of freshly prepared[3] PPA. The clear solution was then heated to 125 °C. A slurry of **12a**[3] (4.1221 g, 8.7606 mmol) and sulfolane (154 g) was heated to 120 °C and added quantitatively to the PPA/**5** solution. The mixture was then heated under nitrogen as follows: 125 °C, 1 h; 140 °C, 0.5 h; 160 °C, 5 h; 175 °C, 1 h; 195 °C, 1.5 h. The polymerization mixture was then precipitated in methanol, washed with methanol, and dried. After reprecipitation from dilute methanesulfonic acid (MSA) solution, a tan polymer with an intrinsic viscosity of 6.5 dL/g (MSA, 30.0 °C) was obtained.

Methods. Intrinsic viscosities were obtained from solutions in freshly distilled methanesulfonic acid (MSA) by extrapolation of $\eta_{rel} - 1/c$ and $\ln \eta_{rel}/c$ to zero concentration. Polymer concentrations were chosen such that the relative viscosity (η_{rel}) was between 1.5 and 1.1. Monomer grade terephthalic acid was obtained from Amoco Chemicals Corp. with an average particle size of 54 μm. The monomer was reduced to a particle size of 95% <10 μm by an air impact method.

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Synthesis, Spinning, and Fiber Mechanical Properties of Poly(*p*-phenylenebenzobisoxazole)

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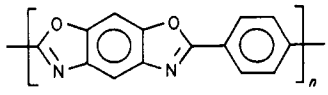
ABSTRACT: The synthesis and the processing of poly(*p*-phenylenebenzobisoxazole) (PBO) into high-modulus organic fibers and films are described. The monomer 4,6-diaminoresorcinol was polymerized with terephthaloyl dichloride in poly(phosphoric acid) at 90–210 °C to attain fibrillar poly(*p*-phenylenebenzobisoxazole). PBO in methanesulfonic acid with a small amount of chlorosulfonic acid was spun into high-modulus fibers and films. The mechanical properties and flammability of the fiber and film are described.

This report covers a part of the work carried out in support of the Air Force effort on the synthesis and solution processing of the high molecular weight rodlike polymers poly(*p*-phenylenebenzobisoxazole) (PBO) and



PBO

poly(*p*-phenylenebenzobisthiazole) (PBT). These polymers are characterized by a high degree of molecular order, their thermal stability, and fabricated shaped items of high strength and modulus.[1]

PBO can be prepared by polycondensation of 4,6-diaminoresorcinol and terephthalic acid in poly(phosphoric acid).[2,3] However, the polymer which is produced exhibits an undesirably low molecular weight and, when spun, yields fibers having undesirably low strength properties, especially modulus. Therefore, it is desirable to provide a process for the production of high molecular weight para-ordered aromatic heterocyclic polymer.

An improvement in the polymerization of linear high molecular weight PBO, the preparation of spinning solution, and the wet-spun fiber properties of PBO are described in this paper. These high molecular weight PBO polymers were prepared by polymerization of 4,6-diaminoresorcinol with an intermediate derived from the reaction of poly(phosphoric acid) and terephthaloyl dichloride, presumably a dipoly(phosphoric) terephthalic anhydride.

Polymerization. The general procedure is to charge the desired quantities of terephthaloyl dichloride and poly(phosphoric acid) into a reaction vessel and dehydrochlorinate by heating at 30–95 °C for 3–24 h in order to form the poly(phosphoric terephthalic anhydride). 4,6-Diaminoresorcinol dihydrochloride is then added and the resulting mixture is again dehydrochlorinated prior to polymerization.

It is also possible to mix 4,6-diaminoresorcinol dihydrochloride, terephthaloyl dichloride, and poly(phosphoric acid) and dehydrochlorinate the entire mixture. Following dehydrochlorination, the polymerization is begun with stepwise heating. Stepwise heating is preferred

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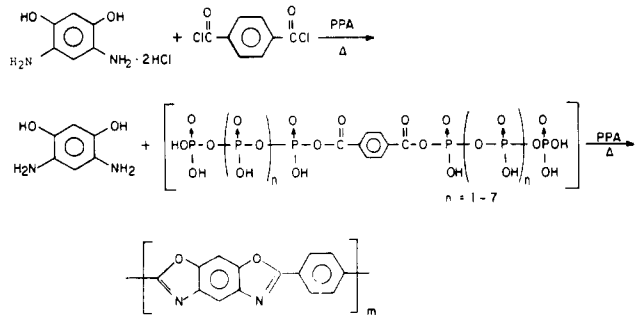

Figure 1. Synthesis of PBO from terephthaloyl dichloride and 4,6-diaminoresorcinol dihydrochloride.

Table I
PBO Polymers from Terephthaloyl Dichloride and 4,6-Diaminoresorcinol Dihydrochloride

polymer no.	PPA,[c] kg	$[\eta]$,[d] dL/g	$[\eta]$,[e] dL/g
1[a]	2	3.88	2.78
2[b]	2	3.57	2.44
3[a]	2	2.10	2.06

[a] 210 °C/48 h. [b] 210 °C/24 h. [c] 1.817% polymer solids. [d] After precipitation from poly(phosphoric acid) (PPA). [e] After precipitation from methanesulfonic acid (MSA).

because immediately exposing the reaction mixture to a relatively high polymerization temperature (~200 °C) may cause decomposition of the monomers. As an example of stepwise heating, the polymerization may be started at a relatively low temperature (e.g., approximately 130 °C) and the polymerization temperature subsequently increased in steps of approximately 20–30 °C at time intervals ranging from 3 to 5 h until the desired maximum polymerization temperature is attained. Polymers produced by this process exhibit a higher molecular weight than corresponding polymers produced by the conventional process, as is evidenced by inherent viscosity. Because of the relatively high molecular weight, the polymers exhibit a fibrillar texture. Fibrils containing many loose strands can be pulled from such polymers during workup. Fibers produced from polymers prepared according to this method exhibit higher strength properties, particularly modulus, than fibers spun from polymers prepared according to the conventional process.

The infrared spectrum of a film from this polymer is identical with that of an authentic sample. While the reaction involved in the process is at present not completely understood, one explanation is presented below, using the reaction of 4,6-diaminoresorcinol dihydrochloride and terephthaloyl dichloride in poly(phosphoric acid).

It appears that terephthaloyl dichloride reacts with poly(phosphoric acid) to form a dipoly(phosphoric) terephthalic anhydride with evolution of hydrochloric acid. The white milky anhydride reacts with 4,6-diaminoresorcinol to give a clear amber solution at 160 °C and polymerizes to PBO. Two advantages of terephthaloyl dichloride in the polymerization are that no sublimation occurs at the end of the reaction and the higher intrinsic viscosity. This proposed reaction sequence is illustrated in Figure 1.

The PBO polymers prepared by this method are summarized in Table I. The inherent viscosities ranged from 2.10 to 3.88 dL/g as determined at 0.2% in methanesulfonic acid when the polymers were precipitated directly into methanol, isolated, washed and dried. Some decrease in viscosity is apparent when the polymer was dissolved

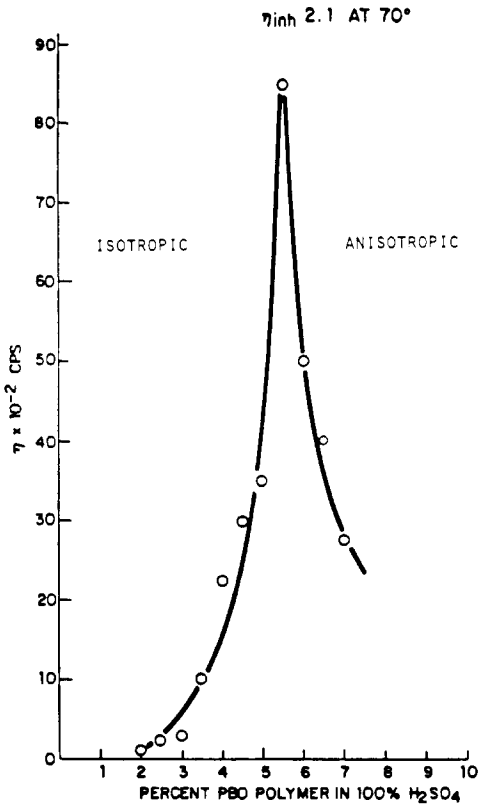

Figure 2. Critical concentration curve for PBO.

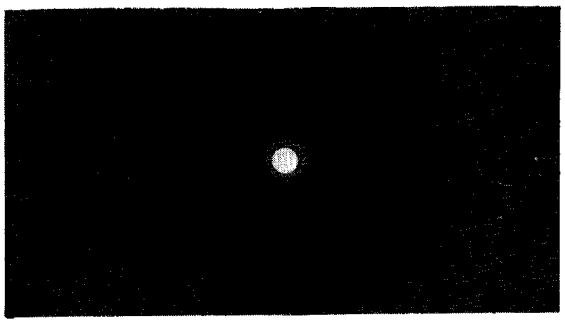

Figure 3. X-ray diffraction pattern for 11% PBO in 100% H_2SO_4

first in methanesulfonic acid, then precipitated into methanol, isolated, washed and dried. The cause is not fully understood at this time.

Spinning Solution. An anisotropic spinning solution (dope) of PBO was prepared by dissolving approximately 10% of the polymer in strong acids, such as 100% sulfuric, methanesulfonic (MSA), or chlorosulfonic (CSA) acid or a 97.5/2.5 mixture of methanesulfonic and chlorosulfonic acids.

Microscopic examination of PBO/MSA dopes show them to be in an anisotropic nematic liquid crystal state at room temperature.

PBO dopes in 100% sulfuric acid were prepared and characterized. A typical critical concentration curve for the rodlike polymers was observed for the PBO ($[\eta]$ 2.1 dL/g) in 100% H_2SO_4 at 70 °C and the curve is shown in Figure 2. The PBO dopes in 100% H_2SO_4 at concentrations greater than 8% solids exhibit crystalline structures (X-ray). They are semisolid at ambient temperature and lyotropic liquids at temperatures above 70 °C. The X-ray diffraction patterns of the dopes were different from those of PBO itself, showing some crystallinity and similarity to that of 16% Kevlar aramid (du Pont's trademark) dopes in 100% H_2SO_4. This might be due to both or either the

Table II
Principal Spacings of PBO (A)

	spacing (intensity)
polymer	3.35, 5.55, 11.35
fiber	3.27, 3.52, 5.52, 11.76
polymer recrystallized from 10% dope in 100% H_2SO_4	1.20 (vw), 1.329 (vw), 1.38 (vw), 1.61 (m), 1.76 (m to s), 1.94 (m to s), 2.38 (m to s), 2.76 (m to s), 3.24 (vvs), 3.51 (vs), 3.92 (vw), 4.14 (vw), 4.38 (vw), 5.50 (vvs), 11.19 (m to s)
polymer recrystallized from 8.6% solution in MSA	2.39 (vw), 2.52 (vvw), 2.86 (vvw), 3.36 (s br), 5.53 (s), 9.16 (vw), 11.26 (w)

Table III
PBO Fiber Properties[a]

spin no.	coagulation bath MSA/H_2O	jet velocity, m/min	spin draw ratio	DPF	elongation, %	tenacity, g/denier	$TE^{1/2}$	modulus, g/denier
1	30/70	4.5	1.4	5.3	1.4	4.2	4.9	502
2	40/60	6.3	1.1	5.5	2.4	3.4	5.3	340
3	40/60	6.3	1.0	9.2	6.6	2.3	5.8	132
4	50/50	6.3	<1.0	13.4	8.7	1.3	3.8	81

[a] Polymer $[\eta]$ = 2.8 dL/g; dope concentration, 8.6% in 97.5% methanesulfonic acid and 2.5% chlorosulfonic acid; dope and coagulation bath temperatures, room temperature; spinneret, 10 × 100 μm.

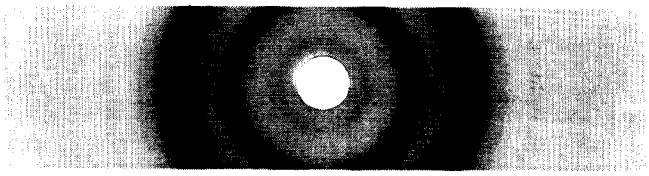

Figure 4. X-ray diffraction pattern for PBO precipitated from 100% H_2SO_4.

formation of a PBO/sulfuric acid complex or the sulfonation of the aromatic rings. An X-ray diffraction pattern for the PBO/H_2SO_4 complex is shown in Figure 3. When the dope was slowly precipitated, PBO crystallized out. The X-ray diffraction patterns of the crystals were extremely well-defined, indicating a very high degree of orientation. The principal spacings are listed in Table II and the X-ray diffraction pattern is in shown Figure 4. A PBO dope in MSA also showed some crystallinity (X-ray) at 11% solids, with the diffraction pattern shown in Figure 5. This is different from those of PBO itself and PBO/H_2SO_4.

Fabrication and Properties of PBO Fibers. Recent advances in spinning and processing of fibers are summarized by Robinson.[4] There are many process variables in fiber spinning and their relative importance depends on the spinning method chosen (i.e., wet, dry spinning, melt spinning, etc.), which, in turn, is dictated by inherent polymer properties such as meltability, solubility, intrinsic viscosity, etc. PBO does not melt and is only soluble in strong acidic solvents such as 100% sulfuric acid or methanesulfonic acid.

An initial approach to PBO spinning was to try wet spinning and then dry-jet wet spinning to increase the spin draw ratio and the orientation. Generally speaking, dry-jet wet spinning, by extruding the polymer dope into air or another gas medium briefly before it touches the coagulating liquid, allows a higher spin draw ratio and consequently higher molecular ordering than does wet spinning. In this way, higher fiber mechanical properties are realized. However, initially PBO fiber was wet spun from a ~10% solution of 97.5/2.5 methanesulfonic acid–chlorosulfonic acid at a jet face temperature of 25 °C, using 10-hole × 75–100-μm spinnerets, into a coagulation bath containing various concentrations of methanesulfonic acid. The yarn was taken up at various speeds to provide a spin stretch.

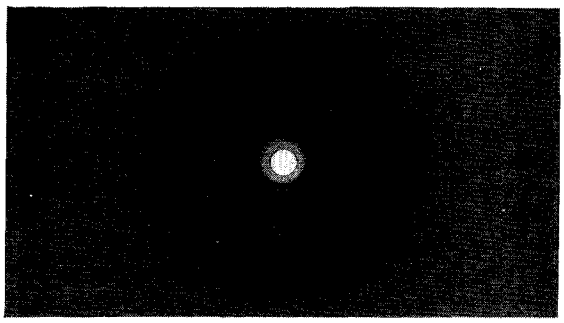

Figure 5. X-ray diffraction pattern of 11% PBO in methanesulfonic acid.

The spin draw ratio is the key to the molecular orientation leading to high fiber mechanical properties. Wet-spun PBO fibers from polymers prepared by the conventional method from terephthalic acid and 4,6-diaminoresorcinol were so weak that they could not be spin stretched and could be taken up only in the relaxed state. The weak wet filament strength is probably attributable to the low intrinsic viscosity. Due to the lack of cohesive strength of the dope, numerous attempts to dry-jet wet spin were not successful.

However, the 8.6% spinning solution (in 97.5/2.5 MSA/CSA) of PBO with inherent viscosity 2.8 dL/g, prepared from terephthaloyl dichloride and 4,6-diaminoresorcinol dihydrochloride, could be wet spun into a coagulation bath containing various concentrations of methanesulfonic acid in water.

The effect of methanesulfonic acid concentration in the coagulation bath on the fiber surface morphology and the fiber mechanical properties was evaluated over the acid concentration from 0 to 90% in water. Examination of SEM micrographs of the fibers indicated that the smoothest and most void-free fiber was obtained with an MSA concentration of 30%. Fiber coagulated from this MSA concentration also yielded the highest property levels. The filaments were slightly spin stretchable (up to ~50%), with the best as-spun properties ($T/E/M$) obtained being 4.2 g/denier/1.4%/502 g/denier. The fiber properties are summarized in Table III. Wide-angle X-ray diffraction patterns showed a significantly higher degree of orientation than those for the previous PBO polymers prepared from terephthalic acid (Figure 6).

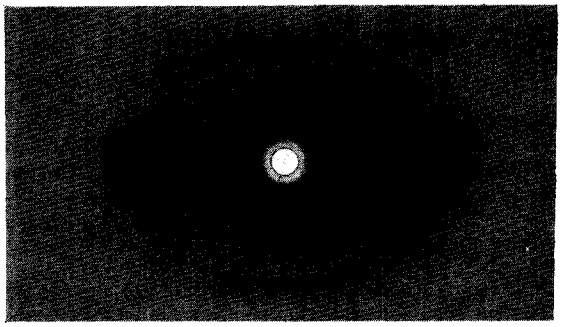

Figure 6. X-ray diffraction pattern of wet-spun PBO fiber prepared from terephthaloyl dichloride before heat drawing (50 kVp, 100 mA, 3-h exposure, Cu Kα radiation).

Table IV
PBO Fiber Properties after Heat Treatment

treatment temp, °C	single-filament fiber properties			
	DPF	tenacity, g/denier	elongation, %	modulus, g/denier
as spun	5.3	4.2	1.4	502
425	4.8	4.8	0.7	711
450	4.9	4.4	0.6	723
475	5.2	3.3	0.5	584
500	5.2	4.5	0.9	559

Table V
Effect of Spin Draw Ratio on PBO Fiber Properties[a]

	spin no.				
	1	2	3	4	5
spin draw ratio	<1	1	1.1	1.2	1.43
jet velocity, m/min	6.3	6.3	6.3	5.3	4.4
fiber properties					
DPF	9.5	9.1	8.3	7.2	6.5
tenacity, g/denier	1.5	1.8	2.1	2.2	2.6
elongation, %	3.4	3.4	2.2	2.5	1.7
modulus, g/denier	120	122	200	198	269
$TE^{1/2}$	2.7	3.3	3.1	3.5	3.3

[a] PBO $[\eta]$ = 2.1 dL/g; dope concentration, 8.6% in 97.5 MSA/2.5% CSA; dope and coagulation bath temperature, room temperature; spinneret, 10 × 100 μm.

The fibers produced by the procedure described above were heat treated at various temperatures within the temperature range 425–500 °C, as shown in Table IV. The heat treatment was conducted by gripping the fiber in the test instrument for 3 min at the heat treatment temperature. The fiber was then drawn during the heating at a 10% strain rate until the fiber broke. The broken sample was then tested at room temperature. As can be seen from the results given in Table IV, a dramatic increase in the modulus of heat-treated fibers over the modulus of as-spun fibers was observed. The best overall fiber properties were obtained after heat treatment at 425 °C. Another PBO sample with an intrinsic viscosity of 2.1 dL/g was wet spun at various spin draw ratios. Results on the fiber properties given in Table V show the effect of spin draw ratio on the fiber properties. Although the physical properties obtained were lower than those from the PBO polymer with an intrinsic viscosity of 2.8 dL/g, presumably because of the lower molecular weight, the results show a trend that the fiber properties, tenacity and modulus, increase as the spin draw ratio increases.

Fiber Flammability. Flammability for a group of polymers was reported recently by Stuetz et al.[5] Critical oxygen concentration (COC) is a measure of the minimum oxygen concentration for onset of combustion as a function of extrinsic parameters. Critical oxygen concentrations

Table VI
Fiber Flammability—Critical Oxygen Concentration[a]

	COC (TW)	COC (BW)
PBO	36.1	22.8
PBT	35.7	22.6
PBI	46.3	28.0
Nomex[b]	26.5	18.0

[a] COC-TW 32.5 and COC-BW 21 signify a material which is "intrinsically noncombustible". [b] Nomex is du Pont's trademark.

greater than 32.5 in top and 21 in bottom ignition modes signify a material which is "intrinsically noncombustible". Critical oxygen concentration was measured for PBO and PBT fiber samples in top and bottom ignition modes, according to the Stuetz procedure.[5] The results given in Table VI indicate that both PBO and PBT are intrinsically noncombustible. Critical oxygen concentrations for PBI and Nomex (du Pont's trademark) are included in the table for comparison.

Fabrication and Properties of PBO Ribbon. A ribbon was extruded through a 6 mm × 0.25 mm (0.25 in × 10 mil) slit die by utilizing the spinning equipment. In the process of coagulation (in 30% MSA in water) and drying, the ribbon shrank to 3 mm ($^1/_8$ in) but it did not split. A tensile strength of 103 MPa (15 000 psi) and a modulus of 7.6 GPa (1.1×10^6 psi) at 0.8% elongation were measured. The ribbon thickness was 0.05 mm. The extrusion continuity (wet extrusion) was good but the properties obtained were significantly lower than the properties obtained with fibers from the same polymer.

A PBO solution in methanesulfonic acid was cast between two glass plates and one of the two plates removed in such a way as to induce a shearing action and an orientation. The resulting film was coagulated in water and dried first at room temperature and then at 80 °C. In conoscopic observation, both films show a centered acute bisectrix figure, which indicates they are well oriented. Wide-angle X-ray patterns for these films show a planar orientation.

Conclusion

4,6-Diaminoresorcinol was polymerized with terephthaloyl dichloride at 90–210 °C to attain fibrillar poly(p-phenylenebenzobisoxazole). PBO spinning solutions in methanesulfonic acid were spun into high-modulus noncombustible fibers and films. The best overall fiber properties demonstrated for PBO were 4.8 g/denier tenacity, 0.7% elongation, and 711 g/denier after heat treatment. Final denier of this sample was 4.8 g/denier. The dope of PBO from the dichloride could be spin stretched up to abut 45% but that of the polymer from terephthalic acid could not be spin stretched. A PBO ribbon was successfully extruded through a 6 mm × 0.25 mm (0.25 in × 10 mil) slit jet but it shrank to 3 mm ($^1/_8$ in) during the coagulation and drying. The as-spun ribbon properties were 103 MPa (15 000 psi) tenacity, 7.6 GPa (1.1×10^6 psi) modulus, and 0.8% elongation.

Experimental Section

IR spectra were measured on a Nicolet 7199 Fourier transform infrared spectrometer in the phases noted. NMR spectra were measured on a Varian EM360 and ^{13}C NMR spectra were measured on a Varian CFT-20. Microanalytical work was performed by Schwarzkopf Microanalytical Laboratory. All inherent viscosities were determined at 25 °C, using methanesulfonic acid as solvent, and at a polymer concentration of 0.2 g/100 mL.

Raw Materials. 4,6-Diaminoresorcinol dihydrochloride monomer was prepared according to the procedures described by Arnold and Wolfe.[3] Terephthaloyl dichloride was purified by

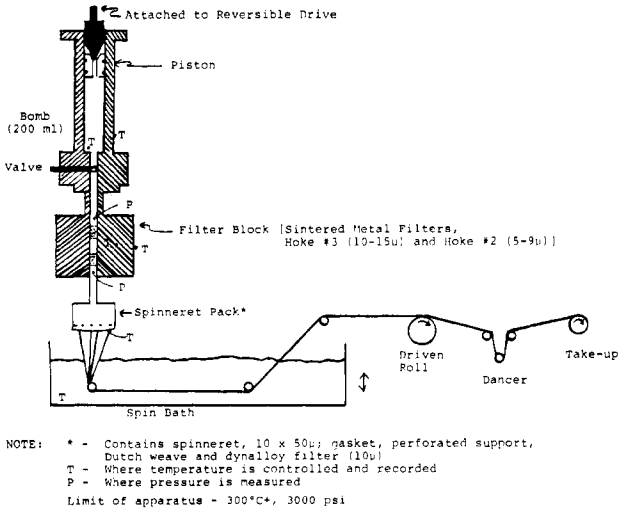

Figure 7. Schematic diagram of PBO spinning apparatus (shown for a dry-jet, wet-spinning operation).

vacuum distillation, followed by recrystallization from hexane. Poly(phosphoric acid) (115%) was acquired from the Food Machinery & Chemical Corp. (FMC) or MCD Manufacturing Chemists, Inc., and was deoxygenated by heating under nitrogen at 150 °C overnight. The polymerizations were carried out under nitrogen in 5-L resin flasks equipped with a spiral agitator.

Poly[(1,7-dihydrobenzo[1,2-*d*:4,5-*d'*]bisoxazole-2,6-diyl)-4-phenylene] [Poly(*p*-phenylenebenzobisoxazole) (PBO)] from Terephthaloyl Dichloride and 4,6-Diaminoresorcinol Dihydrochloride in Poly(phosphoric acid). 4,6-Diaminoresorcinol dihydrochloride (34.09 g, 0.16 mol) and pulverized terephthaloyl dichloride (32.48 g, 0.16 mol) were placed under nitrogen in a 5-L resin flask. Deoxygenated poly(phosphoric acid) (2 kg) was transferred under nitrogen into the flask. The mixture was stirred at 60 °C for 16 h and then at 90 °C for 5 h to dehydrochlorinate. The following heating stages were used for the polymerization: 130 °C for 3 h, 150 °C for 16 h, 170 °C for 3 h, 185 °C for 3 h, and finally 200 °C for 48 h (24 h in the case of run no. 2). At the end of the polymerization, the polymer was scooped out of the flask and precipitated from the poly(phosphoric acid) into 11.4 L of methanol. The polymer was filtered, neutralized with dilute ammonium hydroxide, washed with methanol, and dried at 100 °C. The inherent viscosity of the polymer was measured at a concentration of 0.2% (w/v) of methanesulfonic acid at a temperature of 25 °C. The polymer was dissolved in methanesulfonic acid and filtered. The filtrate was poured into methanol to precipitate the polymer. The polymer was filtered and washed consecutively with water, dilute ammonium hydroxide, water, and finally methanol. The polymer was then dried at 100 °C and a pressure of 0.1 torr.

Preparation of Spinning Solutions (Dopes). The PBO dopes were prepared under nitrogen in a 200-mL glass flask fitted with a helical agitator (Hastelloy B) and immersed in an 85 °C oil bath. The polymer granules were added slowly to the solvent at 85 °C. The agitator speed was controlled between 45 and 50 rpm. The dope was maintained hot until all undissolved particles disappeared. The test counts of undissolved polymer or foreign materials in the dope were conducted with an optical microscope (up to 500×). Methanesulfonic acid (Eastman, 98% minimum assay) and chlorosulfonic acid (MCB, practical grade) were used as solvents. The chlorosulfonic acid was added to remove moisture contaminants, if any, by forming highly volatile HCl.

A spinning apparatus developed previously for dry-jet wet spinning of poly(*p*-phenyleneterephthalamide)[6-8] was used for the PBO spinning. The dope is metered by a piston connected to a ram. The ram speed was accurately controlled by a variable-speed motor with a micrometer (Figure 7). The dope was then filtered in two stages before it reached the spinneret. The spinneret was immersed into the coagulation bath in the same direction as the fiber movement for a wet-spinning operation. Temperatures and pressures at various key points are continuously indicated and recorded. The apparatus requires 200 mL for a full charge and its dead volume is 25 mL. Tantalum spinnerets of 10 × 50 μm were used. The coagulation bath trough was 56 cm (22 in) long. For ribbon spinning, slit jets 6 mm × 0.25 mm (0.25 in × 10 mil) and 13 mm × 0.25 mm (0.5 in × 10 mil) were used.

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