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Technical Report

Molecular Control of Liquid Crystalline Orientation of
Poly(p-phenylene-2,6-benzobisoxazole) and
Poly(p-phenylene-2,6-benzobisthiazole)

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13. ABSTRACT (Maximum 200 words) We studied the effect of molecular orientation on the transverse mechanical properties of poly(p-phenylene-2,6-benzobisoxazole) (PBO) and poly(2,5-benzoxazole) (ABPBO). We prepared ABPBO and PBO chains with radially shaped chain orientations with respect to the anthrone nucleus. The inherent viscosity of the ABPBO in methene-sulfonic acid at 20°C was 0.98 dL/g. The ¹³ C FT NMR spectrum of the star-like polymer showed a chemical shift at 75.0 ppm (relative to TMS) corresponding to the quaternary carbon in the 9-position of the anthrone ring.				
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Molecular Control of the Liquid Crystalline
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INTRODUCTION

The pioneering research of Kwolek (1) in establishing the formation of lyotropic solutions of poly(p-benzamide) and poly(p-phenylene terephthalamide) resulted in the spinning of fibers which maintained the extremely high degree of chain orientation. The resulting fibers exhibit high strength and modulus in the direction of the fiber axis, however, the fibers have poor compressive properties.

Holiday and White (2) showed that a plot of the average transverse modulus against the cohesive energy density for a number of polymers was effectively linear. This dependence on secondary valence forces for strength and modulus perpendicular to the chain direction leads to poor compressive strengths in fibers and delamination problems in biaxially oriented films extruded from lyotropic solutions.

Poly(p-phenylene-2,6-benzobisthiazole) (PBZT) and poly(p-phenylene-2,6-benzobisoxazole) (PBO) were initially prepared at the Air Force Materials Laboratory at Wright Patterson (3). Wolfe (4) discovered that the preparation of PBZT in polyphosphoric acid (PPA) could be achieved at polymer concentrations as high as 21 wt % by increasing the phosphorus pentoxide content of the PPA. This discovery of a method to form more concentrated polymer solutions resulted in the preparation of liquid crystalline solutions of less rigid polymers such as poly(2,6-benzothiazole) (ABPBT) and poly(2,5-benzoxazole) (ABPBO).

Dickstein and Lilly (5) prepared lyotropic star block copolymers containing poly(dimethylsiloxane) flexible segments and poly(p-benzamide) rodlike segments. Dickstein predicted that the unique topology of this system would result in improvements in the multidimensional properties of fibers and films. Furthermore, he suggested that blends of the star-block copolymers and polymers like poly(p-phenylene terephthalamide) would have improved strength in directions other than the chain direction.

We decided to study the effect of molecular orientation on the transverse mechanical properties of PBO and ABPBO by preparing star-like block copolymers. We proposed to use the favorable geometry of 2,6-diamino-9,9-bis(4-aminophenyl)-anthrone to prepare ABPBO and PBO chains with star-like or radially shaped chain orientations with respect to the anthrone nucleus.

EXPERIMENTAL

Preparation of Anthraquinone-2,6-dibenzamide I

Anthraquinone-2,6-dibenzamide I was prepared by the reaction of 2,6-diaminoanthraquinone with benzoyl chloride under reflux. Yield (78 %), IR (KBr pellet) 1679 cm^{-1} (amide I peak) strong, 1660 cm^{-1} (C=O, quinone) strong.

Preparation of 9,9-Bis(4-aminophenyl)anthrone-2,6-dibenzamide II

9,9-Bis(4-aminophenyl)anthrone-2,6-dibenzamide was prepared by essentially the method used by Srinivasan and coworkers (6) to prepare 9,9-bis(4-aminophenyl)anthrone. Aniline hydrochloride (7.77g, 0.06 mole) and 70 ml of freshly distilled aniline were added to 4.46g (0.01 mole) of I in a 500 ml three necked flask equipped with a condenser, thermometer, drying tube, and magnetic stirrer. The mixture was refluxed at 180°C for 24 hrs. The reaction mixture was allowed to cool to room temperature and stand overnight. 9,9-bis(4-aminophenyl)anthrone was collected by filtration and washed with methanol. The crude product was recrystallized from N,N-dimethylacetamide. Yield 2.4g (39 %). IR (KBr pellet) 1651 cm^{-1} (amide I peak) strong, 1624 cm^{-1} (NH, bending) medium. Anal. Found: C, 77.78%; H, 4.87%; N, 9.18% (theoretical, C, 78.17%; H, 4.88%; N, 9.12%).

Preparation of 2,6-Diamino-9,9-bis(4-aminophenyl)-anthrone III

A mixture of II (2.00g, 325 μmole), 30 ml. of 0.3 N potassium hydroxide, and 170 ml. of dimethylsulfoxide was refluxed for 3 hrs. Four hundred milliliters of water were added to the solution. After cooling and filtering, 10% sodium bicarbonate and 15% sodium hydroxide solutions were added to the filtrate. Red-yellow 2,6-diamino-9,9-bis(4-aminophenyl)anthrone was obtained by filtration. Yield, 0.5g (38%). IR (KBr pellet) 1665 cm^{-1} (C=O) medium, 1627 cm^{-1} (NH, bending) medium. Anal. Found: C, 75.51%; H, 5.07%; N, 11.89%. C, 78.70%; H, 5.30%; N, 13.69% (theoretical, C, 76.81%; H, 5.47%; N, 13.79%).

Reaction of 2-Amino-3-hydroxybenzoic Acid with 2,6-Diamino-9,9-bis(4-aminophenyl)anthrone III

A mixture of 8.2 g of 15% PPA and 3.4g of PA (87.5% phosphoric acid) was heated at 100°C for 4 hrs under reduced pressure in a 250 ml 3 necked flask. III (0.190g, 8.448 μmole) and 7.0g (44.8 μmole) of 2-amino-3-hydroxybenzoic acid were introduced into 11.6 ml of the warm PPA. The contents of the flask were deaerated by a vacuum pump. The reaction kettle was heated with an oil bath at 50°C under a stream of nitrogen gas overnight. The kettle was then placed under reduced pressure and heated to 70°C for 23 hrs. Phosphorus pentoxide (10.67g) was added to the reaction mixture to increase the effective P_2O_5 content to 88.5%. After stirring for 3 hrs, the temperature was raised to 100°C and the reaction mixture was maintained under reduced pressure for 21 hrs at this temperature. Then the mixture was heated as follows: for 3 hrs at 115°C under nitrogen; for 2 hrs at 130°C under reduced pressure; for 0.5 hr at 170°C under reduced pressure; and at 190°C under reduced pressure for 17 hrs. The solution was poured into water and the polymer which precipitated was filtered and washed with methanol. The intermediate polymer obtained was then heated under nitrogen for 20 hrs at 270°C. Yield, 4.8g of green black polymer. IR (KBr pellet) 1654 cm^{-1} (amide I peak) small, 1545 (C=N) strong. Anal. Found: C, 70.51%; H, 2.68%; N, 11.60% (theoretical, C, 70.91%; H, 3.09%; N, 11.93%).

RESULTS AND DISCUSSION

Hydrolysis of 9,9-bis(4-aminophenyl)anthrone-2,6-dibenzamide II with sodium hydroxide in refluxing dimethylsulfoxide produced a mixture of 2,6-diamino-9,9-bis(4-aminophenyl)anthrone III and 2,6-diamino-9,10-bis(aminophenyl)anthracene IV. Calcd. (50% III + 50% IV): C, 78.35%; H, 5.58%; N, 14.06. Found: C, 78.70%; H, 5.30%; N, 13.69%. Hydrolysis of II at lower temperatures produced a mixture of IV and benzoic acid. Calcd. (70% III + 30% benzoic acid): C, 75.75%; H, 5.36%; N, 12.21%.

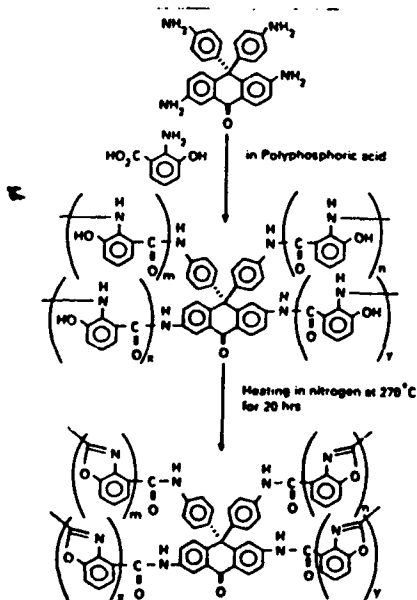
Found: C, 75.51%; H, 3.07%; N, 11.89%. The mixture of III and benzoic acid was used to prepare star-like poly-2,4-benzoxazole. After an intermediate polymer was formed which still contained rings which were not closed, a heat treatment step was needed to form the star-like polymer systems (Scheme 1). The inherent viscosity of the polymer in methane-sulfonic acid at 20°C was determined to be 0.98 dl/g. The proton-decoupled natural-abundance ^{13}C FT NMR spectrum of star-like poly-2,4-benzoxazole in D_2SO_4 is shown in Figure 1. The ^{13}C chemical shifts (relative to TMS) were as follows: δ 75.0, 106.8, 123.0, 126.1, 130.2, 132.3, 150.0, and 161.8 ppm. The peak at δ 75.0 ppm corresponds to the resonance for the quaternary carbon in the 9-position of the anthrone ring. The ^{13}C shifts for benz-oxazole(7) are reported to appear at 111.6, 121.1, 125.2, 126.2, 141.1, 150.7, and 154.1 ppm in acetone- d_6 .

ACKNOWLEDGEMENT

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Scheme 1. Preparation of star-like poly(2,4-benzoxazole).

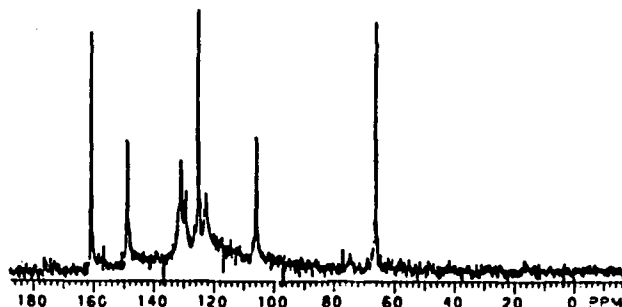
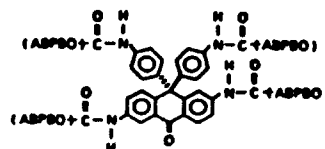


Figure 1. ^{13}C NMR spectrum of star-like poly(2,4-benzoxazole).

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