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Poly(*p*-phenylene terephthalamide)s (PPTAs) having ionic and nonionic side groups and their blends with poly(4-vinylpyridine)

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Modified PPTAs were made by introducing ionic, propanesulfonate groups and nonionic, propyl groups. Ionic groups caused polyelectrolyte behaviour for the modified PPTA in a polar solvent and propyl groups improved solubility of the modified polymer. Modified PPTA having small amounts of side groups (less than 40 mol% in total) showed birefringence, reflecting rigidity of polymer chains. In contrast, modified PPTA having a very high percentage of side groups (nearly 100 mol%), which may be needed for solubility in common, polar, organic solvents, seems to assume more disordered structures. Ionic groups are also responsible for miscibility enhancement of the modified PPTA with a polar polymer, poly(4-vinylpyridine), due to increased interactions through ion–dipole interactions. Propyl groups may make an additional contribution to miscibility enhancement through increased flexibility of PPTA molecules. © 1997 Elsevier Science Ltd.

(Keywords: modified PPTA; ionic groups; blend with PVP)

INTRODUCTION

Poly(*p*-phenylene terephthalamide), PPTA, is a lyotropic liquid crystalline polymer, which forms an anisotropic, partially ordered state in solution. The molecular order is intermediate between the three-dimensional order in a solid crystal and the disorder of an isotropic liquid[1]. PPTA shows a nematic liquid crystalline phase where the molecular chain axes mutually align in one direction, but there is no long-range positional order which might contribute to a crystal lattice[2]. Even though PPTA is considered to be a semi-rigid chain and isolated PPTA molecules are not totally straight, they tend to straighten out in the liquid crystalline phase, showing optical anisotropy[1].

Recently, rigid main-chain polyamides have been synthesized with long alkyl side chains attached to the main chain diaminobenzene units[3–5]. The side chain effect is expected to decrease the melting temperature of rod molecules and to increase their solubility; however, the long alkoxy chains are not thermally stable above 300°C and are highly sensitive to oxidation even at temperatures below 200°C[3]. The addition of side chains may also change an aromatic polyamide from being a lyotropic liquid crystalline polymer to a thermotropic one which forms a partially ordered state on heating[1].

During our efforts in developing molecular composites in which rod-like molecules are dispersed in polymers of coil structure[6,7], via ionic interactions[8–10], we have made various ionic PPTA molecules. Here, ionic interactions are used to counteract the driving force for phase separation typically observed in such composites. In one type of ionic PPTA, we modified PPTA through introduction of both ionic, propanesulfonate groups and nonionic, propyl groups both of which were attached to amide N atoms by combining the methods reported by Takayanagi and Katayose[11] and Gieselman and Reynolds[12]. The introduction of nonionic groups can reduce the softening temperature and increase solubility by increasing the freedom of chain structures. The introduction of ionic groups can increase solubility (in a polar solvent) and enhance miscibility of PPTA with other polar polymers due to ionic interactions. By changing the amounts of nonionic and ionic side groups, one can develop modified PPTAs with a wide range of structures. This paper mainly reports the results on modified PPTA in which all amide N atoms are replaced by side groups (both ionic and nonionic), which were soluble in a common organic solvent, since solution characterization and solution blending need good solubility. Although rigidity is sacrificed by these modifications, some interesting results have been obtained for modified PPTA both in solution behaviour and in miscibility with a polar polymer, poly(4-vinylpyridine).

EXPERIMENTAL

Synthesis

Poly(*p*-phenylene terephthalamide), PPTA, having both ionic and nonionic side groups, N-propyl-poly((*p*-phenylene terephthalamido) propanesulfonate) (N-Pr-PPTA-PS), was prepared from the PPTA anion as the starting material[12]. The PPTA anion was made by metallation of PPTA[11].

The metallation of PPTA was first described by Takayanagi[11] and later modified by Burch *et al.*[13]. The strong base, potassium methyl sulfinyl carbanion, is

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generated by the reaction of dimethyl sulfoxide (DMSO) and potassium hydride (KH). The carbanion is capable of deprotonating the slightly acidic amide hydrogens of PPTA, making the PPTA soluble in DMSO. A three-necked reaction flask, equipped with an overhead stirrer, nitrogen inlet and a septum cap, was flushed with N_2 gas. A 35 wt% KH dispersion in mineral oil was added followed by anhydrous DMSO. The solution was mixed for 5 min or until no hydrogen gas was evolved. Dry hexane was then added to scavenge the mineral oil layer, which was removed with a syringe. This was repeated until no mineral oil remained. The resulting potassium methyl sulfinyl carbanion solution was a clear, greenish-yellow, low viscosity liquid. Vacuum dried PPTA pulp (obtained from DuPont), slightly wetted with DMSO to reduce flocking, was added to the N_2 gas swept carbanion solution. The solution was mixed for 48 h resulting in a thick, red, moisture-sensitive PPTA polyanion solution with no unreacted PPTA fibre visible.

The PPTA anion was then converted to N-Pr-PPTA-PS. The polyanion was alkylsulfonated according to the procedure described by Gieselman and Reynolds[12] and then subjected to an alkylation, as reported by Takayanagi and Katayose[11]. The alkylsulfonation was used to adjust the ion content, while the alkylation enhances the solubility of PPTA. A diagram of the synthesis procedure is shown in *Figure 1*. The correct equivalent weight of 1,3-propane sultone (Aldrich, Milwaukee, WI, USA) for the desired ion content was added to the PPTA polyanion solution. A large decrease in viscosity was observed immediately upon addition of the 1,3-propane sultone. The solution was mixed for 24 h and an excess amount of 1-bromopropane was added. Nucleophilic displacement of bromine attaches propyl groups to the remaining unreacted amide nitrogen atoms. The resulting solution was mixed for 36–48 h with a gradual decrease in viscosity occurring during that time. The final solution was yellow, transparent, and with a viscosity comparable to DMSO. The product was collected by precipitating the solution in acetone and mixing for 48 h. After allowing the product to settle, the supernatant liquid was decanted off and replaced with fresh acetone. After mixing for another 48 h, the acetone was poured off until a slurry of product remained. The remaining acetone was removed under vacuum for 36 h and then dried for 24 h at 120°C also under vacuum.

An example of sample designation is shown here: N-Pr(90)-PPTA-PS(10) represents modified PPTA in which 90 mol% of N atoms are propylated and 10 mol% are attached to propanesulfonate groups. *Table 1* lists the samples used in this study.

Blend sample preparation

Blend samples were made from modified PPTA as described above and poly(4-vinylpyridine) (PVP) (Scientific Polymer Products). PVP has a weight-average molecular weight of 240 000, which was determined by light scattering measurements in DMF. Most blend samples were prepared by vacuum evaporation; some samples were made by compression moulding. First, samples were prepared by dissolving 3 wt% of PVP in DMSO using a magnetic stirrer for 12 h. The appropriate amount of ionic PPTA solution in DMSO (a 3 wt% solution of N-Pr-PPTA-PS) was then added to yield the desired mixing ratio. The solution was poured into an aluminium pan and placed under vacuum for 2 h. The temperature was then increased to 100°C and remained under vacuum for 4 weeks to effectively remove residual DMSO. The resulting 200–300 μm thick film was cut into 1 cm × 1 cm squares and stored in a dry box.

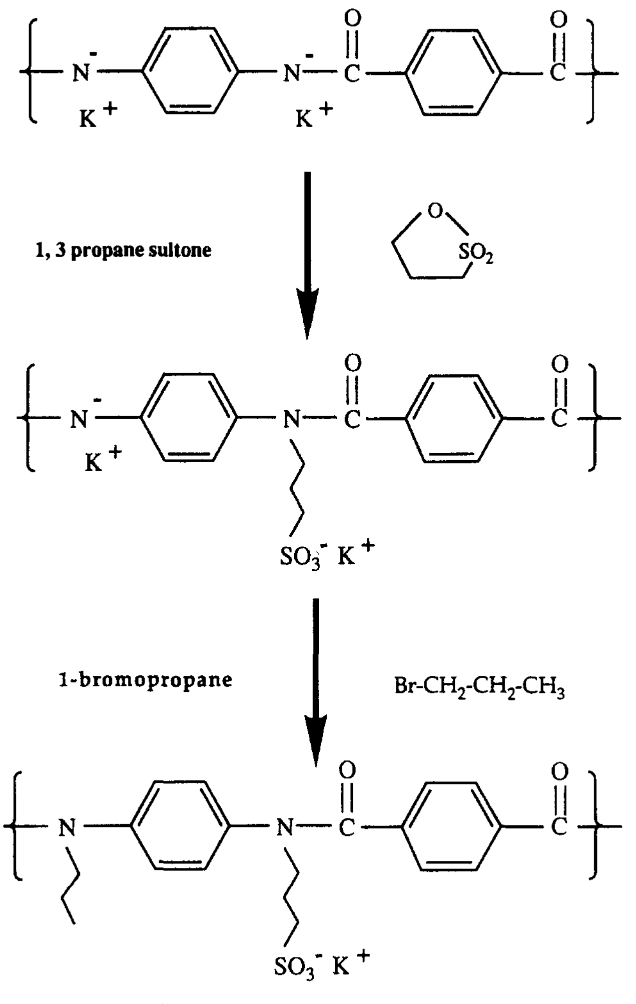

Figure 1 Synthesis of N-Pr-PPTA-PS

Measurements

Viscosity measurements were made at 25 ± 0.1°C with a modified Ubbelohde viscometer that was sealed to prevent solvent evaporation and exposure to air. Solutions were prepared by dissolving a propylsulfonated form of PPTA (i.e. 100 mol% ion content) in water under stirring for 12 h immediately before making measurements. Measurements at each concentration were repeated until the relative error of three successive measurements was less than 0.5%. Details of viscosity measurements are described elsewhere[14].

Light scattering experiments were performed with a KMX-6 low-angle light scattering photometer (Chromatix). Polymer solutions were prepared by

Table 1 Modified PPTA having large amounts of side groups

Propanesulfonate content (mol%)		Propyl content[b] (mol%)
5	(4.9[a])	95
13	(12.8[a])	87
15	(14.6[a])	85
100	(97.5[a])	0

[a] Determined by conductometric titration
[b] Calculated by 100 – (propanesulfonate content)

dissolving the appropriate amount of polymer (modified PPTA or PVP) in dimethylformamide (DMF) and stirring for 12 h at room temperature. Solutions were passed through 0.5 and 0.2 μm filters before entering the scattering cell to remove foreign particles. Measurements were made at three different points of the cell window to make sure that the effects of the roughness of the cell window on scattering were negligible. The specific refractive index increment, d*n*/d*c*, was measured at 25°C using a KMX-16 differential refractometer (Chromatix). Details of low-angle light scattering measurements are described elsewhere[15].

Conductometric titrations were performed in a conductivity cell with conductivity meter (National Instruments Model RC-16B2J). Titrations were performed with 8–12 ml of polyion solution in the conductivity cell, which contained a magnetic stirring bar. The resistance of the solution was measured after each addition of a small volume of reagent. The data were plotted to give two straight lines intersecting at the equivalence point. Measurements made near the equivalence point were excluded in the construction of graphs due to hydrolysis, dissociation or solubility of the reaction products[16].

Thermogravimetric analysis (t.g.a.) measurements were made with a TA Instruments 2100 Thermal Analyst equipped with a 951 Thermogravimetric Analyzer. Samples of 10–30 mg were weighed directly on the test pan. After loading the sample, the sample chamber was flushed with a continual flow of N_2 gas. Heating began at room temperature with a heating rate of 20°C min^{-1}. The test was completed when no appreciable weight loss was detected.

Differential scanning calorimetry (d.s.c.) measurements were made on a TA Instruments 2100 Thermal Analyst equipped with a 910 Differential Scanning Calorimeter. Samples of 5–15 mg were weighted and dried for 48 h at 100°C immediately before testing. Heating began at room temperature with a heating rate of 10°C min^{-1}. The sample cell was continuously flushed with N_2 gas during testing. Glass transition temperatures were determined as a step transition by using a software package on the 2100 Thermal Analyst.

A Leitz Ergolux Inspection Microscope with a vertical camera unit was used for viewing samples under polarized light. A polarizer was used in the substage condenser and another polarizer above the objective lens—one rotated 90° to the other. Some samples were heated with a Mettler F52 hotstage. Heating began at 54°C with a heating rate of 2°C min^{-1}.

Thin film specimens for transmission electron microscopy (TEM) were cast from a 3 wt% solution on a microscope glass slide using a method similar to the procedure described elsewhere[17]. The films were dried in a bell jar that contained an open container of the same solvent as that used for the solution to decrease the evaporation rate. Drying times were usually between 4–6 h, depending on the solvent. The films were cut into 2 mm × 2 mm sections using a razor blade and floated off the glass slide onto the surface of deionized water. The film sections were then picked up onto a copper grid and dried under vacuum at room temperature for at least 48 h. A JEM-100 CX II transmission electron microscope was used to study the morphology of thin films. All micrographs were taken at an accelerating voltage of 100 kV.

RESULTS AND DISCUSSION

Ionic PPTA (N-Pr-PPTA-PS)

Figure 2 shows the results of conductometric titration of N-Pr(87)–PPTA-PS(13) (acid form). The acid sample was prepared by pouring the K-salt solution in DMF into an excess of 1.0 N HCl solution. The ion content, determined by the intersection of two lines of *Figure 2*, is 12.8 mol%. The rate of increase in conductance value beyond the equivalent point is higher because of the contribution of Na^+ and OH^- ions. It should be added that the use of a nonaqueous solvent (DMF) changes the profile of titration curves, usually conducted for aqueous solution, because the mobility of H^+ and OH^- ions are exceptionally high in aqueous solutions due to the proton hopping occurring in water, but such behaviour is not seen for an aprotic solvent, like DMF[16]. Ion contents determined for all the samples are listed in *Table 1*.

Polyelectrolyte behaviour of N-Pr-PPTA-PS was observed using viscosity and light scattering measurements. *Figure 3* shows the viscosity behaviour of N-Pr(0)–PPTA-PS(100) (having nearly 100 mol% propanesulfonate groups) in water. A typical polyelectrolyte behaviour is seen: the reduced viscosity increases remarkably with decreasing polymer concentration. This is a very sensitive method to judge whether there are ionic groups attached to polymer chains[18]. The

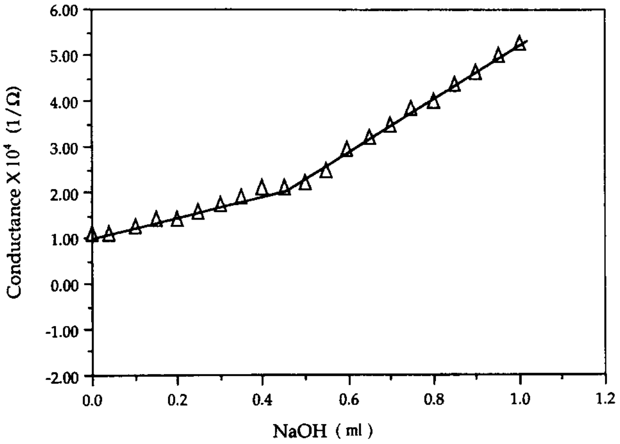

Figure 2 Conductometric titration of N-Pr(87)-PPTA-PS(13) in DMF

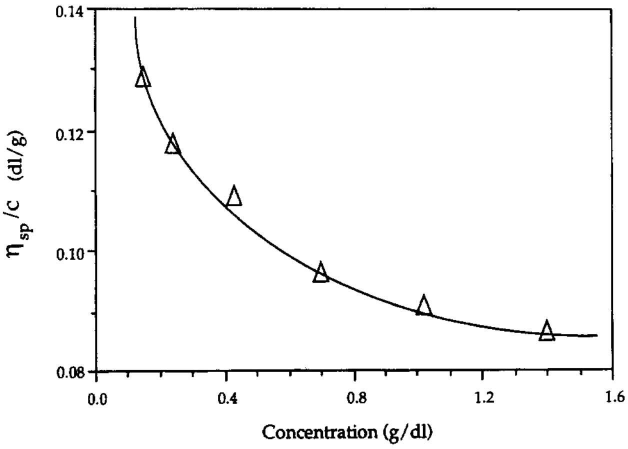

Figure 3 Upturn of the viscosity curve (reduced viscosity vs. polymer concentration) for N-prop(0)–PPTA-PS(100) in water, showing typical polyelectrolyte behaviour

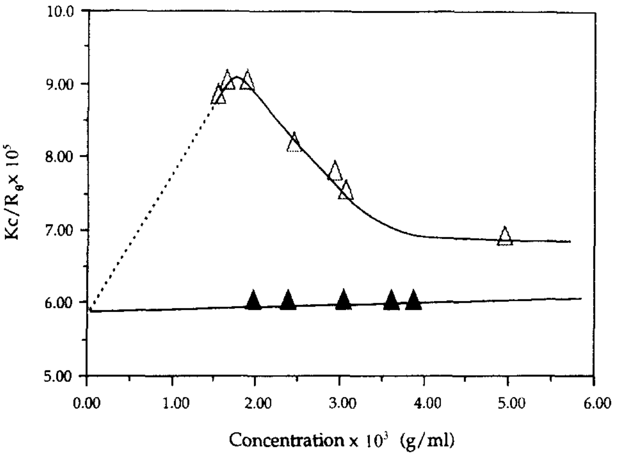

Figure 4 Reciprocal reduced scattered intensity at zero angle, Kc/R_0, against polymer concentration for N-Pr(85)–PPTA-PS(15) in DMF: without salt (△) and with 0.05 M LiCl (▲). Salt-free system shows polyelectrolyte behaviour, which is suppressed by the addition of simple salts

behaviour is conventionally explained by the fact that as polymer concentration decreases, free space increases and some of the previously condensed counterions are dissociated from the polyions. This increases the net charge of the polyions and leads to intramolecular repulsion, causing chain expansion that in turn increases the reduced viscosity. However, more recent results suggest the important role of intermolecular electrostatic interactions in causing such behaviour[18]. In any case, the viscosity clearly demonstrates polyelectrolyte behaviour in salt-free systems.

To confirm polyelectrolyte behaviour, low-angle light scattering experiments were also conducted. *Figure 4* indicates the reciprocal reduced scattered intensity, Kc/R_0, as a function of polymer concentration for N-Pr(85)–PPTA-PS(15) in DMF with and without added salt (LiCl). Here, K is an optical constant, c is a polymer concentration (g cm^{-3}), and R_0 is the scattering intensity measured at very small angle (5–6°), which is safely assumed to be zero for our polymer[15]. In salt-free polyion solutions, it is known that the Kc/R_0 value increases (or scattering intensity, R_0, decreases) sharply from the intercept ($1/M$) with increasing polymer concentration and levels off or even decreases at higher polymer concentrations[18]. The dotted line in *Figure 4* is drawn according to these results. The reduction in scattered intensity arises from the destructive interference of scattered light due to the non-random arrangement of polyions in solution. In contrast, the salt added system (0.05 M LiCl) shows neutral polymer behaviour; Kc/R_0 increases linearly with polymer concentration. This is because added salts (LiCl) shield ionic interactions[18].

PPTA is a lyotropic liquid crystalline polymer that forms an anisotropic, partially ordered state in solution. To determine how structural modifications of PPTA affect liquid crystallinity, the birefringence of N-Pr-PPTA-PS was studied to compare with that of PPTA. *Figure 5* shows a comparison of the birefringence seen for PPTA and N-Pr(85)–PPTA-PS(15). Significant birefringence is observed with the PPTA, but the N-Pr-PPTA-PS exhibits mainly isotropic behaviour having only a faint birefringent phase. Takayanagi also observed isotropic behaviour for modified PPTAs having very high percentage of side groups[11]. To see the effect of degree of substitution, we made small amounts of modified PPTA samples with various ionic and nonionic groups. *Table 2* indicates the effect of increasing side chain content upon the transparency, birefringence and solubility of N-Pr-PPTA-PS. A correlation between increasing side chain content and decreasing rod-like character can be noted. The increasing side chain content improves its transparency and solubility in DMF or DMSO, while steadily decreasing its ability to rotate plane polarized light, i.e. birefringence. Increased solubility, transparency and isotropy under crossed polarizers are all indicative of a more disordered structure. Kim and Calabrese reported that N-allylated PPTA (nearly 100 mol% converted) showed no crystallinity but had a high solubility in chlorinated solvents[19]; by using an X-ray structure determination of a model compound of N-allylated PPTA, they concluded that the N-allylated PPTA can no longer have a rigid rod-like structure due to the changes in the amide bond conformation. Our results on modified PPTA with a high percentage of side groups (nearly 100 mol%) are consistent with their conclusion. However, they also reported that d.s.c. data of N-allylated PPTA showed a broad endotherm and a small exotherm, and the polymer visually melted at 280°C. This may reflect the formation of a thermotropic liquid crystalline structure.

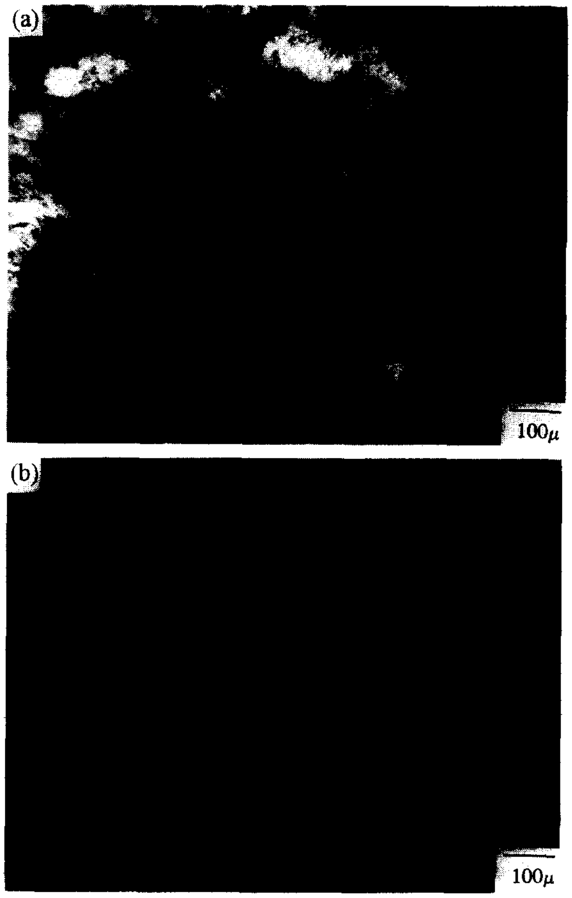

Figure 5 Films under crossed polarizers: (a) PPTA; (b) N-Pr(85)–PPTA-PS(15)

To determine if PPTA was converted to a thermotropic liquid crystalline polymer by the addition of side chains (i.e. propanesulfonate and propyl), N-Pr-PPTA-PS was heated up to 300°C with a Mettler FP52 hotstage and

Table 2 Modified PPTA with various amounts of side groups

Side chain content[a]					Solubility	
Total	Ionic groups	Propyl groups	Visual characterization	Appearance under crossed polarizers	DMF	DMSO
10.0%	5.0%	5.0%	Opaque	Birefringence	ins.	ins.
15.0	5.0	10.0	Opaque	Birefringence	ins.	ins.
20.0	15.0	5.0	Opaque	Birefringence	ins.	ins.
25.0	5.0	20.0	Slightly transparent	Birefringence with large colored phases	ins.	ins.
35.0	5.0	30.0	Mostly transparent	Birefringence with less colored phases	ins.	ins.
40.0	15.0	25.0	Mostly transparent	Birefringence with large colored phases	ins.	swell.
65.0	15.0	50.0	Transparent	Isotropic	ins.	swell.
100.0	15.0	85.0	Transparent	Isotropic	sol.	sol.

[a] Estimated from the amounts of reagents added (propanesulfonate and propyl bromide)

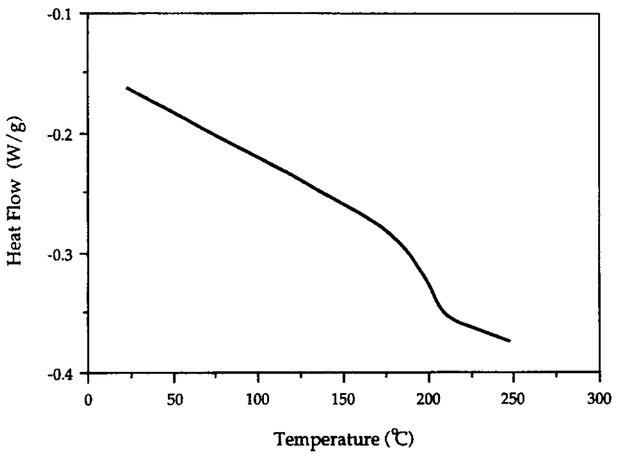

Figure 6 D.s.c. plot of N-Pr(95)-PPTA-PS(5)

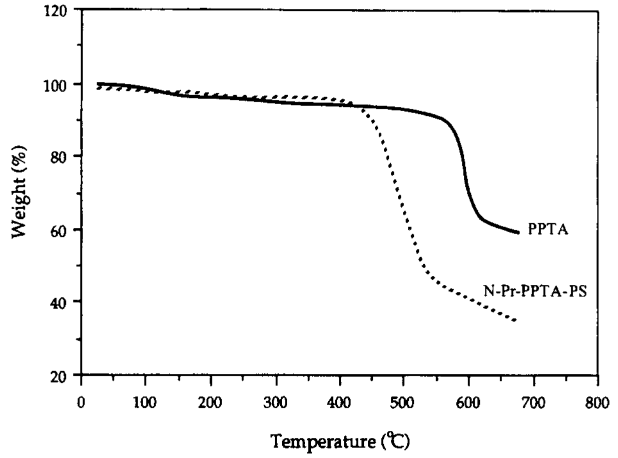

Figure 7 Weight loss as a function of temperature of PPTA and N-Pr(87)-PPTA-PS(13)

observed under crossed polarizers. So far, no liquid crystalline behaviour has been noted before degradation for all samples studied: they either show no melting or show no birefringence after melt. However, this was only a preliminary study of this matter and there is a possibility that a thermotropic liquid crystalline PPTA may be found, in a more systematic investigation which covers a much wider range of substitutions (especially those having a smaller degree of substitution: less than 40 mol%), by applying a shearing stress, or more effectively, an elongational flow[1].

PPTA is known to exhibit no glass transition temperature before its degradation temperature[20]. D.s.c. tests conducted in this study did not detect a glass transition temperature in PPTA. In contrast, the d.s.c. thermogram of N-Pr(95)–PPTA-PS(5), shown in *Figure 6*, indicates a glass transition temperature at 192°C. The appearance of the glass transition temperature in N-Pr-PPTA-PS also suggests that significant changes in the semi-rigid structure of PPTA occurs with the attachment of a large number of side chains to the amide nitrogen atoms.

The occurrence of a more disordered structure in modified PPTA may be explained by two possible causes. One is that the side chains may prevent the rod-like molecules from aligning efficiently; and simultaneously, hydrogen bonding between chains may be eliminated, since the amide hydrogens have been replaced with short alkyl chains. Aromatic polyamides with alkyl side chains attached to the diaminobenzene units have been shown to possess a board-like molecular structure with the alkyl groups preventing rotation about the long axis[4,5]. The board-like molecules pack one on top on the other and show different liquid crystalline transitions than the unmodified aromatic polyamide. The other possibility is a change in the amide bond conformation by substitution of the amide hydrogen by side chains[19]. According to the results obtained, it is believed that the change in the amide bond conformation best accounts for the amorphous-like properties of N-Pr-PPTA-PS with high propyl content.

The attachment of side chains to PPTA's backbone chain at the diaminobenzene unit[3] or at the amide nitrogen[11,12] noticeably reduces the thermal stability of polyamide at high temperatures. In accord with these results, the degradation temperature of N-Pr(87)–PPTA-PS(13) was lowered by *ca.* 100°C in comparison to PPTA, as shown in *Figure 7*, although achievement of thermal stability up to 400°C is still significant for fully substituted, disordered PPTA. The low degradation temperature of hydrocarbon side chains accounts for the lowering of the degradation temperature[12].

Blend system (N-Pr-PPTA-PS/poly(4-vinylpyridine))

To see if modified PPTA has good miscibility with other polymers, we investigated a polymer blend system made of N-Pr-PPTA-PS and PVP. Direct visual observation of polymer blend specimens has been used as a simple test evaluating the degree of miscibility[21,22]. Since transparency in polymer blend films is an indication of miscibility on a scale down to 0.1 μm[22], it was used as an initial test for miscibility in the polymer blend. *Figure 8* is

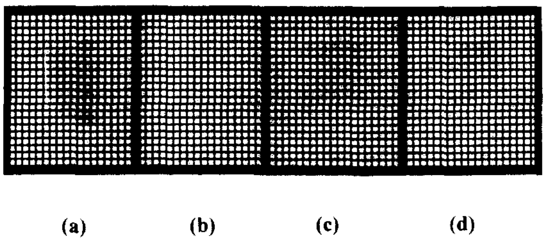

Figure 8 Comparison of the transparency of samples: (a) N-Pr(87) PPTA-PS(13)/S-VP (20/80); (b) PVP; (c) N-Pr(95)–PPTA-PS(5)/PVP (20/80); (d) N-Pr(87)–PPTA-PS(13)/PVP (20/80)

a comparison of transparency between PVP and the blend films. Two samples were made from 20 wt% N-Pr-PPTA-PS and 80 wt% PVP—one system using N-Pr-PPTA-PS containing 5 mol% ions and the other having 13 mol%. A blend system made of 20 wt% N-Pr(87)–PPTA-PS(13) and 80% poly(styrene-*co*-4-vinylpyridine) (50/50) (S-VP) matrix is also shown. The blend films using a PVP matrix have a transparency comparable to that of PVP, while the films having a S-VP matrix are translucent. Also, a blend made of unmodified PPTA and PVP is opaque (not shown here). This is direct evidence that the N-Pr-PPTA-PS/PVP (20/80) system achieves miscibility down to 0.1 μm. Miscible blend films were also heated to 180°C for 24 h and showed no signs of phase separation.

TEM can detect phase domains of less than 100 Å[23]. For this reason, it was decided to further characterize the morphology of blend systems that showed miscibility by visual observation *Figure 9* shows TEM micrographs of the N-Pr(0)–PPTA-PS(100)/PVP (20/80) and N-Pr(0)–PPTA-PS(100)S-VP (20/80) blends. The micrograph of the blend having the PVP matrix shows homogeneity down to 100 Å, while the blend with the S-VP matrix reveals a second phase of 0.1–1 μm—consistent with visual observations. Annealed N-Pr-PPTA-PS/PVP (20/80) films also showed no signs of phase separation.

The results indicate the usefulness of ion–dipole interactions in enhancing miscibility of otherwise immiscible systems; interactions occur between ionic groups of modified PPTA and ionic dipoles of pyridine groups of PVP. Ion–dipole interactions are shown to be effective in enhancing miscibility of otherwise immiscible polymer pairs; one example is seen in a blend of poly(styrene-*co*-lithium methacrylate) ionomer and poly(alkylene oxide)[24]. Our results also show that PVP has better miscibility with N-Pr-PPTA-PS than S-VP. This can be explained by the difference in pyridine content of the two polymers. Since S-VP is a 50/50 copolymer, it only has pyridine groups on 50% of its repeating units and phenyl groups on the remaining units. Since the phenyl rings cannot contribute to ion–dipole interactions, they cannot aid in enhancing miscibility; rather, they probably prevent pyridine groups from interacting with a sulfonate group through steric hindrance.

The most commonly used method for establishing miscibility in polymer–polymer blends is by determining the glass transition temperature of the blends. A miscible polymer blend will exhibit a single glass transition temperature between the components' T_g's with a sharpness of the transition similar to the components[22]. For partially miscible systems, two separate transitions may result between those of the component polymers, one rich in component 1 and the other rich in component 2. Although the level of molecular mixing required to yield a single glass transition temperature for miscible polymer mixtures has not been clearly established, Kaplan suggests a value of 150 Å as the domain size required to contain a 'universal' segmental length associated with the glass transition[25].

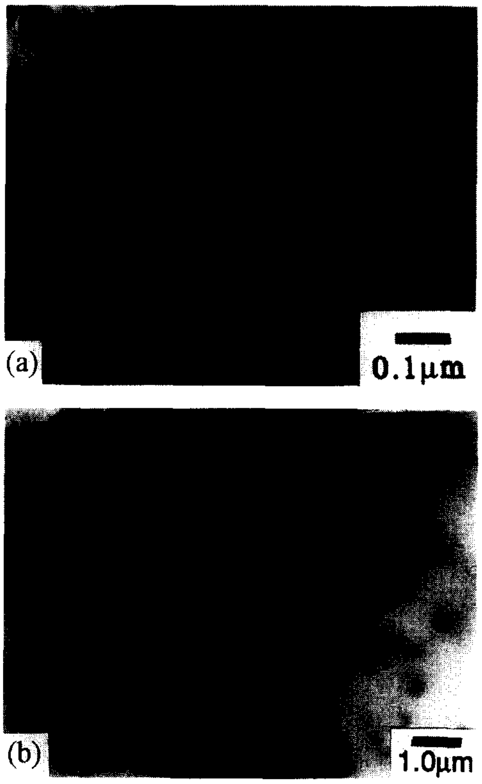

Figure 9 TEM micrographs of (a) N-Pr(0)–PPTA-PS(100)/PVP (20/80) blend and (b) N-Pr(0)–PPTA-PS(100)/S-VP (20/80). Note the difference in magnification. Structures seen at the top left corner are crazes

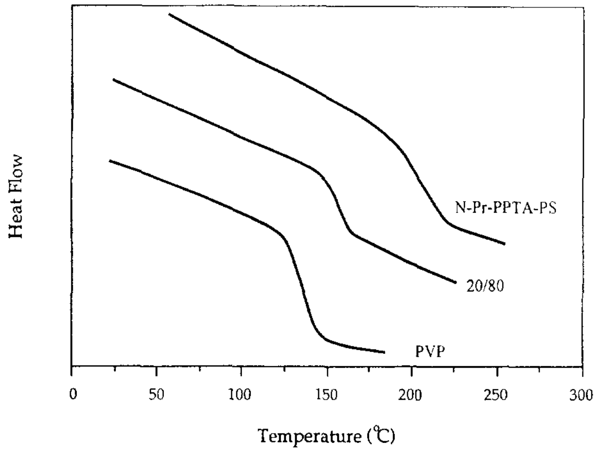

Figure 10 D.s.c. plot of the blend N-Pr(95)–PPTA-PS(5)/PVP (20/80) and the individual components

D.s.c. was used to determine the glass transition temperature of the N-Pr(95)–PPTA-PS(5)/PVP (20/80) blend. *Figure 10* is a comparison of the d.s.c. plots for the 20/80 blend and its individual components. From the plot, the respective T_g values obtained are 137°C for PVP, 191°C for N-Pr-PPTA-PS, and 151°C for the blend. A single, sharp glass transition of the blend, lying between those of its components, indicates miscibility down to *ca.* 150 Å.

The miscibility can also be evaluated by comparing the observed T_g of each polymer phase with that of its respective homopolymers. The random copolymer equation may be used for that purpose[26]:

$$T_g = w_1 T_{g1} + w_2 T_{g2} \tag{1}$$

where T_g is the glass transition temperature of the polymer blend, w_1 and w_2 are the weight fractions of PVP and N-Pr-PPTA-PS, and T_{g1} and T_{g2} are respective glass transition temperatures of PVP and N-Pr-PPTA-PS. This equation simply gives the value from the rule of mixtures. Also, the following Fox equation is widely used for polymer–polymer blends[27]:

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \tag{2}$$

Using the values obtained from d.s.c. results in these equations, glass transition temperatures are calculated as 148°C and 145°C respectively for the 20/80 blend. Although these values are close to the measured value, 151°C, the measured value is higher than the calculated values. It is well known that a positive deviation of the T_g of miscible blends from the rule of mixtures is found in systems with strong intermolecular interactions, such as donor–acceptor interactions[28] and ionic interactions[29]. This further suggests that good miscibility is obtained through the use of strong ion–dipole interactions. Samples were also tested repeatedly to determine if heating induced phase separation. After four consecutive heating and cooling cycles, no shift in the T_g of composites was detected, another indication that the system is not a frozen mixture.

Polarized microscopy was used to further determine the degree of miscibility in the N-Pr-PPTA-PS/PVP (20/80) blend. Characterization using this approach was difficult, since N-Pr-PPTA-PS showed only a very faint birefringent phase—suggesting a mostly disordered structure. Since the motive for using polarized microscopy as a characterization technique is to determine whether a birefringent, reinforcing, second phase exists, the possible amorphous-like structure of N-Pr-PPTA-PS makes it a less effective technique with this system. Even so, the faint birefringent phase, noticeable in the N-Pr-PPTA-PS, was not observed when blended with the amorphous PVP matrix. It may then be concluded that the ion–dipole interactions effectively enhanced miscibility between N-Pr-PPTA-PS and PVP. It should be pointed out that the miscibility may also be enhanced due to the disordered molecular conformation of N-Pr-PPTA-PS, as compared to the initial rod-like conformation of PPTA.

CONCLUSIONS

PPTA was modified by introducing ionic, propanesulfonate groups and nonionic, propyl groups, both of which were attached to amide N atoms. Modified PPTA having less than 40 mol% substitution shows birefringence, but samples having large substitution (nearly 100 mol%) show no birefringence. In this work, we have focused on the latter case which showed good solubility in common solvents, needed for solution characterization and solution blending. Ionic groups caused polyelectrolyte behaviour, observed both by viscosity and low-angle light scattering measurements, for the modified PPTA in a polar solvent. Nonionic propyl groups improved solubility of the modified polymer. Modified PPTA shows rather high thermal stability: no weight loss has been detected up to 400°C. A lack of birefringence and the appearance of a glass transition temperature indicated a disordered structure of modified PPTA in which nearly all N atoms are replaced by side groups.

Polymer blends were made from the modified PPTAs and poly(4-vinylpyridine). Transparency, a single glass transition temperature appearing in the middle between the T_g's of respective component polymers, and TEM observation all show that good miscibility is achieved in this system. This is primarily due to increased interactions through ion–dipole interactions between ionic groups of modified PPTA and ionic dipoles of PVP, although propyl groups may make an additional contribution to miscibility enhancement through increased flexibility of PPTA molecules.

Although this study has mainly focused on modified PPTA having a large percentage of side groups, modified PPTAs having a smaller percentage of side groups may show thermotropic liquid crystal formation under proper conditions (e.g. ion content, propyl content, under elongational flow, etc.). Such a study would be of interest and may lead to melt-processable thermotropic PPTA. PPTA has been widely used as a high performance polymers, but only in fibre or film forms. This is a subject of future work.

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