Molecular Composites via *In Situ* Polymerization: Poly(Phenylene Terephthalamide)–Nylon 3

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Synopsis

All-polyamide molecular level composites composed of rigid rod and flexible coil polymers were prepared using an *in situ* polymerization process in which the anion of the rigid rod poly-(phenylene terephthalamide) (PPTA) was used as the initiator for the anionic polymerization of acrylamide to form the nylon 3 matrix. The rigid aramid component then serves as the reinforcing agent. This polymerization resulted in both graft and homo-nylon 3 formation. Composite films prepared using *in situ* processing showed greatly improved strength and modulus over unmodified nylon 3 with no loss of flexibility. The composites showed aggregation and phase separation of PPTA fibrils at PPTA weight fractions of > 30% as indicated by wide angle X-ray scattering and electron microscopic analysis. The structure of the PPTA formed is that produced from swelled liquid crystalline solutions, indicating that the *in situ* process involves polymerization in the liquid crystalline state.

INTRODUCTION

A new concept recently introduced in composite materials and polymer science is that of the molecular composite.[1-10] This concept is based on a composite material made up of rigid rod and flexible coil polymer molecules in which the reinforcing rigid rod polymer is dispersed at the molecular level in the flexible coil matrix. Composites formed from high temperature polymers useful as aerospace structures have been described by Helminiak and co-workers,[1-3] and Takayanagi has reported on composites of more conventional polymers with aramid reinforcing polymers.[4-10] The properties of aliphatic polyamides nylon 6 and nylon 66 molecularly reinforced with poly(phenylene terephthalamide) (PPTA) have been described in detail by Takayanagi.[4-7] These composites were prepared by coagulation of isotropic ternary sulfuric acid solutions of these polymers followed by compression molding above the nylon melting point to form the composites. The PPTA was found to be present as microfibrils with diameters of 10–30 nm. PPTA was shown to induce crystallization of nylon 6 by a nucleation type mechanism, and this was used to explain the increased crystallinity of the nylon in the composite and the excellent transfer of the PPTA modulus in the composite.

This coagulation approach has a number of drawbacks which reduce its utility. Many polymers are degraded by the strong acid solvents required to dissolve rigid rod polymers, and some will not form the compatible ternary solutions required for successful coagulation processing. Coagulation processing of rigid rod polymers has been shown to lead to the formation of undesirable morphologies such as skin-core structures which have been implicated in the

poor compressive properties of Kevlar fiber reinforced composites. Failure is attributed to the formation of kink defects under compressive stress.[11,12]

An alternative to coagulation processing is an *in situ* polymerization process, in which a solution containing a rigid rod polymer and a monomer is polymerized. The polymerization of monomer-containing liquid crystalline solutions of rigid rod polypeptides and poly isocyanates has been described.[13-16] This paper will discuss the preparation of molecular composites based on an *in situ* polymerization process which uses the rigid rod polymer as both the polymerization initiator and the reinforcing agent.

EXPERIMENTAL

Materials

PPTA was obtained from DuPont in the form of Kevlar pulp. The intrinsic viscosity in 96% sulfuric acid solution was 6.0 dL/g, which represents a viscosity average molecular weight of 29,700 as calculated using the Mark–Houwink parameters given by Arpin and Strazielle.[17] The polymer was dried *in vacuo* at 60°C prior to use. Monomer grade acrylamide obtained from Aldrich was recrystallized from acetone. Dimethylsulfoxide was distilled over calcium hydride prior to use. Sodium hydride was used as a 50% dispersion in oil (Alfa).

Polymerization

PPTA dissolution was accomplished using the procedure of Takayanagi and Katayose.[8] Dimethylsulfoxide (DMSO) (450 g) was charged to a 500-mL three-necked round-bottom flask equipped with a nitrogen inlet, thermometer, and mechanical stirrer. After thorough sparging with nitrogen, 1.82 g (0.038 mol) of sodium hydride was added, and the mixture was heated to 75°C for a period of 1 h. After the sodium hydride dissolved completely, the reaction was cooled to 40°C, and 4.50 g (0.038 mol) of PPTA was added. The solution was stirred for a period of 4 h, during which time the solution took on a deep red color and became extremely viscous as the PPTA dissolved. A sample of the polymer which was precipitated into water after dissolution, dried, and redissolved in sulfuric acid exhibited an inherent viscosity of 10.4 dL/g compared to 10.7 dL/g for the native Kevlar pulp, indicating that the dissolution process, if carried out at sufficiently low temperatures, does not cause degradation of the PPTA. In a typical polymerization reaction, 95.12 g of the PPTA solution, 3.75 g of acrylamide, and 0.01 g of N-phenyl-2-napthylamine were charged to a 250-mL round bottom vacuum flask, and evacuated to 0.05 mm Hg on a rotary evaporator apparatus. The flask was heated gradually to 50°C, at which point the DMSO began to distill. After 1 h at 50–60°C, the temperature was raised to 110°C, and the reaction was continued for 16 h.

The resulting polymer was a clear, tough film which was evenly deposited on the walls of the flask. The polymer was extracted for 48 h with methanol, washed with three additional aliquots of methanol, and dried at 60°C for 24 h *in vacuo*. The yield was 4.46 g, 95.1% of theoretical. The resulting polymer was extracted with 88% formic acid for 48 h at slightly elevated temperature

TABLE I
Compositional Data for PPTA/Nylon 3 Graft Polymers

PPTA (wt %)	Yield (%)	Graft[a] (%)	Graft[b] (%)	Graft[c] (%)	Graft efficency (%)
5	91.7	64.6	—	—	10.5
9.52	—	58.6	64.3	60.6	15.0
10	91.1	47.8	55.7	56.2	11.3
20	95.1	36.4	27.7	38.1	15.3
30	90.2	21.2	22.2	21.7	13.3
40	89.6	16.6	13.0	12.5	15.9
50	88.0	14.2	13.0	12.7	21.7

[a] Determined by extraction.
[b] Determined by proton NMR.
[c] Determined by weight loss (TGA).

(40–50°C), and washed with three additional aliq ots of formic acid. The formic acid solution was partially evaporated unuer vacuum, and the concentrated solution precipitated into methanol. Both fractions were thoroughly washed with methanol and dried *in vacuo* for 24 h. Yields of soluble and insoluble polymer were 2.91 and 1.45 g, respectively. Recovery of the fractions from this procedure was typically 93–95%. The percent grafting and grafting efficiency were calculated as shown:

$$\% \text{ grafting} = \frac{\text{wt formic insoluble} - \text{wt PPTA added}}{\text{wt formic insoluble}}$$

$$\text{graft efficiency} = \frac{\text{wt formic insoluble} - \text{wt PPTA added}}{\text{total wt} - \text{wt PPTA added}}$$

The graft polymer composition was also determined using ^{1}H-NMR spectroscopy and TGA analysis of weight loss. The results for compositional analysis for copolymers varying in the range 15–65% graft polymer are shown in Table I.

In order to form a composite film suitable for mechanical testing, the PPTA anion–acrylamide solution was cast in a 9 cm diameter flat steel dish which was previously coated with Fluoro Glide CP mold release. The dish was carefully leveled in the bottom of a large sublimator, which was then subjected to a heating/vacuum cycle similar to that described above. The film was then extracted with methanol, cut into strips, and dried *in vacuo* at 60°C between Teflon sheets to prevent curling.

Characterization

Proton NMR spectra were obtained on a Bruker AM-300 at 300 MHz in H_2SO_4 solution. Carbon 13 NMR spectra were obtained on a JEOL FX90Q operating at 19.95 MHz. DSC, TGA, and DMA were performed on a DuPont 910 DSC with a heating rate of 10°C/min, a 951 TGA with a heating rate of 20°C/min, and a 982 DMA with a heating rate of 5°C/min and oscillation amplitude of 0.05 mm; all units were interfaced to a DuPont 9900 data

station. Tensile testing was done on an Instron Table Model 1130 at a strain rate of 25%/min. WAXS data were obtained on a Phillips Model 1720 X-ray generator with Nickel-filtered CuK radiation at a sample to film distance of 5.00 cm. FTIR spectra were obtained directly on thin polymer films with a Nicolet 5DX FTIR spectrometer. Optical micrographs were obtained with a Leitz Orthoplan POL light microscope. Scanning electron micrographs were obtained with an AMR-1000A on samples sputter-coated with gold to prevent charging. Solution viscosities were determined at 25°C with a Cannon-Fenske #200 or #100 viscometer.

RESULTS AND DISCUSSION

Polymerization of Acrylamide Initiated with PPTA Anion

The anionic polymerization of acrylamide to form nylon 3 [poly(β-alanine)] was originally described by Breslow et al. in 1957.[18] The polymerization is described as occurring through a hydrogen transfer mechanism, in which the propagating anion is transferred from the α-carbon of the chain end to the amide nitrogen through a proton shift.[18-24] The question of the initiation mechanism has remained something of an enigma, however. This question has had particular significance in the case of grafting reactions, as the initiation mode assumes great importance in these situations. The anionically initiated graft polymerization of acrylamide has been studied for systems utilizing cellulose and poly(vinyl alcohol),[25] polyoxyethylene,[26] rayon,[27] and carbon black.[28] For the first three systems mentioned, no grafting of nylon 3 was observed. In the latter two cases, limited grafting in terms of overall weight gain was reported. The importance of initiation mechanism in these cases can be appreciated most readily by noting the two proposed pathways for the initiation of anionic acrylamide polymerization. As pointed out by Breslow et al., polymerization may proceed by either Michael attack of the initiator species (strong base such as tertiary butoxide) on the acrylamide double bond directly, or by proton abstraction of an acrylamide amide proton by the base. In either case, propagation involves sequential Michael addition of the acrylamide units and intramolecular hydrogen transfers.

In the case of graft polymerizations initiated by an anion attached to a polymer backbone, the mechanism of initiation will be vital in determining the ultimate copolymer structure. A recent evaluation of the anionic polymerization of acrylamide indicated that both base strength and steric factors are important in determining the mechanism of initiation.[29] The two possible initiation modes for the anionic polymerization of acrylamide initiated by PPTA anion are shown in Figure 1. While the basicity of the two amide groups should not be significantly different, the steric hindrance for the acrylamide being attacked by the PPTA chain should be significantly greater than that for the proton abstraction. The relationship between graft efficiency and PPTA anion concentration is given in Figure 2. The graft efficiency is seen to increase slightly with increasing mol % anion, but the low efficiencies indicate a preference for homopolymer formation. The correlation between the graft efficiency and mol % PPTA anion is not high ($R^2 = 70.15\%$) but is statistically significant at the 95% confidence limit.
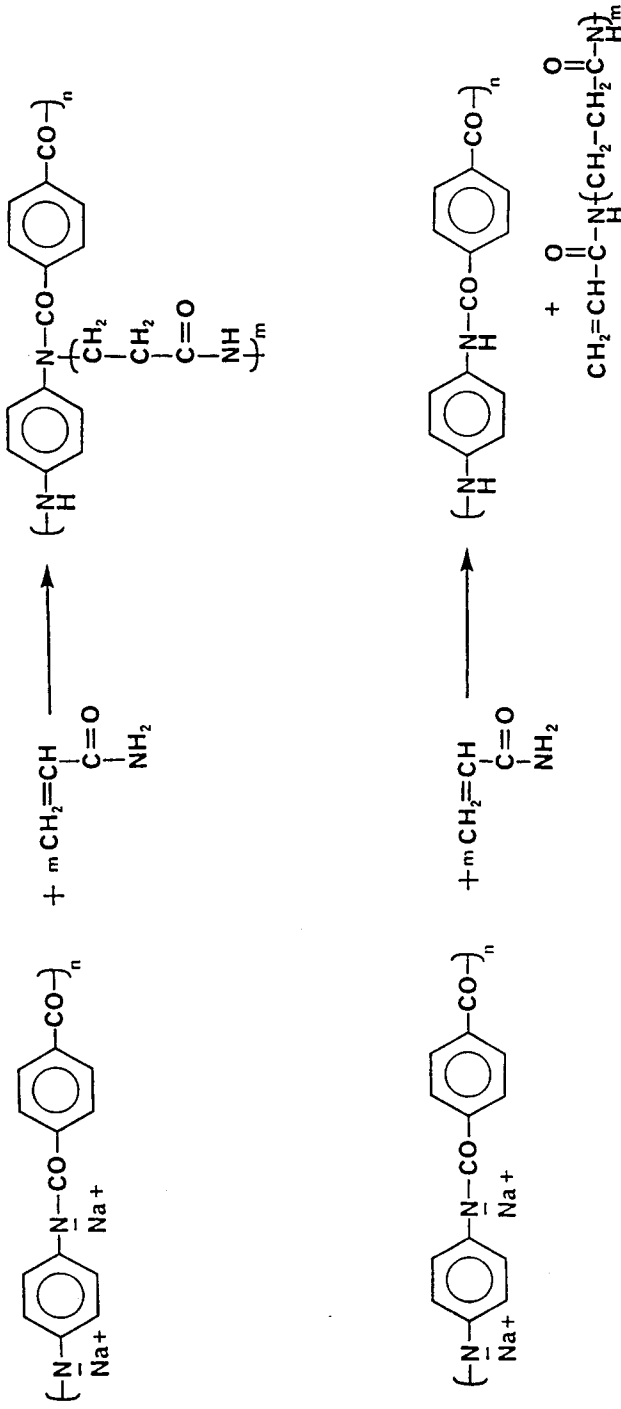
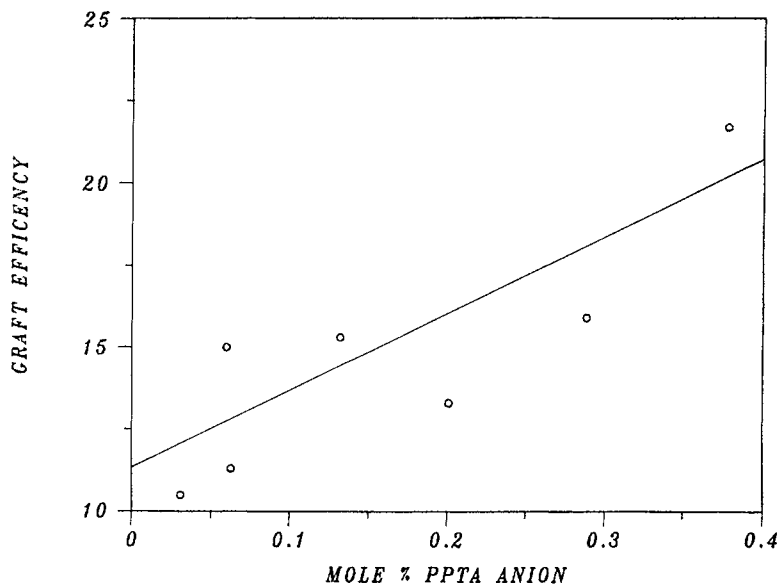Fig. 1. Initiation of anionic polymerization of acrylamide by PPTA anion.

Fig. 2.   Graft efficiency vs. mol % PPTA anion.

The structure of the graft polymer is that of the desired poly(β-alanine) and not poly acrylamide as can be seen from the ^{13}C- and ^{1}H-NMR, shown in Figures 3 and 4, respectively. Chemical shifts for the α and β carbons and protons agree with those reported in the literature.[26,30] The effect of the initiator concentration on the percent grafting and inherent viscosity of the
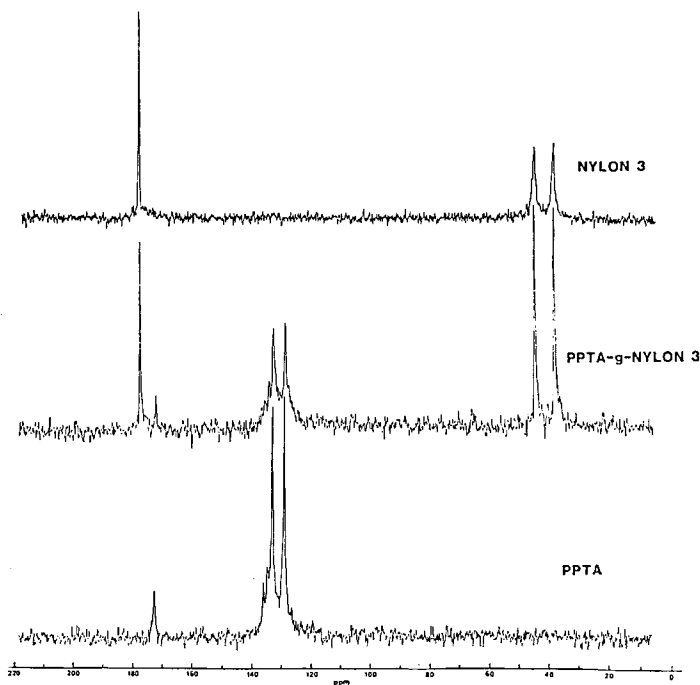
Fig. 3. ^{13}C-NMR spectrum of PPTA-g-nylon 3.
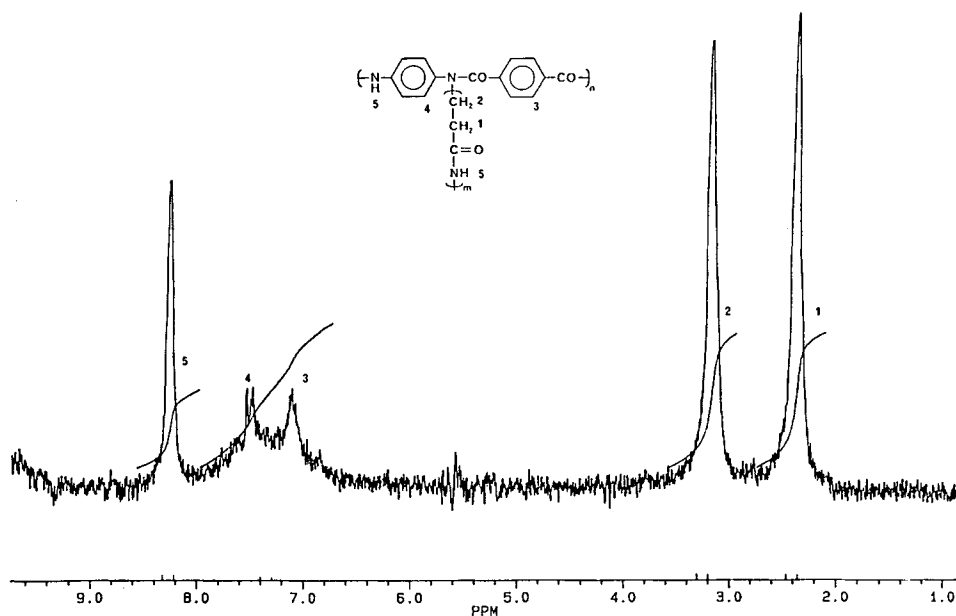
Fig. 4. ^{1}H-NMR spectrum of PPTA-g-nylon 3.
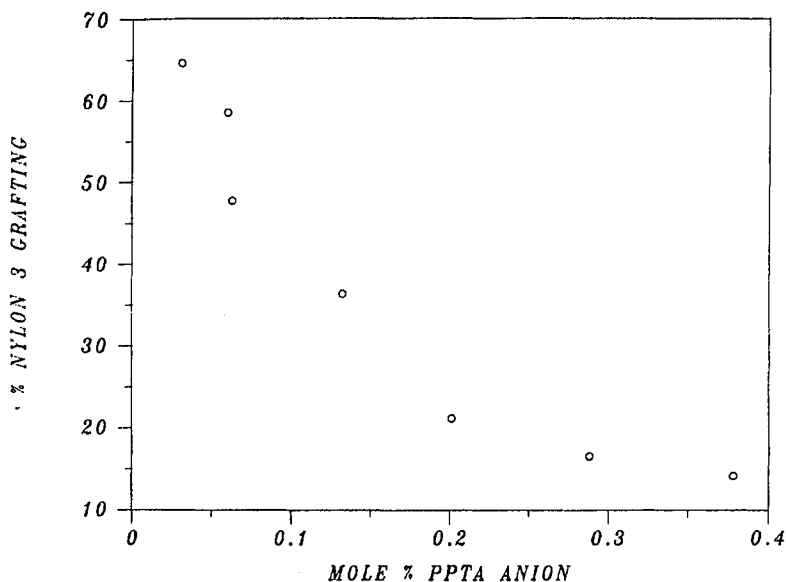
Fig. 5. Percent grafting vs. mol % PPTA anion.

nylon 3 homopolymer is shown in Figures 5 and 6. The trend in these curves is very similar, and indicates a decrease in percentage grafting and homopolymer viscosity with increasing mol % PPTA anion initiator. This indicates an increased length of the graft chain with decreasing initiator concentration, which is normally observed in anionic polymerizations.

The effect of percent grafting on the viscosity of the graft polymer is seen in Figure 7. The increased amount of graft nylon 3 polymer on the PPTA has the
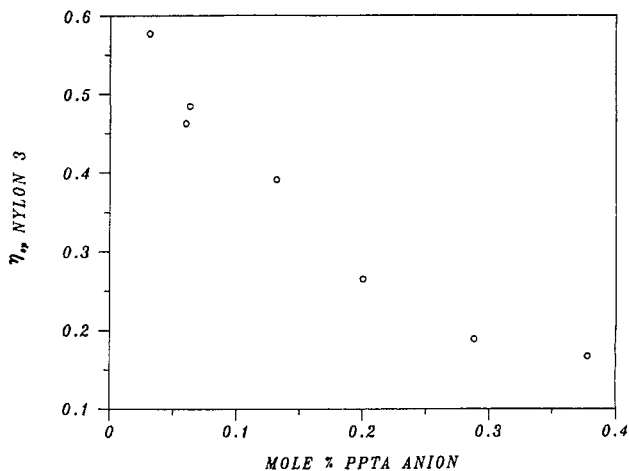
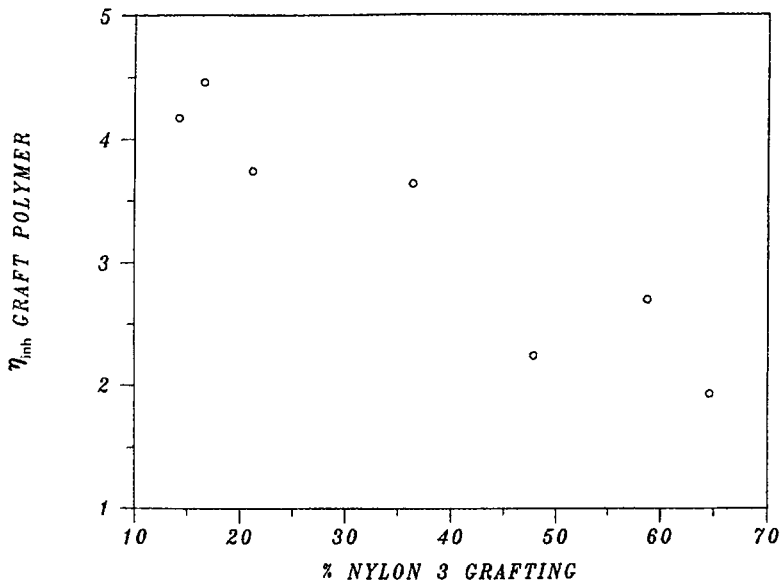Fig. 6. Nylon 3 homopolymer inherent viscosity vs. mol % PPTA anion.

Fig. 7. Graft polymer inherent viscosity vs. percent grafting.

effect of lowering the viscosity of the graft polymer, due to the total co-
polymer assuming a less rigid configuration in solution. The grafting reaction
does not appreciably alter the solubility of the graft polymers, however, as the
polymers were found to be insoluble in nylon 3 solvents such as formic acid,
m-cresol, dimethylacetamide containing lithium chloride, and trifluoroethanol,
but were soluble in sulfuric acid, a common solvent for PPTA and nylon 3.

Composite Characterization

Optical micrographs taken under polarized light of composite films contain-
ing 10 and 50 wt % PPTA are shown in Figures 8 and 9. The 10 wt %
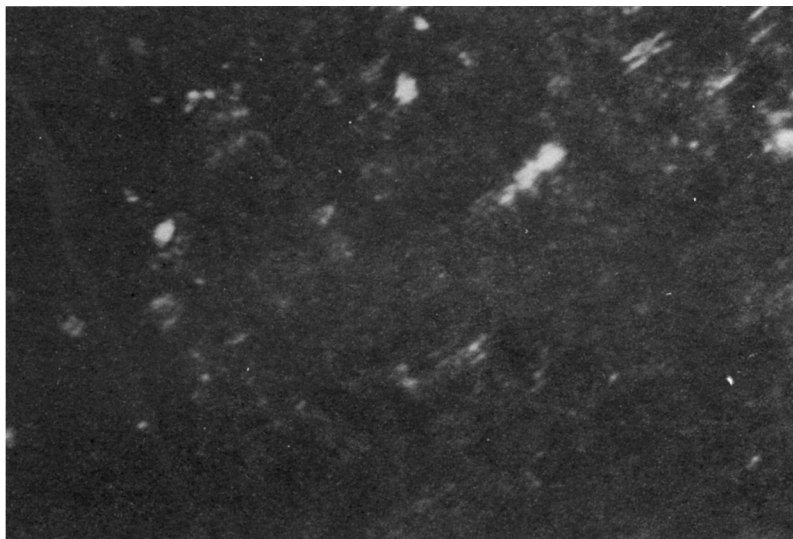composite shows a homogeneous birefringent character with small areas of

Fig. 8. Optical micrograph of a composite film containing 10 wt % PPTA.
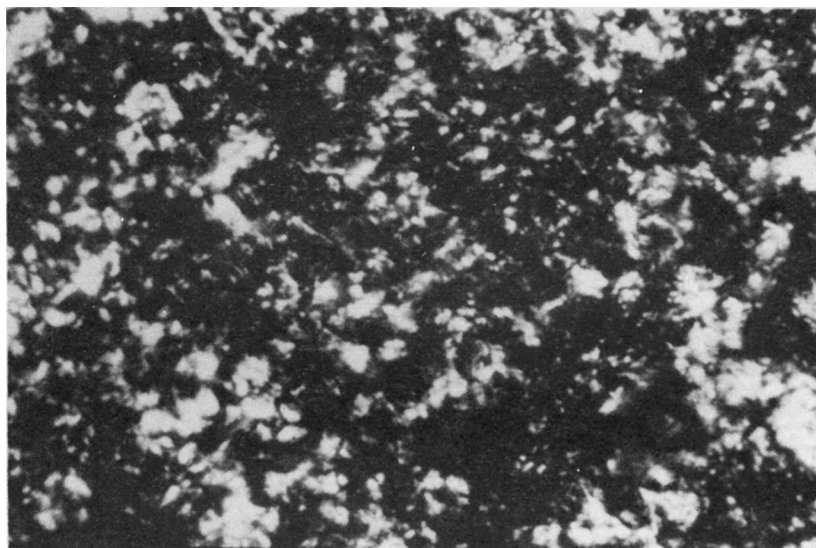

Fig. 9. Optical micrograph of a composite film containing 50 wt % PPTA.

threadlike streaks permeating the material. The 50 wt % sample shows a greater amount of localized, brightly colored domains with the appearance of some large spherulites. The homogeneity of the low weight percentage composites is indication of the excellent dispersion of the PPTA in the nylon 3 matrix. In the case of composites prepared using coagulation techniques, the coprecipitation of PPTA and nylon 3 solutions from sulfuric acid solutions did not lead to homogeneous films, due in part to the incompatibility of these two polymers in solution. Optical micrographs of these samples showed only localized areas of birefringence due to the PPTA.
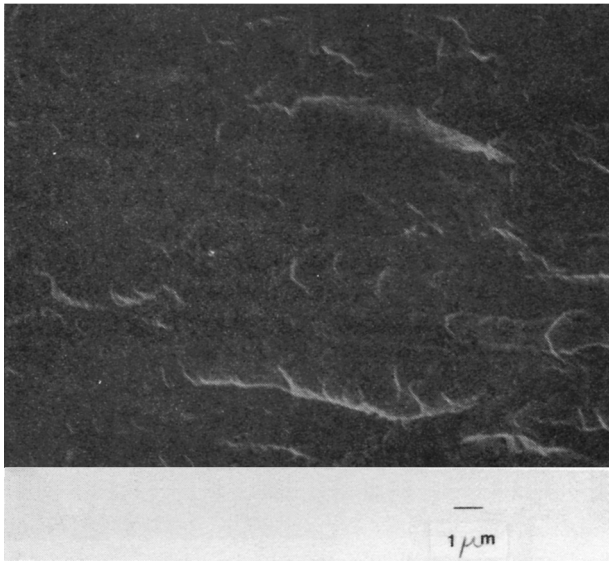
Fig. 10.   SEM of a fracture surface of a composite film containing 20 wt % PPTA.

Solutions of PPTA anion and acrylamide which were examined after solvent removal and prior to polymerization showed a nematic liquid crystalline texture in which a highly colored birefringent background was permeated by black threads. For low levels (< 30% PPTA), heating the solution to the polymerization temperature of 110°C caused this texture to disappear, and the homogeneous texture of the composite to form. In the case of higher levels of PPTA, the liquid crystalline texture persisted during the polymerization.

The effect of polymerization in either liquid crystalline solution or in homogeneous solution on the composite morphology could be seen in electron micrographs of the composite fracture surfaces. Figures 10 and 11 show
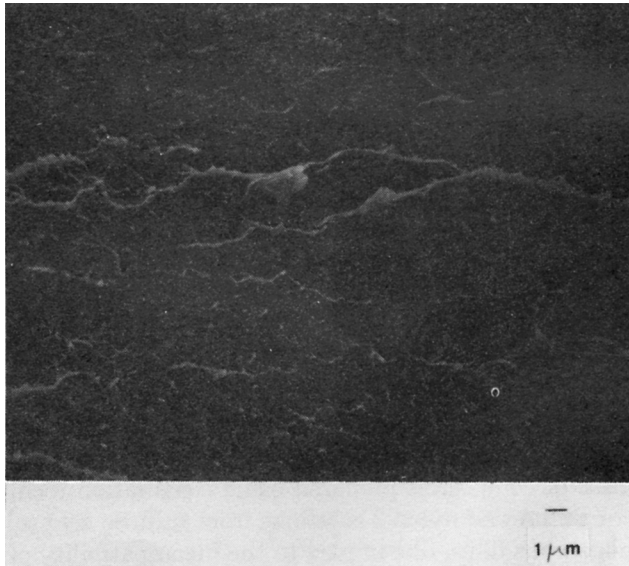

Fig. 11.   SEM of a fracture surface of a composite film containing 30 wt % PPTA.
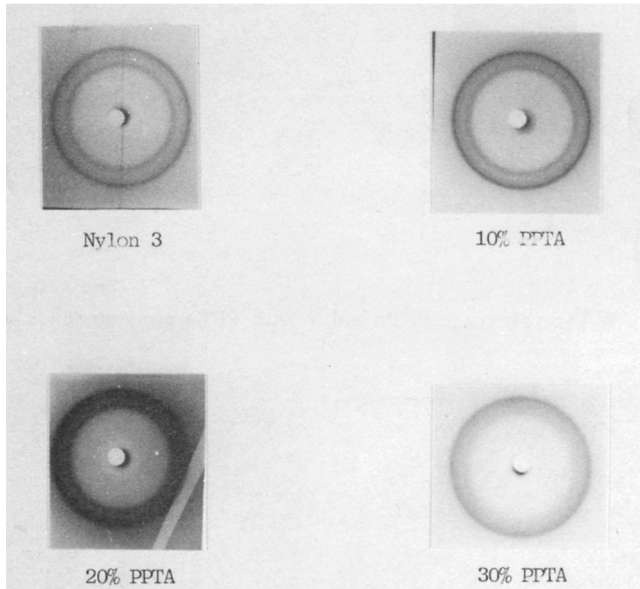
Fig. 12. WAXS patterns of nylon 3 and composites containing 10, 20, and 30 wt % PPTA.

tension fractured surfaces of composites containing 20 and 30 wt % PPTA, respectively. The 30 wt % sample is permeated with a network of fibrils 0.5–1 μm in diameter. These are the result of the formation of aggregated PPTA molecules formed in the liquid crystalline state. Similar behavior was reported by Helminiak et al.,[1-3] who observed phase separation with large diameter fibril formation in composites prepared by coagulating liquid crystalline ternary solutions of the rigid rod poly(p-phenylenebenzobisthiazole) combined with a flexible coil polybenzimidazole in methanesulfonic acid as opposed to the formation of composites with molecular level dispersion in the case of coagulating isotropic solutions. In our case, the liquid crystalline solution which persists at temperatures above the polymerization temperature with concentrations of PPTA above ca. 30 wt % leads to PPTA aggregation and fibril formation.

Wide-angle X-ray scattering (WAXS) was used to study the microscopic properties of the composites. Figure 12 shows WAXS patterns for nylon 3 film prepared according to the procedure of Masamoto et al.[31] and composites containing 10, 20, and 30 wt % PPTA. The nylon 3 sample exhibits reflections at 0.467, 0.407, and 0.374 nm, which are indexed as 111, 202, and 002.[32] These reflections are clearly intensified in the samples containing 10 and 20 wt % PPTA, but become diffuse and ill-defined in the 30 wt % composite. Increased nylon 6 crystallinity in nylon 6–PPTA composites containing low levels (< 10 wt %) of PPTA was reported by Takayanagi, who theorized that PPTA microfibrils could act as nucleating agents for nylon 6 crystallization, and later demonstrated epitaxial crystallization of nylon 6 onto PPTA fiber surfaces.[4,6,7]

The decrease in nylon 3 crystallinity exhibited in our system at high PPTA levels has not been described previously. Figure 13(a) displays two WAXS patterns, one of a PPTA film prepared by vacuum casting a PPTA anion–DMSO solution followed by washing with methanol and water, and the
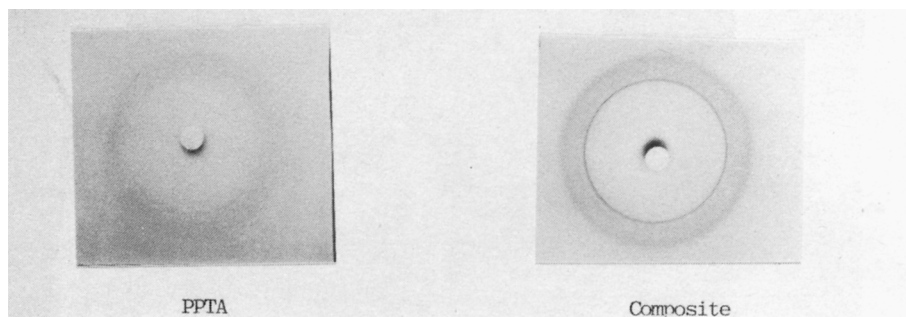
Fig. 13(a).   WAXS patterns of PPTA and 50 wt % PPTA composite films before annealing.
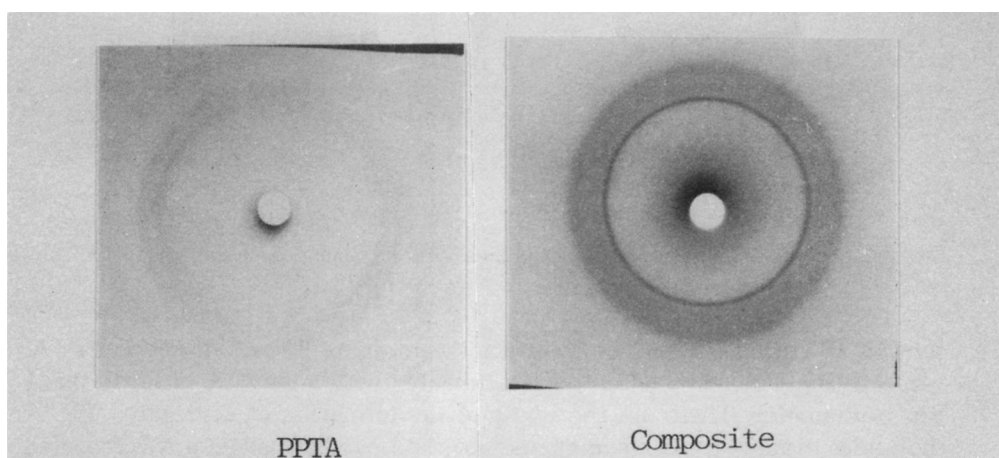

Fig. 13(b).   WAXS patterns of PPTA and 50 wt % PPTA composite films after annealing at 180°C for 24 h.

other of a composite containing 50 wt % PPTA. These patterns show one strong reflection at 0.496 nm, which is indicative of PPTA form II as proposed by Haraguchi et al.[33] This form was found to arise in film samples which had been coagulated in water from liquid crystalline solutions of PPTA in sulfuric acid. This form is significantly different from that found in Kevlar fibers and that of PPTA films coagulated from sulfuric acid solutions into solvents such as methanol. The explanation given for the variation in crystal structure in the two forms was that form II represents a structure formed from a water-swollen liquid crystalline structure which is frozen in place during subsequent drying steps. IR data confirms the presence of form II in the 50 wt % composite as shown in Figure 14. The PPTA band which appears at 730 cm^{-1} in form I and 720 cm^{-1} in form II is found at 720 cm^{-1} in the composite.

Annealing these PPTA films for 24 h at 180°C resulted in conversion to form I as shown in Figure 13(b). This pattern displays reflections at 0.322, 0.394, and 0.439 nm, which are in good agreement with reported values.[34] The 50% PPTA composite film was annealed under the same conditions, and this WAXS pattern is shown in Figure 13(b). The annealing process resulted in a sharpening of the 0.496 nm reflection, but no nylon 3 or form I reflections were detected. Apparently, the nylon 3 acts to "freeze" the PPTA into form II, at
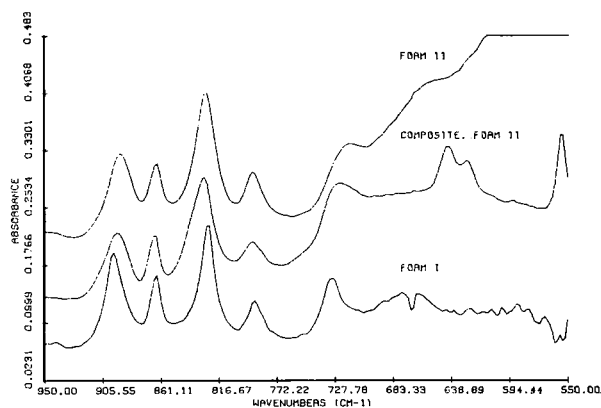
Fig. 14. FTIR spectra of PPTA forms I, II, and a composite containing 50 wt % PPTA.

TABLE II
Mechanical Properties of PPTA/Nylon 3 Composites

Polymer	PPTA (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)
Nylon 3	—	28.0	1.06	5.2
274-36-G	10	60.3	3.15	3.0
274-38-G	20	158.8	5.86	12.0
274-39-B	30	191.1	7.55	9.4

least at the annealing temperatures used for this study. The decreased nylon 3 crystallinity in these composites is presumably due to the poorer efficiency of large diameter PPTA aggregates to act as nucleating agents for the crystallization of nylon 3.

Mechanical Property Evaluation

Table II presents stress–strain data for composites containing 10, 20 and 30 wt % PPTA compared to data for nylon 3. The composites show a dramatic increase in tensile strength and modulus with no significant loss of elongation even at high levels of PPTA. Composites containing lower levels of PPTA exhibited very brittle behavior, and adequate test results could not be obtained on these samples due to fracture in the Instron clamps.

The excellent retention of extensibility in the composites is thought to be due to the nylon 3 graft segments which act to anchor the reinforcing PPTA molecules into the matrix and to slow crack growth by dissipating energy in plastic deformation. The good adhesion between the aggregated PPTA fibrils and the nylon 3 matrix can be seen in the electron micrograph shown in Figure 11. The fibrils are seen to be pulled out of the matrix without losing adhesion to the matrix. Samples broken in liquid nitrogen showed fracture of the fibrils without loss of adhesion to the matrix. Similar behavior was observed by Takayanagi, who studied ionomer reinforced with poly-acrylonitrile-2 grafted PPTA fibers.[35] These composites showed improved

extensibility over those prepared with unmodified PPTA fibers with lower strength and modulus. The lower modulus was ascribed to poor adhesion between the ionomer and the polyacrylonitrile graft. In our case, the nylon 3 graft should have excellent compatibility with the nylon 3 matrix, and this should provide the best possible combination of strength and modulus improvement without sacrificing flexibility.

Reinforcement effectiveness may be evaluated by comparing the behavior of the composites to model systems such as the Tsai–Halpin formulation for modulus prediction. Figure 14 shows a plot of the relative modulus E/E_1 for composites containing 10, 20, and 30 wt % PPTA. The lines represent the Tsai–Halpin equation for random three-dimensional orientation with A values of 1.5, 10, and 20. The A value of 1.5 represents a spherically shaped reinforcement, and A values of 10 and 20 represent L/D values for the reinforcing filler of 15 and 25, respectively. The Tsai–Halpin equation is formulated as follows[36]:

$$E/E_1 = (1 + AB \cdot \phi_2)/(1 - B \cdot \psi \cdot \phi_2)$$

where E is the composite modulus, E_1 is the matrix modulus, A is a constant dependent on the type of composite, and in the case of randomly oriented fiber reinforced composites is proportional to the L/D ratio of the fiber, ϕ_2 is the volume fraction of reinforcement, and ψ is a parameter based on the maximum value of packing fraction of fibers and is close to unity in this case. The value B is given by

$$B = [(E_2/E_1) - 1]/[(E_2/E_1) + A]$$

where E_2 is the fiber modulus. The values of E_1 and E_2 were taken to be 1.06 and 153 GPa based on the modulus of nylon 3 films and the experimental value of the PPTA crystal modulus.[10] As can be seen from the plot, the three experimental points fall on the line for an A value of 20. Similar behavior was
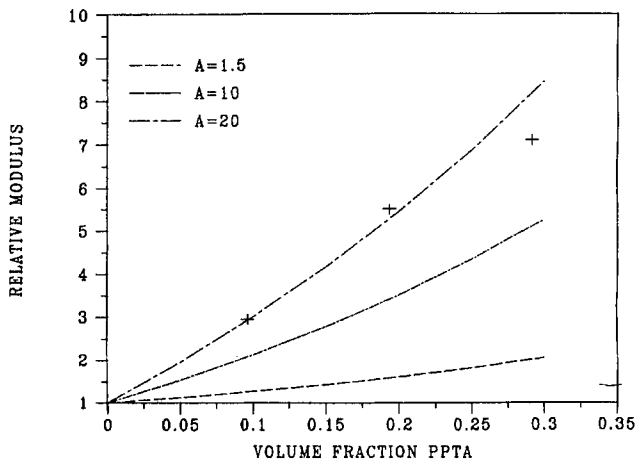

Fig. 15. Relative modulus vs. volume fraction PPTA for the Tsai–Halpin equation and composites containing 10, 20, and 30 wt % PPTA.
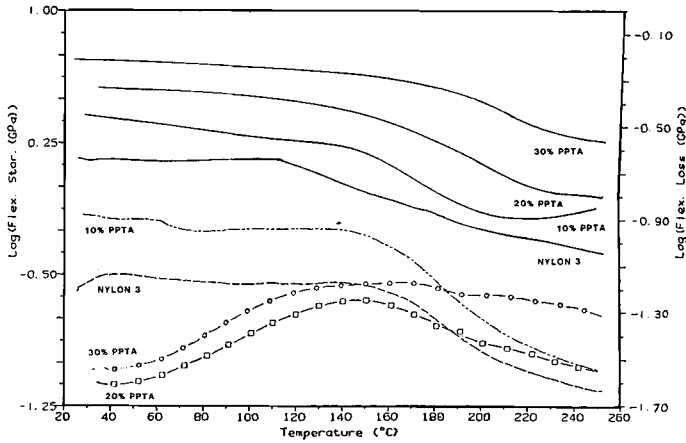
Fig. 16. Flexural storage and loss modulus vs. temperature for nylon 3 and composites containing 10, 20, and 30 wt % PPTA.
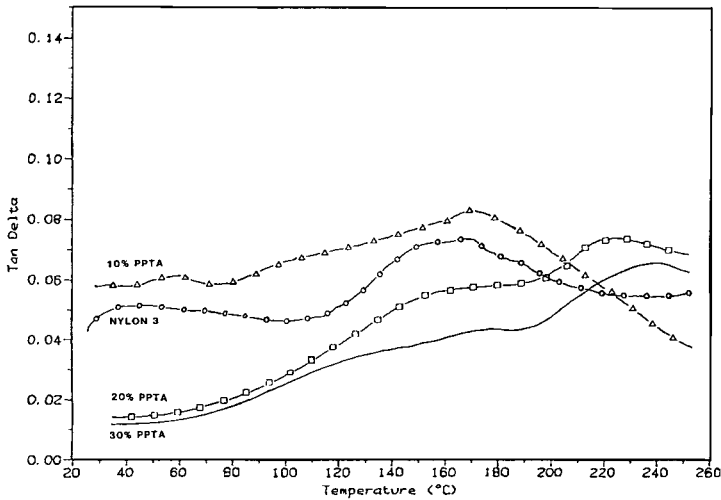

Fig. 17. Tan δ vs. temperature for nylon 3 and composites containing 10, 20, and 30 wt % PPTA.

reported by Takayanagi et al. for nylon 6 based composites employing low levels ($\phi_2 < 0.1$) of PPTA.[4] This analysis implies that molecular level composites are being obtained in this case, as reinforcement by large diameter fibrils would be expected to be less efficient in providing reinforcement compared to small diameter microfibrils or molecules.

Dynamic mechanical measurements for nylon 3 and the 10, 20, and 30 wt % PPTA composites are shown in Figures 15 and 16. The flexural storage modulus shows the expected large increase with increased PPTA levels. The composites also retain good thermal stability beyond the T_g of nylon 3, which is approximately 170°C.[31] The modulus is seen to fall off dramatically at temperatures above 220°C, which is not close to the melting point of nylon 3 (315°C). This decline in modulus is accompanied by the appearance of a

second loss peak which is most easily seen in the tan measurements shown in Figure 16. This peak is centered at 230°C, and is clearly not the T_g transition of the nylon 3, which is still apparent, although weakened at a temperature of 170°C. This transition is thought to be associated with the PPTA, and is believed to be the β^* transition, which is due to conformational changes in the polymer chain caused by thermally stimulated 180° flips of the phenyl rings.[10,37-40] The temperature at which this transition occurs for PPTA has been reported by different groups of workers to be between 160 and 250°C, depending upon the sample preparation and environmental conditioning. One anomaly in the behavior of the composites is the decrease in modulus at temperatures close to that of the β^* transition, which is not exhibited by PPTA samples. We attribute this decrease in modulus to the graft nylon 3, which acts to destiffen the PPTA chain and allow greater conformational mobility. This increases the amplitude of the β^* transition and decreases the effectiveness of PPTA as a reinforcement above 220°C.

CONCLUSIONS

The use of *in situ* polymerization for the fabrication of molecular level composite materials has been proven successful for the case of PPTA–nylon 3. Composites prepared using PPTA anion as the initiator for polymerization and the rigid molecular component show good reinforcement over nylon 3 and improved heat resistance. At very high temperatures, the loss of modulus of the composites is attributed to the graft nylon 3 segments destiffening the PPTA chain. Investigation of the composite morphology revealed the presence of fibrillar aggregates at high PPTA levels which were found to possess the crystal structure found in swelled liquid crystalline PPTA samples. This indicates that *in situ* polymerization processing at high PPTA levels proceeds in the liquid crystalline state.

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