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Notes

Aromatic Polyamides of 3,8-Diamino-6-phenylphenanthridine and Their Molecular Complexes with Sulfonated Polystyrene Ionomers

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Introduction

Fiber-reinforced composites where a polymeric matrix is blended with glass, carbon, or rigid-chain aromatic polyamide fibers are extensively employed in applications requiring high strength and stiffness based on weight. These materials, however, have long suffered from inherent problems imposed usually by the interfacial properties between the two components, such as poor adhesion. Additionally, different thermal expansion coefficients of the two components, fiber imperfections and their tendency to fibrillate, stress concentrations at the fiber ends, and thermal, hydrolytic, and oxidative stability of the matrix are some of the factors that have limited the properties of these materials. Such considerations led to the conception of a "molecular composite" which was conceived by Takayanagi[1] and Helminiak *et al.*[2] independently in the late 1970s.

Molecular composites incorporate rigid-rod polymer molecules with high aspect ratios in a matrix of flexible molecules. The original concept envisioned a homogeneous dispersion of the rigid-rod molecules, but more recently research in this area has been centered around dispersions or microfibrils with dimensions of less than 50 nm in diameter.

The majority of research performed on molecular composites to data has focused on solution blending of the reinforcement and matrix polymers. Some of these systems have included poly(*p*-phenylenebenzobisthiazole) (PBZT)/poly(2,5(6)-benzothiazole) (ABPBT) and poly(2,5(6)-benzimidazole) (ABPBI), PBZT/poly(ether ether ketone) (PEEK), poly(*p*-phenyleneterephthalamide) (PPTA)/Nylon 66, PBZT/Nylon 66, PPTA/Nylon 6, and others which are summarized in a number of review paper.[3-7] The intractability and insolubility in common organic solvents of the rigid-rod components commonly used often necessitates the use of strong protonic solvents such as methanesulfonic acid (MSA) and poly(phosphoric acid) (PPA). Not only does this restriction limit the number of polymer systems that can be used as the matrix materials but also the use of such harsh solvents is a severe limitation to the development of feasible processing technologies. Additionally, the predicted phase separation of the two components,[8] due to the thermodynamically unfavorable free energy of mixing where the ordering of rigid rods rejects the random-coil component, has been an another major problem. A certain amount of success at retaining the molecular dispersion has, nevertheless, been achieved by rapid coagulation of isotropic ternary solutions into films and fibers.

A novel approach aiming to dissolve rigid-rod polymers in aprotic solvents using Lewis acid complexation was recently reported by Jenekhe *et al.*[9] This procedure allowed higher concentration isotropic solutions of the rigid-rod and the matrix polymer to be prepared which could be processed with conventional techniques followed by decomplexation. Good dispersion of the reinforcing phase was obtained by this method, but, similar to other systems, subsequent heat treatment of the composite resulted in an increase in phase separation.

Several modifications have been reported in an attempt to decrease this demixing tendency. The most important approaches are block copolymerization of a rigid and flexible polymer,[7] in-situ polymerization of one component in the presence of the other or the use of thermosetting matrices,[7] and increase of the interactions between rigid/coil polymer chains.[10-14] The use of interactions to improve the miscibility of polymer mixtures is routinely used in studies involving traditional polymer blends. Interactions commonly used include hydrogen bonding, proton transfer, ion–dipole interactions, transition-metal complexation, and charge-transfer complexation.[15]

Recently Tan *et al.*[10] reported the preparation of rigid-rod composites stabilized by ionic interactions based on PBZT and poly[sodium 2-(acrylamido)-2-methylpropanesulfonate] (NaAMPS). Ternary solutions were prepared in MSA followed by rapid coagulation. Even though the wide-angle X-ray diffraction has indicated aggregation of PBZT, scanning electron microscopy (SEM) showed homogeneity down to ca. 50 nm. Partial protonation of PBZT was observed by color changes of the composites in different organic and aqueous environments. A shortcoming of this system is that it relies on the use of MSA which limits the choice of matrix polymers.

A similar approach employing rigid-chain polyamides containing association sites available for ionic interactions that are soluble in organic solvents should have promise in achieving homogeneous blends which might persist in the bulk state. In this paper we report the synthesis of novel rigid-chain polyamides based on 3,8-diamino-6-phenylphenanthridine (DAPP) as potential candidates for such a reinforcing phase. A preliminary investigation into solution blending of these polyamides with ionomeric thermoplastic matrices is also addressed.

Experimental Section

Materials. 3,8-Diamino-6-phenylphenanthridine (DAPP; Aldrich) was used as supplied. Terephthaloyl and isophthaloyl chlorides (Aldrich) were purified by sublimation and recrystallization from hexane, respectively. 2,6-Naphthaloyl chloride was prepared by hydrolysis of 2,6-dimethylnaphthalene dicarboxylate (Fluka) followed by reaction of the resulting diacid with thionyl chloride as described previously.[16] *N*-Methylpyr-

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rolidone (NMP; Aldrich) was vacuum distilled over calcium hydride and was stored over molecular sieves prior to use. Lithium chloride was dried in vacuum at 150 °C for 8 h immediately before use. Sulfonated polystyrenes (SPS) of various sulfonation levels, both in the acid form and as zinc salts, were prepared according to the procedure described by Makowski et al.[17]

Analyses. Thermal properties were measured with a Perkin-Elmer DSC-7 differential scanning calorimeter at a 20 °C/min heating rate under a N_2 atmosphere and with a Perkin-Elmer TGA-7 thermogravimetric analyzer using a 10 °C/min heating rate under nitrogen and air atmospheres. Solution viscosities were determined in NMP containing 4 wt % lithium chloride at 25 °C using an Ubbelohde capillary viscometer and expressed as η_{inh} at 0.5 g/dL concentration. UV–visible spectra at 1.2 wt % polymer solutions in NMP/LiCl (4 wt %) were measured with a Perkin-Elmer UV/vis spectrophotometer using a 1 cm path length cell. SEM micrographs of the fracture surfaces of blends were taken using an AMR Model 1200 scanning electron microscope instrument.

Polymerization. The polyamides were prepared by low-temperature solution polycondensation using the following general procedure described for **1a** and **2**: A three-neck, round-bottomed flask equipped with a reflux condenser, an addition funnel, and a mechanical stirring assembly, flamed and kept under argon, was charged with 1.64 g (5.75 mmol) of DAPP, 2.4 g of LiCl (4 wt % on total solvent), and 50 mL of NMP, and the mixture was stirred until homogeneous (0.5 h). Following the addition of 3 mL of triethylamine (TEA), the greenish–yellow solution was cooled to 0 °C and 1.17 g (5.75 mmol) of terephthaloyl chloride (for **1a**) or 1.45 g (5.75 mmol) of 2,6-naphthaloyl chloride (for **2**) was added rapidly with vigorous stirring from 10 mL of a NMP solution. The viscosity of the solution increased rapidly toward the end of the addition, and within minutes of its completion it solidified, rendering stirring no longer possible. The gelatinous mass was allowed to warm up to room temperature during the next 4 h. It was then broken with a high-speed Waring blender in ethanol. The precipitate was filtered off, Soxhlet-extracted with methanol for 3 days, and dried in vacuum at 100 °C overnight. The yields were quantitative in all cases.

1b and 1c. The same procedure as above was also used for these polymers except that a lower overall polymer concentration was adjusted by using 90 mL total of NMP as solvent. Additionally, in the later case, TEA was omitted from the reaction, which resulted in a dark red solution.

3. This reaction was conducted using 1.17 g (5.75 mol) of isophthaloyl chloride in a total of 30 mL of NMP as solvent. The solution was stirred for 0.5 h at 0 °C and 3 h at room temperature and turned extremely viscous.

Solution Blending. Homogeneous solutions of **1a** or **1b** and SPS with different sulfonation levels (0, 6.75, 8.1, 12.5, 18.1, 22.5, and 57 mol %) were prepared in 1/3 weight ratios of respective polymers at 4 wt % total polymer concentration by adding the appropriate quantity of the SPS component to a solution of the polyamide in NMP containing 4 wt % LiCl. The mixtures were stirred overnight until homogeneous. They were then cast into films over distilled water and washed with distilled water in this state for several days and finally were dried in vacuum at room temperature.

Results and Discussion

DAPP was chosen as the diamine component since all aromatic polyamides based on this monomer were expected to have the desired properties mentioned earlier. The large phenyl side group was expected to be arranged in a head-to-head or head-to-tail fashion along the polymer chain, thus reducing crystallinity and increasing the solubility of the polyamides. Additionally, the polyamides would contain one "pyridinium" residue per repeat unit, avaliable for molecular complexation with complimentary functional groups on another polymer, such as an ionomer.

Scheme 1. Polyamides Based on 3,8-Diamino-6-phenylphenanthridine

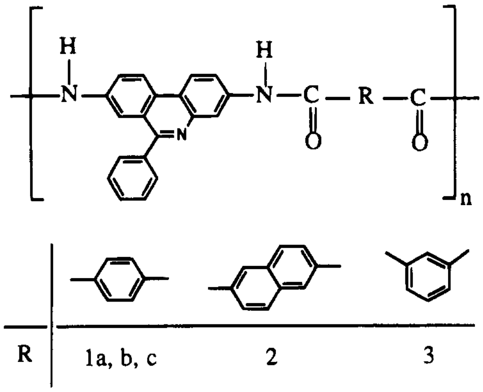

Table 1. Polyamides of 3,8-Diamino-6-phenylphenanthridine

polymer	η^a (dL/g)	emprical formula (formula wt)	elemental anal. (%)	C	H	N
1a	7.19	$(C_{27}H_{17}N_3O_2)_n$ $(415.45)_n$	calc	78.06	4.12	10.11
			found	75.35	4.85	9.74
1b	5.66	$(C_{27}H_{17}N_3O_2)_n$ $(415.45)_n$	calc	78.06	4.12	10.11
			found	67.85	4.30	9.04
1c	10.00	$(C_{27}H_{17}N_3O_2)_n$ $(415.45)_n$	found	75.22	4.69	9.73
2	5.19	$(C_{30}H_{19}N_3O_2)_n$ $(453.50)_n$	calc	79.46	4.22	9.27
			found	79.15	4.68	8.91
3	0.55^b	$(C_{27}H_{17}N_3O_2)_n$ $(415.45)_n$	calc	78.06	4.12	10.11
			found	74.57	4.76	9.35

[a] Measured at 0.5 g/dL concentration in NMP/LiCl (4 wt %) at 25 °C. [b] Measured in NMP.

Table 2. Thermal Properties of Polyamides

polymer	$T_g{}^a$ (°C)	decomposition temp^b (°C) in nitrogen	decomposition temp^b (°C) in air	char^c yield (%)
1a	>500	531	545	61
1c	>500	530	534	56
2	>500	549	545	57
3	335	495	514	62

[a] Determined in DSC at a 20 °C/min heating rate under a nitrogen atmosphere. [b] 10% weight loss temperature in TGA at a 10 °C/min heating rate. [c] Residual yield in TGA at 800 °C under a nitrogen atmosphere.

Three different polyamide compositions based on DAPP and terephthaloyl (**1**), 2,6-naphthaloyl (**2**), and isophthaloyl (**3**) acid moieties (Scheme 1) were synthesized by low-temperature solution polycondensation (see the Experimental Section). As expected, soluble polymers resulted in all cases; **1** and **2** dissolved in NMP/LiCl (4 wt %) at room temperature, and **3** was readily soluble in neat NMP. Table 1 lists the η_{inh} values and elemental analyses of the polyamides. The extended-chain conformation of **1** and **2** is evident from high η_{inh} of these polyamides as opposed to that of **3** which was expected to be a random coil. The higher molecular weight of **1a** than **1b** was due to the higher concentration employed during the polymerization. Both these polyamides were prepared in the presence of excess TEA as the acid acceptor to protect the polymer from protonation by the HCl byproduct. This was not the case during the preparation of **1c**, where the solution turned dark red and the resulting product was red in color due to the protonated phenanthridine residues. Some ionic nature of **1c** was also reflected in its considerably higher

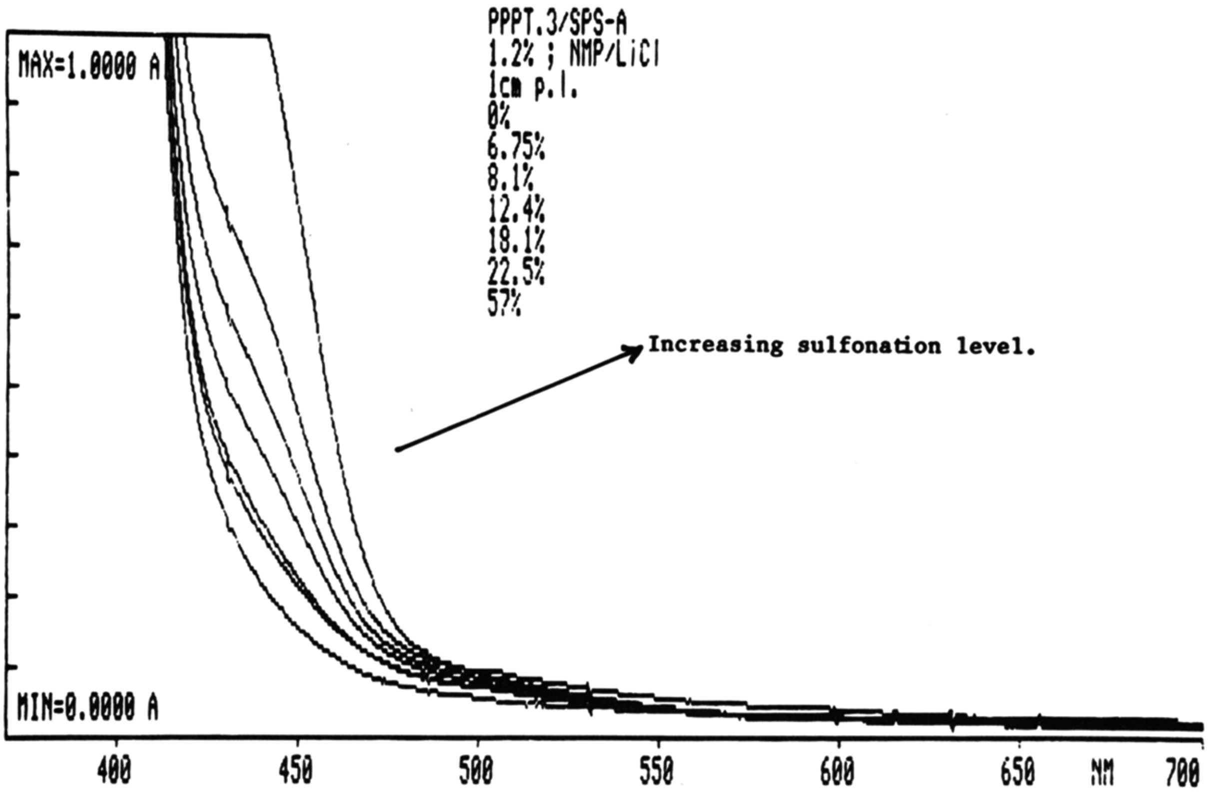

Figure 1. UV–visible spectra of NMP/LiCl (4 wt %) solutions of **1a** and SPS acid form with varying sulfonation levels (0, 6.75, 8.1, 12.5, 18.1, 22.5, and 57 mol %).

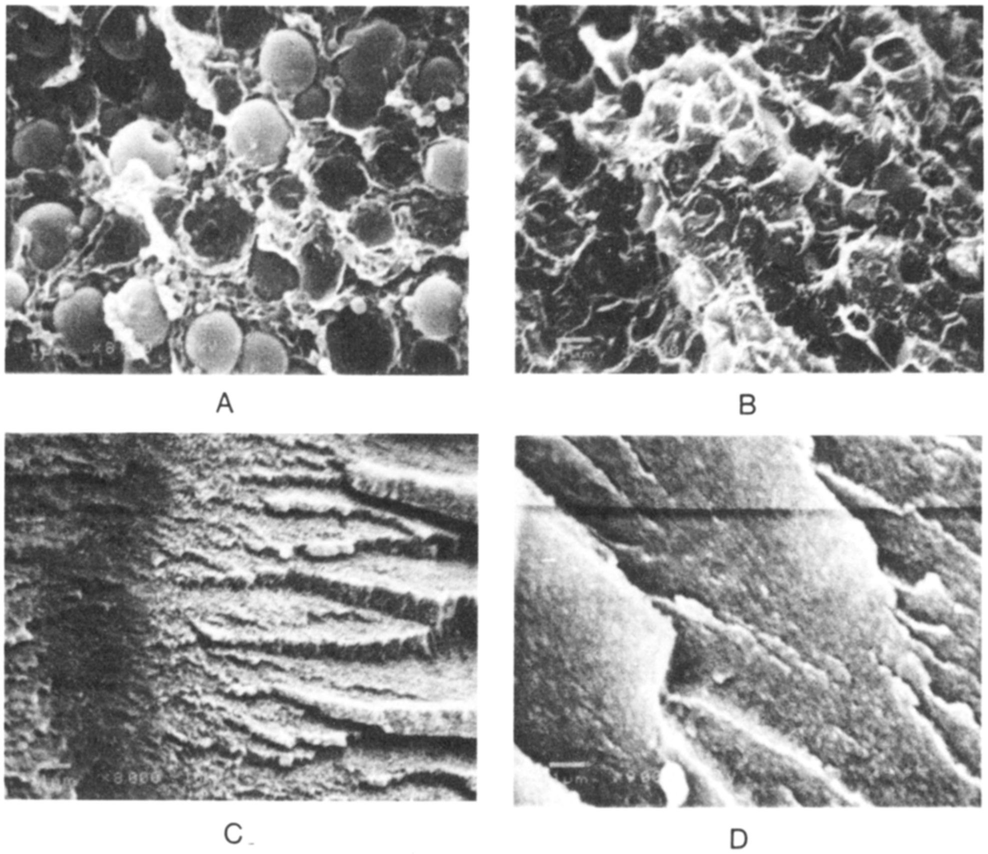

Figure 2. SEM micrographs of the fracture surfaces of blends of **1b** and SPS (neutralized with zinc) with varying sulfonation levels (Zn^{2+}/pyridinium ratio is given in parentheses): (A) polystyrene (0), (B) 8.1 mol % (0.45), (C) 12.5 mol % (0.66), and (D) 22.5 mol % (1.08).

η_{inh} value (Table 1) than that of **1b** even though the polymerization conditions were the same. The elemental analysis of this polymer, however, indicated <0.5% chlorine content. This is believed to be a result of deprotonation occurring during the long methanol extraction stage, which also resulted in a color change of the polymer to orange–yellow. In general, elemental contents of the polymers were lower than the calculated values (with the exception of **2**), which is presumed to be a result of some trapped NMP/LiCl in the products. Confirmation of this was observed during the TGA analysis showing some volatile losses in the 200–300 °C range.

The thermal properties of the polyamides evaluated by DSC and TGA are summarized in Table 2. As expected polyamides **1** and **2** did not show any thermal transitions in DSC before decomposition. Polymer **3** was amorphous and had a T_g at 335 °C. In general, all polyamides exhibited excellent thermal stability in both nitrogen and air atmospheres indicating onset temperatures of around 500 °C. The char yields at 800 °C in nitrogen were as high as 60%.

Homogeneous solutions of **1a** and SPS [1/3 (w/w)] of varying sulfonation levels up to 57 mol %, both in the acid form and neutralized to the Zn salt, could be prepared up to ca. 4 wt % total polymer concentration in NMP/LiCl (4 wt %). Interaction between the two polymers, primarily due to the protonation of the phenanthridine groups in the polyamide, was apparent from the color changes shown by solutions containing SPS with different levels of sulfonic acid groups. A progressive darkening of these solutions from yellow to orange–yellow to yellowish–brown was observed as the sulfonation level increased. The UV–visible spectra of these solutions (Figure 1) show a clear shift in the visible region with increasing the sulfonic acid content of the SPS. Films cast over water from these solutions were opaque when the sulfonation level was <8.1%, whereas for levels higher than 12.5% semitransparent or transparent films were obtained. Those two blends correspond to sulfonic acid to pyridinium ratios of 0.91 and 1.37, respectively. This result suggests the formation of a 1:1 complex. Similar observations were also made using the same series of SPS polymers neutralized with Zn counterion. In this case, the interaction between the polymers involves the formation of a transition-metal complex with the phenanthridine group and the Zn salt. SEM micrographs of the fracture surfaces of films based on SPS-Zn blends with **1b** are shown in Figure 2. Clear phase separation of the polyamide into spherical domains of ~2–5 μm size was observed in a blend with unfunctionalized polystyrene (Figure 2A). When 8.1% SPS–Zn was used, the phase size was reduced to <1 μm (Figure 2B). The micrographs also clearly demonstrate the increase in the interfacial adhesion between the two phases at relatively low sulfonation levels. A further reduction in the dispersed phase size to well below 1 μm resulting with the 12.5% SPS-Zn as the matrix Figure 2C) and above 18.1% sulfonation phase separation was not observed. For the blend composition used, 18.1 mol % sulfonation corresponds to a Zn^{2+}/pyridinium ratio of 0.91, which supports the formation of a molecular complex of one zinc ion (two sulfonate groups) and a pyridinium group. This ratio is consistent with previously reported complexes of zinc sulfonate ionomers and amine-containing polymers.[18–20]

Even though these results are proliminary, clear indications of induced miscibility via strong interaction between these two polymers are evident from both the color changes of ternary solutions and the SEM micrographs. Such intermolecular associations are expected to minimize thermally induced phase separation that is observed in other rigid-rod/coil polymer blends. Melt processing of some of these compositions may therefore be possible without appreciable phase separation.

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