used has not been established yet, and usually, the most symmetric ones have been employed. In the case of PMPS, the modification seems to be in the sense of decreasing the anisotropy of the side group. A tentative explanation of the behavior of the swollen PMPS can be obtained if one imagines a solvation of the phenyl group by the diluent; the resulting solvated ring would be closer to spherical symmetry and hence less anisotropic than the unsolvated group.

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(33) An exception to this rule seems to be chains with asymmetric centers separated by more than two skeletal bonds like poly(3-methyltetrahydrofuran).[31]

Rigid-Rod Polyquinolines with Extended Aryl Ether Pendent Groups: An Approach to Solubility Enhancement

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ABSTRACT: Rigid-rod polyquinolines containing the pendent aryl ether groups *p*-C_6H_4-*p*-$C_6H_4OC_6H_5$, *p*-C_6H_4O-*p*-$C_6H_4C_6H_5$, and *p*-C_6H_4O-*p*-$C_6H_4OC_6H_5$ in the 4,4′ positions of the quinoline rings were prepared by the acid-catalyzed polymerization of the corresponding 3,3′-diaroylbenzidines with 4,4′-diacetylbiphenyl. These polyquinolines were crystalline (T_m = 417–505 °C) and were not soluble in the more common organic solvents. The solubility of these polymers containing the pendent arms was similar to the analogous rigid-rod polymer containing pendent phenyl groups.

Introduction

Although rigid-rod polyaromatics generally display high strength and possess the thermal and mechanical properties necessary for high-temperature applications, they have very limited solubility, or are insoluble, in common organic solvents. Thus they can be difficult to fabricate, and the study of their solution properties is often limited to solutions in strong acids. With a number of polyaromatics, solubility has been improved by the attachment of phenyl groups to the polymer main chain, as is the case with polyquinoxalines,[1] polyphenylenes,[2,3] and polyimides.[4] The solubility of a number of polyheterocycle/polyphenylene copolymers is enhanced by the attachment of phenoxyphenyl and phenylthiophenyl pendent groups.[5] However, improved solubility of the rigid-rod polybenzobis(oxazoles)[6] or polybenzobis(thiazoles)[7] was not realized through phenyl substitution on the phenylene units connecting the benzobis(oxazole) or benzobis(thiazole) units.

The rigid-rod polyquinoline poly[2,2′-(*p*,*p*′-biphenylene)-6,6-bi(4-phenylquinoline)] (1) has excellent thermal and mechanical properties, but it is soluble only in solvents such as trifluoromethanesulfonic acid and its polymerization medium, a mixture of *m*-cresol and di-*m*-cresyl phosphate.[8] Fibers spun from anisotropic solutions of 1 show an X-ray structure in which the parallel chains along the direction of the fiber axis stack in nearly coplanar

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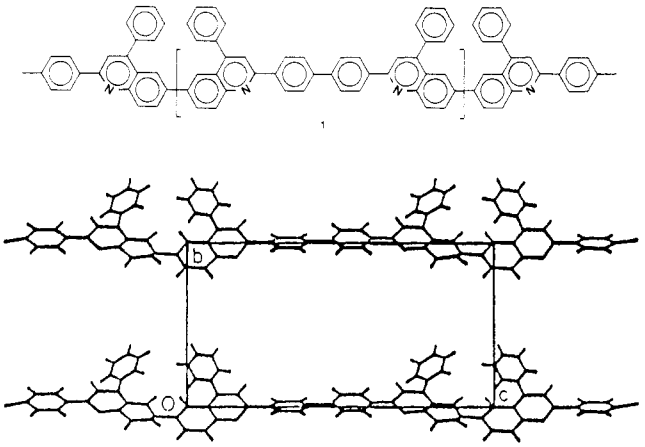
Chart I

Crystal Structure of a Rod Quinoline

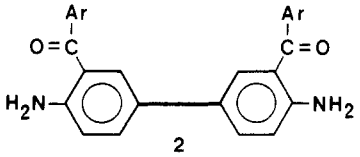


sheets.[9] Thus, the two pendent phenyl groups on the 4-positions of the quinoline unit point toward one another.

Consequently, we sought to modify the structure of rigid-rod polyquinoline 1 by substituting pendent arms longer than the single phenyl unit in an effort to improve the solubility. Placing a pendent group containing two or more phenylene units in the 4-position should reduce the crystallinity by decreasing the overall length-to-width ratio of the rigid rod by disrupting the coplanar array in the polymer chain through steric interference of the pendent groups and by preventing the dense packing of the chains realized by the parallel stacking of the planar sheets. (See Chart I.)

Results and Discussion

In the synthesis of polyquinolines such as 1, the pendent phenyl group originates in the bis(amino ketone) monomer, specifically from the benzoyl phenyl in 3,3′-dibenzoylbenzidine. Thus the critical problem was to be able to develop a synthesis of bis(amino ketone) monomers (2) containing appropriate *o*-aroylamine functions.

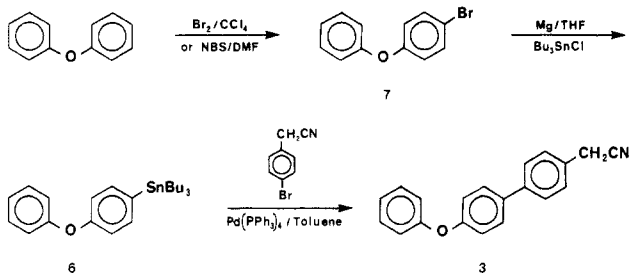


2

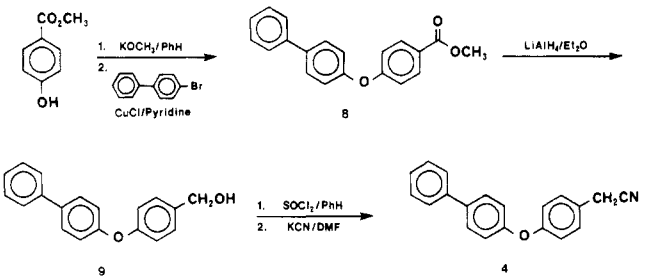
Monomer Synthesis. Acetonitriles 3–5 were initial synthetic targets, since the condensation of phenylacetonitrile with nitroaromatics is known to produce the key benzisoxazole intermediate, which can be hydrogenated to the *o*-benzoylamine.[8] Compound 3 was obtained from the palladium-catalyzed cross-coupling reaction of a tin reagent and an aryl bromide.[10] The coupling of (4-phenoxyphenyl)tributyltin (6) with (4-bromophenyl)acetonitrile gave 3 in 78% yield. The product was easily isolated and purified. No separation by chromatography was required. The tin reagent was obtained by bromination of phenyl ether with either bromine in carbon tetrachloride[11] (68% yield) or *N*-bromosuccinimide in *N*,*N*-dimethylformamide[12] (70% yield) to give 4-bromodiphenyl ether (7). The Grignard reagent prepared from 7 was generated in the presence of tributyltin chloride to produce 6 in 78% yield. (See Scheme I.)

Acetonitrile 4 was prepared by an Ullmann ether condensation reaction[13] between the potassium salt of methyl 4-hydroxybenzoate and 4-bromobiphenyl. This gave methyl 4-(4-phenylphenoxy)benzoate (8) in 58% yield.

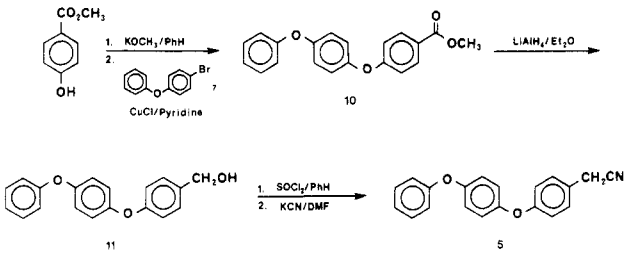
Scheme I



Scheme II



Scheme III



Reduction with lithium aluminum hydride gave benzyl alcohol 9 (94% yield) which, after being converted to the benzyl chloride with thionyl chloride and subsequent reaction with potassium cyanide in *N*,*N*-dimethylformamide, afforded 4 in 89% yield. (See Scheme II).

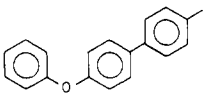
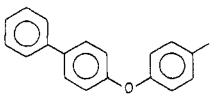
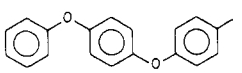
Acetonitrile 5 was prepared similarly. The Ullmann ether condensation reaction between the potassium salt of methyl 4-hydroxybenzoate and 4-bromodiphenyl ether (7) produced methyl 4-(4-phenoxyphenoxy)benzoate (10) in 52% yield. Reduction with lithium aluminum hydride gave benzyl alcohol 11 (93% yield) which, after being converted to the benzyl chloride with thionyl chloride, gave 5 (78% yield) by reaction with potassium cyanide in *N*,*N*-dimethylformamide. (See Scheme III.)

With the synthesis of pendent group acetonitriles 3–5 completed, the synthesis of the *o*-amino ketone monomers through a known synthetic pathway[8] was pursued. Although acetonitriles 3–5 were too insoluble to react with 4-bromonitrobenzene in alkaline methanol/tetrahydrofuran (6.5:1) at 0 °C,[14] when the temperature of the reaction mixture was raised to 55 °C, benzisoxazole formation proceeded smoothly and in a yield comparable to that reported in similar reactions.[8,14] No other modifications of the reported monomer synthesis were required.

Under the modified reaction conditions, 3 was allowed to react with 4-bromonitrobenzene to produce benzisoxazole 12 in 66% yield. Reduction of 12 to *o*-aminobenzophenone 13 was effected in 90% yield with iron and water in glacial acetic acid.[15] Subsequent homocoupling of 13 utilizing a stoichiometric amount of bis(1,5-cyclooctadiene)nickel(0)[16] gave a 65% yield of the benzidine-based *o*-amino ketone monomer 14. (See Scheme IV.)

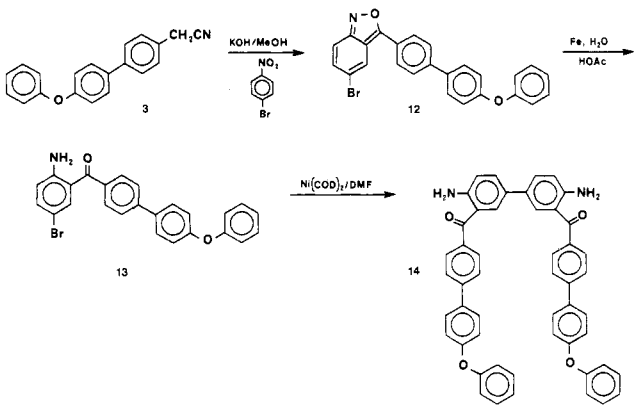
Similarly, a synthesis of monomer 15 was effected. Benzisoxazole 16, obtained in a 66% yield by the reaction

Table I
Thermal Properties of Rigid-Rod Polyquinolines with Pendent Arms[a]

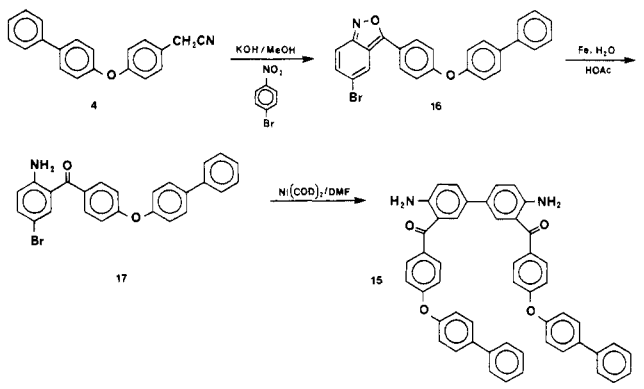
polymer	pendent group (Ar)	heated and quenched[a] T_g	heated and quenched[a] T_m	annealed for 15 min[b] T_g	annealed for 15 min[b] T_m	TGA in air, °C onset	TGA in air, °C break
22a		342 (374)	494 (492)	340	505	440	555
22b		307[c] (283)	416 (414)	364	417	445[d]	545
22c		342 (355)	467 (470)	348	471	450	542

[a] Heating rate for DSC and TGA was 10 °C/min. [b] Sample was heated to annealing temperature at 50 °C/min and then quenched with liquid nitrogen before the DSC trace was recorded. The annealing temperature was calculated from the T_g and T_m of the sample with no thermal treatment: $2/3\ (T_m - T_g) + T_g$ = annealing temperature. Values in parentheses obtained from sample with no thermal treatment. [c] Sample was annealed at the predetermined temperature for 15 min and then allowed to cool to room temperature before the DSC trace was recorded. [d] Sample was contaminated with occluded *m*-cresol. [e] Sample showed a 12% weight loss from 150 to 275 °C due to the volatilization of *m*-cresol.

Scheme IV



Scheme V



of **4** with 4-bromonitrobenzene, was reduced with iron and water in glacial acetic acid to give *o*-aminobenzophenone **17** in 87% yield. The coupling of **17** with bis(1,5-cyclooctadiene)nickel(0) gave monomer **15** in 70% yield. (See Scheme V.)

Monomer **18** also was prepared by following this same sequence of reactions. The formation of benzisoxazole **19** occurred in 70% yield. Subsequent reduction of **19** gave *o*-aminobenzophenone **20** in 90% yield. Monomer **18** was then obtained in a 72% yield by coupling **20** with bis(1,5-cyclooctadiene)nickel(0). (See Schemes VI and VII.)

Polymer Synthesis. Monomers **14**, **15**, and **18** were polymerized with 4,4′-diacetylbiphenyl (**21**)[17] under conditions used for the preparation of high molecular weight rigid-rod polyquinolines.[8] The polymerizations were carried out at 136–138 °C for 48 h in *m*-cresol using the di-*m*-cresyl phosphate catalyst for the Friedlander reaction[18] to yield polyquinolines **22a–c** in 96–98% yields (Table I).

Polymer Properties. Pressed-powder samples of **22a–c** were analyzed by differential scanning calorimetry (DSC). The glass-transition temperatures of the polymers ranged from 307 to 342 °C, although the magnitude of each transition was weak (Table I). The low T_g value of **22b** was attributed to a plasticizing effect due to the presence of *m*-cresol, which could not be completely removed. Although **22b** was precipitated and purified in the same way as **22a** and **22c**, **22b** was a hard, granular material, whereas **22a** and **c** were coarse powders.

Polymers **22a–c** exhibited crystalline-transition temperatures (DSC) ranging from 416 to 494 °C (Table I). The intensity of the crystalline transitions was strong in the case of **22a** and **22b**, but **22c** displayed a moderate transition, suggesting that the degree of crystallinity of **22c** may have been less than that of **22a** and **22b**. Polymer **22c** possesses the pendent group with two flexible ether linkages, and because of the pendent group's spatial bulkiness,

Scheme VI

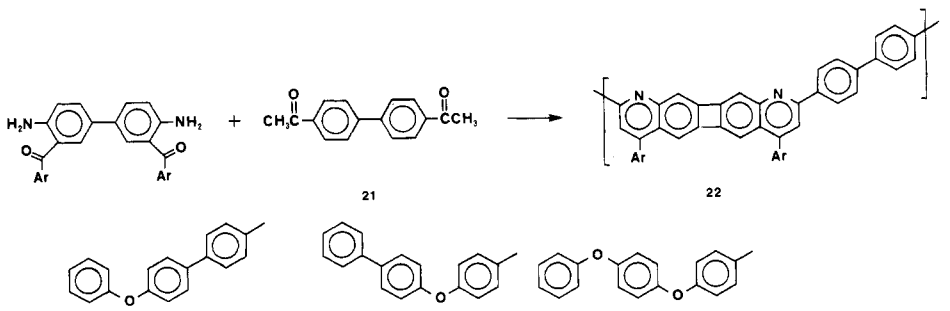
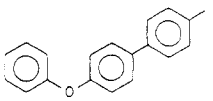
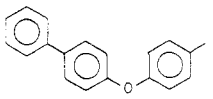
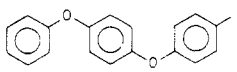
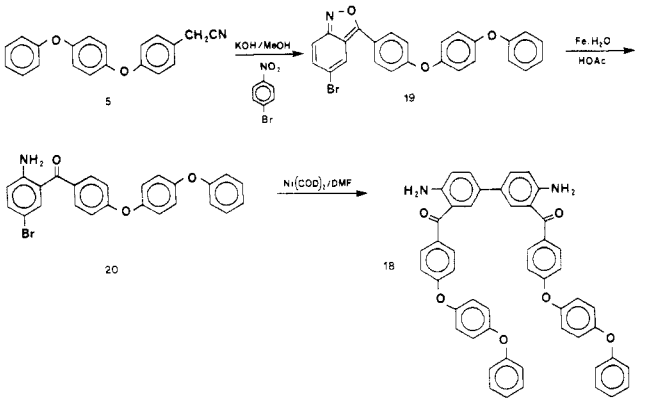


Table II
Solubility Properties of Rigid-Rod Polyquinolines with Pendent Arms in Comparison to a Flexible Polyquinoline

		solubility[a]					
polymer	pendent group (Ar)	chlorinated solvents[b]	THF	benzene, toluene	*m*-cresol	di-*m*-cresyl phosphate/*m*-cresol[c]	$[\eta]^d$
22a		I	I	I	I	S	5.53
22b		I	I	I	I	S	5.26
22c		I	I	I	I	S	26.0

[a] S = ability to dissolve 0.5% by weight of polymer, I = insoluble, SW = swells. Solubility was not improved in hot solvents. [b] Solubility tested in chloroform and 1,1,2,2-tetrachloroethane. [c] A 0.5 mol % solvent mixture. [d] Intrinsic viscosities measured in a 0.5 mol % solvent mixture of di-*m*-cresyl phosphate/*m*-cresol at 25 °C.

Scheme VII



dense packing of the polymer chains may be restricted somewhat, resulting in a lower degree of crystallinity. Possibly the much higher molecular weight of **22c** may have made crystallization more difficult.

Thermogravimetric analysis (TGA) of the polymers in air showed that polymer decomposition began at about 445 °C (Table I) with TGA breaks ranging from 542 to 555 °C. Polyquinolines **22** are not as thermally stable as the parent polymer **1**; the onset of weight loss in air for **1** occurred at 570 °C.[8] The lower stability of **22** in comparison to **1** probably is due to initial scission of the pendent group. Polymer **22b** displayed a gradual 12% weight loss from 150 to 275 °C due to the volatilization of *m*-cresol.

Solubility tests on **22a–c** were carried out in a variety of solvents, but solubility enhancement by pendent group attachment was not realized (Table II). Chloroform, 1,1,2,2-tetrachloroethane, and tetrahydrofuran all failed to dissolve **22a–c**; benzene and toluene had no effect. *m*-Cresol also did not dissolve the rigid-rod polymers, even at 135 °C. When a minimal amount of di-*m*-cresyl phosphate was added to the *m*-cresol, however, to give a 0.5 mol % solvent mixture, the polymers dissolved. This solvent mixture was chosen as the solvent for the dilute solution viscosity measurements (Table II).

Rigid-rod polyquinoline **22c** had the highest intrinsic viscosity ($[\eta]$ = 26.0), which was comparable to rigid-rod polyquinoline **1** ($[\eta]$ = 14.5–26.0).[8] Polymers **22a** and **22b** had much lower intrinsic viscosities, 5.53 and 5.26, respectively. These values were the lowest obtained for any rigid-rod polyquinoline and possibly are a result of having obtained low molecular weight samples.

Experimental Section

Reagents. Cuprous chloride was purified according to a known procedure[19] and used immediately as the catalyst for the Ullman ether syntheses. Tetrakis(triphenylphosphine)palladium(0)[20] and bis(1,5-cyclooctadiene)nickel(0)[21] were prepared as described. The bis(ketomethylene) monomer 4,4′-diacetylbiphenyl (**21**)[17] was purified by sublimation followed by recrystallization from benzene/methanol (2:1), mp 196.0–197.0 °C (lit.[22] mp 189–191 °C). 4-Bromodiphenyl ether[11] (**7**) was distilled, bp 193–197 °C (40 mm) (lit.[11] bp 158–169 °C (10 mm)). The procedure for flash chromatography was followed according to the literature.[23]

(4-Phenoxyphenyl)tributyltin (6). To a stirred mixture of 2.92 g (0.120 mol) of magnesium and 32.5 g (0.100 mol) of tributyltin chloride in 100 mL of dry ether at the reflux temperature under a nitrogen atmosphere was added dropwise over 1.5 h a solution of 27.4 g (0.110 mol) of 4-bromodiphenyl ether in 100 mL of ether. Magnesium salts began to precipitate when about one-third of the solution had been added. The reaction mixture was heated for a total of 24 h and then cooled and suction-filtered through Celite by using 100 mL of ether as a wash. The filtrate was washed with water (2 × 100 mL) and with a saturated salt solution (100 mL) and was then dried over magnesium sulfate. Removal of the solvent followed by fractional distillation of the yellow liquid afforded 35.8 g (78%) of **6** as a colorless liquid: bp 215–219 °C (0.1 mm); IR (neat film) 2970–2840, 1580, 1490, 1260–1220 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.42–6.96 (m, 9 H), 1.58–1.51 (m, 6 H), 1.37–1.29 (m, 6 H), 1.08–1.02 (t, 6 H), 0.92–0.86 (t, 9 H). Anal. Calcd for $C_{24}H_{36}OSn$: C, 62.77; H, 7.90. Found: C, 62.66; H, 7.93.

[4-(4-Phenoxyphenyl)phenyl]acetonitrile (3). A solution of 27.6 g (60.0 mmol) of (4-phenoxyphenyl)tributyltin (**6**) in 100 mL of dry, degassed toluene was transferred via cannula into a nitrogen-flushed reaction flask that contained 9.80 g (50.0 mmol) of (4-bromophenyl)acetonitrile and 1.16 g (1.00 mmol, 2%) of tetrakis(triphenylphosphine)palladium(0). The solution was heated at the reflux temperature for 48 h, by which time palladium black had been deposited. After the reaction mixture had cooled, it was filtered through Celite to afford a yellow solution. The residue obtained after the solvent was removed under reduced pressure was stirred with 200 mL of hexane at 0 °C for 1 h and then suction-filtered to afford a light-yellow solid, which was continuously extracted with hexane for 12 h. Removal of the solvent from the extracts afforded a cream-colored solid which was recrystallized from ethanol (20 mL/g). The product crystallized as 10.7 g (78%) of white plates: mp 121.0–122.0 °C; IR (KBr) 2250, 1280, 1260 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.57–7.04 (m, 13 H), 3.76 (s, 2 H). Anal. Calcd for $C_{20}H_{15}NO$: C, 84.19; H, 5.30; N, 4.91. Found: C, 83.64; H, 5.42; N, 4.79.

3-[4-(4-Phenoxyphenyl)phenyl]-5-bromo-2,1-benzisoxazole (12). To a solution of 23.1 g (0.350 mol, 85% assay) of potassium hydroxide in 48 mL of methanol at 0 °C was added 6.28 g (22.0 mmol) of [4-(4-phenoxyphenyl)phenyl]acetonitrile (**3**). The slurry was mechanically stirred at 0 °C for 5 min, after which time a

solution of 4.04 g (20.0 mmol) of 4-bromonitrobenzene in 32 mL of methanol/tetrahydrofuran (2:1) was added. The dark-blue reaction mixture was stirred at 0 °C for 30 min and then heated at 55 °C for 2.5 h, cooled, and poured into 240 mL of rapidly stirred water. Suction filtration followed by a water wash gave a brown solid, which was placed in an extraction thimble and continuously extracted with methanol for 5 h, after which time the extracts were no longer a dark brown but a light yellow. The contents of the thimble were dried to afford 5.85 g (66%) of **12** as a dull-yellow solid: mp 182.5–184.0 °C. An analytically pure sample was obtained by medium-pressure liquid chromatography (hexane/methylene chloride, 3:7): mp 186.0–186.5 °C; IR (KBr) 1595, 1495, 1260 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.07–8.06 (d, 2 H), 8.03 (s, 1 H) 7.87–7.07 (m, 13 H). Anal. Calcd for $C_{25}H_{16}BrNO_2$: C, 67.89; H, 3.65; N, 3.17. Found: C, 67.75; H, 3.66; N, 3.13.

2-Amino-5-bromo-4′-(4-phenoxyphenyl)benzophenone (13). To a stirred suspension of 4.42 g (10.0 mmol) of benzisoxazole (**12**) in 50 mL of glacial acetic acid at 95 °C was added 3.91 g (70.0 mmol) of iron powder and 9.0 mL of water in six equal portions every 15 min. After the first addition of iron and water, complete dissolution of **12** occurred. When all of the iron and water had been added, the reaction mixture was heated at 95 °C for an additional 2.5 h, cooled, and poured into 250 mL of rapidly stirred water. Suction filtration gave a yellow solid, which was purified by flash chromatography (chloroform/methylene chloride, 1:1) to afford 3.81 g (90%) of **13** as a bright-yellow solid: mp 163.0–164.0 °C; IR (KBr) 3460, 3350, 1635, 1250 (sh), 1240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.74–7.07 (m, 15 H), 6.68–6.65 (d, 1 H), 6.06 (br s, 2 H). Anal. Calcd for $C_{25}H_{18}BrNO_2$: C, 67.58; H, 4.08; N, 3.15. Found: C, 67.25; H, 4.15; N, 3.07.

3,3′-Bis[4-(4-phenoxyphenyl)benzoyl]benzidine (14). To a mixture of 3.55 g (8.00 mmol) of 2-amino-5-bromo-4′-(4-phenoxyphenyl)benzophenone (**13**) and 1.22 g (4.44 mmol) of bis(1,5-cyclooctadiene)nickel(0) in a 100-mL round-bottom flask (prepared in a drybox and fitted with a septum) was added 40 mL of dry, degassed *N,N*-dimethylformamide. The mixture was stirred at room temperature for 30 min and then at 42 °C for 50 h. After the dark solution had cooled, it was suction-filtered through Celite with 200 mL of methylene chloride as a wash. The filtrate was washed with 2% hydrochloric acid (2 × 100 mL) and with a saturated salt solution (100 mL) and was then dried over magnesium sulfate. Removal of the solvent afforded an orange oil, which was placed under reduced pressure (0.05 mmHg) for 12 h and then coated onto silica gel (5 g of silica/g of compound) and prepurified by flash chromatography (hexane/ethyl acetate, 7:3–6:4). Continuous extraction of the product with absolute ethanol followed by suction filtration of the cooled extracts afforded 1.05 g (65%) of **14** as a microcrystalline, bright-yellow solid: mp 208.0–208.5 °C; IR (KBr) 3480, 3350, 1630, 1240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.73–7.03 (m, 30 H), 6.80–6.77 (d, 2 H), 6.03 (br s, 4 H). Anal. Calcd for $C_{50}H_{36}N_2O_4$: C, 82.40; H, 4.98; N, 3.84. Found: C, 82.62; H, 4.96; N, 3.82.

Methyl 4-(4-Phenylphenoxy)benzoate (8). The potassium salt of 38.0 g (0.250 mol) of methyl 4-hydroxybenzoate was prepared with 17.5 g (0.250 mol) of potassium methoxide in 750 mL of dry benzene. To the dry potassium salt was added 3.71 g (37.5 mmol) of cuprous chloride and 64.1 g (0.275 mol) of 4-bromobiphenyl (recrystallized from absolute ethanol) followed by 250 mL of dry pyridine. The reaction mixture was heated to the reflux temperature during which time its color turned from yellow to dark brown. After 24 h, the solvent was removed under reduced pressure, and to the residue was added 500 mL of water, which was then made acidic with concentrated hydrochloric acid. The product was extracted into methylene chloride (3 × 125 mL). The methylene chloride solution was washed with water (2 × 125 mL) and saturated salt solution (125 mL) and dried over magnesium sulfate. Removal of the solvent under reduced pressure gave 73.0 g of a tan solid, which was stirred in methanol (10 mL/g) at the reflux temperature for 30 min and suction-filtered while hot to give 44.0 g (57.8%) of **8** as a light-tan solid: mp 152.5–155.0 °C. Medium-pressure liquid chromatography (methylene chloride: hexane, 9:1) afforded an analytically pure sample of **8** as a white solid: mp 158.0–158.5 °C; IR (KBr) 1720, 1710 (sh), 1285, 1275 (sh) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.04–7.02 (m, 13 H), 3.91 (s, 3 H). Anal. Calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 78.83; H, 5.30.

4-(4-Phenylphenoxy)benzyl Alcohol (9). Because of the poor solubility of methyl 4-(phenylphenoxy)benzoate (**8**) in ether, 15.2 g (50.0 mmol) was continuously extracted into a suspension of 1.90 g (50.0 mmol) of lithium aluminum hydride in 500 mL of dry ether at the reflux temperature for 48 h. The reaction mixture was then diluted with 500 mL of ether and carefully treated with 250 mL of water followed by 50 mL of concentrated hydrochloric acid. Two homogeneous phases were not obtained upon acidification, indicating that the product was very insoluble in ether. The water was separated from the ethereal layer, in which a white solid was suspended. Removal of the solvent followed by recrystallization from chloroform (25 mL/g) afforded 13.0 g (94%) of **9** as a white crystalline solid: mp 160.5–161.0 °C; IR (KBr) 3350, 1270, 1260 (sh) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.59–7.04 (m, 13 H), 4.70–4.68 (d, 2 H), 1.64–1.60 (t, 1 H). (Upon the addition of D_2O to the sample, the doublet at 4.70–4.68 collapsed to a singlet at 4.68 and the triplet at 1.64–1.60 disappeared.) Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.39; H, 5.87.

[4-(4-Phenylphenoxy)phenyl]acetonitrile (4). To a stirred suspension of 9.67 g (35.0 mmol) of 4-(4-phenylphenoxy)benzyl alcohol (**9**) in 105 mL of dry benzene was added 12.5 g (0.105 mol) of thionyl chloride. The solution was heated at 50 °C for 6.5 h, cooled, and carefully treated with 12.3 mL of ethanol. Suction filtration through a column of silica with 150 mL of methylene chloride as a wash and removal of the solvent gave a white solid, which was dissolved in 70 mL of dry *N,N*-dimethylformamide. The solution was stirred with 4.56 g (70.0 mmol) of potassium cyanide at 50 °C for 8 h, cooled, and concentrated under reduced pressure. The residue was stirred for 5 min with 35 mL of methylene chloride and suction-filtered with 70 mL of ether as a wash. The filtrate was washed with water (2 × 35 mL) and with a saturated salt solution (35 mL) and then dried over magnesium sulfate. Medium-pressure liquid chromatography (methylene chloride:hexane, 4:1) afforded 9.48 g (89%) of **4** as a white solid: mp 117.5–118.0 °C; IR (KBr) 2240, 1260 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.59–7.04 (m, 13 H), 3.74 (s, 2 H). Anal. Calcd for $C_{20}H_{15}NO$: C, 84.19; H, 5.30; N, 4.91. Found: C, 84.00; H, 5.30; N, 4.87.

3-[4-(4-Phenylphenoxy)phenyl]-5-bromo-2,1-benzisoxazole (16). To a mechanically stirred solution of 23.1 g (0.350 mol, 85% assay) of potassium hydroxide in 48 mL of methanol at 0 °C was added 6.28 g (22.0 mmol) of [4-(4-phenylphenoxy)phenyl]acetonitrile (**4**). After 5 min, a solution of 4.04 g (20.0 mmol) of 4-bromonitrobenzene in 32 mL of methanol/tetrahydrofuran (2:1) was added. The dark-blue reaction mixture was stirred at 0 °C for 30 min and at 55 °C for 2.5 h and then cooled and poured into 240 mL of water. The precipitate was isolated by suction filtration and then continuously extracted with methanol for 5 h. The yellow solid was dried to afford 5.85 g (66%) of **16**: mp 147.5–148.5 °C. An analytically pure sample was obtained by medium-pressure liquid chromatography (hexane/methylene chloride, 3:7): mp 156.0–157.0 °C; IR (KBr) 1600, 1505, 1255 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.00 (s, 1 H), 7.98–7.95 (d, 1 H), 7.65–7.16 (m, 13 H). Anal. Calcd for $C_{25}H_{16}BrNO_2$: C, 67.89; H, 3.65; N, 3.17. Found: C, 68.02; H, 3.67; N, 3.14.

2-Amino-5-bromo-4-(4-phenylphenoxy)benzophenone (17). To a stirred suspension of 4.42 g (10.0 mmol) of benzisoxazole (**16**) in 50 mL of glacial acetic acid at 95 °C was added 3.91 g (70.0 mmol) of iron powder and 9.0 mL of water in six equal portions every 15 min. When all of the iron and water had been added, the reaction mixture was heated at 95 °C for 2.5 h, cooled, and then poured into 250 mL of water. The yellow precipitate was collected by suction filtration and then purified by flash chromatography (methylene chloride) to give 3.60 g (81%) of **17** as a bright-yellow solid: mp 200.5–201.5 °C; IR (KBr) 3465, 3355, 1635, 1255 (sh), 1240 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.70–7.08 (m, 15 H), 6.67–6.64 (d, 1 H), 5.93 (br s, 2 H). Anal. Calcd for $C_{25}H_{18}BrNO_2$: C, 67.58; H, 4.08; N, 3.15. Found: C, 67.49; H, 4.08; N, 3.14.

3-3′-Bis[4-(4-phenylphenoxy)benzoyl]benzidine (15). To a mixture of 3.55 g (8.00 mmol) of 2-amino-5-bromo-4-(4-phenylphenoxy)benzophenone (**17**) and 1.22 g (4.44 mmol) of bis(1,5-cyclooctadiene)nickel(0) in a 100-mL round-bottom flask (prepared in a drybox and fitted with a septum) was added 40 mL of dry, degassed *N,N*-dimethylformamide. The mixture was stirred at room temperature for 30 min and then at 42 °C for 60 h. After the dark solution had cooled, it was suction-filtered

through Celite with 200 mL of methylene chloride as a wash. The filtrate was washed with 2% hydrochloric acid (2 × 100 mL) and with a saturated salt solution (100 mL) and was then dried over magnesium sulfate. Removal of the solvent afforded an orange oil, which was placed under reduced pressure (0.05 mmHg) for 12 h and then coated onto silica gel (5 g of silica/g of compound) and prepurified by flash chromatography (hexane/ethyl acetate, 7:3–6:4). Continuous extraction of the product with absolute ethanol followed by suction filtration of the cooled extracts afforded 2.03 g (70%) of **15** as a microcrystalline, bright-yellow solid: mp 182.0–182.5 °C; IR (KBr) 3470, 3350, 1625, 1235 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.70–7.00 (m, 30 H), 6.80–6.77 (d, 2 H), 5.93 (br s, 4 H). Anal. Calcd for $C_{50}H_{36}N_2O_4$: C, 82.40; H, 4.98; N, 3.84. Found: C, 82.61; H, 4.96; N, 3.82.

Methyl 4-(4-Phenoxyphenoxy)benzoate (10). The potassium salt of 15.2 g (0.100 mol) of methyl 4-hydroxybenzoate was prepared with 7.01 g (0.100 mol) of potassium methoxide in 300 mL of dry benzene. To the dry potassium salt was added 1.48 g (15.0 mmol) of cuprous chloride followed by 100 mL of dry pyridine. The yellow suspension was heated to its reflux temperature, and then 26.2 g (0.105 mol) of 4-bromodiphenyl ether (**7**) was added over 10 min. After 40 h at the reflux temperature, the solvent was removed under reduced pressure, and to the residue was added 200 mL of water, which was then made acidic with concentrated hydrochloric acid. The aqueous mixture was extracted with methylene chloride (2 × 125 mL), and the extracts were then washed with water (2 × 125 mL) and a saturated salt solution (125 mL). The organic layer was dried over magnesium sulfate. Prepurification by flash chromatography (methylene chloride) gave a white solid, which was stirred with ethanol (30 mL/g) at the reflux temperature for 30 min. The mixture was cooled and suction-filtered to afford 16.8 g (52%) of **10** as a white solid: mp 113.0–114.5 °C. Medium-pressure liquid chromatography afforded an analytically pure sample: mp 114.0–114.5 °C; IR (KBr) 1730, 1715 (sh), 1285, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.02–6.96 (q, 4 H), 7.38–6.99 (m, 9 H), 3.90 (s, 3 H). Anal. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03. Found: C, 74.89; H, 5.08.

4-(4-Phenoxyphenoxy)benzyl Alcohol (11). A solution of 16.0 g (50.0 mmol) of methyl 4-(4-phenoxyphenoxy)benzoate (**10**) in 250 mL of dry ether/tetrahydrofuran, 3:2, was added dropwise over 2 h to a stirred suspension of 1.04 g (27.5 mmol) of lithium aluminum hydride in 50 mL of dry ether at room temperature. The reaction mixture was stirred for an additional 15 min and then carefully treated with 100 mL of water followed by 20 mL of concentrated hydrochloric acid. The aqueous layer was extracted with methylene chloride (100 mL), and the extract was combined with the organic layer. The combined organic layers were washed with water (2 × 100 mL) and a saturated salt solution and were then dried over magnesium sulfate. Removal of the solvent gave a white solid, which was recrystallized from ethanol (7.5 mL/g) to afford 13.6 g (93%) of **11**: mp 117.0–118.0 °C; IR (KBr) 3380, 1250, 1235 (sh) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36–6.99 (m, 13 H), 4.68–4.66 (d, 2 H), 1.63–1.59 (t, 1 H). (Upon the addition of D_2O to the sample, the doublet at 4.68–4.66 collapsed to a singlet at 4.64 and the triplet at 1.63–1.59 disappeared.) Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.93; H, 5.53.

[4-(4-Phenoxyphenoxy)phenyl]acetonitrile (5). A solution of 10.2 g (35.0 mmol) of 4-(4-phenoxyphenoxy)benzyl alcohol (**11**) and 12.5 g (0.105 mol) of thionyl chloride in 105 mL of dry benzene was stirred at 50 °C for 3 h, cooled, and carefully treated with 12.3 mL of ethanol. Suction filtration through silica with 150 mL of methylene chloride as a wash followed by concentration of the filtrate gave a white solid, which was dissolved in 70 mL of dry *N,N*-dimethylformamide. The solution was stirred with 4.56 g (70.0 mmol) of dry potassium cyanide at 50 °C for 10 h, cooled, and concentrated under reduced pressure. The residue was stirred for 5 min with 35 mL of methylene chloride and suction-filtered with 70 mL of ether as a wash. The filtrate was washed with water (2 × 35 mL) and a saturated salt solution (35 mL) and was then dried over magnesium sulfate. Recrystallization from ethanol/petroleum ether (60–90 °C)/benzene (1:1:0.1) afforded 9.20 g (87%) of **5** as a cream-colored solid: mp 96.0–97.5 °C. Further purification by medium-pressure liquid chromatography (hexane/methylene chloride, 1:4) gave an analytically pure sample: mp 98.5–99.0 °C; IR (KBr) 2240, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34–6.98 (m, 13 H), 3.72 (s, 2 H). Anal. Calcd for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65. Found: C, 79.60; H, 5.07; N, 4.64.

3-[4-(4-Phenoxyphenoxy)phenyl]-5-bromo-2,1-benzisoxazole (19). To a mechanically stirred solution of 23.1 g (0.350 mol, 85% assay) of potassium hydroxide in 48 mL of methanol at 0 °C was added 6.63 g (22.0 mmol) of [4-(4-phenoxyphenoxy)phenyl]acetonitrile (**5**). After 5 min, a solution of 4.04 g (20.0 mmol) of 4-bromonitrobenzene in 32 mL of methanol/tetrahydrofuran (2:1) was added. The dark-blue reaction mixture was stirred at 0 °C for 30 min and at 55 °C for 2.5 h and was then cooled and poured into 240 mL of water. The precipitate was isolated by suction filtration and then continuously extracted with methanol for 5 h. The pale-yellow solid was dried to afford 6.41 g (70%) of **19**: mp 91.0–92.0 °C. An analytically pure sample was obtained by medium-pressure liquid chromatography (hexane/methylene chloride, 35:65): mp 95.0–95.5 °C; IR (KBr) 1495 (sh), 1485, 1225 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.99 (s, 1 H), 7.96–7.93 (d, 2 H), 7.53–7.02 (m, 13 H). Anal. Calcd for $C_{25}H_{16}BrNO_3$: C, 65.52; H, 3.52; N, 3.06. Found: C, 65.40; H, 3.53; N, 3.05.

2-Amino-5-bromo-4-(4-phenoxyphenoxy)benzophenone (20). To a solution of 4.58 g (10.0 mmol) of benzisoxazole (**19**) in 50 mL of glacial acetic acid at 95 °C was added 3.91 g (70.0 mmol) of iron powder and 9.0 mL of water in six equal portions every 15 min. After the iron and water had been added, the reaction mixture was heated at 95 °C for 2.5 h, cooled, and poured into 250 mL of water. The product was extracted into methylene chloride (100 mL), and the solution was then suction-filtered through Celite with 100 mL of ether as a wash. The filtrate was washed with a saturated sodium bicarbonate solution (50 mL), water (50 mL), and a saturated salt solution (50 mL) and was then dried over magnesium sulfate. Flash chromatography (methylene chloride) gave 4.15 g (90%) of **20** as a bright-yellow solid: mp 129.0–129.5 °C: IR (KBr) 3450, 3340, 1630 (sh), 1610, 1225 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.68–7.02 (m, 15 H), 6.66–6.63 (d, 1 H), 5.92 (br s, 2 H). Anal. Calcd for $C_{25}H_{18}BrNO_3$: C, 65.23; H, 3.94; N, 3.04. Found: C, 65.09; H, 3.97; N, 2.98.

3,3′-Bis[4-(4-phenoxyphenoxy)benzoyl]benzidine (18). To a mixture of 4.60 g (10.0 mmol) of 2-amino-5-bromo-4-(4-phenoxyphenoxy)benzophenone (**20**) and 1.53 g (5.56 mmol) of bis(1,5-cyclooctadiene)nickel(0) in a 100-mL round-bottom flask fitted with a septum (prepared in a drybox) was added 50 mL of dry, degassed *N,N*-dimethylformamide. The mixture was stirred at room temperature for 30 min and then at 42 °C for 65 h. After the dark solution had cooled, it was suction-filtered through Celite with 200 mL of methylene chloride as a wash. The filtrate was washed with 2% hydrochloric acid (2 × 100 mL) and a saturated salt solution (100 mL) and was then dried over magnesium sulfate. Removal of the solvent afforded an orange oil, which was placed under reduced pressure (0.05 mmHg) for 12 h, coated onto silica gel (5 g of silica/g of compound), and then prepurified by flash chromatography (hexane/ethyl acetate, 7:3–6:4). The product was stirred with 40 mL of absolute ethanol at the reflux temperature to induce crystallization. After it was cooled, the mixture was suction-filtered to afford 1.03 g (72%) of **18** as small, bright-yellow needles: mp 147.0–147.5 °C; IR (KBr) 3480, 3350, 1625, 1220 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.69–6.95 (m, 30 H), 6.79–6.75 (d, 2 H), 5.90 (br s, 4 H). Anal. Calcd for $C_{50}H_{36}N_2O_6$: C, 78.93; H, 4.77; N, 3.68. Found: C, 78.09; H, 4.88; N, 4.64.

Poly[2,2′-(*p*,*p*′-biphenylene)-6,6′-bi[4-(4-(4-phenoxyphenyl)phenyl)quinoline]] (22a). Into the bottom of a resin flask was weighed 0.7288 g (1.000 mmol) of 3,3′-bis[4-(4-phenoxyphenyl)benzoyl]benzidine (**14**) and 0.2383 g (1.000 mmol) of 4,4′-diacetylbiphenyl (**21**) followed by 6.96 g (25.0 mmol) of di-*m*-cresyl phosphate and 2.16 g of *m*-cresol. The resin flask was assembled, fitted with a mechanical stirrer, and then flushed with nitrogen for 10 min. The dark-red solution was heated with stirring at 136–138 °C for 48 h under a static atmosphere of nitrogen. After this time the polymerization dope was diluted with 30 mL of *m*-cresol and stirred for 1 h until homogeneous and then poured, while still hot, into a rapidly stirred mixture of 250 mL of ethanol and 27.5 mL of triethylamine. The mixture was stirred until all of the precipitated polymer was yellow and was then ground in a Waring blender set at high speed for 3 min. The polymer was isolated by suction filtration, was continuously extracted with a mixture of 250 mL of ethanol and 27.5 mL of triethylamine for 24 h, and was then dried at 110 °C at 0.05 mmHg

for 24 h to afford 0.862 g (96%) of **22a** as a coarse, yellow powder: $[\eta]$ = 5.25 dL/g (25 °C; di-*m*-cresyl phosphate/*m*-cresol, 0.5 mol % ratio). Anal. Calcd for $C_{66}H_{42}N_2O_2$: C, 88.57; H, 4.73; N, 3.13. Found: C, 88.67; H, 4.74; N, 3.10.

Poly[2,2′-(*p*,*p*′-biphenylene)-6,6′-bi[4-(4-(4-phenylphenoxy)phenyl)quinoline]] (22b). The above procedure was followed except 0.7288 g (1.000 mmol) of 3,3′-bis[4-(4-phenylphenoxy)benzoyl]benzidine (**15**) and 0.2383 g (1.000 mmol) of 4,4′-diacetylbiphenyl (**21**) were used as the monomer reagents. The monomers were polymerized, precipitated, and purified as above to afford 0.985 (110%) of **22b** as hard granules, which were contaminated with occluded *m*-cresol: $[\eta]$ = 5.26 dL/g (25 °C; di-*m*-cresyl phosphate/*m*-cresol, 0.5 mol % ratio). Anal. Calcd for $C_{66}H_{42}N_2O_2$: C, 88.57; H, 4.73; N, 3.13. Found: C, 84.81; H, 4.62; N, 3.06.

Poly[2,2′-(*p*,*p*′-biphenylene)-6,6′-bi[4-(4-(4-phenoxyphenoxy)phenyl)quinoline]] (22c). The above procedure was followed except 0.7608 g (1.000 mmol) of 3,3′-bis[4-(4-phenoxyphenoxy)benzoyl]benzidine (**18**) and 0.2383 g (1.000 mmol) of 4,4′-diacetylbiphenyl (**21**) were used as the monomer reagents. The monomers were polymerized, precipitated, and purified as above to afford 0.904 g (98%) of **22c** as a coarse, bright-yellow powder: $[\eta]$ = 26.0 dL/g (25 °C; di-*m*-cresyl phosphate/*m*-cresol 0.5 mol % ratio). Anal. Calcd for $C_{66}H_{42}N_2O_4$: C, 85.51; H, 4.57; N, 3.02. Found: C, 85.58; H, 4.61; N, 3.00.

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Registry No. **3**, 99113-95-8; **4**, 99113-96-9; **5**, 99113-97-0; **6**, 99128-02-6; **7**, 101-55-3; **8**, 48198-80-7; **9**, 99113-98-1; **10**, 99113-99-2; **11**, 99114-00-8; **12**, 99114-01-9; **13**, 99114-02-0; **14**, 99114-03-1; $(\mathbf{14}\cdot\mathbf{21})_x$, 99128-03-7; **15**, 99114-04-2; $(\mathbf{15}\cdot\mathbf{21})_x$, 99114-10-0; **16**, 99114-05-3; **17**, 99114-06-4; **18**, 99114-07-5; $(\mathbf{18}\cdot\mathbf{21})_x$, 99114-11-1; **19**, 99114-08-6; **20**, 99114-09-7; **22a**, 99128-04-8; **22b**, 99114-12-2; **22c**, 99114-13-3; Bu_3SnCl, 1461-22-9; 4-$BrC_6H_4CH_2CN$, 16532-79-9; 4-$BrC_6H_4NO_2$, 586-78-7; 4-$KOC_6H_4CO_2CH_3$, 26112-07-2; 4-BrC_6H_4Ph, 92-66-0.

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Study of Surface Composition and Morphology of Block Copolymers of Bisphenol A Polycarbonate and Poly(dimethylsiloxane) by X-ray Photoelectron Spectroscopy and Ion Scattering Spectroscopy

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ABSTRACT: X-ray photoelectron spectroscopy and ion scattering spectroscopy results are presented for block copolymers of bisphenol A polycarbonate (BPAC)/poly(dimethylsiloxane) (DMS). Analysis of these results shows surface enrichment in the copolymer of the lower surface energy DMS segments over the range 25–65% DMS. Models are presented for the morphology of the top 50 Å of the sample surface consisting of discrete regions of DMS and BPAC oriented perpendicular to the surface.

Introduction

Previous work[1,2] has shown that composition at the surface of AB block copolymers can differ greatly from that of the bulk. Since many of a polymer's properties depend on its surface bonding and composition (weathering,[3] adhesion,[4] biocompatibility,[5] etc.), the ability to predict the extent of surface speciation of one component should add greatly to the development of structure-specific polymers.

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