Miscibility in Poly-p-Phenylene Terephthalamide/Nylon 6 and Nylon 66 Molecular Composites

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Synopsis

Miscibility and crystallization of poly-p-phenylene terephthalamide (PPTA)/nylon 6 and nylon 66 composites prepared by coagulation of isotropic ternary sulfuric acid solutions were studied. The apparent crystallinity of nylon 6 and nylon 66 in molecular composites was investigated by differential scanning calorimetry and Fourier transform infrared spectroscopy. The solvation of nylon 6 crystals in PPTA matrix was observed when the PPTA content exceeds 70 wt%. Cross-hydrogen bonding seems to be responsible for the virtual disappearance of nylon 6 crystals. Specific interaction between PPTA and nylon 6 macromolecules and phase separation during thermal treatment has been discussed.

INTRODUCTION

A molecular composite is essentially a mixture of stiff chain and flexible coil macromolecules which is conceptually similar to a fiber-reinforced plastic, except that the reinforcement takes place at a microscopic level.[1-10] The optimum reinforcement can generally be expected if mixing occurs at a molecular level. However, such expectation is difficult to achieve due to the low entropy of mixing and the high tendency of self alignment of the rigid macromolecules.[11] Thus molecular composites may be thermodynamically unstable and undergo phase segregation either during coagulation or thermal treatment. The morphology of such molecular composites depends on the extent of phase segregation which can exert profound effect on the mechanical properties of the system. Prior to processing of molecular composites, understanding the miscibility or the demixing behavior is crucial.

Molecular composites based upon poly-p-phenylene terephthalamide (PPTA) with various flexible matrices, notably polyamides, were first developed by Takayanagi and co-workers.[1,2,6] The authors have demonstrated significant improvement in modulus and tensile strength in the PPTA/nylon 6 system. Another interesting molecular composite system is the mixture of poly-p-phenylene benzobisthiazole (PPBT)/poly 2,5 (6) benzimidazole (ABPBI) prepared by rapid coagulation in water from a homogeneous methane sulfonic acid (MSA) solution. These PPBT-based molecular composites revealed outstanding mechanical performance.[3-5,10]

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In the present study, we focus on the structural characteristics of PPTA-based molecular composites. We choose PPTA as considerable information on this polymer has been accumulated in the literature,[12-27] which includes morphology of Kevlar fiber, lattice defects, effect of coagulation conditions on crystal modification of PPTA, solution properties of PPTA, surface characteristics of Kevlar fibers, etc. The characteristics of PPTA and nylon 6 blends are examined by means of differential scanning calorimetry (DSC) and optical microscopy. The specific interaction between PPTA and nylon 6 molecules is investigated using Fourier transform infrared spectroscopy (FTIR).

EXPERIMENTAL

Materials

Poly-*p*-phenylene terephthalamide (PPTA) in the form of quarter inch fiber (Kevlar) was provided by E. I. Du Pont de Nemours. Nylon 6 was obtained from the Allied Signal Company. Nylon 66 was obtained from the Monsanto Co. The solvent used was 96% sulfuric acid from Fisher Scientific Co.

Preparation of Molecular Composites

Various ratios of Kevlar/nylons were dissolved in H_2SO_4 in an ultrasonic vibration bath at about 40°C. The polymers were dissolved completely within two or three days depending on the composition and/or concentration of polymers.

A drop aliquot of the completely dissolved solution was placed on a spectrophotometer cell with a path length of 0.1 mm, and sealed with Teflon tape to minimize moisture contamination. The solutions were examined in an optical microscope under cross polars. Concentrated solutions exhibited an anisotropic appearance. Varying known amounts of H_2SO_4 were gradually added until the solutions become isotropic.

The concentrations, at which anisotropic–isotropic transition occurred, depend on the composition of PPTA and nylon. The 2.8 wt% solution generally shows an isotropic structure. Coagulation was undertaken by pouring the isotropic ternary solution into distilled water. The solvent power is thereby rapidly decreased, causing the polymer mixture to precipitate. These precipitates were filtered and washed with hot distilled water until the acid was completely removed, then dried under vacuum at 80°C for two days. The precipitates were used in the subsequent characterization studies.

For the optical and infrared spectroscopic studies, thin films were prepared by smearing various PPTA/nylon/H_2SO_4 isotropic solutions on glass slides at room temperature and subsequently dipping in a running water bath. The pH of the water bath was determined to show the absence of sulfuric acid. The films were transferred to a Teflon sheet and dried in an vacuum oven at 80°C. The thickness of these thin films were typically 6–10 μm. The pure nylon films prepared according to the above procedure resulted in a cloudy appearance; thus transparent nylon films were prepared differently by casting from formic acid.

Characterization

Infrared spectra were obtained in the range of 400–4800 cm^{-1} on an IBM IR/32 FTIR spectrophotometer with a nitrogen purge. Five hundred scans at a resolution of 2 cm^{-1} were signal-averaged. All films used in this study were within the range where the Beer-Lambert law is operative.

A Du Pont 9900 Differential Scanning Calorimeter was utilized with a nitrogen purge. Heating and cooling rates were undertaken at 10 and 6°C/min, respectively. Indium was used as the reference substance for temperature calibration.
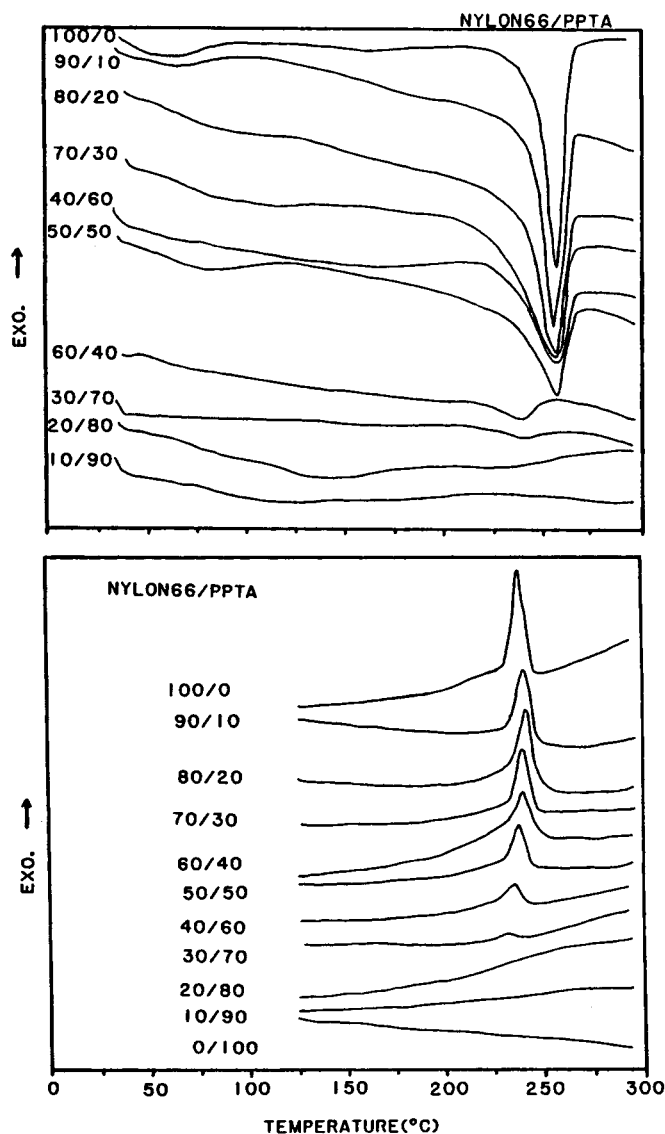

Fig. 1. DSC crystallization exotherms and melting endotherms for various compositions of PPTA/nylon 66.

RESULTS

Optical Microscopy

The thin films of PPTA/nylon used in this study were yellowish, but transparent. Optical microscopic investigations showed no clearcut sign of phase-separated regions. Occasionally, slightly cloudy films were obtained during coagulation. These were found to exhibit interconnected biphase structures, characteristics of spinodal decomposition. These phase separated films were not used in the present study.
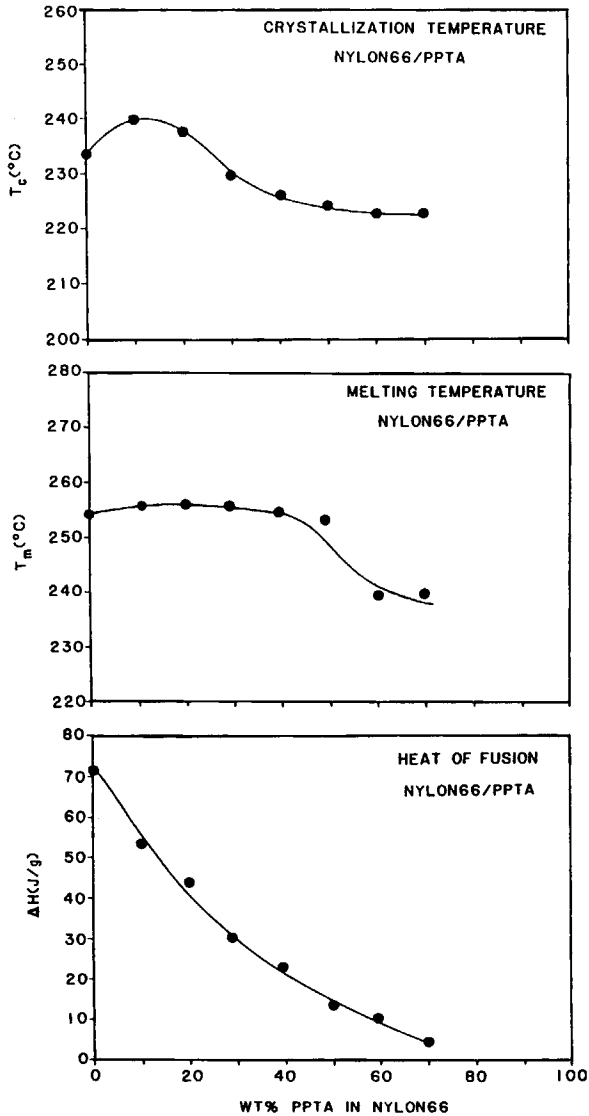

Fig. 2. The variation of T_c, T_m, and ΔH with composition for PPTA/nylon 66.

Differential Scanning Calorimetry

Figure 1 exhibits the crystallization exotherms and the melting endotherms of PPTA/nylon 66 as a function of compositions. Both exotherms and endotherms of pure nylon 66 crystals were clearly seen, but shifted to slightly higher temperatures when a small amount of PPTA was added. When an excessive amount of PPTA were present, that is to say, beyond 10 wt%, this effect was no longer discernible. Instead, melting depression occurs. A similar trend was observed in the case of PPTA/nylon 6 system.

When the PPTA content approaches 70 wt% of PPTA/nylon 66 composites, the melting endotherm (T_m) and the crystallization exotherm (T_c) diminish
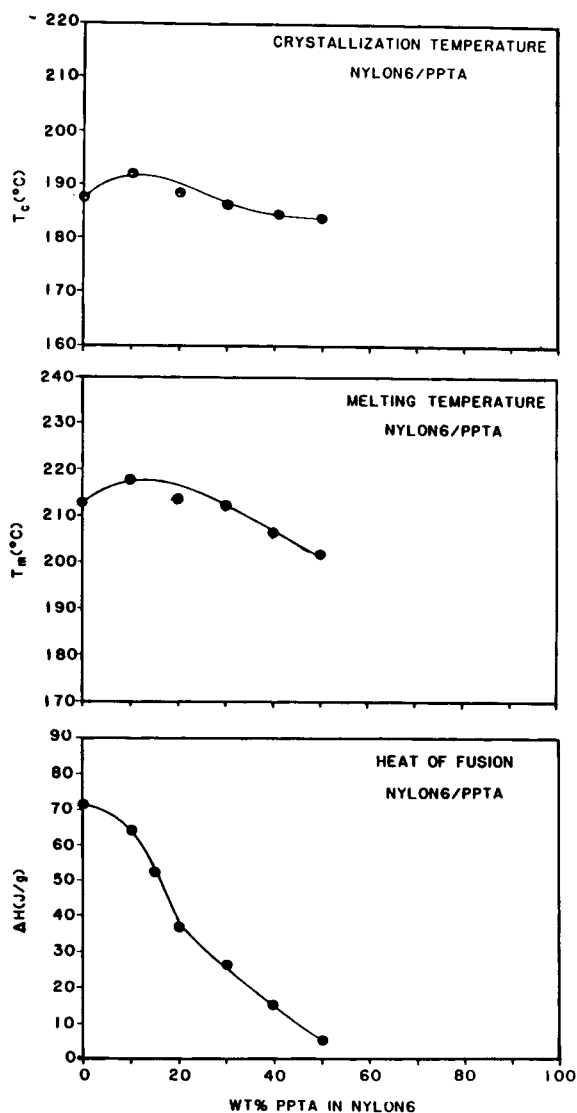

Fig. 3.   The variation of T_c, T_m, and ΔH with composition for PPTA/nylon 6.

and almost disappear. Such behavior is even more prominent with the PPTA/nylon 6 system, in which the T_c and T_m are no longer detectable in the composition in excess of 50 wt%. Figures 2 and 3 illustrate the change in T_c, T_m, and ΔH (heat of fusion) with composition, respectively, for the PPTA/nylon 66 and PPTA/nylon 6 systems.

FTIR

FTIR scans were obtained in the range of 400–4800 cm^{-1} for both PPTA/nylon 66 and PPTA/nylon 6 systems. The characteristic IR bands for PPTA, nylon 66 and nylon 6 are summarized in Table I together with respective band assignments.[28-32]

Figures 4 and 5 exhibit the IR spectra of the symmetric and asymmetric C—H stretching of nylons for the PPTA/nylon 66 and PPTA/nylon 6 composites. In the 2800–3000 cm^{-1} region of C—H stretching, there is no IR absorption of PPTA, thus it is unique to the nylon components. The symmetric and asymmetric C—H stretching bands correspond to the combined crystal and amorphous phases of nylon. A shift of a few wavenumbers (6–9 cm^{-1}) can be noted in the two peaks with composition, suggesting a change of relative contribution from crystalline and amorphous phase.

Another band (929 cm^{-1}) associated with the skeletal vibration of C—H is displayed together with the 2867 cm^{-1} and 2942 cm^{-1} C—H stretching in

TABLE I
Characteristic IR Bands for PPTA, Nylon 6 and Nylon 66

| Band location (cm^{-1}) | | | Assignment |
PPTA	Nylon 6	Nylon 66	(refs. 28 and 29)
523	523	534	Amide 4,6
	579	580	Amide 4,6
	692	692	Amide 5
720*	731	729	CH$_2$ rocking and ring mode
791*			Ring mode
825*			Ring mode
864*			Ring mode
892*			Ring mode
	929	935	Skeletal vibration
1017*			Ring mode
	1171	1180	CH$_2$ twisting or wagging
	1201	1201	CH$_2$ twisting or wagging
1262*	1265	1277	Amide 3, CH$_2$ wagging, and ring mode
	1372	1371	Amide 3 and CH$_2$ wagging
1407*	1417	1417	CH$_2$ scissoring and ring mode
	1464	1441	CH$_2$ scissoring
	1477	1474	CH$_2$ scissoring
1515*			Ring mode
1552	1548	1544	Amide II
1610*			Ring mode
1655	1643	1640	Amide I
	2867	2859	Symmetric C—H stretching
	2942	2936	Asymmetric C—H stretching
3329	3297	3302	N—H stretching
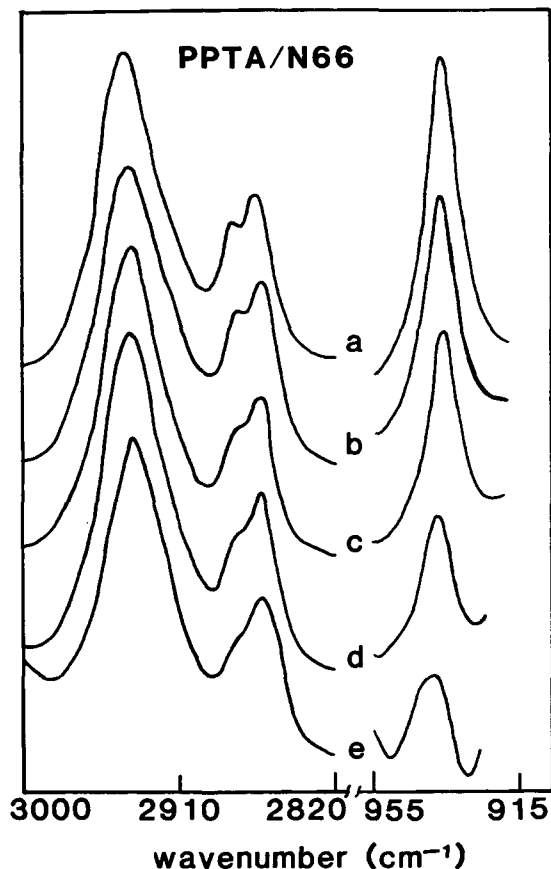
Fig. 4.   Infrared spectra of CH_2 skeletal vibration of nylon 66 crystals and C—H stretching bands corresponding to the combined crystal and amorphous phase of nylon 66 in their composites with PPTA. The composites containing: (a) 10; (b) 30; (c) 50; (d) 70; (e) 90 wt% PPTA.

Figures 4 and 5. According to Schneider et al.,[28] the 929 cm^{-1} band can be exclusively assigned to the nylon 6 crystal. The striking observation here is that this 929 cm^{-1} band is observable up to 50 wt%, but disappeared with further increase of PPTA content. The ratio of absorbance of crystalline band with respect to that of the combined contribution of crystalline and amorphous bands are shown in Figure 6. The crystalline band vanishes when the PPTA content exceeds 70 wt%. In the case PPTA/nylon 66, the crystalline band (935 cm^{-1})[30-32] clearly exists even up to 90 wt% PPTA.

Figures 7 and 8 exhibit the IR spectra corresponding to amide I and II (1600–1800 cm^{-1}) and N—H stretching (3100–3580 cm^{-1}) regions, respectively, for PPTA/nylon 66 and PPTA/nylon 6 systems. The amide I and II bands of pure PPTA are located at 1655 and 1552 cm^{-1}, while those of pure nylon 66 are centered at 1643 and 1548 cm^{-1}. The intermediate compositions exhibit respective peaks intermediate between the pure components. These bands appear to shift by a few wavenumbers. Because of the proximity of the two peaks and considerable noise level, no detailed analysis is warranted. The
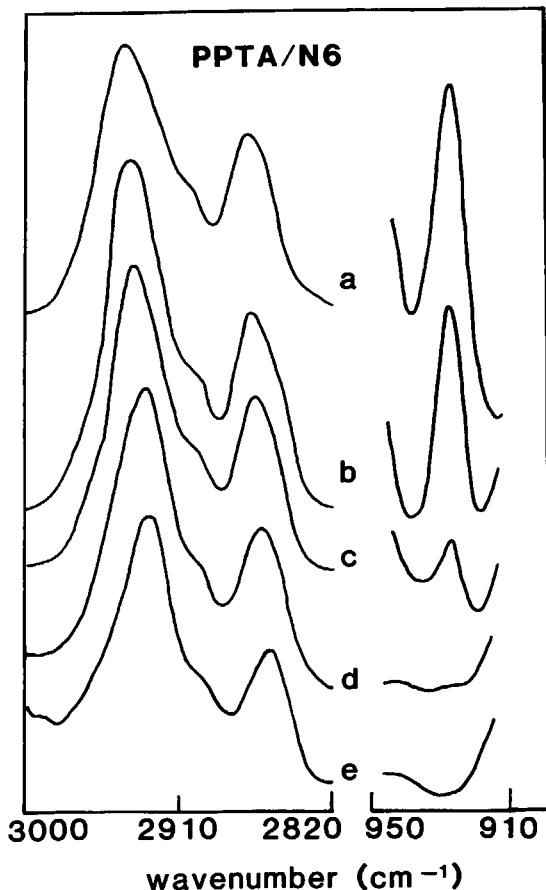
Fig. 5. Infrared spectra of CH_2 skeletal vibration of nylon 6 crystals and C—H stretching bands corresponding to the combined crystal and amorphous phase of nylon 6 in their composites with PPTA. The composites containing: (a) 10; (b) 30; (c) 50; (d) 70; (e) 90 wt% PPTA.

IR signal is more stable in the region where N—H stretching is observed. The N—H stretching peak of PPTA is located 30 cm^{-1} higher than that of nylon 66 or nylon 6. The intermediate composition shows a slight movement at low PPTA content, which becomes more appreciable at large PPTA content. A similar trend has been observed with PPTA/nylon 6.

DISCUSSION

Let us first turn our attention to the DSC studies. The shifting of the crystallization exotherms and melting endotherms to slightly higher temperatures is of interest. This observation is consistent with that of Takayanagi and co-workers,[2] who attributed this to the enhanced crystallization of nylon. It seems PPTA acts as a nucleus, thereby expediting the rate of crystallization (or nucleation) of nylon crystals.

The most striking DSC observation is the virtual disappearance of nylon 6 crystals in the PPTA/nylon system. A substantial amount of nylon 6, specifically 50 wt%, was present in these systems. It is interesting to point out that
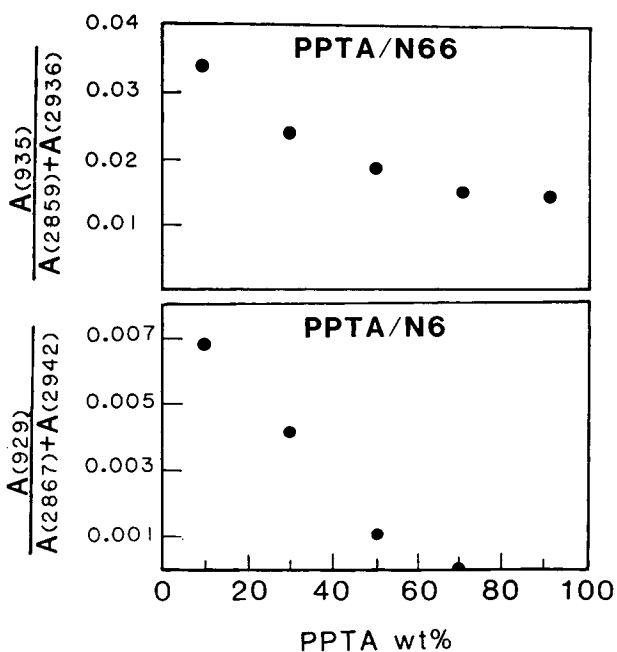
Fig. 6. The ratio of crystalline band absorbance to the combined crystal and amorphous band absorbance with composition for PPTA/nylon 66 and PPTA/nylon 6 composites.
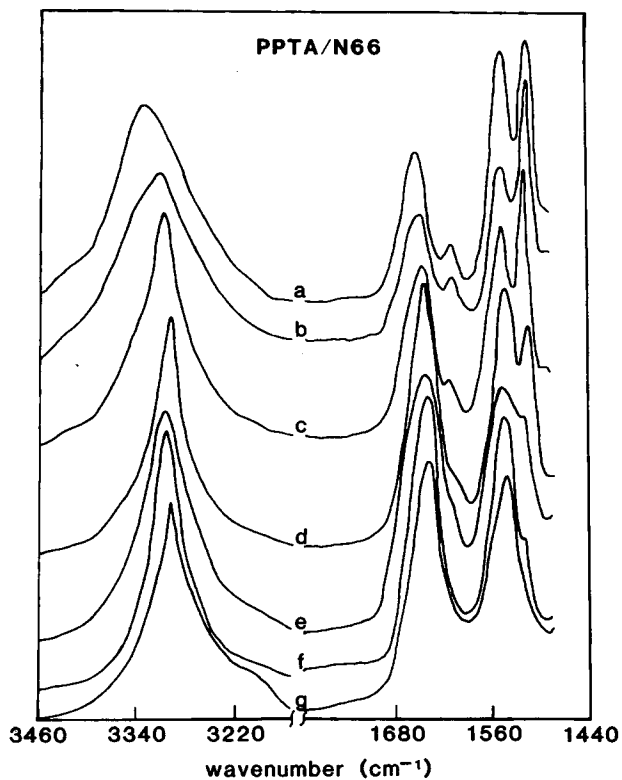

Fig. 7. FTIR spectra in the regions of amide I and amide II (1500–1700 cm^{-1}) and N—H stretching (3300 cm^{-1}) of PPTA/nylon 66. The composites containing: (a) 100; (b) 90; (c) 70; (d) 50; (e) 30; (f) 10; (g) 0 wt% PPTA.
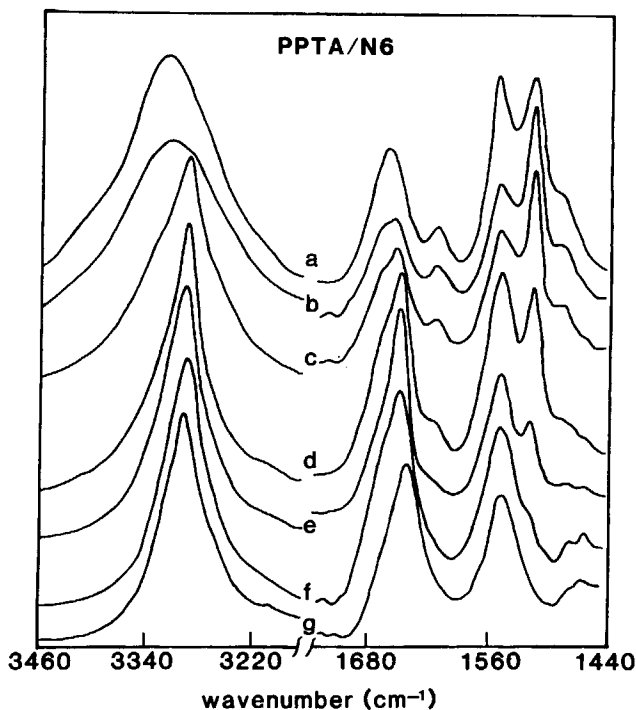
Fig. 8. FTIR spectra in the regions of amide I and amide II (1500–1700 cm^{-1}) and N—H stretching (3300 cm^{-1}) of PPTA/nylon 6. The composites containing: (a) 100; (b) 90; (c) 70; (d) 50; (e) 30; (f) 10; (g) 0 wt% PPTA.

T_m and T_c have been clearly observed in our laboratories in a 90/10 composition of PPTA/nylon 11 and PPTA/nylon 12 systems.[33]

The contrasting behavior of PPTA/nylon 6 and PPTA/nylon 66 may be associated with the differences in the crystallization rate of nylon 6 and nylon 66, that is, the thermal crystallization of nylon 66 is significantly faster than that of nylon 6.[34,35] This may be important in the coagulation process, although one should not directly translate the behavior of thermal-induced crystallization to that in the solution.

At present, it is unclear how PPTA perturbs the crystallization of nylons. It is well documented that hydrogen bonding plays an important role in the crystallization of nylon crystals as well as of PPTA crystals.[14,36,37] When these materials were coprecipitated together, there is a high probability of cross-hydrogen bonding between PPTA and polyamide chains, thereby mutually interfering with their crystallization behavior. If such cross-hydrogen bonding were strong and the rate of crystallization were slow, as in the case of nylon 6, there is a possibility that nylon 6 crystals will dissolve completely in the PPTA continuum. In the case of fast crystallization such as nylon 66, self-association prevails, thus crystallization may occur in nylon 66 even when its content may be less. It seems that cross-hydrogen bonding is important not only in the crystallization process, but also can be important for miscibility enhancement in PPTA/nylon composites.
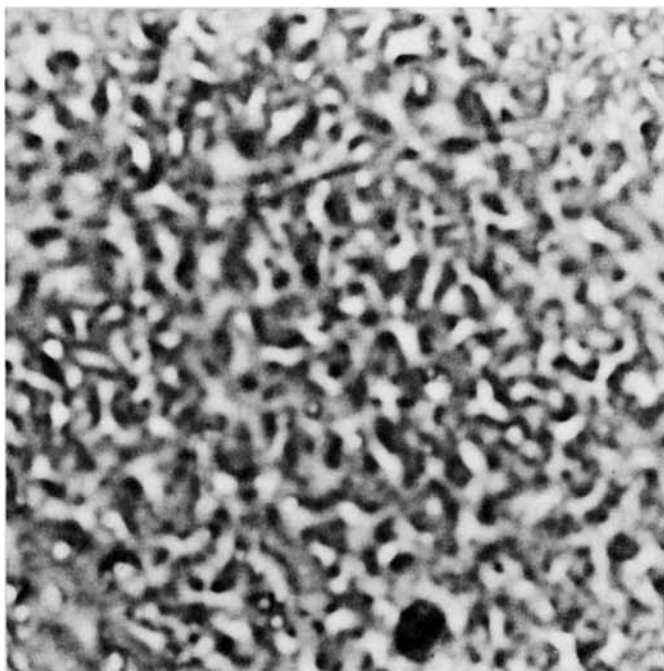
30 µm   240°C

Fig. 9.   Optical micrograph of 30/70 PPTA/nylon 6 annealed at 240°C for 5 min, exhibiting biphase structure.

We now turn to the FTIR observations. The shifts of the amide I, II, and N — H stretching must surely be attributed to the CO...NH hydrogen bonding between PPTA and nylon molecules. The above observation is, by no means, conclusive because hydrogen bonding is expected to occur between pure PPTA/PPTA or nylon/nylon molecules. Since both PPTA and nylons are semicrystalline polymers, the changing crystallinity with composition, in principle, can cause some movement of the peaks. To see the specific interaction between the PPTA and nylon, the 30/70 PPTA/nylon 6 was heated above the melting temperature (240°C) for 5 min. The optical microscopic investigation revealed the interconnected biphase structure characteristic of spinodal decomposition as shown in Figure 9. The IR spectra of the heat-treated 30/70 and 70/30 PPTA/nylon 6 showed the splitting of N — H stretching band. As can be seen in Figure 10, the pure PPTA or nylon 6, which were annealed under the same condition (240°C for 5 min), showed only a single peak. This strongly suggests that thermal-induced phase separation has occurred. In other words, the development of a single peak in unheated PPTA/nylon 6 blends may be suggestive of enhanced miscibility presumably due to hydrogen bonding between PPTA and nylon 6 molecules.

Thermal-induced phase separation in rod/coil systems appears to be a general phenomenon. Recently, Chuah et al.[38] observed thermal-induced phase separation in PPBT/nylon 66 molecular composites with a miscibility window
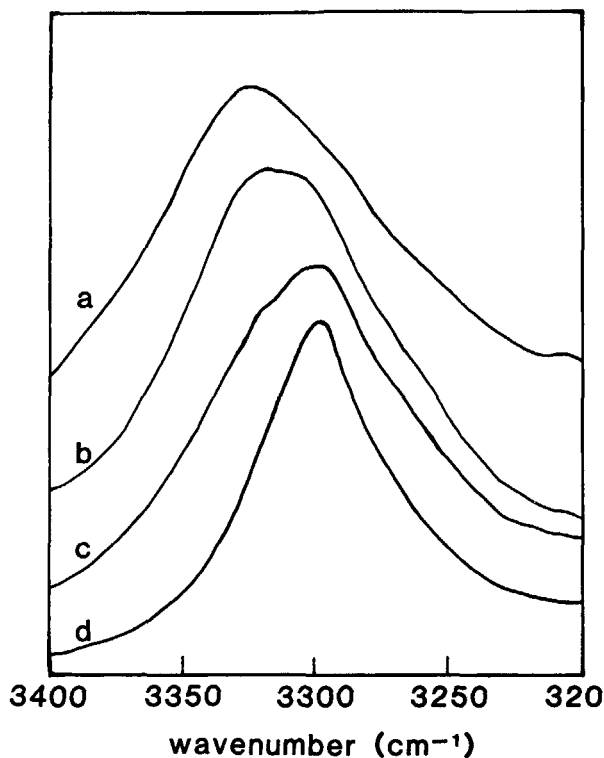
Fig. 10. FTIR spectra in the regions of N—H stretching for various compositions of PPTA/nylon 6 after annealing at 240°C for 5 min. The composites containing: (a) 100; (b) 70; (c) 30; (d) 0 wt% PPTA.

reminiscent of an LCST (lower critical solution temperature). Nakai et al.[39] recently reported that thermotropic liquid crystalline copolyester (PHB-PET) and polyethylene terephthalate (PET) exhibit thermally induced phase separation above the crystal melting temperature of PET phase. A similar observation was also made by Kyu and Zhuang[40] with the PHB-PET/polycarbonate (PC) system exhibiting a cloud point phase diagram similar to an LCST.

CONCLUSIONS

We observed that nylon 6 crystals virtually dissolve in PPTA matrix when PPTA content exceeds 70 wt%. This has been attributed to the interruption associated with the cross-hydrogen bonding between PPTA and nylon 6 crystals. Miscibility enhancement takes place due to hydrogen bonding between amorphous PPTA and nylon 6, but the composites phase separate during thermal treatment above the melting temperature of nylon.

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