300 mL of water was added and the product was extracted with CH_2Cl_2 and dried over anhydrous K_2CO_3. Crude **5a** was obtained by vacuum evaporation of solvent at room temperature; IR $\nu_{N\equiv C}$ 2120 cm^{-1}).

***trans*-4,5-Cyclohexano-2-oxazoline (1a).** A solution of crude **5a** and cuprous oxide (600 mg) in 430 mL of anhydrous benzene was heated to reflux until the infrared N≡C band of **5a** disappeared. After filtration, the solvent was evaporated, and distillation of the residue gave analytically pure **1a**: 13.4 g, 41% yield from **4a**; bp 68–69 °C (14 mmHg); IR 1592 ($\nu_{N=C}$), 1072 cm^{-1} (ν_{C-O-C}); mass spectrum, *m/e* 125 (M^+). Anal. Calcd for $C_7H_{11}NO$: C, 67.17; H, 8.86; N, 11.19. Found: C, 66.90; H, 8.95; N, 11.16.

***cis*-4,5-Cyclohexano-2-oxazoline (1b)** was similarly obtained from **4b** prepared by the procedure previously reported,[4] to give **1b** in 31% yield [Kugelrohr, bp 75 °C (18 mmHg)]: IR 1628, 1612 ($\nu_{N=C}$), 1090 cm^{-1} (ν_{C-O-C}); mass spectrum, *m/e* 125 (M^+). Anal. Calcd for $C_7H_{11}NO$: C, 67.17; H, 8.86; N, 11.19. Found: C, 67.01; H, 9.01; N, 11.25.

Cooligomerization. A typical procedure was as follows. In a sealed tube **1a** (3 mmol), AA (3 mmol), and *p*-methoxyphenol (0.01 mmol) were placed in 1.0 mL of benzonitrile under nitrogen. The mixture was allowed to react at 130 °C. After 100 h, the reaction mixture was poured into a large amount of diethyl ether to precipitate the oligomeric materials. The product was isolated by decantation and purified further by reprecipitation from chloroform into diethyl ether. The pale yellow solid cooligomer obtained was dried in vacuo and weighed.

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A Cardo Polyquinoline from an AB Monomer

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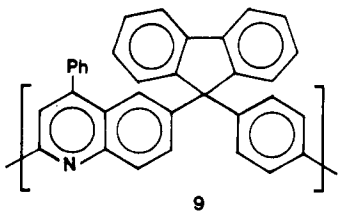
Aromatic polymers containing pendent rings in which a carbon of the ring is also a member of the polymer main chain—and therefore a quaternary carbon—have been shown to possess enhanced solubility in organic solvents and higher glass transition temperatures than the analogous polymers without this ring or cardo structure.[1] Cardo polyquinolines prepared from symmetrical AA bis(*o*-amino ketone) and BB bis(ketomethylene) monomers containing the appropriate ring structures are amorphous.[2] These AA–BB cardo polyquinolines, in which the quaternary carbon in the ring has replaced oxygen links connecting quinoline and biphenylene units in the chain, have better solubility in organic solvents and glass transition temperatures that are as much as 140 °C higher than the oxygen-linked analogues. In this paper, the synthesis of an AB cardo monomer and the polymer obtained therefrom are reported.

Results and Discussion

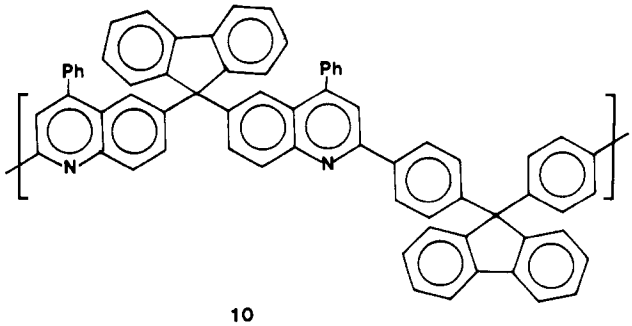
In order to construct the aromatic *o*-amino ketone and ketomethylene groups attached to the cardo unit, it was advantageous to generate the unsymmetric cardo carbon early in the synthesis by introducing functionalities that later could be converted into the appropriate polyquinoline-forming groups. The synthesis was accomplished in eight relatively simple steps (Scheme I). Reaction of (4-ethylphenyl)magnesium bromide[3] and 9-fluorenone produced the carbinol 9-hydroxy-9-(4-ethylphenyl)fluorene (**1**) in isolated yields of 90%. The crude alcohol underwent condensation with aniline[4] to introduce the arylamine portion, thus forming the unsymmetric arylalkyl amine 9-(4-aminophenyl)-9-(4′-ethylphenyl)fluorene (**2**) in 50% yields. Oxidation of the amino group with *m*-chloroperbenzoic acid (*m*-CPBA)[5] gave 9-(4-nitrophenyl)-9-(4′-ethylphenyl)fluorene (**3**). Oxidation of the benzylic carbon with catalytic amounts of silver persulfate[6] in an acetonitrile–water two-phase system generated the acetyl unit. The 40% yields of 9-(4-nitrophenyl)-9-(4′-acetylphenyl)-fluorene (**4**) were low compared to the yields reported[6] for substrates that were liquid under the reaction conditions. Protection of the carbonyl group and subsequent base-assisted condensation of **5** with phenylacetonitrile[7] gave the benzisoxazole **6**. Finally, hydrogenation of the benzisoxazole ring over palladium-on-charcoal generated the *o*-amino ketone function on one side of the monomer while deketalization of **7** with a dilute hydrochloric acid–tetrahydrofuran mixture released the ketomethylene group on the other side of the monomer to give 9-(4-amino-3-benzoylphenyl)-9-(4′-acetylphenyl)fluorene (**8**).

The polymerization of **8** was carried out in a mixture of *m*-cresol and di-*m*-cresyl phosphate at 135–140 °C for 4–6 h to give polyquinoline **9**.



9

Surprisingly, the AB cardo polyquinoline was not soluble in chloroform or *sym*-tetrachloroethane whereas those cardo polyquinolines obtained from the polymerization of AA with BB monomers are soluble in these solvents.[2] Polymer **9** was soluble in strong acids and in *m*-cresol (>20% w/v; $[\eta]_{m\text{-cresol}}$ = 0.24 dL/g). The glass transition temperature of **9** (powdered samples) is 365 °C, 25 °C lower than that of the analogous AA–BB polymer **10** containing fluorene in each monomer unit. Both **9** and **10** are amorphous.



10

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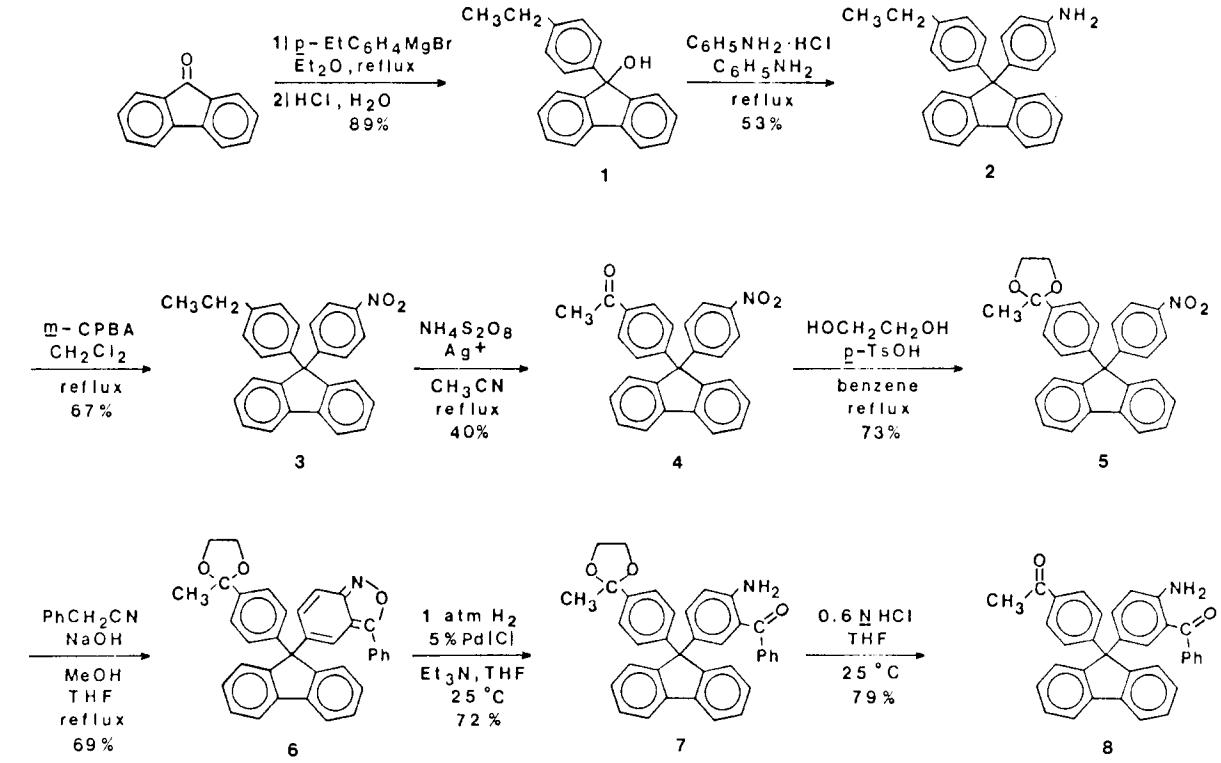
Scheme I
Synthesis of 9-(4-Amino-3-benzoylphenyl)-9-(4'-acetylphenyl)fluorene (8)



Annealing **9** at 470–480 °C for 1–1.5 h under nitrogen did not lead to crystallization; the glass transition temperature remained the same. As expected, polyquinoline **9** showed good thermal stability, with a break in air, at 520 °C.

Experimental Section

9-Hydroxy-9-(4-ethylphenyl)fluorene (1). Thirteen grams (0.54 mol) of magnesium contained in a flask was flame-dried under a nitrogen flow while being stirred mechanically. Following cooling, 50 mL of diethyl ether and 10–15 mL of an aryl bromide solution composed of 50 g (0.27 mol) of *p*-(bromoethyl)benzene in 75 mL of diethyl ether were added in succession via an addition funnel. The remaining halide–ethereal mixture was dropped into the preformed solution of Grignard reagent so as to maintain a steady reflux. After the halide addition was completed, the reaction mixture was heated at reflux for 30 min with an oil bath.

To the refluxing Grignard reagent was added dropwise an ethereal solution of ketone prepared from 43 g (0.24 mol) of 9-fluorenone in 400 mL of diethyl ether, with continued heating at reflux. After the ketone solution was completely dispensed, the presence of a copious quantity of white solid was noted. The mixture was heated at reflux for 16 h and then cooled to ambient temperature. Quenching the reaction mixture into 1 L of a chilled (ice) hydrochloric acid solution produced two layers. Following separation of the ethereal layer, the aqueous layer was extracted with diethyl ether (2 × 500 mL). Combining the ether layers followed by drying over sodium sulfate and removal of solvent gave 71 g (89%) of a red-orange viscous oil, which was not purified further: IR (NaCl plates, film) 3565 (OH, non-H-bonded), 3455 (OH, H-bonded), 3090 (Ar, C–H), 2990 (Et, C–H), 2930, 2800, 1595, 1500, 1440, 1150, 1010, 800, 750, 725, 620 cm^{-1}; ^1H NMR ($CDCl_3$–1% Me_4Si) δ 1.07 (t, J = 7 Hz, 3 H, $ArCH_2CH_3$), 2.42 (q, J = 7 Hz, 2 H, $ArCH_2CH_3$), 2.48 (s, br, 1 H, COH; disappears with D_2O), 6.50–7.48 (m, 20 H).

9-(4-Aminophenyl)-9-(4'-ethylphenyl)fluorene (2). A mixture of 67.6 g (0.236 mol) of aniline hydrochloride and 156 mL (152 g, 1.63 mol) of aniline was heated at reflux for 16 h. After cooling to ambient temperature, the reaction mixture was quenched into a 2:1 mixture of ice and concentrated hydrochloric acid. Collection of the blue-gray solid by suction filtration, followed by washing with 2 L of water and air-drying, provided damp light green amine hydrochloride. Stirring the salt in 10% sodium hydroxide regenerated the free amine, which was collected by suction filtration. Finally, two crystallizations from ethanol (charcoal) afforded 38 g (44%) of light green-gray solid **2**: mp 195–196 °C; IR (KBr) 3480 (NH_2), 3390 (NH_2), 3060, 3030 (Ar, C–H), 2930 (Et, C–H), 2870, 1630, 1520, 1455, 1290, 810, 750 cm^{-1}; ^1H NMR ($CDCl_3$–1% Me_4Si) δ 1.11 (t, J = 7 Hz, 3 H, $ArCH_2CH_3$), 2.49 (q, J = 7 Hz, 2 H, $ArCH_2CH_3$), 3.38 (s, br, 2 H, $ArNH_2$), 6.13–7.0 (m, 16 H, ArH). Anal. Calcd for $C_{27}H_{23}N$: C, 89.71; H, 6.41; N, 3.87. Found: C, 89.10; H, 6.37; N, 3.85.

9-(4-Nitrophenyl)-9-(4'-ethylphenyl)fluorene (3). A solution of 26 g (0.072 mol) of **2** in 150 mL of dichloromethane was slowly added dropwise to a refluxing solution of 62 g (0.36 mol) of *m*-chloroperbenzoic acid in 393 mL of dichloromethane over a 1-h period. The mixture was heated at reflux for 16 h and then cooled to 25 °C. Filtration of the reaction mixture removed the suspended *m*-chloroperbenzoic acid. The filtrate was then washed with 10% potassium carbonate until the washings became colorless. Removal of the solvent and drying [25 °C (0.5 mmHg)] afforded 25 g (89%) of an orange-brown solid. Chromatography of impure **3** on a column of silica gel (toluene elution), crystallization from ethanol, and drying [105 °C (0.5 mmHg)] afforded 19 g (67%) of **3** as yellow crystals: mp 144.5–145.5 °C; IR (KBr) 3080 (Ar, C–H), 3040, 2980 (Et, C–H), 2950, 2890, 1615, 1605, 1525 (NO_2), 1460, 1355 (NO_2), 860, 835, 755, 750, 705 cm^{-1}; ^1H NMR ($CDCl_3$–1% Me_4Si) δ 1.18 (t, J = 7 Hz, 3 H, $ArCH_2CH_3$), 2.46 (q, J = 7 Hz, 2 H, $ArCH_2CH_3$), 6.96 (s, 4 H, $C_6H_4NO_2$), 7.00–8.16 (m, 12 H, ArH). Anal. Calcd for $C_{27}H_{21}NO_2$: C, 82.84; H, 5.41; N, 3.58. Found: C, 82.79; H, 5.47; N, 3.46.

9-(4-Nitrophenyl)-9-(4'-acetylphenyl)fluorene (4). A two-phase liquid–liquid system consisting of 18.5 g (0.0473 mol) of **3** dissolved in 335 mL of acetonitrile and 23.1 g (0.104 mol) of ammonium persulfate dissolved in 113 mL of water was heated with mechanical stirring until reflux was achieved. A solution of 0.21 g (1.3 mmol) of silver nitrate in 0.6 mL of water was added in one portion to the reaction mixture and reflux was continued for 8 h. Then 23.1 g (0.104 mol) of ammonium persulfate and 0.21 g (1.3 mmol) of silver nitrate dissolved in 0.6 mL of water were introduced in succession, followed by continued refluxing for an additional 8 h. The mixture was cooled to ambient temperature. After separation of the aqueous and organic layers, the

acetonitrile was removed in vacuo. Drying the isolated material [25 °C (0.5 mmHg)] produced an orange-yellow solid. Chromatography on a column of silica gel (chloroform elution) provided 10 g (53%) of a yellow solid. Crystallization of **4** from ethanol provided 7.7 g (40%) of fluffy, light yellow crystals: mp 171.5–172.5 °C; IR (KBr) 3080, 3020 (Ar, C–H), 2960 (Et, C–H), 2916, 2860 (Et, C–H), 1690 (C=O), 1610, 1520 (NO_2), 1450, 1350 (NO_2), 1270, 850, 820, 730, 695 cm^{-1}; ^1H NMR ($CDCl_3$–1% Me_4Si) δ 2.47 (s, 3 H, $COCH_3$), 6.76–8.14 (m, 16 H, ArH). Anal. Calcd for $C_{27}H_{19}NO_3$: C, 79.98; H, 4.72; N, 3.46. Found: C, 79.69; H, 4.76; N, 3.39.

9-(4-Nitrophenyl)-9-[4′-(2-methyl-1,3-dioxolan-2-yl)-phenyl]fluorene (5). A liquid–liquid suspension of 2.0 g (4.9 mmol) of **4**, 0.86 mL (1.5 mmol) of ethylene glycol, 0.035 g (0.56 mmol) of *p*-toluenesulfonic acid monohydrate, and 40 mL of benzene was heated at reflux for 22 h, and approximately 15 mL of the benzene–water azeotrope was siphoned from the Dean–Stark trap. Following 16 h of additional reflux, 15 mL of the benzene–water azeotrope was again removed. Reflux was continued for 53 h and the mixture was cooled to ambient temperature. The reaction mixture was diluted with 80 mL of benzene, and washed with 10% sodium hydroxide (3 × 5 mL) and 5% sodium bicarbonate (2 × 10 mL). The benzene layer was dried with magnesium sulfate, and the solvent was removed to give 1.9 g (86%) of yellow solid **5**. Crystallization of **5** from a benzene–hexane solvent mixture gave, after drying [105 °C (0.5 mmHg)], 1.6 g (73%) of fluffy light green **5**: mp 215–216 °C; IR (KBr) 3040 (Ar, C–H), 3000, 2950, 2890 (CH_2), 1610, 1525 (NO_2), 1455, 1350 (NO_2), 1200, 1040, 830, 750, 700 cm^{-1}; ^1H NMR ($CDCl_3$–1% Me_4Si) δ 1.57 (s, 3 H, CH_3), 3.82 (A_2B_2, m, 4 H, CH_2), 6.82–8.10 (m, 16 H, ArH). Anal. Calcd for $C_{29}H_{23}NO_4$: C, 77.49; H, 5.16; N, 3.12. Found: C, 77.20; H, 5.01; N, 2.85.

9-[5-(3-Phenyl-2,1-benzisoxazolyl)]-9-[4′-(2-methyl-1,3-dioxolan-2-yl)phenyl]fluorene (6). A mixture of 0.88 g (22 mmol) of sodium hydroxide, 5 mL of methanol, and 15 mL of tetrahydrofuran was stirred for 15 min. This mixture was cooled (ice), and 0.49 mL (0.5 g, 4.2 mmol) of phenylacetonitrile was added. After 15 min of stirring, 1.27 g (2.83 mmol) of **5** and 1.0 mL of tetrahydrofuran were added. The dark green reaction mixture was stirred and cooled (ice) for 30 min and then heated at reflux for 16 h. While the mixture was still warm, 100 mL of methanol was added, followed by cooling of the heterogeneous mixture to ambient temperature. Filtering the suspended solid provided a beige powder that, when washed with 500 mL of methanol (or until the washings turned colorless), air-dried (aspirator), and dried under reduced pressure [25 °C (0.5 mmHg)], afforded 1.3 g (89%) of light beige powder **6**. This material was crystallized from a benzene–hexane mixture, affording 1.0 g (69%) of fluffy, light beige crystalline **6** after drying [105 °C (0.5 mmHg)]: mp 247–248 °C; IR (KBr) 3170 (Ar, C–H), 2990, 2890 (CH_2), 1645 (C=N), 1560, 1525, 1500, 1475, 1445, 1370, 1250, 1040, 800, 740, 680 cm^{-1}; ^1H NMR ($CDCl_3$–1% Me_4Si) δ 1.58 (s, 3 H, CH_3), 3.82 (A_2B_2, m, 4 H, CH_2), 6.89–7.87 (m, 20 H, ArH). Anal. Calcd for $C_{36}H_{27}NO_3$: C, 82.90; H, 5.22; N, 2.69. Found: C, 82.94; H, 5.42; N, 2.79.

9-(4-Amino-3-benzoylphenyl)-9-[4′-(2-methyl-1,3-dioxolan-2-yl)phenyl]fluorene (7). A suspension of 0.80 g (1.5 mmol) of **6**, 0.061 g of 5% palladium-on-charcoal, 6.5 mL of tetrahydrofuran, and 0.21 mL of triethylamine was subjected to a hydrogen atmosphere, at ambient temperature, until gas uptake ceased. Filtration of the resulting mixture, followed by removal of the solvent from the filtrate, provided 0.79 g (98%) of a yellow solid. This solid was crystallized from a benzene–hexane solvent mixture, providing, after drying [105 °C (0.5 mmHg)], 0.58 g (72%) of **7** as yellow crystals: mp 165.0–166.5 °C; IR (KBr) 3480 (NH_2), 3350 (NH_2), 3060 (Ar, C–H), 2990, 2890 (CH_2), 1625 (C=O), 1580, 1545, 1445, 1245, 1030, 815, 740, 700, 645 cm^{-1}; ^1H NMR ($CDCl_3$–1% Me_4Si) δ 1.55 (s, 3 H, $COCH_3$), 3.78 (A_2B_2, m, 4 H, CH_2), 5.83 (s, br, 2 H, $ArNH_2$), 6.28–7.72 (m, 20 H, ArH). Anal. Calcd for $C_{36}H_{29}NO_3$: C, 82.58; H, 5.58; N, 2.68. Found: C, 81.83; H, 5.59; N, 2.58.

9-(4-Amino-3-benzoylphenyl)-9-(4′-acetylphenyl)fluorene (8). To a solution of 1.8 g (3.4 mmol) of **7** in 12 mL of tetrahydrofuran was added 12 mL of 0.6 N hydrochloric acid, and the mixture was stirred at 25 °C for 24 h. Dilution of the reaction mixture with 12 mL of water, followed by removal of the tetrahydrofuran in vacuo, produced a suspension of yellow solid in water. The solid was removed by filtration and washed with water until the washings were neutral (pH paper). The precipitate was then dissolved in chloroform, washed with a 10% sodium bicarbonate solution and water, and dried over sodium sulfate. Removal of the chloroform in vacuo provided 1.5 g (91%) of a green-yellow solid. Chromatography of this solid on a column of silica gel (dichloromethane elution) and recrystallizations from benzene–methanol, followed by drying [105 °C (0.5 mmHg)], gave 1.3 g (79%) of yellow crystalline **8**: mp 205.5–206.5 °C; IR (KBr) 3480 (NH_2), 3350 (NH_2), 3060 (Ar, C–H), 2930 (Me, C–H), 1680 (C=O), 1600, 1550, 1450, 1265, 1250, 1170, 820, 735, 700, 650 cm^{-1}; ^1H NMR ($CDCl_3$–1% Me_4Si) δ 2.40 (s, 3 H, $COCH_3$), 5.90 (s, br, 2 H, $ArNH_2$), 6.25–7.81 (m, 20 H, ArH); ^{13}C NMR ($CDCl_3$–1% Me_4Si) δ 198.2 (C=O), 197.3 (C=O), 151.1, 150.3, 149.6, 139.8, 139.2, 135.4, 133.8, 133.6, 131.5, 129.1, 128.2, 127.6, 125.6, 120.2, 117.5, 117.1, 64.4, 26.6. Anal. Calcd for $C_{34}H_{25}NO_2$: C, 85.15; H, 5.25; N, 2.92. Found: C, 85.36; H, 5.09; N, 2.89.

Polymerization. Poly[2-(*p*-phenylene)-4-phenyl-6-[9-(*p*-phenylene)-9′-fluorenylidene]quinoline] (**9**) was prepared by using polymerization conditions similar to those for the AA–BB polyquinolines.[2] A mixture of 1.000 g (2.085 mmol) of 9-(4-amino-3-benzoylphenyl)-9-(4′-acetylphenyl)fluorene (**8**), 15 g (50 mmol) of di-*m*-cresyl phosphate, and 4.8 mL of *m*-cresol was heated at 135–140 °C under a static nitrogen atmosphere, with mechanical stirring, for 46 h. Precipitation of this amber-colored reaction mixture into 350 mL of a 10% triethylamine–90% ethanol mixture afforded fibrous material. Collection of the polymer by suction filtration and extraction in an amine–ethanol mixture for 48 h afforded 0.918 g (99.3%) of small, beige fiber strands. Anal. Calcd for $(C_{39}H_{21}N_7)$: C, 92.07; H, 4.77; N, 3.16. Found: C, 91.00; H, 5.01; N, 3.43, residue 0.57.

Solution viscosities were measured in *m*-cresol with a Cannon-Ubbelohde microdilution viscometer at 25.0 ± 0.1 °C. The intrinsic viscosity, $[\eta]$ = 0.24 dL/g, was obtained from extrapolation of reduced and inherent viscosities to zero concentration.

Thermal analyses were conducted with a Du Pont 990 differential thermal analyzer equipped with a differential scanning calorimeter (DSC) cell base module II and a 950 thermogravimetric analyzer (TGA). The DSC analysis was obtained on pressed powder samples at a heating rate of 10 °C/min under a nitrogen flow of 50–60 mL/min. Thermogravimetric analysis was carried out on slightly pressed, powdered polyquinolines at a 5 °C/min heating rate in both flowing air and nitrogen atmospheres (flow rate 50–60 mL/min).

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Does a Glassy Polymer on Annealing Relax toward the Equilibrium State?

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When a glassy polymer is brought to a temperature moderately below its T_g, it undergoes a slow relaxation toward a limiting structural state. Such relaxation is

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