Synthesis of 2,2-Bis[4-(3,4-diaminophenoxy)phenyl]propane and Its Polymerization

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ABSTRACT: Two synthetic routes have been examined that use nucleophilic aromatic substitution of 2,2-bis(4-hydroxyphenyl)propane either with 5-chloro-2,1,3-benzothiadiazole or with 5-chloro-2-nitroaniline. Subsequent reductions lead to the tetraamine 2,2-bis[4-(3,4-diaminophenoxy)phenyl]propane that has been converted to the corresponding polybenzimidazole by an oxidative heteroaromatization reaction with isophthalaldehyde. Conditions are described which provide η_{inh} = 0.47–0.97 dL/g and tough, flexible films.

Introduction

Polybenzimidazole (PBI) polymers have been attractive because of their outstanding mechanical and dielectric properties at high temperatures.[1] They also have desirable properties for producing fibers and fabrics that are nonflammable and have excellent moisture regain. Ion-selective resins have been prepared recently from PBI beads that have been derivatized with chelating agents.[2] In addition, polybenzimidazoles have been successfully used for sea water desalination using reverse osmosis membranes or hollow filaments.[3] They have good mechanical properties as well as high flux and selectivity. They do not require the cumbersome alternate approach of using a nondurable, selective polymer coated on a sturdy, unselective fiber. This work is aimed at producing new polybenzimidazoles with greater processability that might be useful in making membranes or hollow filaments used for gas separations. They probably will have somewhat less high-temperature stability, but, in the hollow filament area, high-temperature stability is not as important as how readily the polymer can be processed and what permeability selectivity it will exhibit to gas mixtures. The polybenzimidazoles have another potential advantage in that the benzimidazole ring is a good ligand so that metal could be complexed to the polymer, which could enhance the selectivity.[4]

The early methods[5] of PBI synthesis used the high-temperature reaction of diesters, e.g., **1a** or **2a**, with tetraamines such as 3,3′-diaminobenzidine (DAB) to form PBI-1 or the para analogue of PBI-1 (see Scheme I and Table I). Later methods[6] used diacids, e.g., **1b**, in highly acidic media such as PPA or PPMA (phosphorus pentoxide–methanesulfonic acid). Another variation[7] is to use bis(orthoesters), e.g., **1c**, which react at lower temperatures. A different methodology[8] uses dialdehydes, e.g., **1d**, to make a polyazomethine "prepolymer" that is subsequently oxidized to the PBI, or this can be done in a one-step process.[9] Another recent approach[10] is to use bisazlactones with tetraamines although only low molecular weight materials were formed (η_{inh} = 0.10–0.12 dL/g). Aromatic aldimines with tetraamines have also been used.[11] PBI ureas have also been formed starting with bibenzimidazolediamines.[12]

When the dialdehydes (or diacids or diesters) are aromatic, the polymers will be quite stiff, which can make them difficult to work with because of poor solubility. Several approaches currently are being pursued to improve the processability of PBI polymers. Putting units in the polymer that provide more flexibility can overcome this problem. For example, O, CH_2O, SO_2, and CMe_2 units have been used for this purpose.[13] Other approaches to modifying the properties of PBI's are to make PBI copolymers,[14] to make mixed polymers such as PBI–polyimides[15] or PBI–polyamides,[16] or to blend them with other polymers such as polyimides.[17]

Results and Discussion

This research examines the preparation of PBI polymers with O and CMe_2 flexible links in the chain. Two routes have been investigated (see Schemes II and III) in which bisphenol A (**3**) reacts in a nucleophilic aromatic substitution reaction to form either **4** or **5**. Reduction of either **4** or **5** produces the desired monomer **6**, which can be polymerized to PBI-2.

Earlier work[18] on nitro-substituted phthalimides (where the nitro group is displaced by a phenoxide) suggested that nitro-2,1,3-benzothiadiazoles might undergo such a reaction. However, 4-nitro-2,1,3-benzothiadiazole (**7**) did not undergo this displacement when treated with sodium 4-*tert*-butylphenoxide in DMSO in the same way that nitrophthalimides do. Earlier work[19] has noted that sodium methoxide in methanol also does not give displacement of the nitro group on **7**. On the other hand, we have found that 5-chloro-2,1,3-benzothiadiazole (**8**) does react with **3** to give the desired product **4**, but the conditions used [20] only gave a 27:36:21 ratio of compound **4**, the "monosubstitution product", **9**, and the starting compound, **8**. Thin-layer chromatography (TLC) was used to follow the reaction to completion. Compound **8** is not commercially available but was prepared in one step from the corresponding chloro diamine **10** in 95% yield after sublimation.[21] Variations in conditions have been tried for the nucleophilic aromatic displacement step in Scheme II to improve the rather poor yield (<20% after purification). Longer times reduced the amount of recovered starting materials but did not improve the overall yield. Recycling the recovered monosubstitution product, **9**, was not very effective either. Compounds **8** and **4** do not separate on flash chromatography with 30% EtOAc–hexane, but the separation was satisfactory using 5% EtOAc–hexane.

Although low yields are a problem with this route, enough **4** was obtained to test this novel approach to producing **6**. The reduction[22] of **4** was carried out with Raney nickel in 51% yield. The spectral data for **6** agree with the spectral data of **6** generated by the chloronitroaniline route outlined in Scheme III.

The nucleophilic aromatic substitution approach should be possible with other aromatic compounds that have a

Scheme I

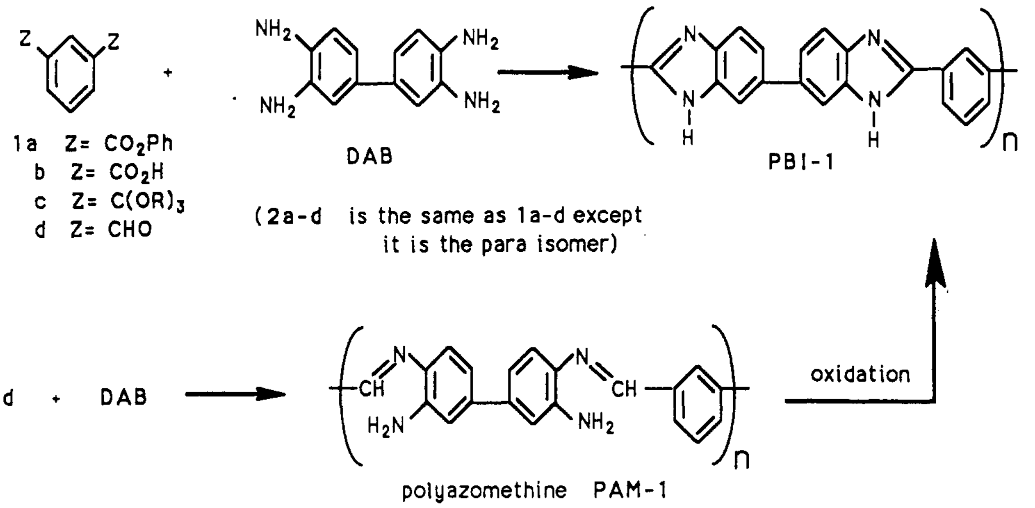


Table I
Polymerizations Generating Polybenzimidazoles

type	monomer[a]	method	η_{inh}	comments	ref
1	diester	melt, 400 °C	0.6–0.8	sensitive to air	5
2	diester	PhSO$_2$Ph, 379 °C	0.6–0.9	solvent hard to remove	5
3	bis(orthoester)	DMSO, 110 °C	0.5–0.7	flexible films	7
4	dialdehyde	DMAC, 50–150 °C/air	0.1–0.7	some films OK	9
5	dialdehyde	DMAC, −20 °C, 60 °C/air	0.8–0.9	flexible films	8

[a] Both the meta and para isomers were tested (e.g., **1a–d** and **2a–d**); the meta isomer generally gave better films. The other monomer in all cases is 3,3′-diaminobenzidine (DAB).

good leaving group para to an activating substituent like nitro. 1,2-Dinitro-4-chlorobenzene would seem to be an inviting compound except that it is known[23] that the ortho nitro group is displaced rather than the chloro group in that compound. The related 5-chloro-2-nitroaniline (**11**) was chosen instead.

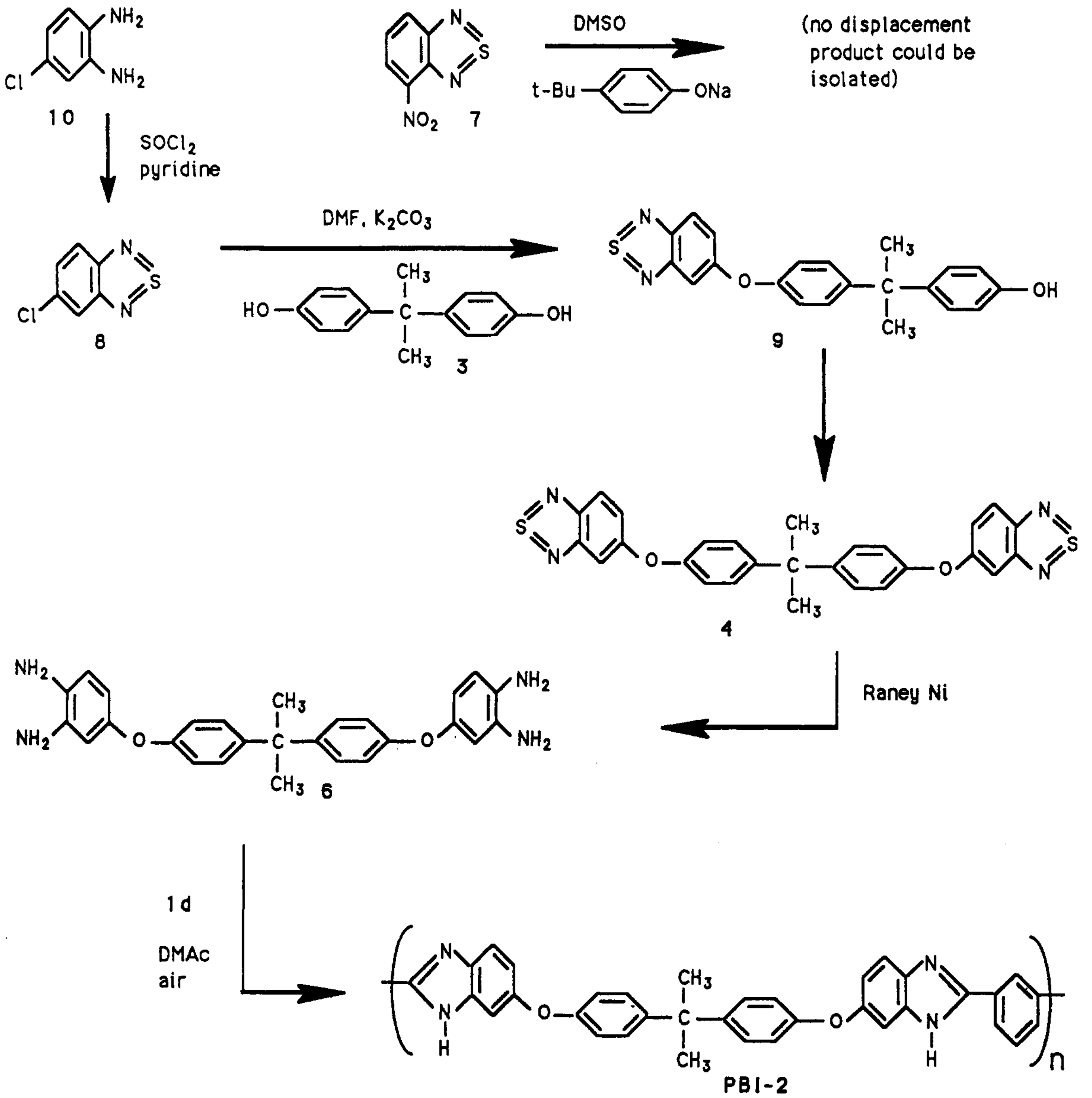
The chloronitroaniline route is outlined in Scheme III. Compound **11** is commercially available, but, for larger amounts, it was prepared by reacting 2,4-dichloronitrobenzene with liquid ammonia in an autoclave.[24] Phase-transfer conditions[25] using 30% NaOH-chlorobenzene and either tetrabutylammonium bromide or Aliquat 336 were initially explored for the nucleophilic aromatic displacement of **3** and **11** to form **5**. The phase-transfer reaction did proceed, but it was slow and TLC analyses appeared less clean than the product mixture formed using K$_2$CO$_3$–dry DMF. Adding KF, in an attempt to provide a better incoming group to displace Cl and a better leaving group to be displaced by **3**, did not improve the yield. A brief look at the THF–18-crown-6–K$_2$CO$_3$ and THF–18-crown-6–KH conditions did not look promising. The K$_2$CO$_3$–dry DMF conditions produced yields of **5** ranging from 20 to 82% after purification, but the yields were usually in the 50–65% range. Running the reaction for several hours at 100 °C followed by 8 h at 140 °C generally gave ca. 50% yields, but running the reaction for a longer period at 110 °C produced **5** that was lighter in color and easier to purify. In all cases, it required some purification before it could be crystallized. Extraction with 5% NaOH removed unreacted **3** but not the monoadduct **12**. Extraction with 30% NaOH removes **12**, which improves the subsequent flash chromatography, since **5** and **12** have similar R_f values with ethyl acetate–hexane as eluent (**5** and **12** are separable on TLC using 30:70 EtOH–hexane as eluent). After chromatography, **5** crystallized readily. Reduction of **5** with Raney nickel and hydrazine[21] gave a 79% yield of the polybenzimidazole precursor **6** after crystallization. The Ni–hydrazine reduction seems to give good results if the starting material is pure and the reduction is run long enough, as determined by TLC, to ensure that the intermediate stage is fully reduced.

Before examining the polymerizations of **6**, several polymerization methods were tried using readily available DAB and the diphenyl ester of terephthalic acid or the diphenyl ester of isophthalic acid (or the corresponding bis(orthoesters) or dialdehydes). Two criteria were used to estimate whether the polymerizations were producing materials with useful properties: (1) Could an inherent viscosity, η_{inh} of 0.8 dL/g or higher be achieved and (2) could films be formed that were tough and flexible? The classic diphenyl diester thermal methods worked (types 1 and 2), but we sought a milder method since the monomers in this study are less thermally stable than DAB. The type 3 method is attractive, but the bis(orthoesters) are less available. Types 4 and 5 were chosen for further study because dialdehydes are available, and type 5 generally gave good viscosity and film properties.

The simplicity of type 4 was initially attractive, and the preliminary studies gave viscosities approaching what was thought to be the useful range. Table II shows a sample of test runs using DAB and **1d**. Some films could be made with good properties (reasonably tough and flexible, but they did not always maintain good strength and flexibility when all the solvent and water was removed). In many cases, the viscosity was low, indicating low molecular weights, and attempts to make films generally gave something that fell apart during the cure process. Effective conditions using FeCl$_3$ to catalyze the oxidation step were not found although one run (η_{inh} = 0.410 dL/g) suggests that it might be feasible given more study. The two-stage method generally gave better results, so this one-stage method was abandoned except for a few further test trials with **1d** and **6** (see Table IV). Those runs gave low viscosities, but, surprisingly, some flexible films could be formed.

The two-stage method is intended to preform a polyazomethine (PAM) "prepolymer" at −20 °C, which is subsequently oxidized to the PBI at higher temperature (see PAM-1) in Scheme I). In this study, viscosity measurements at the PAM stage gave η_{inh} = 0.06–0.31

Scheme II



dL/g, indicating a rather low molecular weight. Normally η_{inh} increases considerably during the oxidation to the PBI solution, indicating loss of flexibility associated with the cyclization and an increased molecular weight. This could be due to driving the equilibrium by removing the cyclic component, or it also could be that some cross-linking is taking place. In a number of runs, a gel or precipitate formed that was insoluble in DMAc even with heating, which suggests that cross-linking occurs under some conditions. The success of this polymerization depends on several factors. The concentrations used in Table III seemed to give the best results. Preliminary runs indicated that more dilute conditions gave poor films and a higher concentration caused precipitation problems. Regarding the oxidation step, the $FeCl_3$ catalyst[8] made it harder to control so most of the work was done without the catalyst. The air flow rate seems to show an optimum value of 100 mL/min in one comparison (see Table III, entries 3–5), but that is just for one particular time. The series of runs at 80 °C show that viscosity increases with time and that rather long times are needed. The reaction time at −20 °C also seems important (compare the η_{inh} = 0.439 dL/g run with the η_{inh} = 0.710 dL/g).

The results with DAB and **1d** were used to predict reasonable conditions for **6** and **1d** (see Table IV). The best viscosities and films of PBI-2 resulted from conditions using 100 mL/min air flow for 72 and 204 h. We had expected that viscosity would provide a good guide of molecular weight and would be a good predictor of whether the polymer would produce a durable, flexible film. This was not always the case as shown in Table IV. Inherent viscosities below 0.6 dL/g usually meant poor or no film, but there were exceptions. It may be that, in some cases, the film can undergo further oxidation during the cure that may be hard to control or predict. The films listed as excellent were clear yellow-brown, tough (but would tear if started), and flexible and would fold without breaking. They were generally of better quality than any of the films from the DAB and **1d** studies, which suggests that the more flexible nature of the **6** component produces a more workable polymer for films.

Commercial PBI-1 has a reported[1] T_g of 435 °C while PBI-2 has a T_g of 279 ± 10 °C, which is consistent with its greater flexibility. PBI-2 shows a distinct inflection point for 10% weight loss at 296 ± 10 °C while PBI-1 is reported[1] to have a very gradual slope with 4.1% weight loss at 250 °C. The onset of the steep portion of the weight-loss curve in air is ca. 530 °C for PBI-2 vs ca. 580 °C for PBI-1.

Scheme III

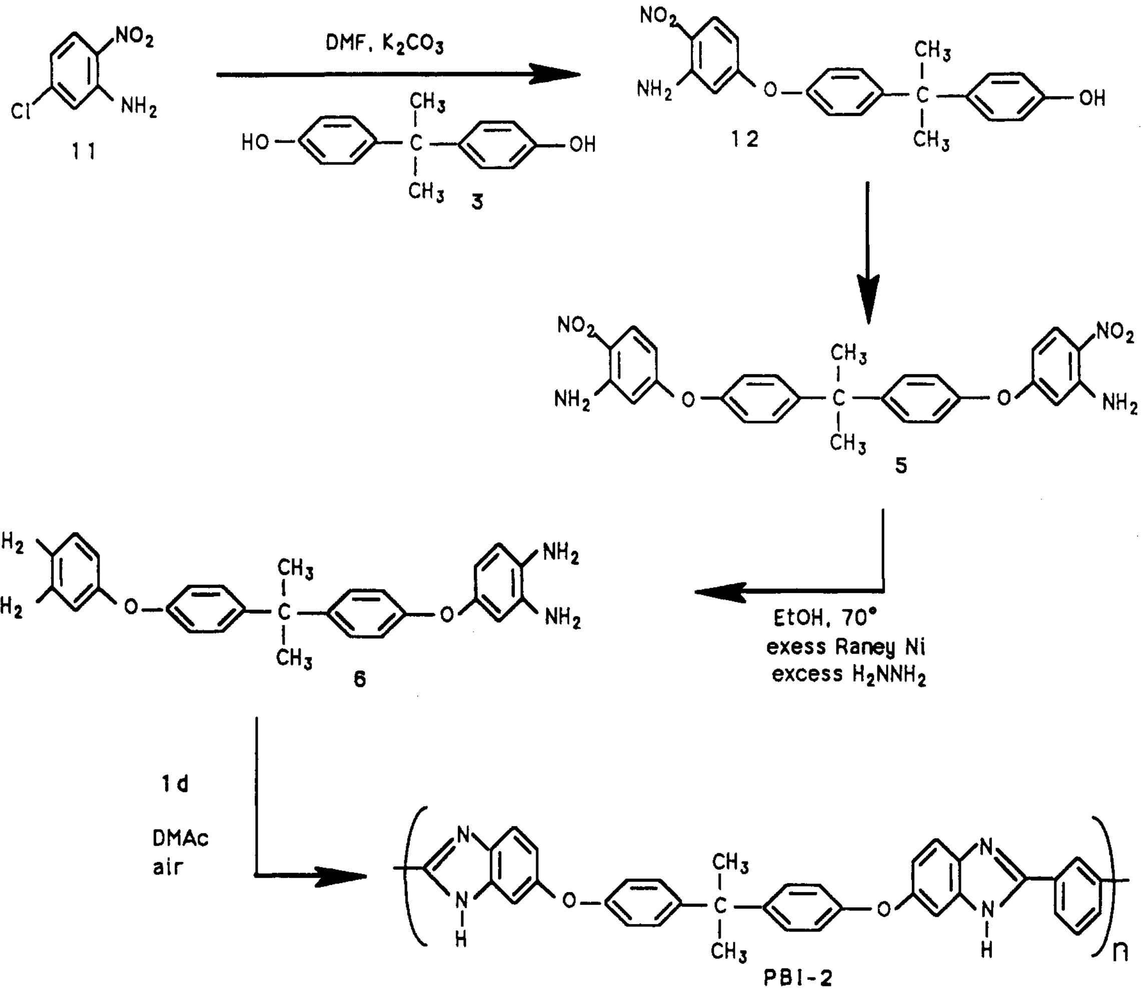


Table II
One-Stage[a] Polymerization of DAB and 1d

drip, mL	pot, mL	T, °C	t, h	FeCl$_3$, mmol	air, mL/min	η_{inh}, dL/g	film[b]
5	3	50	5		*c*	0.717	good
10	5	50	3		300	0.130	decom
10	5	50	72		150	0.130	decom
7	3	50	72		150	0.144	decom
5	3	50–150	3		200	gelled	no
10	10	100	24		200	0.710	fair
12	3	110	2		*c*	0.446	good
12	3	110	2		*c*	0.531	good
12	3	110	2.5		*c*	0.624	good
7	5	50	2	0.02	120	0.149	decom
6	3	50	22	0.02	175	0.410	decom
10	10	100	0.25	0.02	200	ppt'd	no

[a] 2.5 mmol of **1d** in dry DMAc (drip, mL) was dripped over 30 min into 2.5 mmol of DAB in dry DMAc (pot, mL) with stirring and air the whole time. [b] A film was judged to be "fair" if it broke easily if bent, "good" if it was reasonably tough and flexible, and "very good" if it could be folded without breaking. [c] Not accurately measured; estimated at 200 mL/min.

Conclusions

Nucleophilic aromatic substitution chemistry has been used in two ways to generate a tetraamine which was polymerized in an oxidative heteroaromatization reaction with isophthalaldehyde. Conditions are described which provide viscosity, T_g, TGA, and film results indicating a new polybenzimidazole with acceptable manufacturing characteristics.[1]

Experimental Section

General Procedures. Spectral measurements utilized Perkin-Elmer 727B and 621 and Nicolet 510P infrared, Hewlett Packard 8452 UV, Bruker 300- or 400-MHz NMR, and CDC mass spectrometer instruments. Flash chromatography[26] used EtOAc–hexane eluent with the percent indicated in parentheses. Dimethylacetamide (DMAc) and dimethylformamide (DMF; Aldrich Gold Label) were dried by storing over 13X molecular sieves (predried under nitrogen at 350 °C for 4 h). All reactions were conducted under nitrogen with magnetic stirring unless otherwise stated.

5-Chloro-2,1,3-benzothiadiazole (8). A solution of 250 g (1.75 mol) of 4-chloro-1,2-diaminobenzene (**10**) in 2200 mL of toluene was mechanically stirred as 350 mL of thionyl chloride was added over 30 min (some heat generated).[21] The temperature was increased gradually over 5 h to 110 °C as gas evolved. After 24 h at 110 °C, IR and TLC analysis indicated mainly the di-*N*-sulfinyl compound, ClC$_6$H$_3$(N=S=O)$_2$; 127 mL of pyridine was added[27] in several portions and heating continued for 3 h, at

Table III
Two-Stage Polymerization[a] of DAB and 1d

T_1, °C	t_1, h	T_2, °C	t_2, h	air flow, mL/min	η_{inh}, dL/g	film[b]	notes
-20	3	35	6	200	gelled		
-20	5	50	12	175	precip		10 mL into 2 mL
-20	3	60	78	200	0.627	good[b]	
-20	3	60	78	100	0.822	good	
-20	3	60	78	50	0.576	good	
-20	3	35-80	88	200	0.751	good	
-20	3	35-80	77	100	0.435	good	
-20	3	35-100	63	100	0.778		
-20	3.5	80	8	200	0.647	good	
-20	6.5	80	8	200	0.287	good	
-20	7	80	2	200	0.202		
-20	7	80	4	200	0.307		
-20	7	80	6	200	0.314		
-20	7	80	8	200	0.363		
-20	7	80	25	200	0.710	good	
-20	3.5	80	24	200	0.439	decomp	
-20	3	100	20	200	precip		
-20	5	50	2	150	precip		4 mL into 2 mL, 0.02 mmol of $FeCl_3$

[a] 2.5 mmol of **1d** in 10 mL of dry DMAc was dripped into 2.5 mmol of DAB in 10 mL of dry DMAc over ca. 3 h and then kept at -20 °C until time t_1 (includes the 3 h) unless otherwise noted. The temperature was raised to T_2, and air was bubbled through for t_2. [b] A film was judged to be "fair" if it broke easily if bent, "good" if it was reasonably tough and flexible, and "very good" if it could be folded without breaking.

Table IV
Polymerization[a] of 6 and 1d

T_1, °C	t_1, h	T_2, °C	t_2, h	air, mL/min	η_{inh}, dL/g	film[b]	notes
		50	5	?	0.115	flexible	10 to 4 mL[c]
		50	5	?	0.108	flexible	18 to 8 mL[c]
		50	2.25	?	gelled		10 to 4 mL[c]
		50	5	?	0.295	brittle	10 to 4 mL[c]
-20	3	35-100	63	100	0.611	very good	c
-20	3	60	85	100	0.635	good	c
-20	3	60	72	100	0.836	good[d]	c
-20	3	60	78	200	0.740	good	
-20	3	60	78	100	0.970	very good	
-20	3	60	78	50	0.680	fair	
-20	3	60	204	100	0.956	(none made)	
-20	7	80	24	200	0.380	brittle	
-20	6.5	80	48	200	0.246	brittle	
-20	6.5	80	60	200	0.500	very good	
-20	6	80	3	200	0.411	brittle	
-20	7	100	16	200	0.376	brittle	
-20	3	80	*e*	200	0.471	very good	

[a] The first four entries are one-stage polymerizations (see Table II); the mL shown under notes are for a 2.5-mmol scale, but they were actually run at approximately half-scale. The others are two-stage: 2.5 mmol of **1d** in 10 mL of dry DMAc was dripped into 2.5 mmol of DAB in 10 mL of dry DMAc over ca. 3 h and then kept at -20 °C until time t_1 (includes the 3 h) unless otherwise noted. The temperature was raised to T_2 and air was bubbled through for t_2. [b] A film was judged to be "brittle" if it broke readily when touched, "fair" if it broke easily if bent, "good" if it was reasonbly tough and flexible, and "very good" if it could be folded without breaking. [c] Half-scale. [d] Also precipitated in MeOH. When redissolved in DMAc, a very good film was cast. [e] Toluene Dean-Stark trap and air at 100 mL/min; 60 °C for 72 h.

which time the 1165- and 1190-cm^{-1} IR peaks were gone. Most of the volatiles were removed with a rotary evaporator, the brown liquid was poured over ice, and the resultant solid was washed with water and dried to give 333 g of dark brown solid, mp = 49–53 °C. The material was sublimed in 60–90-g batches in a Kugelrohr apparatus, which gave 283 g (94%) of pale yellow **8** that was one spot on TLC [mp = 53–54 °C (lit.[28] mp 57 °C)].

5,5′-[(1-Methylethylidene)bis(4,1-phenyleneoxy)]bis-[2,1,3-benzothiadiazole-*2-S*^{IV}] (4). A slurry of 0.8832 g (5.18 mmol) of **8**, 0.5043 g (2.21 mmol) of 2,2-bis(4-hydroxyphenyl)-propane (**3**), 1.0939 g (7.93 mmol) of anhydrous K_2CO_3, 25 mL of DMF, and 10 mL of toluene was stirred and heated in a flask equipped with a Dean-Stark trap.[20] The toluene was removed with the trap, and the reflux was continued for 24 h. The reaction mixture was shaken with 200 mL of CH_2Cl_2 and 100 mL of 5% NaOH. The organic layer was washed with 5% NaOH and water and then dried over $MgSO_4$. After removal of the $MgSO_4$ and CH_2Cl_2, a Kugelrohr apparatus at 45 °C (1.1 Torr) was used to remove residual DMF. The dark crude product was dissolved in EtOAc, Celite was added, and the EtOAc was removed. The Celite/crude product was then flash chromatographed (5%), which gave **8** (R_f = 0.33), **4** (R_f = 0.15), and **9** (R_f = 0.03). The ratio of **8**:**4**:**9** in an earlier 6-h run was 21:27:36 (**3** was removed by the 5% NaOH while **9** was not). Spectra for **9**: IR 3380, 880, 840, 820 cm^{-1}; NMR ($CDCl_3$) δ 8.0 (d, J = 8 Hz, 1 H), 6.6–7.6, (m, 10 H), 5.6 (s, 1 H), 1.7 (s, 6 H). The ratio was not quantified in this 24-h run, but the TLC of the crude product looked similar to that of the earlier 6-h run. The fractions of reasonably pure **4** were treated with hexane, which removed a colored, hexane-soluble impurity. A second flash chromatographic separation was performed on some fractions. Crystallization from EtOAc–hexane gave 0.205 g of **4** (19% yield): mp 110–111 °C; IR 880, 840, 820 cm^{-1}; NMR ($CDCl_3$) δ 8.0 (d, J = 8 Hz, 2 H), 7.0–7.6 (m, 12 H), 1.8 (s, 6 H). Anal. Calcd for $C_{27}H_{20}N_4O_2S_2$: C, 65.30; H, 4.06. Found: C, 65.18; H, 3.99.

2,2-Bis[4-(3,4-diaminophenoxy)phenyl]propane (6). A 199.1-mg sample of **4** was dissolved in 60 mL of absolute ethanol at 70 °C in an open flask.[22] Eight 0.05-g protions of Raney nickel were added (less vigorous at the end, and TLC showed no starting material). The reaction mixture was filtered through sintered glass to remove Raney nickel, which was kept wet to avoid a fire. Removal of solvent gave 89.7 mg of **6** with spectral properties identical with **6** prepared from **5** (see below).

5-Chloro-2-nitroaniline (11). This material could be purchased or prepared from 2,4-dichloronitrobenzene by reacting with liquid ammonia in a pressure reactor [ca. 85% yields, mp 122–123 °C crystallized from methanol (lit. mp 126.5–127 °C)] as described previously.[22] Some 1,3-diamino-4-nitrobenzene is also formed, but it is in minor amounts and is water soluble (mp = 153–154 °C).

2,2-Bis[4-(3-amino-4-nitrophenoxy)phenyl]propane (5). A slurry of 23.62 g (0.137 mol) of **11**, 15.80 g (0.068 mol) of **3**, 10.53 g (0.85 mol) of anhydrous K_2CO_3, and 50 mL of dry DMF was stirred and heated at 110 °C for 80 h.[20] No toluene and Dean-Stark trap was used to remove water for this run, but it was used in other runs. The reaction mixture was added to 500 mL of ether and was washed with 350-mL portions of the following: water (twice), 5% NaOH (twice), 30% NaOH. After drying ($MgSO_4$), removal of ether gave crude product that was flash chromatographed (5%). This eluted **11**, which was recycled and purified for later use. To elute the pure diadduct (**5**), 30% EtOAc–hexane was used, and then 50% EtOAc–hexane was used to flush the column. Crystallization from 30:70 EtOAc–hexane gave 34.65 g (56.3%) of **5**: mp = 168–169 °C; NMR ($CDCl_3$) δ 8.10 (d, J = 8 Hz, 2 H), 7.30 (d, J = 8 Hz, 4 H), 7.00 (d, J = 8 Hz, 4 H), 6.35 (dd, J = 8 and 2 Hz, 2 H), 6.20 (d, J = 2 Hz, 2 H), 6.3–5.9 (br s, ca. 4 H), 1.75 (s, 6 H); IR (KBr) 3480, 3350, 1640, 1580, 1510, 1440, 1340, 1260 cm^{-1}; high-resolution MS m/e 500.1696 (calcd for $C_{27}H_{24}N_4O_6$, 500.1697).

Acidification of the 30% NaOH wash gave the half-reacted product **12**: mp = 180–181 °C; NMR ($CDCl_3$) δ 8.10 (d, J = 8 Hz, 1 H), 6.6–7.20 (m, 8 H), 6.35 (dd, J = 8 and 2 Hz, 1 H), 6.15 (d, J = 2 Hz, 1 H), 1.70 (s, 6 H); IR 3480 (br) 3350, 1640, 1580, 1500, 1430, 1340, 1240 cm^{-1}; MS (relative intensity) m/e 364 (37.6), 350 (35.7), 349 (100), 311 (20.6), 152 (15.9), 119 (16.9). A 5% NaOH wash would not remove **12**, and it has essentially the same R_f value as **5** in EtOAc–hexane eluents. TLC analysis with 30% EtOH–hexane was effective with R_f values for **11** of 0.58, for **12** of 0.47, and for **5** of 0.37.

2,2-Bis[4-(3,4-diaminophenoxy)phenyl]propane (6). A 1.243-g sample of **5** was warmed in 125 mL of ethanol and 50 mL of acetone in an open flask.[21] A total of 1.2 g of Raney nickel (50% in water) and 8 mL of hydrazine hydrate were added in small portions. The reaction was monitored by TLC to ensure that all of **5** and all of an intermediate stage had reduced (silica plates with 30:70 EtOAc–hexane: **6**, the intermediate stage, and **5** have R_f values of 0.38, 0.22, and 0.04). The residual nickel catalyst was removed by filtration, keeping the nickel wet. The ethanol was evaporated down to ca. 40 mL, and this was added to 200 mL of a 60:40 water–ethanol mixture with heat. Crystals formed overnight, and the product was crystallized again in 60:40 water–ethanol, which gave a 79% yield of pale brown crystals of **6**: mp 147–148 °C; NMR ($CDCl_3$) δ 7.5–6.2 (m, 14 H), 3.2 (br s, ca. 8 H), 1.7 (s, 6 H); IR 3440, 3360, 3040, 2970, 1620, 1490, 1225, 1175, 1010, 970, 860, 825 cm^{-1}; MS m/e (relative intensity) 440 (100), 425 (45), 334 (95), 319 (65), 220 (55). Anal. Calcd for $C_{27}H_{28}N_4O_2$: C, 73.61; H, 6.41. Found: C, 73.79; H, 6.48.

Poly[2,5-benzimidazolediyloxy-1,4-phenylene(dimethylmethylene)-1,4-phenyleneoxy-5,2-benzimidazolediyl-1,3-phenylene] (PBI-2). A solution of 0.168 g (1.125 mmol) of isophthalaldehyde (**1d**) dissolved in 5 mL of dry DMAc was added dropwise over 3 h to 0.550 g (1.125 mmol) of **6** dissolved in 5 mL of dry DMAc at −15 to −20 °C in an oxygen-free environment. The temperature of the solution was raised to 60 °C, and dry air was bubbled through the mixture at a rate of ca. 100 mL/min for 72 h. This gave η_{inh} = 0.826 dL/g and a strong resilient film. The film was cast by dripping the dissolved polymer (DMAc) onto a microscope slide until covered and letting the slide sit for 1 h at 50–60 °C in air and then pulling a vacuum (−95 kPa) at 100 °C for 1.5–2.5 h. The PBI was separated from the slide by placing the slide in water: IR (KBr) 3440, 1700, 1685, 1650, 1640, 1620, 1560, 1545, 1505, 1475, 1460, 1230, 1175, 1150, 1010, 875, 810, 700 cm^{-1} (quite similar to poly(2,5-benzimidazolediyloxy-5,2-benzimidazolediyl-1,4-phenylene)[8]); UV (DMAc) 322 ($\epsilon = 3.2 \times 10^4$), 266 ($\epsilon = 1.1 \times 10^4$), flat base line from 370 to 500 nm (PAM region); T_g = 279 ± 10 °C (average deviation of four samples); TGA 10% weight loss of 296 ± 10 °C (average deviation of three samples). Anal. Calcd for $C_{35}H_{26}N_4O_2$ (and 2.88% water determined by Karl-Fischer analysis): C, 76.39; H, 5.08; N, 10.18. Found: C, 76.32; H, 5.11; N, 9.72.

Measurements. Viscosity measurements, using a Cannon–Ubbelohde type viscometer, were conducted at 24.0 °C in DMAc at a concentration of 0.4–0.5 g/dL (in a few cases, they were measured at a higher concentration, and the value shown is corrected to the 0.4–0.5 range using a graphical plot). Glass transition temperatures (T_g), taken as the midpoint of the change in slope of the base line, were measured on a Du Pont 1090 differential scanning calorimeter with a heating rate of 10 °C/min. Thermal gravimetric analyses (TGA) were conducted in air at 20 °C/min.

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References and Notes

(1) Powers, E. J.; Serad, G. A. *High Performance Polymers: Their Origin and Development*; Seymour, R. B., Kirshenbaum, G. S., Ed.; Elsevier: New York, 1986; pp 355–373. Cassidy, P. E. *Thermally Stable Polymers*; Marcel Dekker: New York, 1980; pp 163–173.

(2) Chandra, M.; Rempel, G. L. *React. Polym.* **1989**, *11* (2), 165.

(3) Belohlav, L. R. *Angew. Chem., Makromol. Chem.* **1974**, *40/41*, 465.

(4) Li, N.-H.; Frechet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1100. For membranes using cobalt complexes to give facilitated oxygen transport, see: Nishide, H.; Ohyanagi, M.; Okada, O.; Tsuchida, E. *Macromolecules* **1988**, *21*, 2910.

(5) Vogel, H.; Marvel, C. S. *J. Polym. Sci.* **1961**, *50*, 511. Hedberg, F. L.; Marvel, C. S. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1823. For more recent examples, see: Gordon, B., III; Kumpf, R. J.; Painter, P. C.; *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27* (1), 311. Gordon, B., III; Kumpf, R. J.; Painter, P. C. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, *26* (1), 146.

(6) Ueda, M.; Sugita, H. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 2815. Ueda, M.; Sato, M.; Mochizuki, A. *Macromolecules* **1985**, *18*, 2723.

(7) Vogl, O.; Dudgeon, C. D. *J. Polym. Sci. (A)* **1978**, *16*, 1815.

(8) Neuse, E. W. *Adv. Polym. Sci.* **1982**, *47*, 2. Neuse, E. W.; Loonat, M. S.; Rabilloud, G. *Macromolecules* **1986**, *19*, 481. Neuse, E. W.; Loonat, M. S. *Macromolecules* **1983**, *16*, 128.

(9) D'Alelio, G. F. U.S. Patent 3,763,107, 1973; *Chem. Abstr.* **1974**, *80*, 71350b.

(10) Katritzky, A. R.; Sakizadeh, K.; Swinson, J. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 1781. Katritzky, A. R.; Sakizadeh, K.; Swinson, J.; Rassmussen, J. K.; Kaepski, L. K.; Pathre, S. V. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 1515.

(11) Engel, A. K.; Yoden, T.; Sanui, K.; Ogata, N. *Polym. Mater. Sci. Eng.* **1986**, *54*, 119.

(12) Reddy, T. A.; Srinivasan, M. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 2805.

(13) Scariah, K. J.; Krishnumarthy, V. N.; Rao, K. V. C.; Srinivasan, M. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 2675. Izyneev, A. A.; Varga, I.; Mazurevskaya, Sh. P.; Novak, I. S.; Mazurevski, V. P.; Mognonov, D. M.; Angotkina, A. A.; Radnaeva, L. D. *Acta Polym.* **1988**, *39* (8), 429. For a hydroquinone-linked tetramine monomer like **6**, see: Koton, M. M.; Sazanov, Y. N. *Vysokomol. Soedin., Ser. A* **1975**, *17* (7), 1469 and earlier papers in that series.

(14) Korshak, V. V.; Berestneva, G. L.; Pelzbauer, Z.; Nikol'skii, K. V.; Dubovik, I. I. *Acta Polym.* **1986**, *37* (5), 281.

(15) Radnaeva, L. D.; Mognonov, D. M.; Batotsyrenova, A. L.; Izyneev, A. A.; Erzh, B. V.; Varga, I. *Acta Polym.* **1988**, *39* (8), 437.

(16) Mandric, G.; Neamtu, G. A.; Peccincu, S.; Racaru, G. *Rev. Roum. Chim.* **1986**, *31* (1), 25.

(17) Lee, D. S.; Quin, G. *Polym. J.* **1989**, *21*, 751. Leung, L.; Williams, D. J.; Karasz, F. E.; MacKnight, W. J. *Polym. Bull. (Berlin)* **1986**, *16* (5), 457.

(18) White, D. M.; Takekoshi, T.; Williams, F. J.; Relles, H. M.; Donahue, P. E.; Klopfer, H. J.; Loucks, G. R.; Manello, J. S.; Mathews, R. O.; Schluenz, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1635.
(19) Nunno, L. D.; Florio, S. *Tetrahedron* **1977**, *33*, 855.
(20) Loewe, H.; Urbanietz, J.; Kirsch, R.; Duewel, D. Ger. Patent 2,365,362, 1975; *Chem. Abstr.* **1975**, *82*, 156391g (used on 5-chloro-2-nitroaniline with phenol).
(21) Sharma, K. S.; Singh, R. P.; Singh, V. *Indian J. Chem.* **1979**, *17B*, 13.
(22) Ross, J. M.; Smith, W. C. *J. Am. Chem. Soc.* **1964**, *86*, 2861.
(23) Markert, J.; Schwander, H. Ger. Patent 2,620,791, 1976; *Chem. Abstr.* **1977**, *86*, 89376y. Latham, D. W. S.; Meth-Cohn, O.; Suschitzky, H. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2216.
(24) Archer, G. A.; Kalish, R. I.; Ning, R. Y.; Sluboski, B. C.; Stemple, A.; Steppe, T. V.; Sternbach, L. H. *J. Med. Chem.* **1977**, *20*, 1312.
(25) Starks, C. M.; Liotta, C. *Phase-Transfer Catalysis*; Academic Press: New York, 1978.
(26) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 3861.
(27) Komin, A. P.; Carmack, M. *J. Hetrocycl. Chem.* **1975**, *12*, 829.
(28) Dal Monte, D.; Sandri, E.; Di Nummo, L.; Florio, S.; Todesco, P. E. *J. Chem. Soc. B* **1971**, *2209*.

Registry No. 3, 80-05-7; **4**, 137964-67-1; **5**, 137946-71-5; **6**, 137946-72-6; **8**, 2207-32-1; **11**, 89-63-4; **12**, 137946-73-7; PBI-1 (copolymer), 27288-38-6; PBI-1 (SRU), 25734-65-0; PBT-2 (copolymer), 137946-74-8; PBI-2 (SRU), 137946-75-9.