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Solubilization, Solutions, and Processing of Aromatic Heterocyclic Rigid Rod Polymers in Aprotic Organic Solvents: Poly(*p*-phenylene-2,6-benzobisthiazolediyl) (PBT)

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ABSTRACT: We report the solubilization of aromatic heterocyclic rigid rod polymers, exemplified by poly(*p*-phenylene-2,6-benzobisthiazolediyl) (PBT), in *aprotic organic solvents* via reversible complex formation with Lewis acids. It is shown that the soluble PBT complex is not due to a π-electron charge transfer but a result of complexation at specific heteroatom donor sites (S, N). The resulting solutions of PBT in nitroalkanes and nitrobenzene, which appear to exhibit liquid crystallinity at high concentrations (>5 wt %), were investigated by viscosity measurements, electronic absorption, polarized light microscopy, and ^{1}H NMR. The textures of the lyotropic PBT solutions were those characteristic of the nematic mesophase. The PBT solutions were processed to optical quality transparent yellow free-standing films and coatings on various substrates by precipitation of the complexes in nonsolvents. Films prepared from liquid-crystalline solutions were turbid and birefringent. The PBT films produced from aprotic organic solvents were characterized by elemental analysis, infrared and UV–visible near-IR spectroscopies, and thermal analysis to confirm the complete regeneration of pure PBT polymer from its soluble complexes. It is suggested that the reported method of solubilization and processing of PBT in aprotic organic solvents holds promise for the large-scale processing of the rigid rod polymers to films, coatings, and fibers.

Introduction

The aromatic heterocyclic rigid rod polymers, poly(*p*-phenylene-2,6-benzobisthiazolediyl) (PBT), poly(*p*-phenylene-2,6-benzoxazolediyl) (PBO), and poly(*p*-phenylene-2,6-benzimidazolediyl) (PBI) whose structures are shown in Figure 1, have been of considerable interest because of their many exceptional properties.[1-8] These polymers exhibit high-temperature resistance, unusual resistance to organic solvents, and excellent mechanical properties especially in the highly ordered state. More recently, interesting electrical and nonlinear optical properties have been found in these conjugated polymers. For example, a high electrical conductivity ($\sim$20 Ω^{-1} cm^{-1}) in electrochemically doped samples[9] and a large third-order nonlinear optical susceptibility ($\chi^{(3)}$) of the order 10^{-11} esu[10] have been demonstrated in PBT.

One of the major barriers to the extensive characterization of the structural and solid-state properties and application of these rigid rod polymers is their insolubility in aprotic organic solvents from which they could be more readily processed into films, coatings, fibers, and other forms. However, they are soluble in strong concentrated acids such as methanesulfonic acid (MSA), trifluoromethanesulfonic acid, and chlorosulfonic acid (CSA), forming liquid-crystalline solutions at high concentrations.[1] The major disadvantages of using such strong concentrated acids as solvents for potential large-scale processing include their highly corrosive nature and the difficulty of removing the relatively nonvolatile acids from films, coatings, or fibers.

In this paper we report the successful solubilization, preliminary study, and processing of aromatic heterocyclic rigid rod polymers, exemplified by PBT, in aprotic organic solvents such as nitroalkanes and nitrobenzene. It is demonstrated that the PBT solutions in organic solvents can exhibit liquid crystallinity at high concentrations. Although PBO has also been solubilized in the same organic solvent systems as PBT, its solutions have not as yet been fully investigated and hence will not be discussed in detail here. A more general discussion of our laboratory's method of mediated solubilization and processing of rigid rod as well as ladder polymers in aprotic organic solvents by means of reversible polymer complex formation is present elsewhere.[11]

Experimental Section

The PBT polymer sample (PBT-2895-2C) was provided by Dr. Ivan J. Goldfarb of the Polymers Branch, Air Force Wright Aeronautical Laboratories, Dayton, OH. The PBT sample has an intrinsic viscosity of 18.3 dL/g in methanesulfonic acid at 30 °C; this translates to a M_w of about 29470, using the known Mark–Houwink relation for PBT:[1,3,12] $[\eta] = 1.65 \times 10^{-7} M_w^{1.8}$.

All organic solvents, Lewis acids, and protic acids were used without further purification: nitromethane, 99+% purity (Aldrich); nitroethane (Aldrich); nitrobenzene (Aldrich); 1,1-dichloroethane (Baker); 1-nitropropane (Aldrich); 2-nitropropane (Aldrich); methyl alcohol; $AlCl_3$ (Aldrich); $FeCl_3$ (Aldrich); $GaCl_3$ (Aldrich); $SbCl_5$ (Alfa); AsF_3 (Alfa); SbF_5 (Alfa, Aldrich); $SbCl_3$ (Aldrich); sulfuric acid (Baker); and methanesulfonic acid (Kodak).

Initial solubility tests consisted of a qualitative scan of the effectiveness of various Lewis acid/organic solvent systems in solubilizing PBT. These initial tests were done by placing a small amount of the polymer, ca. 5–10 mg, in about 6 mL of the solvent system. The polymer/solvent mixtures were monitored for signs of swelling, partial dissolution, or complete dissolution at room temperature and after heating to 60 °C. Heating on a hot plate up to 60 °C was observed to accelerate the polymer dissolution rate.

With the exception of PBT solutions in $FeCl_3$/organic solvents and protic acids, which were prepared in ambient conditions, all the PBT and PBO solutions were prepared in a Vacuum Atmospheres Dri Lab filled with nitrogen. Once prepared, the solutions were stored in the drybox and brought into air only when necessary. The polymer solutions were prepared by placing a known weight of the polymer into a solution of Lewis acid in organic solvent in a wide-mouth jar or vial. The resulting mixture of solid polymer/liquid Lewis acid/organic solvents was stirred, when feasible, as in the case of dilute solutions, until complete polymer dissolution was achieved. Dilute PBT solutions (<2 wt %) were in general prepared at room temperature. However, the concentrated and more viscous solutions, which could not be stirred, were prepared at 40–60 °C.

The PBT solutions in aprotic organic solvents, particularly solutions in $AlCl_3$/nitroalkanes, $GaCl_3$/nitroalkanes, and $FeCl_3$/nitroalkanes, were investigated spectroscopically. The electronic absorption spectra of solutions and films deposited on sapphire substrates were obtained in the 200–1500-nm wavelength range using a Perkin-Elmer Lambda 9 UV–vis near-IR spectrophotometer. The ^{1}H NMR spectrum of a 2 wt % PBT solution in a 30 wt % $AlCl_3$/deuterated nitromethane was obtained using a General Electric QE 300 instrument at 300 MHz.

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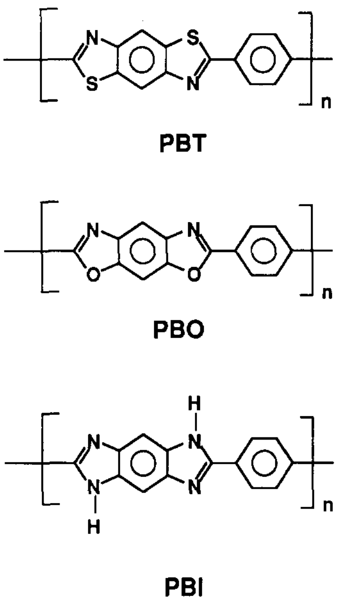

Figure 1. Structures of rigid rod polymers.

The rheological properties of dilute and concentrated solutions of PBT in Lewis acids/organic solvents were investigated by intrinsic viscosity and absolute viscosity measurements, respectively. Intrinsic viscosity, $[\eta]$, of PBT in $AlCl_3$/nitromethane and $GaCl_3$/nitromethane was determined at 30 °C using a Cannon–Ubblehode dilution viscometer. The solution concentrations were such that the elution times were between 1.1 and 1.8 times the elution time of the pure solvents (MX_n/CH_3NO_2). The viscosity of the concentrated solutions was measured at 25 °C using a Wells–Brookfield cone and plate digital viscometer Model RTV DV-II and cones of different angles that provided about three decades of shear rate (s^{-1}).

The pure polymer was recovered or regenerated from its complex in solutions by precipitation into a nonsolvent, deionized water or methanol, thoroughly washed in the nonsolvent, filtered, and dried at 105 °C. Elemental analysis was performed on regenerated PBT samples by Galbraith Laboratories, Inc. (Knoxville, TN). Theoretically calculated for $(C_{14}H_6N_2S_2)_n$: C, 63.15; H, 2.27; N, 10.52; S, 24.06. Found: C, 61.84; H, 2.34; N, 10.06; S, 23.24; Cl, 0.44. Thermal analysis on the pristine and regenerated PBT samples was performed using a Du Pont Thermal Analyst Model 2100 based on an IBM PS/2 Model 60 computer and equipped with a Model 910 differential scanning calorimeter (DSC) and a Model 951 thermogravimetric analyzer (TGA). Both TGA and DSC were done in nitrogen atmosphere and at a heating rate of 20 °C/min.

Films and coatings of PBT were prepared by casting of the dilute solutions (<2 wt %) onto a substrate (glass, sapphire, or silicon wafer) and evaporation of the aprotic organic solvent to give continuous polycrystalline films of the PBT/MX_n complex and any excess MX_n. The polycrystalline complex films/substrates were immersed in a beaker of methanol or water to produce continuous, uniform gold yellow and apparently amorphous films of PBT on the substrate; alternatively, the nonsolvent was sprayed onto the polycrystalline complex films until the pure polymer film is regenerated on the substrate. The free-standing films were similarly produced but removed from the substrates after precipitation and while the films were still wet with nonsolvent. The feasibility of fiber spinning of these organic solutions of PBT was crudely assessed by extruding viscous solutions or gels through an orifice using the pressure from a nitrogen gas tank. The extruded fibers of PBT/MX_n complex were precipitated in a nonsolvent to give short fibers of the pure PBT. The thickness of free-standing films or coatings produced by solution casting was varied by varying the concentration or viscosity of the PBT solutions. Electronic absorption spectra of thin films of PBT were obtained for comparison with the solution spectra. FTIR spectra of thin PBT films were obtained using a Nicolet Model 2SXC spectrometer.

Investigation of liquid crystallinity and morphology of PBT solutions in organic solvents containing Lewis acids was done by observation of thin layers of solutions under crossed polarizers in transmitted light using an Olympus Model BHSP 300 polarized light microscope. The thin layers of solutions were placed between microscope cover glass slides. Effects of shear on optical properties and on films were examined by sliding the top cover glass over the bottom one containing the thin layer of solution. Even in the case of nitromethane solutions, the thin layers of PBT solutions remained true solutions without evaporation, except at the edges, for days.

Initial investigation by polarized light microscopy showed that a 5 wt % PBT solution in 18.2 wt % $AlCl_3$/nitromethane showed both anisotropic and isotropic phases. Solutions of higher concentration (>5 wt %) expected to be more anisotropic or completely liquid crystalline were prepared by placing the required amount of the polymer sample into the Lewis acid nitroalkane solvents in jars on a hot plate at 40–60 °C. The jars were carefully sealed to prevent solvent evaporation. PBT dissolution at high concentrations (>5 wt %) took more than 1 week for a 6 wt % solution and still longer for higher concentrations in $AlCl_3$/nitroalkane solvents; the dissolution time for similar solutions in $GaCl_3$/nitroalkane solvents was about half the time for $AlCl_3$-containing solvents.

Results and Discussion

Solubilization in Organic Solvents. Heretofore, the rigid rod polymers in Figure 1 were known to be generally insoluble in organic solvents. Even methyl or 2,5-dimethyl substitution on the *p*-phenylene ring of the rigid rod polymers of Figure 1 does not result in solubility in aprotic organic solvents.[8] However, we have now found that aprotic organic solvents containing metal halide Lewis acids (MX_n) readily dissolve PBT and PBO to form stable viscous solutions. In the case of PBT, its solutions of varying concentration up to 7.5 wt % polymer have been prepared in nitroalkanes containing a varying amount of a Lewis acid ($MX_n = AlCl_3$, $GaCl_3$, $FeCl_3$, etc.).

PBT is insoluble in the pure liquid Lewis acids SbF_5 and $SbCl_5$; however, it dissolves in pure AsF_3 to give a yellow solution. The polymer swells in liquid $SbCl_5$ but swells and partially dissolves in $SbCl_5$/nitromethane to give brown solutions. In liquid SbF_5, the copper-colored PBT was doped to a black conductive solid, which is insoluble in SbF_5 or organic solvents. This interesting behavior of PBT in pure SbF_5 and $SbCl_5$ sheds light on the mechanism of solubilization in aprotic organic solvents containing Lewis acids (MX_n), as will be discussed further later. Clearly, since PBT is a conjugated polymer (Figure 1) with a delocalized π-electron system, the black conductive solid formed by reaction with the strong electron acceptor SbF_5 is a π-electron charge-transfer (CT) complex. The electrical properties of SbF_5-doped BPT, which is expected to be a p-type conductor in contrast to electrochemically n-type doped PBT recently reported,[9] are currently being investigated and will be reported elsewhere.

In the case of solubilization studies with $AlCl_3$ and $GaCl_3$ in nitroalkanes, it was found that true solutions were obtained only if the mole ratio $AlCl_3$:PBT (repeating unit) or $GaCl_3$:PBT is 4:1 or greater. At mole ratios, $GaCl_3$:PBT or $AlCl_3$:PBT, of 1:1, 2:1 and 3:1 red gels were formed.

PBT Solutions in Organic Solvents. Our spectroscopic investigation of the PBT solutions in organic solvents include ^1H NMR since only the protonated form of PBT has heretofore been available in solution.[1,2,4] The ^1H NMR spectrum of PBT in $AlCl_3$/deuterated CH_3NO_2 showed two broad resonances at 9.25 ppm (4 protons) and 6.9 ppm (2 protons), relative to TMS, which are due respectively to the *p*-phenylene protons and the benzobisthiazole protons. Figure 2 shows the electronic absorption spectrum of PBT in nitromethane containing 30 wt % aluminum chloride. This solution electronic absorption spectrum in nitromethane ($\lambda_{max} = 442$ nm, $\epsilon = 585\,150$

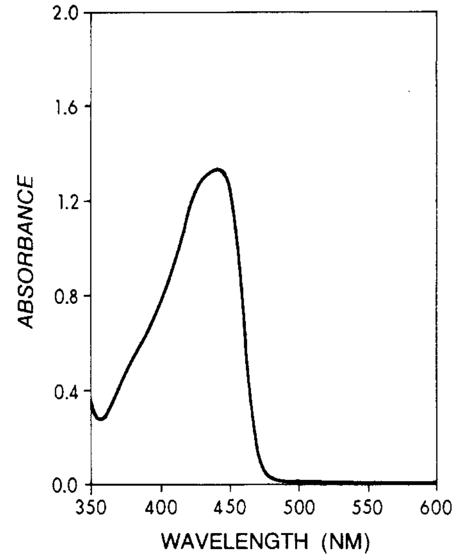

Figure 2. Electronic absorption spectrum of PBT in nitromethane/$AlCl_3$.

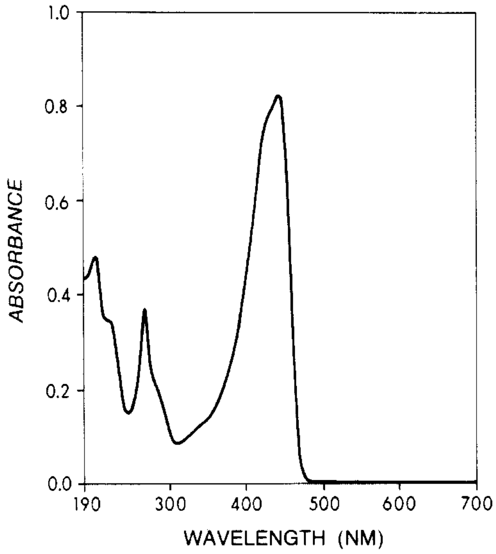

Figure 3. Electronic absorption spectrum of PBT in methanesulfonic acid.

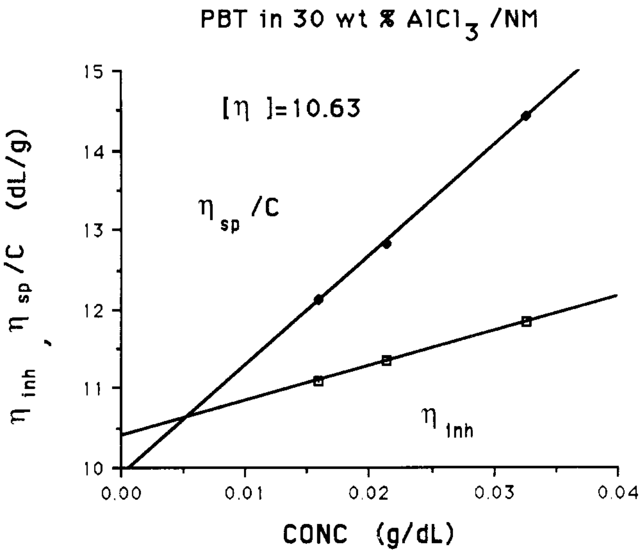

Figure 4. Plots of reduced and inherent viscosities versus concentration for PBT in 30 wt % $AlCl_3$/nitromethane.

Table I
Intrinsic Viscosity [η] of PBT in Protic Acid and Various Aprotic Organic Solvents at 30 °C

polymer	solvent	solvent viscosity, mPa·s	[η], dL/g
PBT	100% MSA (CH_3SO_3H)	24.5	17.3[a]
PBT	30 wt % $AlCl_3$/NM	2.2	10.63
PBT	18.2 wt % $AlCl_3$/NM		12.03
PBT	9.0 wt % $AlCl_3$/NM		11.12
PBT	30 wt % $GaCl_3$/NM		11.15
PBT	18.2 wt % $GaCl_3$/NM		11.95
PBT	9.0 wt % $GaCl_3$/NM		11.33

[a] This value determined in our laboratory is less than the 18.3 dL/g provided by AFWAL with the sample.

L/mol·cm) is similar to that in methanesulfonic acid (λ_{max} = 444 nm, ϵ = 607 400) shown in Figure 3.

The PBT solutions in nitroalkanes containing Lewis acids were generally quite viscous. Figure 4 shows plots of the reduced viscosity (η_{sp}/c) and inherent viscosity (η_{inh} = [ln η_{rel}]/c) at dilute solution concentrations in $AlCl_3$/nitromethane (30 wt %/wt). An intrinsic viscosity value of 10.63 dL/g was extracted from Figure 4. The intrinsic viscosities, [η], of PBT in several Lewis acid/nitromethane solvent systems at 30 °C are shown in Table I. The average value of [η] in the six aprotic organic solvents in Table I is 11.4 dL/g; the intrinsic viscosity of PBT in the different nitromethane solutions of $AlCl_3$ and $GaCl_3$ is within 5–7% of this average. The identical value of [η] in $AlCl_3$/nitromethane and $GaCl_3$/nitromethane solvents suggests that the nature of PBT/$AlCl_3$ and PBT/$GaCl_3$ complexes in dilute solution is the same. This similarity of the dilute solution viscosity, [η], of PBT in $AlCl_3$/nitromethane and $GaCl_3$/nitromethane is to be contrasted with the corresponding concentrated solutions (≥0.25 wt % PBT) where a striking difference is obseved as will be discussed later. It is also noteworthy that the intrinsic viscosity of PBT in Lewis acid/aprotic organic solvents is significantly less (~34%) than in methanesulfonic acid (MSA).

The rheological properties of the concentrated PBT solutions in Lewis acid/nitroalkane solvents were investigated at 25 °C. Figure 5 shows the solution viscosity of PBT in $AlCl_3$/nitromethane (30 % wt/wt) as a function of shear rate at three different concentrations. A true zero-shear viscosity is obtained only in the most dilute (0.25 wt %) solution. At higher polymer concentrations some shear thinning is evidenced at the shear rates accessible with our viscometer. The $AlCl_3$/nitromethane (30 % wt/wt) solvent had a viscosity η_s of 2.2 mPa·s (cps). Figure 6A shows the specific viscosity ($\eta_{sp} = \eta/\eta_s - 1$) versus concentration of PBT solutions in $AlCl_3$/nitromethane. A rapid solution viscosity increase with polymer concentration is observed. In contrast, the solution viscosity of PBT in $GaCl_3$/nitromethane was generally less viscous. Newtonian flow behavior and a zero-shear viscosity were obtainable up to 5 wt % PBT in this solvent system. Figure 6B shows the concentration dependence of the solution viscosity of PBT in 18.2 wt % $GaCl_3$ in nitromethane. The solution viscosity in $GaCl_3$/nitromethane was about 1 order of magnitude less than that in $AlCl_3$/nitromethane at similar concentrations. We similarly found that PBT solutions in nitroalkanes containing iron(III) chloride were generally more viscous than those containing gallium chloride at similar concentrations. The reason for this significant dependence of the rheological properties of concentrated PBT solutions on the nature of the complexing Lewis acid (MX_n) is as yet not clear especially in view of the lack of such dependence in dilute solution properties.

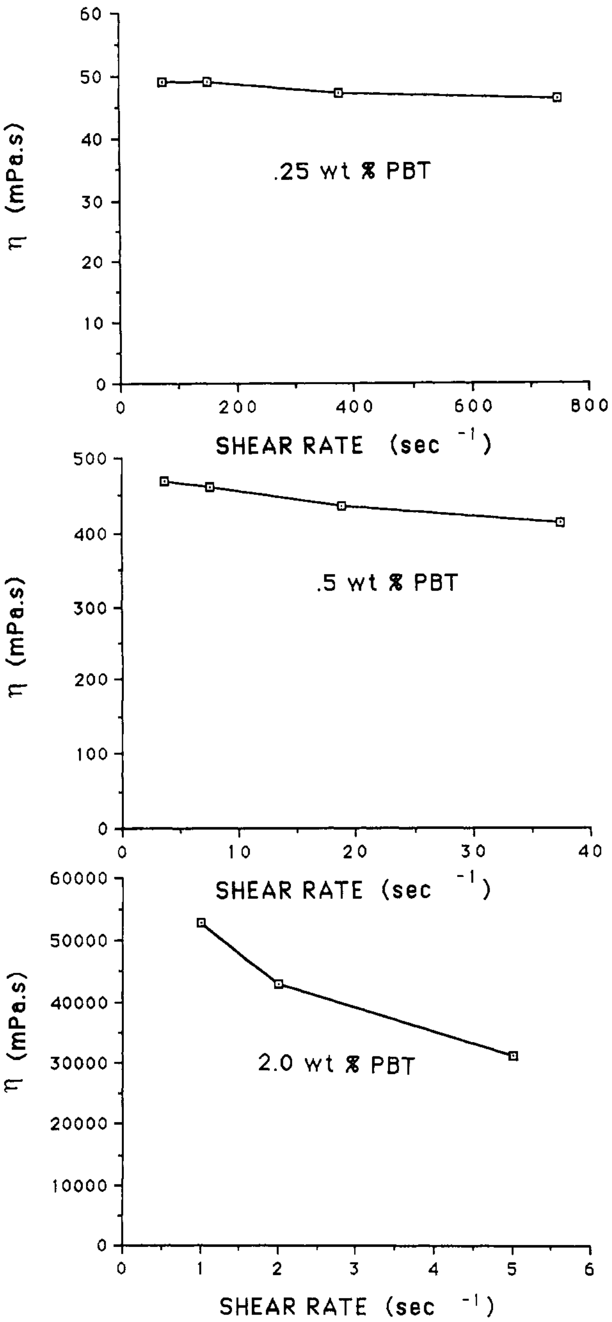

Figure 5. Shear-rate dependence of the viscosity of PBT solutions in $AlCl_3$/nitromethane at 0.25, 0.50, and 2.0 wt %.

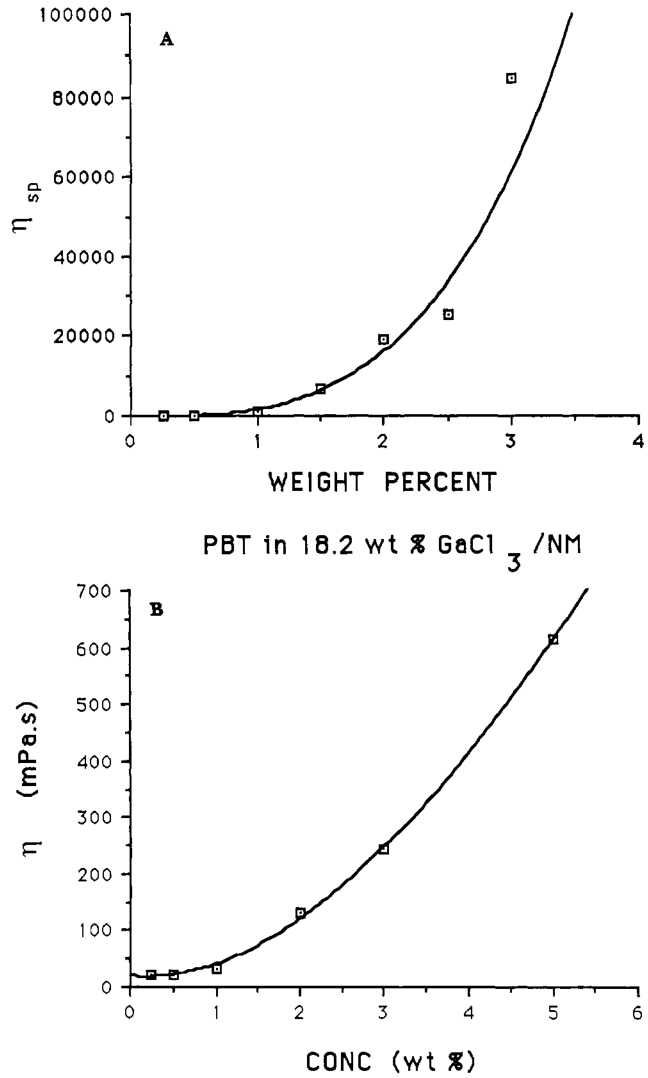

Figure 6. (A) Specific viscosity (η_{sp}) versus concentration of PBT solutions in organic solvent ($AlCl_3$/nitromethane). (B) Viscosity versus concentration of PBT solutions in $GaCl_3$/nitromethane.

The fact that PBT and the other rigid rod polymers in Figure 1 can form liquid-crystalline solutions in protic acids, such as methanesulfonic acid (MSA) and polyphosphoric acid, is well-known.[1-4] For example, PBT typically forms liquid-crystalline (nematic) solutions in MSA at 7 wt % at room temperature. Thus, it can be expected that liquid-crystalline solutions of PBT may be similarly obtained in organic solvents provided the solubility is high enough. However, since the present solubilization in organic solvents is achieved by complex formation, it can also be expected that the effective axial ratio of the polymer chains—a key factor that determines the critical concentration for isotropic to nematic transition—may significantly change due to complexation. Our observations of solutions of PBT in $AlCl_3$/nitromethane show that liquid-crystalline phases can indeed be obtained at high concentrations (> 5 wt %). More dilute solutions are isotropic: they appear transparent yellow and do not transmit light under crossed polarizers. However, though a 5 wt % PBT solution is still largely isotropic, it contains a distribution of anisotropic phases, which appear cloudy or turbid. Thin layers of the 5 wt % solution viewed under crossed polarizers showed large regions of liquid-crystalline phases evidenced by the transmitted light and colorful textures.

Figures 7 and 8 show the typical textures of the birefringent regions of a 5 wt % solution in $AlCl_3$/nitromethane. Although the liquid-crystalline solutions of PBT, PBO, and PBI in protic acid solvents are generally believed to be nematic mesophases,[1-4] as far as we know the textures of the lyotropic mesophases of these rigid rod polymers have not previously been reported. Our observed textures of liquid-crystalline PBT solutions in organic solvents containing Lewis acids are consistent with those of the nematic mesophase and similar to textures of lyotropic nematic solutions of extended-chain aromatic polyamides.[13,14]

The fact that a 5 wt % PBT solution in $AlCl_3$/nitromethane contains both isotropic and anisotropic phases indicates that the critical concentration for isotropic to anisotropic phase transition is higher than 5 wt %. Ongoing studies of isotropic/anisotropic phase equilibria and effect of the Lewis acid concentration on this equilibria in PBT solutions in organic solvents together with rheological measurements will allow precise determination of the critical concentration, as well as the isotropic, biphasic,

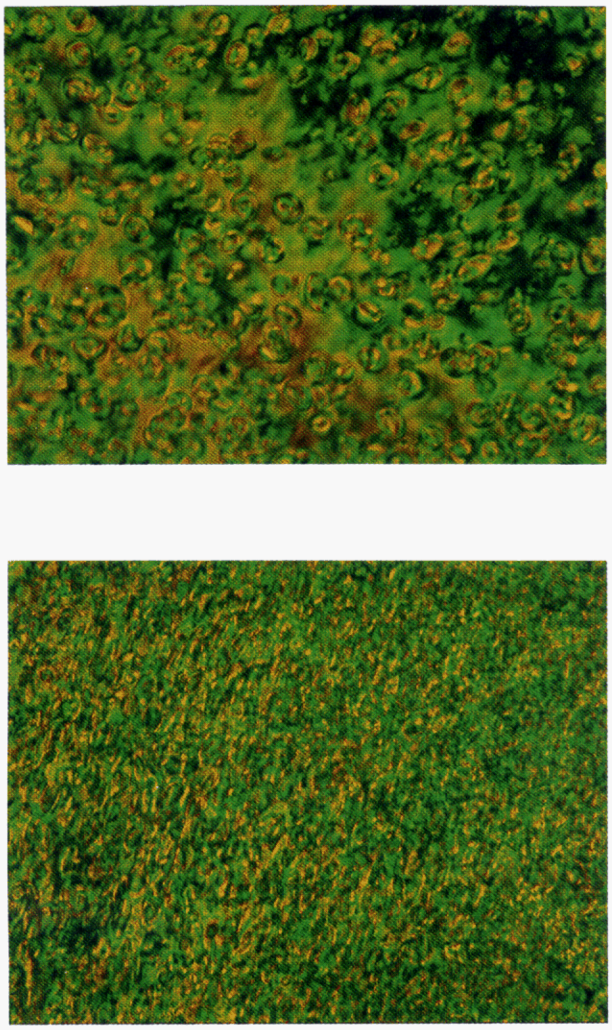

Figure 7. Photomicrograph of liquid-crystalline regions of a 5 wt % PBT solution in $AlCl_3$/nitromethane viewed under crossed polarizers (500×).

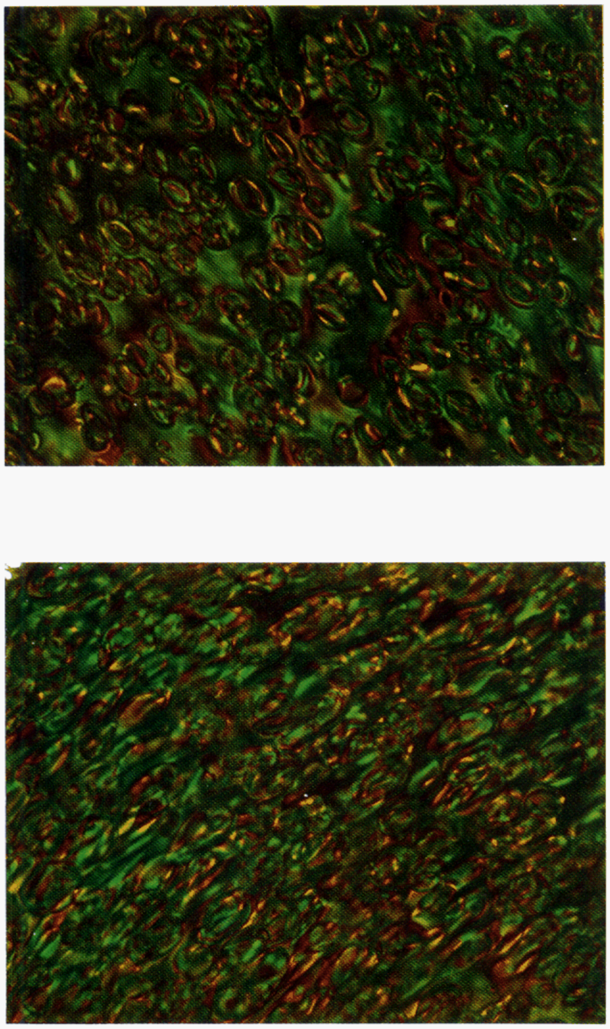

Figure 8. Photomicrograph of liquid-crystalline regions of a 5 wt % PBT solution in $AlCl_3$/nitromethane viewed under crossed polarizers (500×).

and liquid-crystalline regions.

Solution Processing to Films and Coatings. Solvent casting of the dilute PBT solutions on glass, sapphire, and silicon wafers gave films of the PBT/MX_n complex, which after immersion in a nonsolvent such as alcohol or water produced good yellow films or coatings of the pure PBT on a substrate. However, films or coatings produced from liquid-crystalline solutions were birefringent and had turbid appearance.

The complete regeneration of the pure polymer from its soluble complex was investigated by elemental analysis, infrared and UV–vis near-IR spectroscopies, and thermal analysis, including both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The analytical results showed only a trace amount (0.44 atomic % Cl) of Lewis acid in a PBT sample regenerated from a 30 wt % $AlCl_3$/nitromethane solution by precipitation in water at room temperature. The analytical results for the regenerated polymer were also in good agreement with theoretical and pristine PBT values. The FTIR spectrum of a thin film of PBT regenerated from an $AlCl_3$/nitromethane solution is shown in Figure 9. This spectrum is that expected for the PBT structure shown in Figure 1 and is similar to those originally reported for the model compound and polymer.[2a]

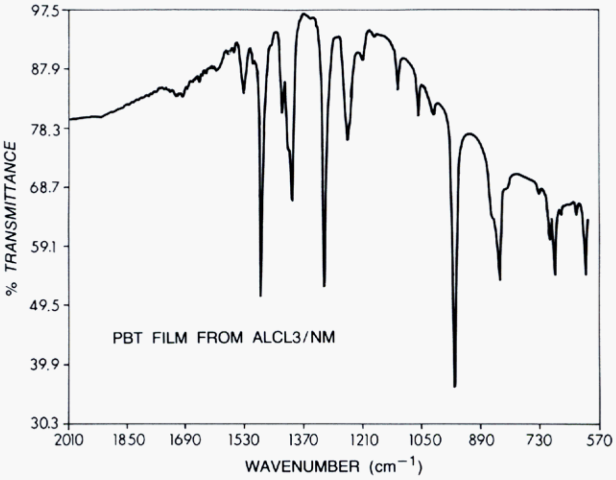

Figure 9. FTIR spectrum of a PBT thin film cast from $AlCl_3$/nitromethane solution.

Figure 10 shows the electronic absorption spectrum of a PBT thin film (~10 μm) cast from a 0.5 wt % PBT solution in $AlCl_3$/nitromethane. The absorption edge at ~500 nm gives a solid-state band gap value of 2.48 eV, which is slightly smaller than the value obtainable from the PBT solution spectra in either Lewis acid/organic solvents or methanesulfonic acid. It is to be noted that the observed spectrum of Figure 10 is that anticipated for the neutral and pure conjugated PBT.

The TGA of both the *pristine* and *regenerated* PBT showed similar thermooxidative stability as revealed in

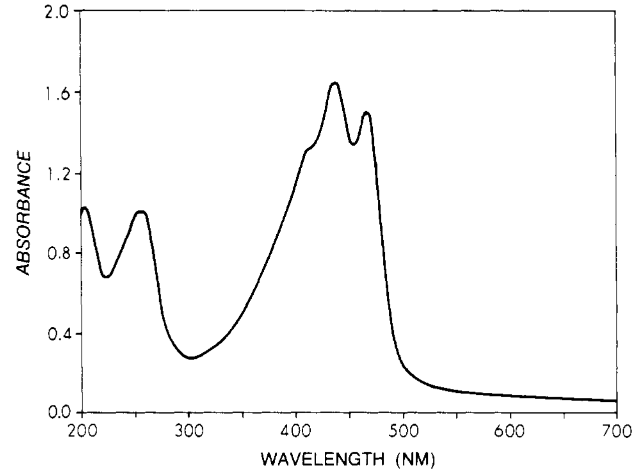

Figure 10. Electronic absorption spectrum of PBT thin film prepared from nitromethane/$AlCl_3$ solutions.

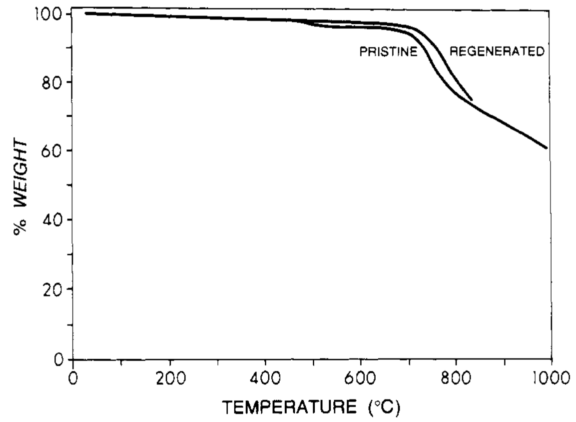

Figure 11. TGA thermogram of pristine PBT and sample recovered from nitromethane/$AlCl_3$ solution.

Figure 11. DSC scans of both pristine and regenerated pure PBT were similar, showing no transitions up to 600 °C as shown in Figure 12A. On the other hand, DSC thermograms of solvent cast PBT/$AlCl_3$ complexes containing varying amount of Lewis acid always revealed an endothermic transition at $\sim$190–305 °C, which is in the range of the melting or decomposition of $AlCl_3$ as shown in Figure 12B. The TGA weight loss curves of such PBT/$AlCl_3$ complexes similarly revealed a low-temperature decomposition product in contrast to Figure 11. All the above analytical, spectroscopic, and thermal analysis results confirm the recovery of the pure polymer by precipitation of its complexed solutions in nonsolvents. Furthermore, these results confirm that there is no polymer degradation or adverse side reactions when solubilized in organic solvents by complex formation with Lewis acids (MX_n). Finally, it is also clear that these results confirm the facile reversibility of complexation of PBT with certain Lewis acids in organic solvents.

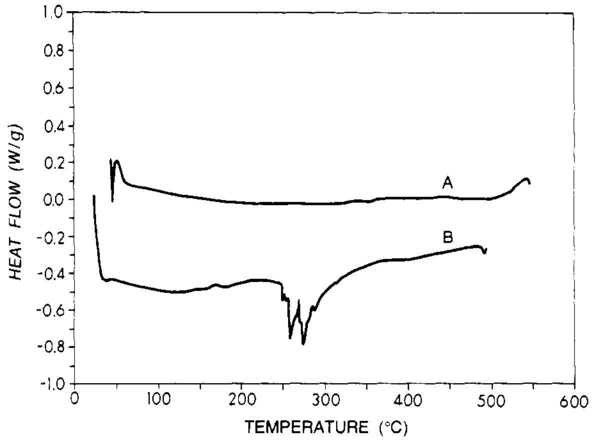

Figure 12. DCS thermogram of pristine and regenerated PBT (A) and PBT/$AlCl_3$ complex (B).

Mechanism of Solubilization. The observed solubilization of PBT and PBO, mediated by the presence of a Lewis acid (MX_n), is attributed to the *reversible in situ formation* of an electron donor–acceptor (EDA) complex of the rigid rod polymer in organic solvents. We believe that the soluble complex is not a π-electron charge-transfer complex but rather one formed between the Lewis acid and the unshared pairs of electrons of the heteroatoms (S, N, O) in the polymers. This means that the heteroatom sites on the polymers are sufficiently basic to react with Lewis acids to form complexes in essentially a reversible acid–base reaction. All the present results negate the possibility that the soluble complex is of the π-electron charge-transfer type: (1) The one instance where a π-electron charge-transfer complex of PBT was clearly formed, i.e. SbF_5-doped conductive PBT, it was insoluble. (2) The solution electronic spectra, facile decomplexation in nonsolvents, and a MX_n:PBT mole ratio of 4:1 are not characteristic of a charge-transfer complex. Furthermore, the isolated solid complex $AlCl_3$/PBT whose DSC scan is shown in Figure 12B is an insulator. There are four complexable heteroatom sites per repeating unit for the formation of EDA complexes in each of the rigid rod polymers of Figure 1. In the case of PBT, there are two thio (–S–) and two imino (=N–) sites. On the average all the four sites are actually complexed as the solubilization results suggest. Further studies of the detailed mechanisms of solubilization of PBT and other polymers via complex formation with Lewis acids in organic solvents are in progress and also discussed elsewhere.[11]

Conclusions

The aromatic heterocyclic rigid rod polymer, PBT, has been solubilized in *aprotic organic solvents* via reversible complex formation with Lewis acids. The resulting PBT solutions were found to be isotropic at low concentrations and appear to be liquid crystalline at high concentrations ($>$5 wt %). The textures of the lyotropic PBT solutions in organic solvents were those characteristic of the nematic mesophase. It was shown that the soluble PBT complex is not a π-electron charge-transfer type but one formed at specific heteroatom donor sites (S, N). Solutions of PBT in nitroalkanes containing $AlCl_3$ or $FeCl_3$ were significantly more viscous than solutions in $GaCl_3$/nitroalkanes at similar polymer concentrations. The solution electronic absorption spectrum of PBT in organic solvents containing metal halide Lewis acids (MX_n) was found to be similar to the spectrum in methanesulfonic acid. The solutions of PBT in organic solvents were stable indefinitely and were readily processed to films and coatings of the pure polymer by conventional solution casting followed by regeneration or precipitation in nonsolvents. Thus, the method of solubilization and processing of PBT in aprotic organic solvents presented here holds promise for the large-scale processing of the rigid rod polymers to films, coatings, and fibers.

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Modified Hammett Treatment on Copolymerizations of 7,8-Dibenzoyl- and 7,8-Bis(butoxycarbonyl)-7,8-dicyanoquinodimethane with Para-Substituted Styrenes: Differences between Alternating and Random Copolymerizations

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ABSTRACT: Copolymerizations of 7,8-dibenzoyl- (BzCQ) and 7,8-bis(butoxycarbonyl)-7,8-dicyanoquinodimethane (BCQ) with five kinds of para-substituted styrenes were carried out under a few different polymerization conditions considering the equilibrium monomer concentration of BzCQ or BCQ. The monomer reactivity ratios obtained were analyzed by the modified Hammett equation of Yamamoto and Otsu to determine the polar and resonance reaction constants of the cross-propagation steps in these copolymerizations. On the basis of these results is discussed the mechanism of the cross propagations in the copolymerizations.

Recently it was found out that some quinodimethane compounds with two different groups at the 7,8 positions such as 7,8-bis(alkoxycarbonyl)-7,8-dicyanoquinodimethane (1),[1,2] 7,8-diacyl-7,8-dicyanoquinodimethane (2),[3] and 7,8-bis(alkylthio)-7,8-dicyanoquinodimethane[4] are obtainable as stable crystals at room temperature and also are homopolymerizable with radical and other initiators in spite of being very highly conjugative. In the previous work[5] it was reported that 1 and 2 undergo typical of equilibrium polymerization with characteristic thermodynamic parameters of polymerization. Their values of entropy of polymerization are a third as large as those of conventional vinyl compounds, which generally exhibit values of entropy of polymerization in a given range of 100–130 J/(K·mol), and those of enthalpy of polymerization also lie in a low level from 21.6 to 26.4 kJ/mol, resulting in a negative but small free energy of polymerization. As another interesting feature of their polymerization behaviors it was found in their copolymerizations with styrene (St) that when their monomer concentrations in feed are higher than their respective equilibrium monomer concentrations, their copolymerizations are in a random fashion, whereas when the concentrations are lower than the equilibrium concentration, their copolymerizations change from a random to an alternating fashion. On the basis of this finding, a new mechanism[5] for alternating copolymerization has been proposed that when the more highly conjugative monomer between a pair of monomers loses its homopolymerizability due to participation of its depolymerization, their copolymerizations become alternating, and that the very stable and unreactive polymer radical with the terminal unit of the more conjugative monomer undergoes a bare cross propagation under the favor of a strong charge-transfer interaction with the comonomer such as St, conceivably composing the rate-determining process of an alternating copolymerization.

Moreover, in the previous studies of the terpolymerizations among two donor and a common acceptor monomers[6] and among two acceptor and a common donor monomers,[7] which can be regarded as combination of a pair of alternating copolymerization systems, it was pointed out that an alternating copolymerization is controlled much more with polar effect of component monomers and much less with general reactivity (resonance) effect compared to conventional random copolymerization.

Therefore, it was considered to be interesting and significant that the cross-propagation steps in copolymerizations of 1 and 2 with St would be investigated by the linear free energy principle to attain characteristics of an alternating copolymerization in a quantitative sense.

In this work were studied the copolymerizations of 7,8-dibenzoyl-7,8-dicyanoquinodimethane (BzCQ) and 7,8-bis(butoxycarbonyl)-7,8-dicyanoquinodimethane (BCQ) with five kinds of para-substituted styrenes under some polymerization conditions considering the equilibrium monomer concentrations of BzCQ and BCQ, to obtain the

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