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Thiophene-Based Liquid Crystalline Poly(benzobisoxazole)s

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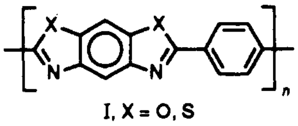
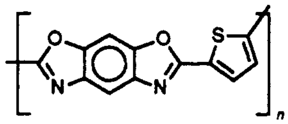
Introduction. Poly(benzobisthiazole)s and poly(benzobisoxazole)s are high-performance polymers exhibiting ultrahigh strength fibers with phenomenal thermal stability.[1] Abbreviated PBX (I, where X stands for oxygen or sulfur and these atoms are diagramed in the cis geometry), the rigid, rodlike primary and secondary structure of PBX accounts for the unusual properties of these polymers: it lends itself to an extended-chain crystal habit which, in turn, exhibits a solid-state morphology with an unusually high degree of order and crystallinity. Both the large-scale morphology and the local crystal perfection may be traced to the fact that the solid state of PBX is derived from a liquid crystalline phase—a lyotropic mesophase wherein the rodlike PBX chains assume a virtually parallel (nematic) supramolecular arrangement in concentrated polymer solutions. Although the rigid, rodlike, molecular structure confers exceptional solid-state properties, there is concomitant intractability which limits the processability of and, consequently, the applications for PBX. For example, aggressive solvents such as methanesulfonic acid are necessary to solubilize PBX. Herein we describe the synthesis of a modified poly(*p*-phenylenebenzobisoxazole) (PBO) wherein we have replaced the 1,4-phenylene unit in the backbone with the 2,5-thiophene unit, poly(2,5-thienylbenzobisoxazole) (PBOT, II).


I, X = O, S


II

We explore some general properties of this heterocyclic PBX derivative with some ulterior motives, namely, with the suspicion that PBOT's nonlinear backbone secondary structure could impact tractability, processing, and other issues in this class of polymers. Although the thiophene heterocycle introduces a "bend" into the structure of the chain ($\sim$148° between the thiophene unit's 2–5 exocyclic bonds), we know from recent work in our laboratory on thiophene-based model mesogens[2] and the findings of Chow et al.[3] on poly(2,6-benzothiazole) and poly(2,5-benzoxazole)—ABPBO having a $\sim$150° bend in the backbone chain—that this marked deviation from backbone linearity does not deleteriously effect liquid crystal formation. Hence, we anticipated finding mesomorphism in concentrated solutions of PBOT.

In the synthesis of the control polymer PBO, we used a route that employed the terephthalic acid chloride;[1b] this appears to circumvent the solubility problems of the diacid (the necessity for using ultrafine diacid particle sizes).[1c] Although the 2,5-thiophene diacid is more soluble than terephthalic acid, use of the heterocyclic acid chloride does facilitate preparations with final PBOT concentrations (in the poly(phosphoric acid) reaction solvent) that are rather high by the standards reported for PBO. After confirming the viability of the diacid chloride route to PBO, we extended the synthesis to PBOT and describe some preliminary data on selected properties of this new polymer.

Experimental Section. Each polymer was synthesized in freshly prepared poly(phosphoric acid) (PPA) using the P_2O_5 adjustment method[1] to control the PPA composition at various stages of the synthesis. The polymerization was carried out to give predetermined, target polymer concentrations in order to ensure that the critical concentration for mesophase formation was exceeded.

Poly(1,4-phenylbenzobisoxazole) (PBO). Phosphorus pentoxide (3.76 g) was added to 85% phosphoric acid (5.62 g) while the mixture was stirred under argon at room temperature. The solution was then heated at 115 °C overnight to produce a clear, homogeneous PPA. 4,6-Diamino-1,3-benzenediol dihydrochloride (2.13 g, 0.01 mol; Dow Chemical Co.) was added while stirring under argon at 115 °C. These conditions were maintained for 4 days to allow complete dissolution and dehydrochlorination of the monomer before the terephthaloyl chloride (2.03 g, 0.01 mol + 5%) was added (a 13% wt final polymer solution is targeted). During the reaction, a total of 5.517 g of P_2O_5 was added to the solution in small increments as described in ref 1. (A few milliliters of toluene was refluxed above the reaction mixture to return sublimed terephthaloyl chloride to the reaction.) The following temperature profile was employed during polymerization: 24 h @ 95 °C; 2 h @ 130 °C; 24 h @ 155 °C; 24 h @ 170 °C; 22 h @ 180 °C; 24 h @ 195 °C. Over this time the solution evolved into an inky, opalescent mixture which was extremely viscous and exhibited spontaneous birefringence, the signature of a lyotropic liquid crystal.

The workup consisted of dissolving the polymer in methanesulfonic acid (MSA), precipitating the polymer in methanol, washing with methanol and water, and then continuously extracting with methanol in a Soxhlet overnight. The inherent viscosities of PBO in MSA routinely gave values in the range of 2–4.4 dL/g.

Poly(2,5-thienylbenzobisoxazole) (PBOT). The PBOT polymer was prepared using a slightly altered version of the procedure outlined for PBO. 2,5-Thiophenedicarbonyl chloride was substituted for terephthaloyl chloride, and the polymerization was carried out to give a higher final polymer concentration (20 wt % instead of 13 wt % for PBO). This change required using less solvent and the corresponding modifications of the poly(phosphoric acid) (PPA was prepared with 2.14 g of P_2O_5 and 3.18 g of phosphoric acid, and only 3.92 g of P_2O_5 was added during the dehydrochlorination). As there was no serious foaming of the liberated HCl, instead of incremental heating, the temperature of the solution was raised to 185 °C within 1 h of the addition of the thiophene monomer. A few hours later, the reaction mixture became extremely viscous. At this point the reaction mixture exhibited spontaneous birefringence (Figure 1). The

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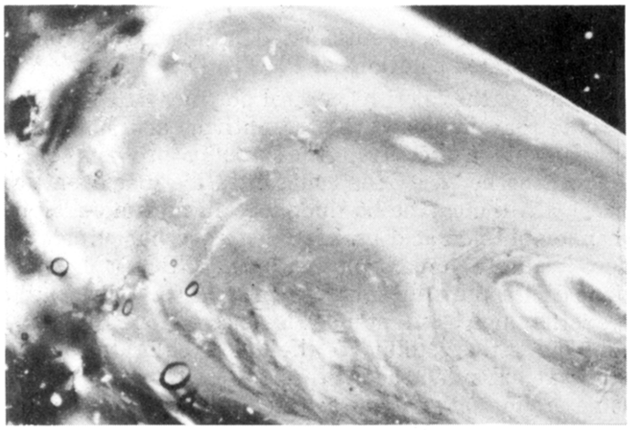

Figure 1. Photomicrograph of the PBOT reaction mixture (18% wt polymer in poly(phosphoric acid)) under crossed polars. The birefringent texture is nematic.

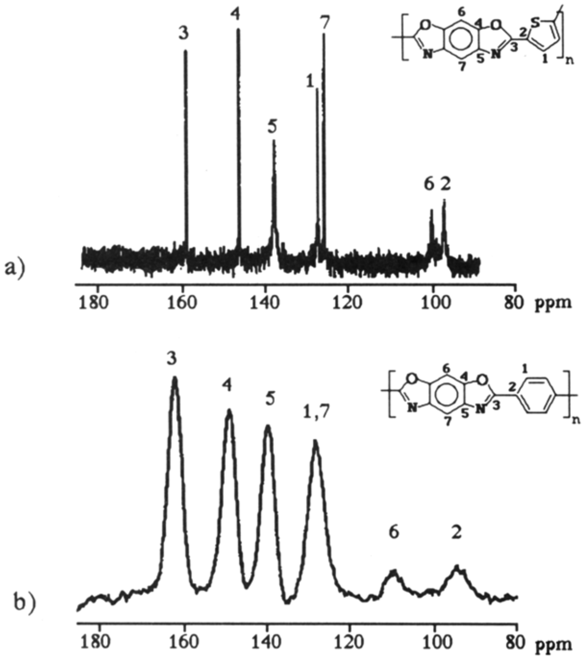

Figure 2. (a) Carbon-13 NMR spectrum of PBOT in deuterated sulfuric acid (90.56 MHz). (b) Solid-state carbon-13 NMR spectrum of PBO (MAS spinning rate 3.4 kHz, 5-ms mixing time, and TOSS side-band suppression; 90.56 MHz with external adamantane reference).

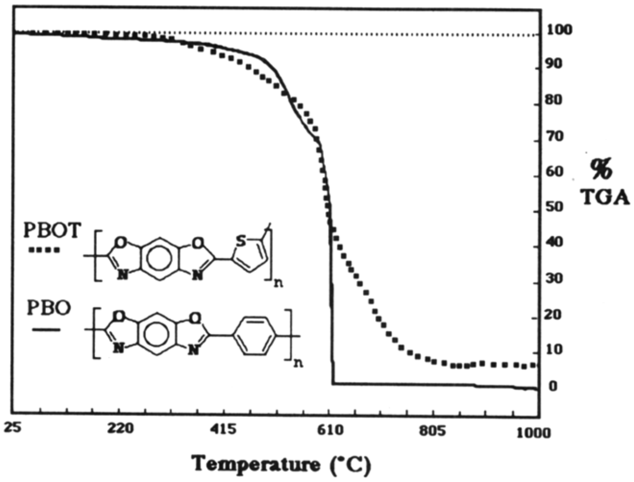

Figure 3. Thermogravimetric analysis of PBO and PBOT in air; 20 °C/min.

workup was the same as that used for PBO. Inherent viscosity values of 1.6–1.8 dL/g were obtained for this polymer in MSA.

In Figure 2a, we show the ^{13}C NMR spectrum with assigned chemical shifts supporting the structure of PBOT. The assignment of the spectrum was conducted by referring to the spectra of 4,6-diamino-1,3-benzenediol dihydrochloride (106.2, 153.6, 112.0, and 121.7 ppm for carbons 1–4, respectively) and 2,5-thiophenedicarbonyl chloride (145.9 and 136.5 ppm for the ring carbons 1 and 2). The solution spectrum of PBOT is contrasted with the solid-state NMR spectrum of PBO (Figure 2b). Thermogravimetric analysis (TGA) was carried out in nitrogen and in air (with a Seiko 320 TG/DTA at a heating rate of 20 °C/min).

Results and Discussion. We have demonstrated that nonlinear 2,5-thiophene can be substituted for the linear *p*-phenylene linkage in PBO to give a nonlinear PBX-type polymer. The lower inherent viscosities exhibited by PBOT relative to PBO are undoubtedly due to the nonlinearity introduced into the polymer backbone by the thiophene heterocycle. The degree of polymerization (dp) for our control sample PBO is about 30; without Mark–Houwink constants for PBOT we cannot determine its dp but estimate that both polymers are of comparable molar mass. When the final PBOT concentration was targeted to be above ~18% polymer in PPA, the reaction mixture is birefringent and readily flows when warmed. The schlieren texture shown in Figure 1 is indicative of a lyotropic nematic phase. Hence, the important precursor phase to ultrahigh strength fibers—the mesophase—is present in concentrated solutions of both the linear PBO and the nonlinear PBOT macromolecules.

In Figure 3 we contrast TGA scans of PBO and its thiophene analogue PBOT in air; there is no indication of weight loss up to 500 °C for either polymer. Subsequent thermal analysis studies of thiophene-containing polyesters,[4] polyamide,[5] and poly(arylene ether ketone)s[6] confirm that the thiophene unit has good thermooxidative stability. We therefore conclude that, despite insinuations to the contrary,[7] PBOT shows thermal stability comparable to that of PBO itself; i.e., we do not weaken the primary structure on introducing the sulfur-containing heterocyclic unit into the backbone.

Recently it has been suggested that chain persistence is a critical variable for mesophase formation in semiflexible polymers.[8,9] We have attempted to qualitatively contrast the persistence length, R_x, for the new PBOT polymer with that of the essentially rectilinear PBO chain and that of the nonlinear poly(2,5-benzoxazole) (ABPBO) chain. The ABPBO is an example of another secondary structure in this class of polymers having a 150° bend in the polymer backbone and similarly exhibits a mesophase.[3] The persistence length values for all three structures were obtained via a numerical simulation technique wherein we randomly varied dihedral angles about the single bonds connecting the bisoxazole unit to the "aromatic" ring in the primary structure (i.e., the $>$N–C$_{ar}$ bonds) to "grow" chain configurations. Using half of the linear bisoxazole unit as the initial segment, we averaged the projection of the end-to-end distance R on the direction of the initial segment (along the x-axis) for several hundreds of such randomly generated chain configurations to obtain the average persistence length at a given degree of polymerization N, $\langle R_x(N) \rangle$. It is important to note that these calculations were based on freely rotating chains—no preferential weighting of the dihedral angles—and therefore represent "high-temperature" limiting values of $\langle R_x \rangle$. Consequently, the results in Figure 4 represent lower limits for $\langle R_x(N) \rangle$ and are not directly comparable with more

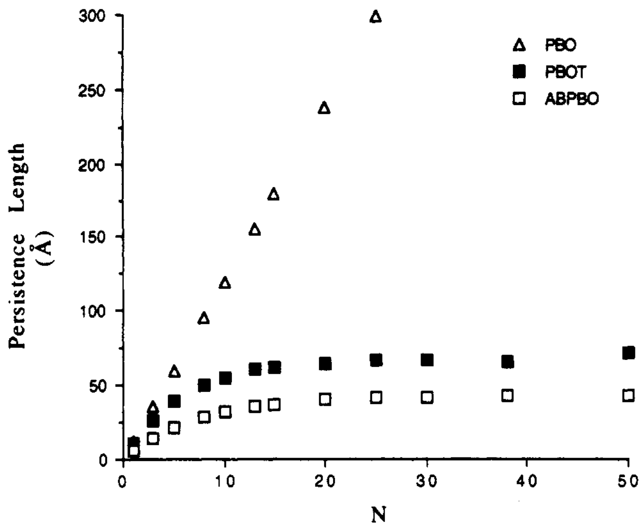

Figure 4. Computed persistence lengths for freely rotating chains of PBO (triangles), PBOT (solid squares), and ABPBO (open squares) versus degree of polymerization N.

exact modeling of this class of polymers recently reported.[10,11] While PBOT and ABPBO have limiting persistence lengths that differ by a factor of 2 ($\langle R_x(\infty)\rangle \sim 75$ Å and $\langle R_x(\infty)\rangle \sim 45$ Å, respectively), these values are much smaller than that computed for PBO ($\langle R_x(N)\rangle \sim N$). (In fact, in order to introduce structural realism into the calculation of $\langle R_x(N)\rangle$ for PBO, we performed a MM2 minimization on the benzoxazole unit and found a 2.4° deviation from linearity with respect to this unit's exocyclic bonds. However, this small structural nonlinearity, when incorporated into the idealized calculation of $\langle R_x\rangle$ for PBO, produces a negligible deviation from linearity in the plot of $\langle R_x(N)\rangle$ vs N and is not apparent on the scale of Figure 4.) Our computations for PBOT are in qualitative agreement with recent (high-temperature limit) calculations of $\langle R_x(N)\rangle$ by Windle[12] using more realistic torsion angle potentials. All three polymers considered in the computations span a wide range of $\langle R_x(N)\rangle$ values *and* experimentally have been shown to yield liquid crystalline phases. Thus, in conjunction with the widely accepted thesis that excluded-volume interactions dominate low molar mass mesophase stability, we are led to conclude that the global persistence length of a polymer chain may be a less relevant indicator of a chain's propensity for liquid crystal formation than some measure of the facility of short-range packing of chain contours.

In several classes of high-performance polymers based on thiophene we generally observed increased tractability (solubility) relative to the *p*-phenylene polymers.[2,4-6] While we do not have firm evidence of increased tractability of PBOT relative to PBO, i.e., increased solubility of the isolated PBOT polymer itself, the possibility of targeting high PBOT concentrations in PPA (≥20% wt) relative to those readily achieved in PBO (≤15% wt) points toward greater tractability; minimally it suggests that PBOT might possess advantageous processing attributes. Lastly, the potential nonlinear optical activity of PBOT has not escaped our attention; model compounds based on bisthiazoles linked to thiophene and the PBX class of materials in general show promising $\chi^{(3)}$ values;[10,13,14] however, additional characteristics of PBOT are needed before we can say more about this aspect of the polymer.

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