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Articulated All-Para Polymers with 2,6-Benzobisoxazole, 2,6-Benzobisthiazole, and 2,6-Benzobisimidazole Units in the Backbone[1]

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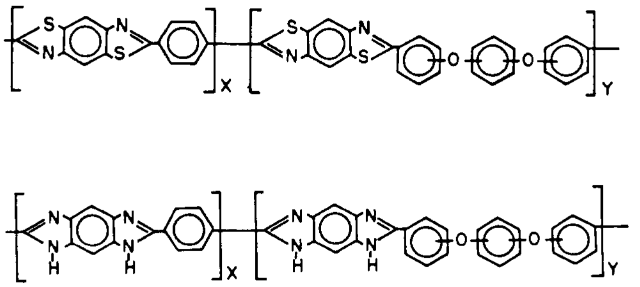
ABSTRACT: Articulated all-para polymers with 2,6-benzobisoxazole, 2,6-benzobisthiazole, and 2,6-benzobisimidazole units in the backbone were synthesized by copolycondensation in poly(phosphoric acid) of 4,6-diamino-1,3-benzenediol dihydrochloride, 2,5-diamino-1,4-benzenedithiol dihydrochloride, and 1,2,4,5-tetraaminobenzene tetrahydrochloride, respectively, with terephthalic acid and reactive diphenoxybenzene monomers. Inherent viscosities of up to 12.57 dL/g (CH_3SO_3H, 25 °C, 0.2 g/dL) were achieved. The average length of the rodlike all-para segments between the relatively flexible diphenoxybenzene units was controlled by the stoichiometry of the copolycondensation reactions. Films which exhibited optical birefringence under crossed polars could be cast from methanesulfonic acid solutions of the polymers. Modulus and tensile strength values as high as 4696 and 93 mPa, respectively, were recorded. Thermooxidative stability of the articulated polymers was evaluated by isothermal aging in air at 316 °C. Stability for the articulated poly(benzobisoxazoles) was found to decrease with increased content of the diphenoxybenzene structure. The articulated poly(benzobisoxazole) structure was shown to be less stable than the analogous poly(benzobisthiazole) structure but much more stable than the articulated poly(benzobisimidazole) structure.

Considerable research effort in recent years has been directed toward the synthesis, characterization, and fabrication of extended-chain or rodlike polymers. The unique ordering properties of these polymers into liquid crystalline solutions has resulted in the preparation of extremely high modulus fibers, exemplified by the fibers from poly(*p*-benzamide).[2] Examples of thermooxidatively stable, aromatic heterocyclic polymers which exhibited liquid crystalline behavior in concentrated solution are poly[(benzo[1,2-*d*:5,4-*d*′]bisoxazole-2,6-diyl)-1,4-phenylene] (PBO),[3] poly[(benzo[1,2-*d*:4,5-*d*′]bisthiazole-2,6-diyl)-1,4-phenylene] (PBT),[4] and poly[(benzo[1,2-*d*:4,5-*d*′]bisimidazole-2,6-diyl)-1,4-phenylene] (PBI).[5] Two of these all-para, rodlike polymers, PBO and PBT, have been spun into highly oriented fibers from methanesulfonic acid solutions;[6,7] fibers from the latter exhibited exceptionally high modulus and tensile strength values.[7]

In an attempt to improve the processability of these polymers through improved solubility and to modify the properties of the resultant fabricated specimens, we carried out the synthesis of articulated all-para polymers containing 2,6-benzobisoxazole, -thiazole, and -imidazole units in the polymer backbone. The synthesis of these articulated PBOs, PBTs, and PBIs was achieved through the introduction into the polymer backbone of a predetermined number of diphenoxybenzene units. The resultant polymers were expected to exhibit differences from the parent polymers (PBO, PBT, and PBI) in solubility, thermal characteristics, morphology, etc. On the basis of the theoretical considerations of Flory[8] and dependent on the number and isomeric structure of the diphenoxybenzene units,[9] the polymers were also expected to retain the ability to form liquid crystalline solutions.

Chart I



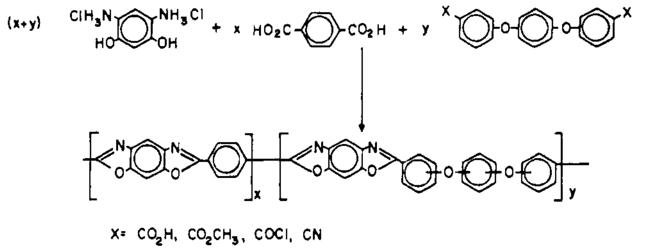
The initial synthesis effort entailed the preparation of the articulated PBOs through copolycondensation in poly(phosphoric acid) (PPA) of 4,6-diamino-1,3-benzenediol dihydrochloride with terephthalic acid and appropriately substituted diphenoxybenzene monomers (Scheme I). The average length of the all-para, rodlike PBO segments was determined by the stoichiometry of the reaction mixture and could be varied by adjusting the mole proportions (*x* and *y*, respectively) of terephthalic acid and diphenoxybenzene monomer. Various isomeric diphenoxybenzene structures were used, with emphasis initially being placed on incorporation of the $-p-C_6H_4-O-p-C_6H_4-O-p-C_6H_4-$ (p-p-p) structural isomer into the polymer backbone. Subsequently, the syntheses of articulated PBTs and PBIs (Chart I) were carried out in a similar fashion, with 2,5-diamino-1,4-benzenedithiol dihydrochloride and 1,2,4,5-tetraaminobenzene tetrahydrochloride as key monomers. The synthesis and preliminary characterization of the articulated polymers are described below.

Results and Discussion

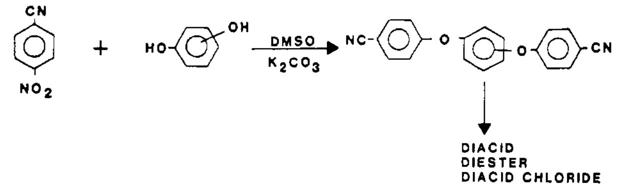
Monomer Synthesis. The key step in the preparation of the p-p-p, p-m-p, and p-o-p isomeric diphenoxybenzene structures entailed the base-promoted reaction of 4-nitrobenzonitrile with hydroquinone, resorcinol, and catechol, respectively. These nitro-displacement reactions were carried out according to the general procedure described by Heath and Wirth.[10] Yields of purified products in the range 45–85% were recorded. These dinitriles [referred to here as p-p-p$(CN)_2$, p-m-p$(CN)_2$, and p-o-p$(CN)_2$] could then be readily converted into the corresponding diacid, dimethyl ester, or diacid chloride derivatives (Scheme II).

However, this synthetic reaction was not applicable to the preparation of the m-p-m and m-m-m diphenoxybenzene structures. The key intermediates in their syntheses were prepared by the cuprous chloride catalyzed reaction of sodium *m*-cresylate with *p*-dibromobenzene and *m*-dibromobenzene, respectively. Alternatively, these compounds could be prepared in lower yield by the reaction of *m*-bromotoluene with the disodium salts of hydroquinone and resorcinol.[11] The resultant dimethyl

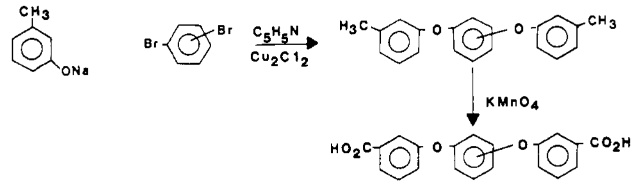
Scheme I



Scheme II



Scheme III



compounds then underwent oxidation with potassium permanganate to give the corresponding diacids [m-p-m-$(CO_2H)_2$ and m-m-m$(CO_2H)_2$] which could be converted to the dinitrile or diacid chloride derivatives (Scheme III).

Polymer Synthesis. In order to determine the solubility and demonstrate the reactivity of the diphenoxybenzene monomers, we directed initial polymer synthesis efforts toward the polycondensation of 4,6-diamino-1,3-benzenediol dihydrochloride with p-p-p$(CO_2H)_2$ and its derivatives. The results are shown in Table I. The polycondensation reactions were run in freshly prepared PPA at a solids content of approximately 1% by weight. After dehydrochlorination of the dihydrochloride salt was effected at 80–110 °C over a period of several hours, the reaction temperature was gradually raised over several days to 190 °C. Both the diacid monomer (trial no. 1) and the dimethyl ester monomer (trial no. 3) exhibited limited solubility in PPA. Suspended, undissolved monomer was still present at the termination of the polycondensation reaction. This factor probably limited the polymer DP and led to polymer discoloration due to monomer decomposition at higher temperatures. In a sulfolane/PPA reaction medium (trial no. 2), rapid and complete dissolution of the diacid monomer took place but did not lead to an improvement in the η_{inh} or quality of the polymer. However, polycondensation reactions in PPA involving the dinitrile or diacid chloride derivatives (trial no. 4 and 5, respectively) quickly became homogeneous and yielded golden-colored polymer, albeit of no greater η_{inh}. Polycondensation of p-m-p$(CO_2H)_2$ and p-m-p$(CN)_2$ with 4,6-diamino-1,3-benzenediol dihydrochloride (trial no. 6 and 7, respectively) resulted in the formation of extremely viscous, apparently homogeneous solutions of polymer in PPA. Upon workup, the isolated polymers proved to be insoluble in a variety of solvents. The reason for this insolubility has not been determined.

Table I
Polycondensation of 4,6-Diamino-1,3-benzenediol Dihydrochloride and Diphenoxybenzene Monomer

trial no.	diphenoxybenzene monomer	η_{inh},[b] dL/g
1	p-p-p$(CO_2H)_2$	1.90
2[a]	p-p-p$(CO_2H)_2$	1.60
3	p-p-p$(CO_2CH_3)_2$	0.67
4	p-p-p$(CN)_2$	1.93
5	p-p-p$(COCl)_2$	1.97
6	p-m-p$(CO_2H)_2$	insol[c]
7	p-m-p$(CN)_2$	insol[c]

[a] 1.5 PPA/sulfolane (w/w) used as polycondensation solvent. [b] CH_3SO_3H, 25 °C, 0.2 g/dL. [c] Solvents tested include CH_3SO_3H, H_2SO_4, $ClSO_3H$, and *m*-cresol.

Table II
Copolycondensation of 4,6-Diamino-1,3-benzenediol Dihydrochloride with Terephthalic Acid and Diphenoxybenzene Monomer

trial no.	diphenoxybenzene monomer	*y*, mole proportion	η_{inh},[b] dL/g
1	p-p-p$(CN)_2$	0.50	1.41
2	p-p-p$(CN)_2$	0.25	1.99
3	p-p-p$(CO_2H)_2$	0.25	1.94
4	p-p-p$(COCl)_2$	0.25	2.34
5	p-p-p$(CN)_2$	0.10	3.18
6[a]	p-p-p$(CN)_2$	0.10	7.08
7[a]	p-p-p$(CN)_2$	0.05	8.58
8	p-p-p$(CN)_2$	0.03	6.75[c]
9	p-m-p$(CN)_2$	0.50	insol
10	p-m-p$(CN)_2$	0.25	insol
11	p-m-p$(COCl)_2$	0.10	4.37
12	p-m-p$(CN)_2$	0.05	3.77
13	p-m-p$(CN)_2$	0.03	9.88
14	p-o-p$(CN)_2$	0.10	5.44
15	p-o-p$(CN)_2$	0.05	6.74
16	p-o-p$(CO_2H)_2$	0.05	7.73
17	p-o-p$(CN)_2$	0.03	6.86
18	m-p-m$(CN)_2$	0.05	7.67
19	m-m-m$(COCl)_2$	0.03	7.84

[a] Concentration 2.4–2.6% (w/w). [b] CH_3SO_3H, 25 °C, 0.2 g/dL. [c] $[\eta]$ = 8.10 dL/g (CH_3SO_3H, 25 °C).

Synthesis of the articulated PBOs was carried out by copolycondensation in PPA of 4,6-diamino-1,3-benzenediol dihydrochloride with terephthalic acid and the diphenoxybenzene monomers. The results are shown in Table II. After dehydrohalogenation was complete, polycondensation of terephthalic acid and 4,6-diamino-1,3-benzenediol was allowed to proceed at 130 °C to give a clear yellow solution. Addition of the diphenoxybenzene monomer followed by a gradual increase in the reaction temperature over several days to 190–210 °C yielded soluble fibrous polymers which varied in color from pale yellow to brown. The latter color was observed when a large mole proportion of relatively insoluble p-p-p$(CO_2H)_2$ was used (trial no. 3). In the interest of polymer quality, the more soluble and consequently more reactive diacid chloride and dinitrile derivatives were usually used. The articulated PBOs generally exhibited higher η_{inh} than the homopolymers described in Table I. This increase was most pronounced in the articulated PBOs containing small mole proportions (0.03–0.10) of the diphenoxybenzene structure; a maximum η_{inh} of 9.88 dL/g was recorded. Substantial differences in the solution viscosity–polymer DP relationships as well as increased polymer DP were probably responsible for the increase in η_{inh} values. In general, the solution viscosity values reported for the articulated PBOs were substantially higher than those reported for PBO synthesized by a similar experimental procedure (programmed heating rate)[3] and equivalent to

Table III
Copolycondensation of 2,5-Diamino-1,4-benzenedithiol Dihydrochloride with Terephthalic Acid and Diphenoxybenzene Monomer

trial no.	diphenoxybenzene monomer	y, mole proportion	η_{inh},[a] dL/g
1	p-o-p$(CN)_2$	0.10	7.97
2	m-p-m$(CN)_2$	0.10	12.02
3	m-p-m$(CN)_2$	0.03	12.57

[a] CH_3SO_3H, 25 °C, 0.2 g/dL.

Table IV
Copolycondensation of 1,2,4,5-Tetraaminobenzene Tetrahydrochloride with Terephthalic Acid and Diphenoxybenzene Monomer

trial no.	diphenoxybenzene monomer	y, mole proportion	η_{inh},[a] dL/g
1	p-p-p$(COCl)_2$	0.10	9.92
2	p-o-p$(CN)_2$	0.10	9.13

[a] CH_3SO_3H, 25 °C, 0.2 g/dL.

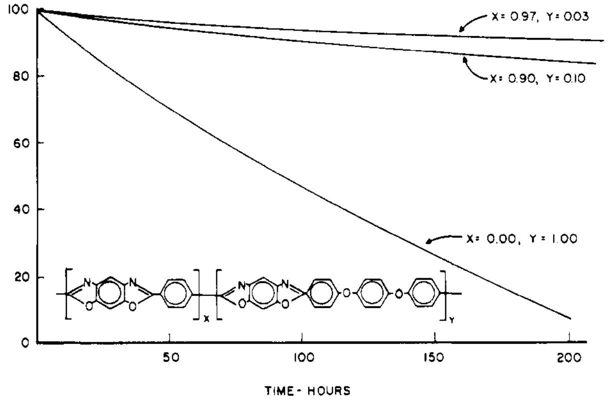


Figure 1. Isothermal aging in air at 316 °C for articulated PBOs.

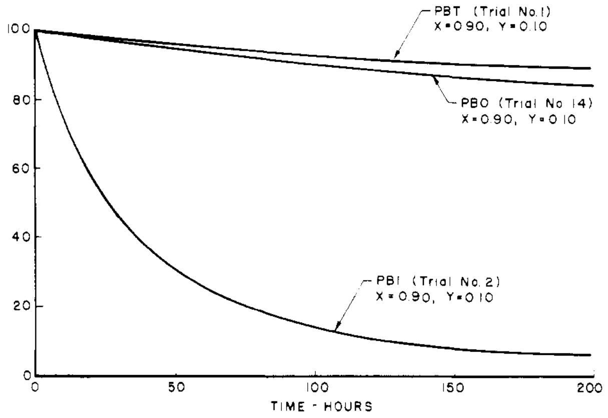


Figure 2. Isothermal aging in air at 316 °C for articulated PBO, PBT, and PBI.

those obtained from PBO prepared by isothermal polycondensation reactions.[12]

As in the case of the polycondensation reactions of p-m-p$(CN)_2$ and p-m-p$(CO_2H)_2$ with 4,6-diamino-1,3-benzenediol described above, the copolycondensation reactions of p-m-p$(CN)_2$ and p-m-p$(COCl)_2$ gave rise to extremely viscous, apparently homogeneous reaction mixtures (trial no. 8–12). The isolated articulated PBOs, however, were soluble only when mole proportions of 0.10 or less of the diphenoxybenzene monomers were used.

Although the copolycondensation reactions were generally run at a solids content of approximately 1%, higher concentrations could be used (trial no. 6 and 7); high η_{inh} were obtained even though stirring could not be effectively employed in the latter stages of the reaction.

Synthesis of the articulated PBTs was performed under conditions similar to those described for preparation of the articulated PBOs. Loss of hydrogen chloride occurred at 60–80 °C and a clear yellow solution formed upon several hours of heating at 130 °C. Addition of a readily soluble diphenoxybenzene monomer [p-o-p$(CN)_2$, m-p-m(CN_2)] followed by a rapid temperature increase to 150 °C and a gradual increase to 195–200 °C over several days yielded yellow-orange, fibrous polymers. The results are summarized in Table III.

Several articulated PBIs were also synthesized in a similar manner to yield red-brown, fibrous polymers in high yields. The results are summarized in Table IV. Although small amounts (approximately 10%) of insolubles were present, the articulated PBIs exhibited solubility in methanesulfonic acid. By comparison, PBI prepared by the polycondensation of 1,2,4,5-tetraaminobenzene tetrahydrochloride with terephthalic acid in PPA is reported to be completely insoluble.[5]

Polymer Characterization. The articulated PBOs, PBTs, and PBIs described above were soluble in methanesulfonic, chlorosulfonic, and sulfuric acids. They were insoluble in all aprotic solvents tested. Solution behavior studies of the articulated PBOs in methanesulfonic acid are currently under way in another laboratory to determine their capability to order into liquid crystalline solutions and to determine their solubility relative to PBO.[13]

Solution viscosity data on the articulated polymers were determined by using methanesulfonic acid as a solvent. The η_{inh} or $[\eta]$ values recorded were found to be quite dependent upon the workup history of the respective polymer samples and were found to decrease substantially upon dissolution and reprecipitation of the polymer. For example, an articulated PBO (trial no. 14) initially exhibited an η_{inh} of 5.44 dL/g. Dissolution and reprecipitation from methanesulfonic acid into methanol resulted in an η_{inh} of 3.57 dL/g. Although the possibility of polymer chain scission existed, irreversible molecular aggregation of the polymer chains during the dissolution–reprecipitation process was a more likely cause for this phenomenon. Similar changes in solution viscosity data have been observed with PBT.[4,13]

As would be expected, the presence of the diphenoxybenzene structure in the articulated polymers resulted in decreased thermooxidative stability compared to the parent polymers. This decrease in thermooxidative stability could be readily determined by isothermal aging studies in air at elevated temperatures. Articulated PBOs, for example, in air at 316 °C exhibited greater weight losses as the diphenoxybenzene unit content increased (Figure 1).

Isothermal aging in air at 316 °C of articulated PBOs, PBTs, and PBIs of analogous structure demonstrated the superior thermooxidative stability of the articulated PBTs and the relative poor thermooxidative stability of the articulated PBIs compared to the articulated PBOs (Figure 2). This order of thermooxidative stability (PBT > PBO ≫ PBI) was also observed in the parent polymers.[14]

Films which exhibited optical birefringence under crossed polars could be cast from methanesulfonic acid solutions of the articulated polymers. Tensile strength and modulus values for films of articulated PBOs are shown in Table V. In comparison, continuous films could not be cast from methanesulfonic acid solutions of the parent

Table V
Film Properties of Articulated PBOs

trial no.	diphenoxy- benzene structure	y, mole propor- tion	tensile strength, mPa	modulus, mPa
6	p-p-p	0.10	56	1558
14	p-o-p	0.10	77	3765
15	p-o-p	0.05	49	2317
17	p-o-p	0.03	62	2365
18	m-p-m	0.05	93	3068
19	m-m-m	0.03	52	4696

polymers. Excessive shrinking led to extensive cracking of these films.

Conclusions

Articulated PBOs, PBTs, and PBIs can be synthesized in moderate-to-high molecular weight through incorporation of diphenoxybenzene units into the polymer backbone. This is best achieved in the copolycondensation reactions through the use of the dinitrile or diacid chloride of the appropriate diphenoxybenzene structure. Incorporation of the flexible diphenoxybenzene unit into the polymers does not lead to observable solubility in aprotic solvents. As expected, thermooxidative stability of the articulated polymers decreases with increased content of the diphenoxybenzene structure. Continuous films of the articulated polymers can be cast from methanesulfonic acid. In comparison, films cast from solutions of the parent polymers show extensive cracking because of excessive shrinkage.

Experimental Section

Synthesis of Monomers. The requisite monomers were either obtained from commercial sources and purified as necessary or synthesized according to the procedures described below.

Terephthalic acid was obtained from Amoco Chemicals Corp. The monomer-grade terephthalic acid was finely ground to an average particle size of 95% <10 μm (courtesy of Dr. J. F. Wolfe).[4]

1,2,4,5-Tetraaminobenzene tetrahydrochloride was obtained from Burdick and Jackson. It was carefully recrystallized from hydrochloric acid and dried prior to use.

4,6-Diamino-1,3-benzenediol dihydrochloride was prepared by Midwest Research Institute according to the procedure of Wolfe and Arnold.[3] It was also purified by recrystallization from hydrochloric acid.

2,5-Diamino-1,4-benzenedithiol dihydrochloride was prepared by Dr. J. F. Wolfe according to his published procedure.[4]

4,4′-(*p*-Phenylenedioxy)dibenzoic Acid [p-p-p(CO_2H)$_2$]. 4,4′-(*p*-Phenylenedioxy)dibenzonitrile[15] (15.0 g, 0.048 mol) and potassium hydroxide pellets (45.0 g, 0.800 mol) were stirred under nitrogen in 375 mL of redistilled ethylene glycol. The white slurry was heated to reflux to produce a vigorous evolution of ammonia. The resultant pale yellow solution became cloudy after a few minutes and a flocculent white precipitate was formed. After 20 h at 175 °C, 75 mL of ethylene glycol was distilled off and the reaction mixture was cooled in an ice bath. The white precipitate was isolated by filtration and washed on the frit with 2-propanol. The crude dipotassium salt (18.3 g) thus isolated was dissolved in 200 mL of dilute potassium hydroxide solution. After being refluxed for 30 min, the cloudy solution was treated with charcoal, filtered, and reduced in volume to 90 mL. Cooling of the solution gave 15.6 g of the dipotassium salt, which was isolated by filtration and washed on the frit with 2-propanol. Dissolution of this salt in 200 mL of water gave a hazy solution, which was heated to reflux and then acidified with concentrated hydrochloric acid. The resultant white slurry was refluxed for 4 h, cooled, and filtered to give 13.5 g of the crude diacid. After extraction of the crude diacid with a 1 L of refluxing tetrahydrofuran, 1.2 g of insoluble material remained. The tetrahydrofuran solution was diluted with an equal volume of hexane to precipitate the diacid (10.4 g). Recrystallization from 900 mL of dioxane (charcoal) gave 7.2 g (43% yield) of powdery white product, mp 331–333 °C (lit.[16] mp 313–315 °C). The product could not be further purified by recrystallization. Anal. Calcd for $C_{20}H_{14}O_6$: C, 68.57; H, 4.03; mol wt 350. Found: C, 68.24; H, 4.11; mol wt 350 (mass spectrum).

4,4′-(*p*-Phenylenedioxy)dibenzoyl chloride [p-p-p($COCl$)$_2$] and dimethyl 4,4′-(*p*-phenylenedioxy)benzoate) [p-p-p(CO_2CH_3)$_2$] were prepared from the diacid as described by Malichenko and co-workers.[16]

4,4′-(*m*-Phenylenedioxy)dibenzonitrile [p-m-p(CN)$_2$]. Resorcinol (11.0 g, 0.100 mol) and dry potassium carbonate (82.8 g, 0.600 mol) were stirred for 2 h at room temperature under nitrogen in 300 mL of freshly distilled dimethyl sulfoxide. 4-Nitrobenzonitrile (32.56 g, 0.220 mol) was then added and the reaction temperature was raised to 75 °C for 20 h. The dark solution was poured with vigorous stirring into 1500 mL of ice water and the resultant suspension was stirred for an additional hour. The gray, lumpy product was isolated by filtration, washed well with water, and allowed to dry overnight on the frit. It was taken up in 1600 mL of 2-propanol (some insoluble material) and the solution was treated with charcoal. Reduction of the solution volume to 700 mL followed by cooling in ice water gave 25.5 g (82% yield) of white crystalline product, mp 123.5–125 °C (lit.[17] mp 123–124 °C).

4,4′-(*m*-Phenylenedioxy)dibenzoic acid [p-m-p(CO_2H)$_2$] was prepared by hydrolysis of the dinitrile in a procedure very similar to that described above for the p-p-p isomer. Recrystallization from dioxane gave a 64% yield of powdery white product, mp 300–302 °C.

Anal. Calcd for $C_{20}H_{14}O_6$: C, 68.57; H, 4.03; mol wt 350. Found: C, 68.36; H, 3.80; mol wt 350 (mass spectrum).

4,4′-(*m*-Phenylenedioxy)dibenzoyl chloride [p-m-p($COCl$)$_2$] was prepared through reaction of the corresponding diacid (7.0 g, 0.020 mol) with phosphorus pentachloride (10.5 g, 0.074 mol) in 37 g of phosphorus oxychloride. After the solution was allowed to reflux for 2 h, the phosphorus oxychloride was distilled off under reduced pressure and the residue was extracted with 75 mL of hexane. Recrystallization from hexane gave 2.40 g (31% yield) of product, mp 77–78.5 °C.

Anal. Calcd for $C_{20}H_{12}Cl_2O_4$: C, 62.04; H, 3.13; Cl, 18.31; mol wt 387. Found: C, 62.40; H, 3.16; Cl, 17.98; mol wt 387 (mass spectrum).

4,4′-(*o*-Phenylenedioxy)dibenzonitrile [p-o-p(CN)$_2$] was prepared by reaction of the dipotassium salt of catechol with 4-nitrobenzonitrile in dimethyl sulfoxide. Reaction conditions and workup were similar to that described for the analogous p-m-p isomer. Successive recrystallizations from heptane and 2-propanol afforded a 45% yield of white crystals, mp 116.5–117.5 °C.

Anal. Calcd for $C_{20}H_{12}N_2O_2$: C, 76.91; H, 3.87; N, 8.97; mol wt 312. Found: C, 76.97; H, 3.65; N, 8.75; mol wt 312 (mass spectrum).

3,3′-(*p*-Phenylenedioxy)dibenzonitrile [m-p-m(CN)$_2$]. To a solution of 3,3′-(*p*-phenylenedioxy)ditoluene[18] (9.9 g, 0.034 mol) in 255 mL of pyridine was added a slurry of potassium permanganate (42.6 g, 0.270 mol) in 150 mL of water. After being stirred for 1 h at room temperature, the reaction mixture was heated at 70 °C overnight. The cooled reaction mixture was diluted with 125 mL of water and then made strongly acidic by the addition of 280 mL of concentrated hydrochloric acid. The acidified reaction mixture was heated to 70 °C for 1 h, cooled, and filtered. The filter cake was thoroughly washed with water and allowed to dry on the frit. The solid was placed in a continuous extraction apparatus and extracted with ether and then with methylene chloride. Evaporation of the combined extracts gave 9.4 g of crude material. Two recrystallizations from glacial acetic acid yielded 6.7 g (56% yield) of white powdery 3,3′-(*p*-phenylenedioxy)dibenzoic acid, mp 305–313 °C (lit.[19] mp 300–308 °C).

Anal. Calcd for $C_{20}H_{14}O_6$: C, 68.57; H, 4.03; mol wt 350. Found: C, 68.79; H, 3.96; mol wt 350 (mass spectrum).

The diacid (24.0 g, 0.069 mol) was refluxed under nitrogen with 80 mL of thionyl chloride for 5 h to give a clear tan solution. Excess thionyl chloride was stripped off under reduced pressure and the residue was distilled to give 18.3 g of a pale yellow liquid, bp 220–234 °C (2.5 mmHg). The solidified crude product was recrystallized from heptane (charcoal) to give 12.2 g (46% yield) of 3,3′-(*p*-phenylenedioxy)dibenzoyl chloride as white needles, mp 73.5–76 °C.

Anal. Calcd for $C_{20}H_{12}Cl_2O_4$: C, 62.04; H, 3.13; Cl, 18.31; mol wt 387. Found: C, 62.03; H, 2.87; Cl, 18.24; mol wt 387 (mass spectrum).

The diacid chloride (20.0 g, 0.052 mol) was dissolved in 200 mL of ether and the resultant solution was added dropwise to 150 mL of vigorously stirred concentrated ammonium hydroxide at 0–5 °C. When addition was complete after 2 h, the white slurry was allowed to warm to room temperature. After 2 h at room temperature, the reaction mixture was filtered and the white filter cake was washed with ammonium hydroxide and with water. The filter cake was allowed to dry on the frit overnight and was then recrystallized from 2-propanol to give 9.7 g (54% yield) of 3,3′-(*p*-phenylenedioxy)dibenzamide, mp 244–246 °C.

Anal. Calcd for $C_{20}H_{16}N_2O_4$: C, 68.96; H, 4.62; N, 8.04; mol wt 348. Found: C, 68.86; H, 4.36; N, 8.15; mol wt 348 (mass spectrum).

The diamide (9.7 g, 0.028 mol) was dissolved in 160 mL of *N*,*N*-dimethylformamide. Thionyl chloride (25 mL) was added dropwise to the solution over a period of 3 h, with the temperature maintained at 0–5 °C. During the addition period, the reaction mixture changed from a clear, water-white solution to a milky suspension and then to a clear yellow solution. The solution was stirred at ice bath temperature for 6 h and then poured over ice. Acidification of the aqueous solution was effected with concentrated hydrochloric acid. The addition of 200 mL of water followed by filtration gave a white filter cake, which was washed repeatedly with water. After being allowed to dry on the frit, the crude white product (7.9 g, mp 116–124 °C) was recrystallized once from heptane and three times from 2-propanol to give 3,3′-(*p*-phenylenedioxy)dibenzonitrile as fine white needles, mp 139.5–141 °C.

Anal. Calcd for $C_{20}H_{12}N_2O_2$: C, 76.91; H, 3.87; N, 8.97; mol wt 312. Found: C, 76.81; H, 3.58; N, 8.74; mol wt 312 (mass spectrum).

3,3′-(*m*-Phenylenedioxy)dibenzoyl Chloride [m-m-m-(COCl)$_2$]. *m*-Cresol (27.5 g, 0.254 mol) and sodium methoxide (13.0 g, 0.242 mol) were refluxed with stirring under nitrogen in 350 mL of benzene for 90 min. The benzene was then stripped off under reduced pressure and 500 mL of dry pyridine was added to the white sodium salt. *m*-Dibromobenzene (27.9 g, 0.119 mol) and cuprous chloride (9.0 g) were added to the reaction mixture, which was then refluxed for 5 days. Approximately 400 mL of pyridine was then distilled from the reaction flask and the residue was poured into ice water. Following acidification of the aqueous slurry with concentrated hydrochloric acid, the insolubles were isolated by filtration. Both the filter cake and the filtrate were extracted repeatedly with light petroleum ether and the combined extracts were washed once with water. The petroleum ether extracts were dried over anhydrous magnesium sulfate and the solvent was stripped off under reduced pressure. Distillation of the dark brown residual oil (38.4 g) afforded 23.5 g (68% yield) of pure 3,3′-(*m*-phenylenedioxy)ditoluene, bp 159–163 °C (3 mmHg).

Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.74; H, 6.23; mol wt 290. Found: C, 82.54; H, 6.02; mol wt 290 (mass spectrum).

Subsequent oxidation of this intermediate with potassium permanganate in an aqueous pyridine reaction medium afforded a low yield of white 3,3′-(*m*-phenylenedioxy)dibenzoic acid which exhibited a melting point of 269–274 °C after repeated recrystallization from glacial acetic acid.

Anal. Calcd for $C_{20}H_{14}O_6$: C, 68.57; H, 4.03; mol wt 350. Found: C, 68.69; H, 3.76; mol wt 350 (mass spectrum).

The diacid was subsequently refluxed under nitrogen with thionyl chloride. Reaction conditions and workup procedures very similar to those described above for the analogous m-p-m isomer gave a 61% of yield of 3,3′-(*m*-phenylenedioxy)dibenzoyl chloride as white crystals, mp 117.5–120 °C.

Anal. Calcd for $C_{20}H_{12}Cl_2O_4$: C, 62.04; H, 3.13; Cl, 18.31; mol wt 387. Found: C, 62.22; H, 2.97; Cl, 18.44; mol wt 387 (mass spectrum).

Synthesis of Polymers. Typical experimental procedures for the synthesis of the articulated PBOs, PBTs, and PBIs are given below.

Articulated PBO (Trial No. 7). A slurry of terephthalic acid (0.790 g, 4.75 mmol) and 4,6-diamino-1,3-benzenediol dihydrochloride (1.065 g, 5.00 mmol) in 75 g of freshly prepared PPA was stirred under nitrogen at 90–110 °C for 4 h to effect dehydrochlorination. The temperature was raised to and held at 130 °C for 20 h. 4,4′-(*p*-Phenylenedioxy)dibenzonitrile (0.079 g, 0.25 mmol) and 80 g of PPA were added to the clear yellow solution and the resultant slurry was heated at 150 °C for 19 h. The clear red reaction mixture was then heated at 175 °C for 7 h, 185 °C for 2 h, and 195 °C for 16 h. Addition of the cooled, extremely viscous solution to water gave fibrous polymer, which was vigorously washed three times with water in a blender and extracted for 3 days with water in a continuous extraction apparatus. Drying at room temperature (0.01 mmHg) for 20 h and at 145 °C (0.01 mmHg) for 6 h yielded 1.1 g (92% yield) of pale yellow polymer; η_{inh} = 8.58 dL/g (methanesulfonic acid, 25 °C, 0.2 g/dL).

Anal. Calcd for $(C_{14}H_6N_2O_2)_{0.95}(C_{26}H_{14}N_2O_4)_{0.05}$: C, 72.06; H, 2.63; N, 11.50. Found: C, 72.99; H, 2.19; N, 11.68.

Articulated PBT (Trial No. 3). Terephthalic acid (0.806 g, 4.85 mmol) and 2,5-diamino-1,4-benzenedithiol dihydrochloride (1.226 g, 5.00 mmol) were stirred with 110 g of freshly prepared PPA at room temperature under nitrogen for 2 h. The viscous white slurry was then heated at 70 °C for 6 h to effect dehydrochlorination and the temperature was then gradually raised over 2 h to 130 °C. 3,3′-(*p*-Phenylenedioxy)dibenzonitrile (0.047 g, 0.15 mmol) and an additional 104 g of PPA were added and stirring was continued at 130 °C for 3 h to give a clear, deep red solution. The solution was then heated with stirring as follows: 150 °C for 16 h, 185 °C for 8 h, and 200 °C for 16 h. After several hours at 200 °C, the viscous reaction mixture was climbing the stirrer shaft and stirring was not effective. The cooled polymerization mixture was added to 1 L of water in a blender. The precipitated polymer was vigorously washed three times with water in the blender and was extracted with water in a continuous extraction apparatus for 3 days. Drying at room temperature (0.01 mmHg) for 16 h and 188 °C (0.01 mmHg) for 6 h yielded 1.2 g (91% yield) of fibrous yellow-orange polymer; η_{inh} = 12.57 dL/g (methanesulfonic acid, 25 °C, 0.2 g/dL).

Anal. Calcd for $(C_{14}H_6N_2S_2)_{0.97}(C_{26}H_{14}N_2O_2S_2)_{0.03}$: C, 63.44; H, 2.31; N, 10.30; S, 23.59. Found: C, 63.90; H, 1.86; N, 10.44; S, 23.67.

Articulated PBI (Trial No. 1). 1,2,4,5-Tetraaminobenzene tetrahydrochloride (1.420 g, 5.00 mmol) and terephthalic acid (0.748 g, 4.50 mmol) were stirred in 105 g of freshly prepared PPA at 90–100 °C for 2 h. When evolution of HCl subsided, the temperature was slowly raised to 130 °C to give a clear yellow solution. 4,4′-(*p*-Phenylenedioxy)dibenzoyl chloride (0.194 g, 0.50 mmol) was added along with an additional 65 g of PPA. The reaction mixture was heated as follows: 150 °C for 4 h (clear red solution), 175 °C for 16 h, 190 °C for 8 h, and 210 °C for 4 h. The polymer solution exhibited a blue coloration and was climbing the stirrer shaft well before the end of the heating period. The cooled reaction mixture was added to water and the precipitated polymer was vigorously washed with water three times in a blender. Extraction with water in a continuous extraction apparatus for 3 days followed by drying at room temperature (0.01 mmHg) for 16 h and 100 °C (0.01 mmHg) for 4 h yielded 1.1 g (87% yield) of red-brown polymer; η_{inh} = 9.92 dL/g (methanesulfonic acid, 25 °C, 0.2 g/dL). This sample contained approximately 10% by weight of insoluble polymer.

Anal. Calcd for $(C_{14}H_8N_4)_{0.90}(C_{26}H_{16}N_4O_2)_{0.10}$: C, 72.84; H, 3.53; N, 22.35. Found: C, 70.81; H, 3.31; N, 20.60.

Films could be prepared from the articulated polymers by vacuum casting from dilute solutions. The general procedure followed was to prepare a 2% polymer solution in methanesulfonic acid and put the solution in a specially fabricated circular flat-bottomed casting dish. The dish was then placed and leveled in the bottom of a sublimator. The cold finger of the sublimator was maintained at 25 °C and sublimator was continuously evacuated and heated to 60 °C to facilitate the removal of the methanesulfonic acid. After the films were formed and removed from the casting dish, they were generally dried at 100 °C in a vacuum oven for 24–48 h. The films produced were approximately 5 cm in diameter and 5.0 × 10^{-3} cm in thickness. Most of the films retained approximately 15% residual solvent. Mechanical property data for an average of five test specimens were obtained on an Instron Tensile Tester, Model 1102, at 0.02 in/min.

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Polymerization Kinetics of Rigid Rodlike Molecules: Polycondensation of Poly([benzo(1,2-*d*:5,4-*d'*)bisoxazole-2,6-diyl]-1,4-phenylene)

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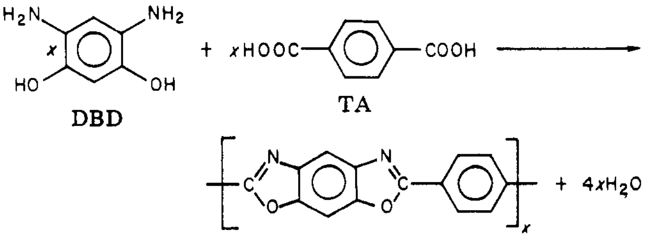
ABSTRACT: The molecular weight and molecular weight distribution of the rigid rodlike polymer poly([benzo(1,2-*d*:5,4-*d'*)bisoxazole-2,6-diyl]-1,4-phenylene) (PBO) have been measured as a function of the extent of reaction to conversions up to 98%. The analysis of the molecular weight data indicates that the polymerization rate decreases sharply with increasing molecular weight. This conclusion—based on measurements of the intrinsic viscosity, size-exclusion chromatography, and an end-group analysis of the number-average molecular weight—is in accord with a diffusion-limited polymerization rate for the condensation of rigid rods.

The statistical analysis of polycondensation reactions is based on the understanding that reaction rates are independent of molecular weight.[1] The reactive end groups of flexible coils indeed diffuse, reorient, and react in solution at a rate independent of the polymer molecular weight. For rigid rods, however, diffusion of reactive end groups must be coordinated with that of the entire molecule. The transport properties[2] of rodlike molecules in general show a greatly enhanced dependence on molecular weight, in comparison with flexible macromolecules. In view of the extraordinary thermomechanical properties[3] that rodlike heteroaromatic polymers display, we have characterized the polymerization kinetics of poly([benzo-(1,2-*d*:5,4-*d'*)bisoxazole-2,6-diyl]-1,4-phenylene) (PBO) to determine if shape anisotropy affects the polymerization process and its products. PBO is prepared by the step-growth polymerization of 4,6-diamino-1,3-benzenediol (DBD) and terephthalic acid (TA):



The reaction is carried out in poly(phosphoric acid) (PPA), which serves to remove the water formed in the polymerization step.

Experimental Section

The monomer 4,6-diamino-1,3-benzenediol dihydrochloride was synthesized under conditions reported in ref 9. Polymerizations were carried out in freshly prepared poly(phosphoric acid) (85% P_2O_5) following the general procedure outlined in ref 9, but several important features were changed to facilitate quantitative kinetic analysis. To avoid complications due to the ordering of polymer molecules in liquid crystalline domains, polymerizations were

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