wt % blend, (b') PBI/Ultem 1000, 50/50 wt % blend after annealing at 300 $^\circ\text{C}$, and (b'') PBI/Ultem 1000, 50/50 wt % blend after annealing at 350 $^\circ\text{C}$.

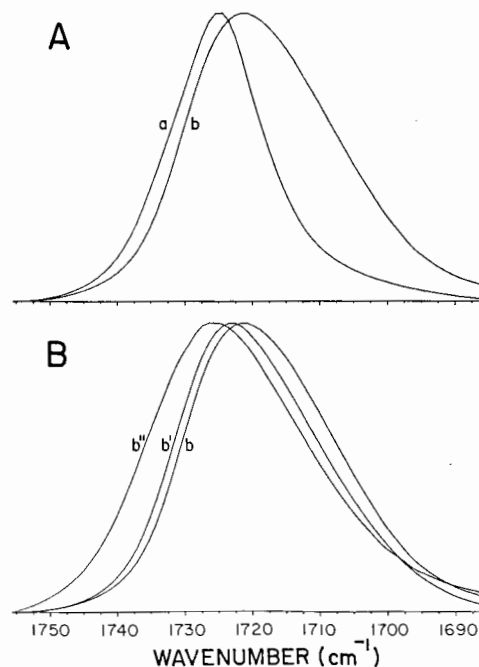


Figure 7. IR spectra of the phthalimide carbonyl band for (a) pure Ultem 1000, (b) PBI/Ultem 1000, 75/25 wt % blend, (b') PBI/Ultem 1000, 75/25 wt % blend after annealing at 350 $^\circ\text{C}$, and (b'') PBI/Ultem 1000, 75/25 wt % blend after annealing at 400 $^\circ\text{C}$.

With the same annealing procedures, there is no change in any portion of the IR spectra of the polymer; in particular there is no shift in the N–H and C=O stretching bands. These results indicate that no major chemical change occurs and that the reversible displacements of the two bands are indeed related to the phase separation phenomena in the blends.

In addition to the N–H stretching band, two other bands that are affected by the blending process are shown in

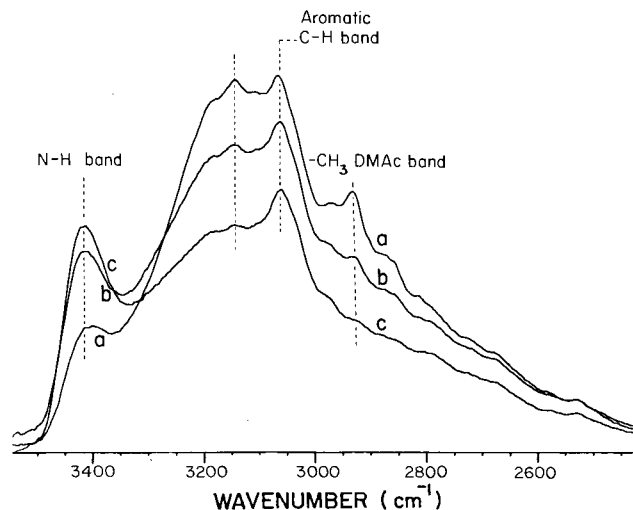


Figure 8. IR spectra in the N-H stretching region of a PBI film cast at 80 °C and then annealed at (a) 180 °C, (b) 300 °C, and (c) 450 °C in order to remove residual DMAc.

Figure 2. We note that the two broad absorptions of PBI, located at about 3190 and 3150 cm^{-1} , diminish in amplitude with respect to the N-H stretching band with increasing XU 218 content. The amplitude of these bands is strongly dependent on the presence of residual solvent as well as on adventitious water. For instance, Figure 8 shows the IR spectra in the 3500–2500 cm^{-1} region of a PBI film containing differing amounts of DMAc. The film was cast at 80 °C from DMAc solution without the usual successive washing in water and then heated to 180 °C (curve a), 300 °C (curve b), and 450 °C (curve c) to incrementally reduce the solvent content of the film from about 15 wt %. This is consistent also with the observed reduction in amplitude of the DMAc CH_3 stretching band at 2940 cm^{-1} . These changes in the IR spectra are reversible; in fact spectra identical to curve a can be again obtained by absorption of DMAc. The 3420 cm^{-1} peak may be identified as an N-H free stretching band, since its amplitude decreases with increasing DMAc content. In contrast the 3150 cm^{-1} peak is consistent with an >N-H hydrogen bonded stretching band, since its amplitude increases with increasing DMAc content. The IR spectra in the 3700–2800 cm^{-1} region of PBI film cast, washed (curve a) and then dried at 200 °C (curve b), as described in the experimental part, are shown in Figure 9. Also in this case the changes are reversible and a spectrum analogous to curve a can be achieved by renewed absorption of water.

Since the amplitude of the bands in the region 3300–3000 cm^{-1} is strongly dependent on the residual amount of solvent and water, it is not surprising that the blending of the polymers, which generally affects solvent absorption, generates changes in the amplitude of these bands.

In summary the changes observed in the N-H region stretching bands of PBI and the presence of shifts in all the carbonyl stretching bands of XU 218 in the spectra of the blends strongly suggests that specific interactions occur between these polymers and that these interactions are related to their miscibility. At least three possible sources of interactions are possible: (a) hydrogen bonding between the carbonyl groups and the >NH groups, (b) π -orbital interaction between the imide and imidazole rings, or (c) a charge-transfer interaction between the phthalimide and

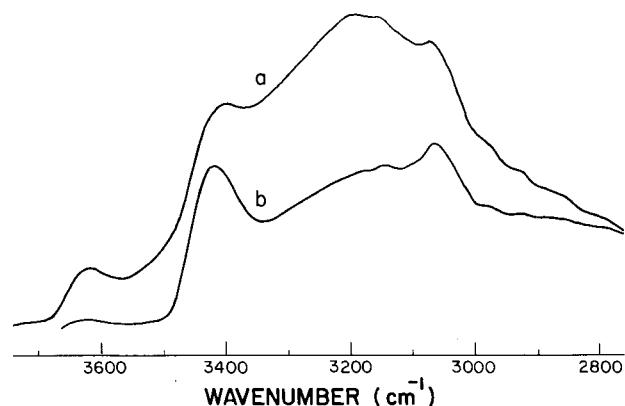


Figure 9. IR spectra in the N-H stretching region of a PBI film cast at 80 °C washed in water for (a) 24 h and (b) then dried under vacuum at 200 °C.

benzimidazole fused-ring systems. Spectroscopic and other studies of model compounds are underway to clarify the precise nature of the contributions to the overall interaction.

Conclusions

Composition-dependent IR spectral shifts of up to 55 cm^{-1} for the N-H stretching band and 6 cm^{-1} for the carbonyl stretching bands of PBI/PI blends have been observed in a number of miscible PBI/PI blends. In one representative system it was observed that these shifts were eliminated upon phase separation. These observations suggest that PBI/PI blend miscibility is related to intermolecular interactions involving the carbonyl and >NH groups in which PBI is the sole source of >NH groups and PI is the sole source of carbonyl groups.

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Registry No. PBI, 25734-65-0; UHem 1000 (SRU), 61128-24-3; UHem 1000 (copolymer), 61128-47-0; XU 218, 62929-02-6.

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