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the Navy later developed into an interest in scuba diving, generally off the shores of Florida and Mexico.

John and Dolores married in 1958 and have two sons: John Robert, who is a faculty member in the Chemistry Department at Michigan State University, and James Kenneth, who is a chemical engineer in the Ciba Geigy Corp. in New Jersey.

John is claimed as their own by two distinctly different groups of chemists because he made especially important contributions to both of their fields: polymer chemistry and organometallic chemistry. His 270 publications, two books, and several book chapters include basic, pioneering contributions to both of these fields as well as to synthetic organic chemistry. This issue of *Macromolecules* contains the last paper that John submitted before his death to this journal.

Perhaps first and foremost John was an organic chemist, who brought his wide-ranging interests and unique perspective to the original application of organic reactions both to polymer synthesis and to the reactions of organometallic compounds. He also served both fields professionally as the first Associate Editor for organic-polymer manuscripts for *Macromolecules* from 1967 to 1981 and then as an Associate Editor for the *Journal of the American Chemical Society* from 1982 to 1987. For his many important contributions to polymer chemistry he received the prestigious American Chemical Society Award in Polymer Chemistry in 1982. For his excellence in research in organic, organometallic, and polymer chemistry he was named a Colorado State University Distinguished Professor in 1986. He was given the ACS Colorado Section Award in 1988, and he was to receive the Arthur C. Cope Scholar Award in 1990. Over the years John made numerous contributions to the professional activities of the American Chemical Society by serving as chairman of the Iowa Section in 1965, as organizer and chairman of the Biennial Polymer Symposium in 1972 and in 1974, and as chairman of the Division of Polymer Chemistry in 1975.

The graduate students and visiting scientists who had the opportunity to work with John will always remember him fondly as a teacher who provided encouragement and insisted on excellence. He is also remembered as a "boss" who was deeply concerned with their professional development and welfare and as a co-worker who shared his wonderful sense of humor and love for life with them on a daily basis both in the laboratory and in research group get togethers and parties. John was viewed by his co-workers as a role model who expected much but always gave much more.

John had the ability to instill his fascination and enthusiasm for science in those around him—his family, his co-workers, and his colleagues. He was an outstanding research scientist and teacher, but a teacher of more than science. To his students he taught discipline, responsibility, and hard work. To his sons he was a friend who taught love and caring and the fun of a career in science. To us, his colleagues, he taught the importance of total commitment to creativity, originality, and excellence.

The Chemistry Department faculty at Colorado State University has established a memorial lectureship in his name in recognition of that dedication to research and that commitment to teaching, in all its forms.

The contributions from John R. Stille, Denise R. Rutherford, Dirk M. Sutherlin, and David R. Tueting in the preparation of this memorial are gratefully acknowledged.

Robert W. Lenz

Articles

Thermal Rigidification of Polyquinolines by Thermolytic Elimination of Ethylene from a 9,10-Dihydro-9,10-ethanoanthracene Unit

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ABSTRACT: Polyquinolines 7 and 8 containing the 9,10-dihydro-9,10-ethanoanthracene unit as the connecting group between bis(4-phenylquinoline) units were prepared by the condensation of 2,6-diacetyl-9,10-dihydro-9,10-ethanoanthracene (4) with 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (5) and 3,3′-dibenzoylbenzidine (6), respectively, in the presence of diphenyl phosphate and *m*-cresol. Both of the polymers were soluble in chloroform and tetrachloroethane, exhibiting T_gs of 270 and 295 °C, respectively. Heating 7 or 8 at 200 °C for 6 h followed by 300 °C for 2 h resulted in the extrusion of ethylene via a retro [4 + 2] reaction to yield polyquinolines 9 and 10, now containing the 2,6-diacetylanthracene connecting group. These thermally stable polymers were insoluble in chloroform and tetrachloroethane, exhibited T_gs at 308 and 360 °C, respectively, and showed increased storage moduli over the uncured samples.

Introduction

Conjugated polymers, particularly polyaromatics possessing a rigid-rod configuration, often attain considerable crystallinity with correspondingly high melting temperatures and poor solubility in common organic solvents. Such polymers, which are valuable light-weight, thermally stable engineering materials, are especially difficult to fabricate. In addition, their syntheses often are

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† Deceased.

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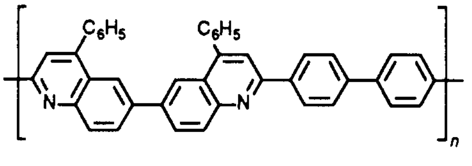
limited by poor solubility, yielding low molecular weight polymers as a result of premature precipitation from the polymerization medium.

Polyquinolines have been synthesized by a polymerization reaction that allows the introduction of a wide range of structural features.[1] As a result, the linearity and rigidity of the polymer can be adjusted to provide materials that are amorphous and have good solubility in common organic solvents and relatively low glass transition temperatures (250 °C) or materials that are highly crystalline, insoluble in the common organic solvents, and have crystalline transition temperatures greater than 500 °C. Poly[(4,4′-diphenyl-6,6′-biquinoline-2,2′-diyl)-4,4′-biphenylene] (1), for example, is highly crystalline (T_m > 500 °C) and insoluble in common organic solvents, including chloroform and tetrachloroethane. Films and fibers are cast or spun from the polymerization dope (di-*m*-cresyl phosphate/*m*-cresol). The polymer also is soluble in trifluoromethanesulfonic acid. Thus fabrication is limited to processing from strong acid solutions.



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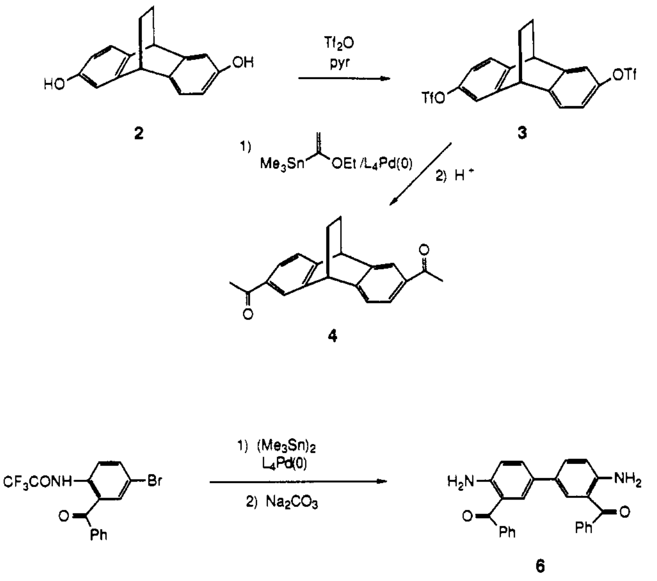
This report describes an approach to soluble, thermally stable polyquinolines that can be solution processed in common organic solvents and then thermally converted to crystalline, insoluble, rigid-rod materials by utilizing a monomer containing a 2,6-disubstituted 9,10-dihydro-9,10-ethanoanthracene (DEA) unit. It was hoped that the nonplanar nature of the DEA unit would allow for the polymers to be amorphous (with a relatively low T_g) and soluble in common organic solvents. The thermolysis (200–400 °C) of 2,6-disubstituted dihydroethanoanthracenes is known[2] to result in a retro [4 + 2] reaction with the extrusion of ethylene. In this process, the angle made by the two benzene rings changes from approximately 120° to 180°, and planar anthracene is obtained. This is roughly comparable to effecting a change from a *m*-phenylene group in a polyaromatic chain to a *p*-phenylene unit. The thermal elimination of ethylene occurs at temperatures well below the decomposition temperature of the precursor polymer. This methodology in fact has been used in the synthesis of polyesters of 2,6-dihydroxyanthracene[3] and polyamides of 2,6(7)-diaminoanthracene.[4]

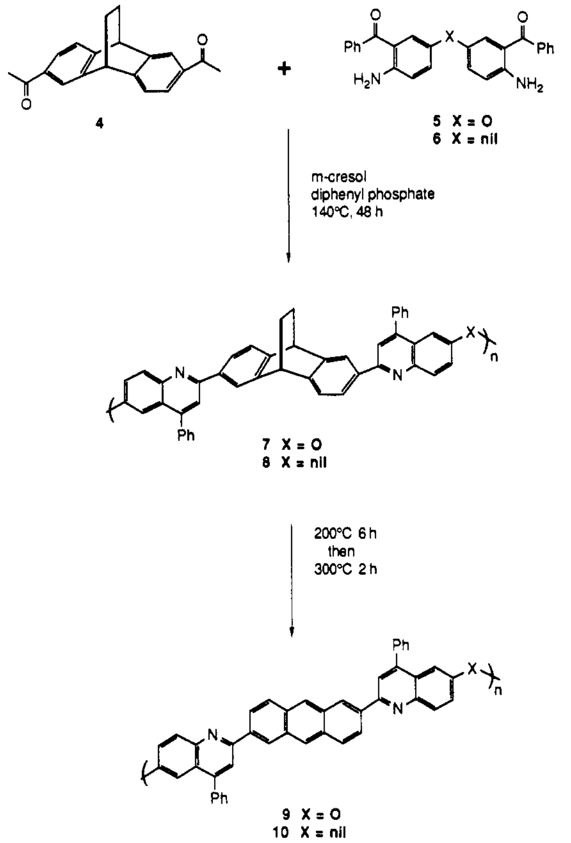
Results and Discussion

Monomer Synthesis. Using a known procedure, 2,6-dihydroxy-9,10-dihydro-9,10-ethanoanthracene (2) was synthesized from anthraflavic acid (2,6-dihydroxyanthraquinone).[3] Treatment of 2 with trifluoromethanesulfonic anhydride in pyridine afforded a 78% yield of 2,6-bis[(trifluoromethanesulfonyl)oxy]-9,10-dihydro-9,10-ethanoanthracene (3) (Scheme I). By way of the palladium-catalyzed coupling[5] of (α-ethoxyvinyl)trimethylstannane with 3, 2,6-diacetyl-9,10-dihydro-9,10-ethanoanthracene (4) was obtained in 83% yield. Recrystallization from ethanol yielded polymerization-grade monomer. The amino ketone 4,4′-diamino-3,3′-dibenzoyldiphenyl ether (5) was synthesized according to the known procedure.[6] An improved method was used in the synthesis of 3,3′-dibenzoylbenzidine (6). Homocoupling of 5-bromo-2-(trifluoroacetamido)benzophenone with hexamethyldistannane and tetrakis(triphenylphosphine)palladium(0), followed by deprotection of the amine, yielded 3,3′-dibenzoylbenzidine (6) in good yield. This procedure overcame the low yields and the hazards of coupling with stoichiometric amounts of Ni(COD)$_2$.[7]

Scheme I



Scheme II



Polymer Synthesis. Monomers 4 and 5 were polymerized in a *m*-cresol/diphenyl phosphate solvent/catalyst system at 140 °C for 48 h, according to a known procedure (Scheme II).[8] Polymer 7 was soluble in chloroform, 1,1,2,2-tetrachloroethane (TCE), and trifluoromethanesulfonic acid. GPC analysis showed polymer 7 to have a number-average molecular weight of 84 000 (polystyrene standards). The presence of the ethylene

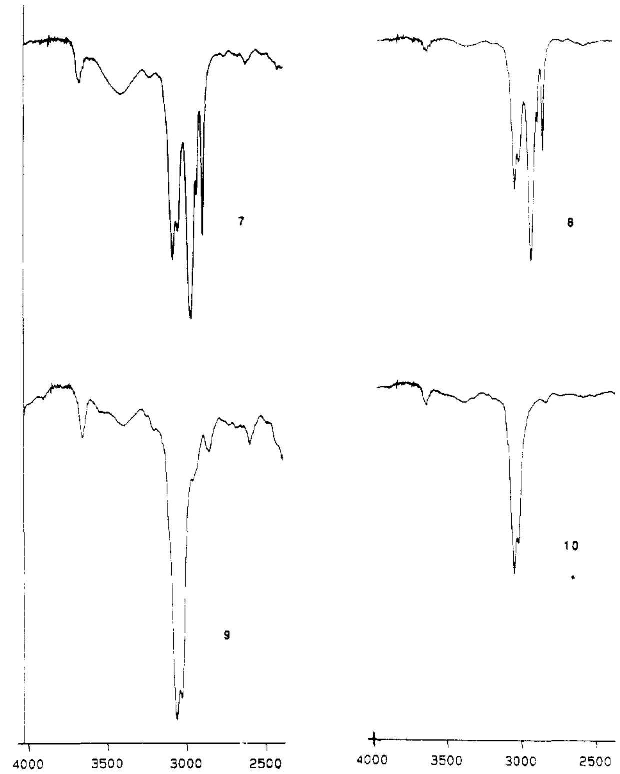


Figure 1. FT-IR of polymers **7**–**10**.

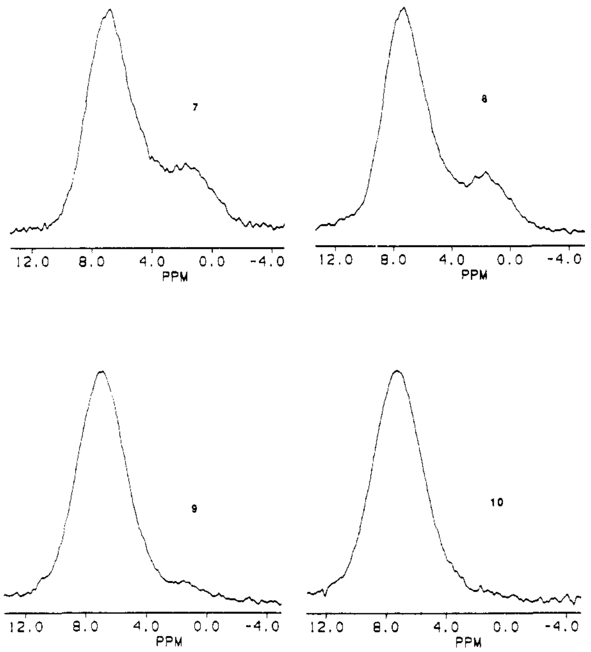


Figure 2. Solid-state ^{1}H NMR of **7**–**10**.

Table I
Thermal Properties of Polyquinolines

polyquinoline	T_g, °C	T_{endo} (T_{max}),[a] °C	C_2H_4 loss	T_d, °C Ar	T_d, °C air
7	270	324 (354)	315	530	450
8	295	352 (362)	329	575	500
9	308			540	
10	360			590	

[a] Ethylene loss.

bridge was confirmed by the aliphatic C–H stretching frequencies at 2943 and 2868 cm^{-1} in the IR (Figure 1) and the peaks at 1.81 ppm for the bridging $-CH_2-$ groups and at 4.59 ppm for the bridgehead –CH– groups in the ^{1}H NMR spectrum.

Monomers **4** and **6** were similarly polymerized to yield polymer **8** (Scheme II).[9] Since polymer **8** was soluble in chloroform, the GPC could be obtained, revealing polymer **8** to have a number-average molecular weight of 136 400 (polystyrene standards). Polymer **8** was also soluble in TCE and trifluoromethanesulfonic acid. The presence of the ethylene bridge was confirmed by the aliphatic C–H stretching frequencies at 2943 and 2868 cm^{-1} in the IR spectrum (Figure 1) and the peaks at 1.81 ppm for the bridging $-CH_2-$ groups and at 4.59 ppm for the bridgehead –CH– groups in the ^{1}H NMR spectrum.

Polymers **9** and **10** were obtained by heating **7** and **8**, respectively, at 200 °C for 6 h and then at 300 °C for 2 h under argon. A color change from yellow to red-orange was observed for both polymers, which were no longer soluble in common organic solvents. Films of **9** and **10**, obtained by heating films of **7** and **8**, remained flexible and did not break upon bending. The absence of the ethylene bridges in **9** and **10** was confirmed by the IR spectra (Figure 1), which showed an absence of aliphatic C–H stretches. The solid-state ^{1}H NMR CRAMPS spectra (Figure 2) were especially useful for verification of the loss of the ethylene bridge. Although solid samples of **7** and **8** showed the presence of aliphatic protons (~1.8 ppm), these were absent in the samples of **9** and **10**.

The most notable observation in these polymers is that polymer **8**, the precursor to rigid rod **10**, is soluble in chloroform and tetrachloroethane. After thermal treatment and loss of ethylene, neither polymer **9** nor **10** is soluble in these common organic solvents or in trifluoromethanesulfonic acid. Polymer **9** containing the flexible oxygen link could be expected to be soluble in chloroform or tetrachloroethane, and **10** could be expected to be soluble in trifluoromethanesulfonic acid. The observed insolubility probably is due to some cross-linking taking place during the thermal treatment.

Properties. The DSC of pressed powder samples of **7** and **8** showed only endotherms corresponding to the loss of ethylene at 304 °C (max 344 °C) and 293 °C (max 347 °C), respectively. Although T_gs were not readily observed with powder samples, a cast film of **7** exhibited at T_g at 270 °C and an endotherm for ethylene loss at 324 °C (max 354 °C) (Table I). When a film sample of **7** was heated to 310 °C, cooled, and reheated to 400 °C, the T_g observed on the first heating was not seen in the second cycle, but only the endotherm for ethylene loss was observed. These observations indicate that ethylene loss starts just above or at the T_g.

Polyquinoline **8** exhibited a higher T_g than **7**, although its detection was much more difficult due to its coincidence with ethylene loss. The DSC of a cast film of **8** showed a T_g at 295 °C and the endotherm for ethylene loss at 352 °C (max 362 °C). On the basis of a study of monomeric DEAs, the loss of ethylene was expected to be an exotherm. However, it has been shown[3,4] that the loss of ethylene from polymeric systems containing the DEA unit does appear as an endotherm.

Polyquinolines **9** and **10**, containing the anthracene units, showed T_gs at 308 and 360 °C, respectively. In neither case was there any observation of an endotherm due to the loss of residual ethylene, indicating that complete thermolysis had been achieved.

Thermogravimetric analyses of **7** and **8** showed a weight loss of ethylene at 315 and 329 °C, respectively. Thermal decomposition of **7** began at 530 °C under argon and at 450 °C under air (Table I). Thermal decomposition of **8** began at 575 °C under argon and at 500 °C under air. The TGA of **9** under argon showed no weight loss

Table II
Dynamic Mechanical Analysis

polyquinoline	7	8	9	10
E' (GPa, 50 °C)	2.1	2.6	2.6	4.1
$E''_{\max}$	253	305		
	318	348	345	328
	343	378		
tan δ (max)	293	310		
	353	393	358	403

below the onset of thermal decomposition at 540 °C; **10** showed no weight loss prior to thermal decomposition at 590 °C.

The dynamic mechanical analyses of films of **7** and **8** (Table II) clearly indicated the structural changes occurring during heating. Polymer **7**, with a storage modulus (E') of 2.1×10^9 Pa at 50 °C, exhibited a change in slope at 181 °C. E' leveled off at 0.4×10^9 Pa at 280 °C and then increased to 0.9×10^9 Pa before decreasing again at 332 °C. The loss modulus (E'') had maxima at 253, 318, and 343 °C, the first and third maxima corresponding to changes in E'. The second maximum could be due to changes occurring in the polymer caused by ethylene loss. The DMA data for **7** is interesting since it shows that as the T_g for **7** is reached, the polymer is losing ethylene and becoming more rigid as it is transformed into **9**, leading to the second maxima for E' and tan δ. Polymer **8** exhibited a storage modulus (E') of 2.6×10^9 Pa at 50 °C, which decreased to 1.1×10^9 Pa at 275 °C, followed by a second decrease at 335 °C. E'' showed maxima at 305, 348, and 378 °C, and tan δ showed maxima at 310 and 393 °C. This data indicates that the T_g for **8** is coincident with or higher than the temperature at which the loss of ethylene begins, leading to the extra maximum in E''. The final E'' and tan δ maxima correspond to the T_g of polymer **10**.

The storage modulus of **9** at 50 °C was 2.6×10^9 Pa. The T_g was indicated by a change in the slope of E' at 340 °C, a maximum in E'' at 345 °C, and a maximum in tan δ at 358 °C. These data correspond with both the T_g from the DSC and with the second transitions in the DMA of **7**. The storage modulus of polymer **10** at 50 °C was 4.1×10^9 Pa. The T_g was indicated by a change in the slope of E' at 337 °C, a maximum in E'' at 328 °C, and a maximum in tan δ at 403 °C. These data correspond with both the T_g from the DSC and with the second transitions in the DMA of **8**. Studies of the mechanical properties of fiber specimens of **7**–**10** are in progress and will be reported at a later date.

Conclusion

Polyquinolines **7** and **8** containing the 9,10-dihydro-9,10-ethanoanthracene unit were soluble in chloroform and tetrachloroethane and had T_gs between 250 and 300 °C. Prolonged heating at 300 °C resulted in rigidification of the polyquinolines through thermolytic elimination of ethylene, giving polyquinolines **9** and **10** containing the 2,6-diacetylanthracene unit. The absence of the ethylene bridge in **9** and **10** was confirmed by IR and ^{1}H CRAMPS NMR spectrometry. The rigidification process was followed by mechanical analysis. Polyquinolines **9** and **10** were insoluble in chloroform and tetrachloroethane, exhibited T_gs of greater than 300 °C, and showed increased storage moduli over the uncured samples.

Experimental Section

The ^{1}H NMR spectra were obtained on a Bruker AC-300 (300 MHz) with tetramethylsilane (0.00 ppm) or chloroform (7.24 ppm) as the internal standard. The ^{13}C NMR spectra were obtained on a Bruker AC-300 (75.5 MHz) with tetramethylsilane (0.00 ppm) or chloroform (77.00 ppm) as the internal standard. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR. The ^{1}H CRAMPS spectra were obtained at a proton Larmor frequency of 187 MHz on a severely modified NT-200 spectrometer. The BR-24 sequence, with τ = 3 μs and a 90° pulse width of 1.24 μs, was used. MAS rates were approximately 2 kHz.

Starting materials were obtained from commercial supplies or prepared according to standard procedures. Toluene and 1,4-dioxane were freshly distilled under argon from sodium prior to use. All reactions were carried out under an inert atmosphere and in flame-dried glassware unless otherwise stated. All melting points are uncorrected. Intrinsic viscosities were obtained with Cannon-Ubbelohde microdilution viscometers size 50 (chloroform), 75 (tetrachloroethane), and 100 (trifluoromethanesulfonic acid).

Thermal analyses were conducted with a Du Pont 9900 differential thermal analyzer equipped with a 910 differential scanning calorimeter (DSC) and a 951 thermogravimetric analyzer (TGA). The DSC analyses were obtained on film samples (20 °C/min) under a flowing-argon atmosphere (50 mL/min). Thermogravimetric analyses were obtained with a heating rate of 10 °C/min on both pressed powder and film samples in both flowing air and argon atmospheres. Elemental analyses were performed by Atlantic Microlabs, Inc., of Norcross, GA. Mechanical analyses were conducted on a Du Pont 983 dynamic mechanical analyzer (DMA) at a heating rate of 5 °C/min under a flowing-argon atmosphere.

Films of **7** and **8** were cast from tetrachloroethane (TCE). Once a cast film of **8** had been dried, the film could not be redissolved in chloroform or TCE to form a homogeneous solution. Films of **9** and **10** were obtained through thermal treatment of cast films of **7** and **8**, respectively, as described.

2,6-Bis[(trifluoromethanesulfonyl)oxy]-9,10-dihydro-9,10-ethanoanthracene (3). To a solution of 12.2 g (0.0520 mol) of 2,6-dihydroxy-9,10-dihydro-9,10-ethanoanthracene[3] (**2**) in 450 mL of dry pyridine at 0 °C was added 52.44 g (0.1900 mol) of trifluoromethanesulfonic anhydride.[10] The resulting mixture was stirred at 0 °C for 5 min and then at room temperature for 36 h. The reaction mixture was poured into water and extracted with ether. The ether extract was washed sequentially with water, 10% hydrochloric acid (2×), water, and saturated NaCl solution, dried ($MgSO_4$), and concentrated to yield a yellow solid. Chromatography (hexanes/EtOAc, 3:1) followed by recrystallization from hexanes afforded 20.21 g (78%) of off-white crystals of **3**, mp 109–110 °C. ^{1}H NMR ($CDCl_3$): δ 1.73 (s, 4 H), 4.42 (s, 2 H), 7.04 (dd, J = 8 and 2 Hz, 2 H), 7.21 (d, J = 2 Hz, 2 H), 7.33 (d, J = 8 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ 25.88, 43.51, 116.78, 118.62, 124.97, 142.86, 145.24, 147.62. Anal. Calcd for $C_{18}H_{12}F_6O_6S_2$: C, 43.05; H, 2.39. Found: C, 43.10; H, 2.43.

2,6-Diacetyl-9,10-dihydro-9,10-ethanoanthracene (4). To a solution of 7.000 g (13.94 mmol) of 2,6-bis[(trifluoromethanesulfonyl)oxy]-9,10-dihydro-9,10-ethanoanthracene (**3**) in 300 mL of dry 1,4-dioxane were added 4.20 g (96.0 mmol) of lithium chloride, 8.37 g (34.9 mmol) of freshly distilled (α-ethoxyvinyl)trimethylstannane,[11] and 330 mg (0.29 mmol) of tetrakis(triphenylphosphine)palladium(0).[12] The resulting suspension was heated at reflux for 24 h. After cooling to room temperature, 75 mL of 10% hydrochloric acid was added, and the resulting mixture was stirred at room temperature for 30 min. The reaction mixture was poured into water and extracted with ether. The ether extracts were washed (water), dried ($MgSO_4$), and concentrated. Chromatography (flash, hexanes/EtOAc, 3:1) followed by recrystallization from 95% ethanol yielded 3.38 g (83%) of white needles of **4**, mp 152–153 °C. IR (NaCl, neat): 3008, 2953, 2866, 1676, 1610, 1419, 1354, 1256, 1131, 907, 826, 749 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.71 (s, 4 H), 2.55 (s, 6 H), 4.46 (s, 2 H), 7.34 (d, J = 8 Hz, 2 H), 7.73 (dd, J = 2 and 8 Hz, 2 H), 7.88 (d, J = 2 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ 25.85, 26.42, 43.97, 123.03, 123.39, 126.72, 135.01, 142.90, 148.65, 197.86. Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.78; H, 6.20. Found: C, 82.56; H, 6.20.

3,3′-Dibenzoylbenzidine (6). (A) Coupling. A mixture of 64.8 g (0.17 mole) of 5-bromo-2-(trifluoroacetamido)benzophenone,[13] 29.2 g (89.0 mmol) of hexamethyldistannane,[14] and 2.06 g (1.79 mmol, 1 mol %) of tetrakis(triphenylphosphine)palladium(0)[12] in 800 mL of dry toluene was heated at reflux under argon for 15 h. The reaction mixture was filtered hot to remove the spent catalyst. Upon cooling to room temperature, dichloromethane (1 L) was added to dissolve the crystalline product, and the organic solution was washed with water (3 × 500 mL), dried ($MgSO_4$), and concentrated. Recrystallization from toluene yielded 47.1 g (90.5%) of *N,N'*-bis(trifluoroacetyl)-3,3'-dibenzoylbenzidine as greenish yellow crystals, mp 215–218 °C. ^1H NMR ($CDCl_3$): δ 7.44 (m, 4 H), 7.61–7.71 (m, 6 H), 7.79 (m, 4 H), 8.69 (m, 2 H), 11.96 (s, 2 H).

(B) Deprotection. To a degassed solution of 1.45 L of ethanol and 360 mL of water were added 47.1 g (0.08 mol) of *N,N'*-bis(trifluoroacetyl)-3,3'-dibenzoylbenzidine and 65.5 g (0.62 mol) of sodium carbonate. The resulting slurry was heated at reflux for 72 h. Upon cooling to room temperature, the reaction mixture was separated between 1 L of water and 1 L of dichloromethane. The organic layer was dried ($MgSO_4$) and concentrated. Recrystallization from benzene yielded 25.6 g (80%) of **6** as yellow crystals, mp 195–196 °C (lit.[7] 195.0–196.0 °C). ^1H NMR ($CDCl_3$): δ 5.90 (br s, 4 H), 6.78 (m, 2 H), 7.34–7.64 (m, 14 H).

Poly[2,2'-[2,6-(9,10-dihydro-9,10-ethanoanthracenyl)]-6,6'-oxybis(4-phenylquinoline)] (7). A mixture of 0.564 350 g (1.381 65 mmol) of 4,4'-diamino-3,3'-dibenzoyldiphenyl ether[6] (**5**), 0.401 193 g (1.381 65 mmol) of 2,6-diacetyl-9,10-dihydro-9,10-ethanoanthracene (**4**), 8.60 g (34.5 mmol) of diphenyl phosphate, and 1.60 mL (15.5 mmol) of freshly distilled *m*-cresol was placed in a three-necked polymerization flask equipped with an argon inlet, an overhead stirrer, and an argon outlet. The reaction mixture was flushed with argon for about 5 min and then heated in an oil bath from room temperature to 135–140 °C in about 30 min. It was maintained at this temperature for 48 h under a static argon atmosphere. The resulting clear, highly viscous, orange-yellow solution was poured slowly into a stirred solution of 500 mL of ethanol containing 50 mL of triethylamine to yield an off-white, fibrous material. This fibrous polymer was suspended in a small amount (about 10 mL) of ethanol containing 10% v/v of triethylamine, chopped in a blender, and collected by filtration. The polymer was continuously extracted in a Sohxlet apparatus with ethanol containing 10% v/v of triethylamine for 48 h. It was air-dried and then further dried at 100 °C under reduced pressure for 18 h. The polymer was redissolved in 30 mL of chloroform and reprecipitated by slow addition to a stirred solution of 500 mL of ethanol containing 50 mL of triethylamine. The precipitated fibrous polymer was suspended in about 15 mL of ethanol containing 10% v/v of triethylamine, chopped in a blender, collected by filtration, air-dried, and then further dried at 100 °C under reduced pressure for 24 h to afford an off-white fibrous polymer. $[\eta]$ = 1.4 ($CHCl_3$ or $CHCl_2CHCl_2$), 4.3 (CF_3SO_3H). IR (film): 3063, 2942, 2867, 1612, 1590, 1545, 1485, 1458, 1390, 1348, 1237, 1207, 1134, 988, 942, 883, 831, 765, 700, 584, 556 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.82 (s, 4 H), 4.59 (s, 2 H), 7.12–7.22 (m, 2 H), 7.46 (m, 14 H), 7.79 (m, 2 H), 7.89 (m, 2 H), 8.21 (m, 4 H). ^{13}C NMR ($CDCl_3$): δ 26.56, 44.21, 112.48, 119.93, 122.57, 122.76, 123.81, 125.05, 126.47, 128.48, 128.62, 129.28, 131.86, 138.05, 144.11, 145.24, 154.53, 156.25. Anal. Calcd for $C_{46}H_{30}N_2O$: C, 88.14; H, 4.79; N, 4.47. Found: C, 86.99; H, 4.82; N, 4.43.

Poly[2,2'-[2,6-(9,10-dihydro-9,10-ethanoanthracenyl)]-6,6'-bis(4-phenylquinoline)] (8). A mixture of 0.773 591 g (1.97113 mmol) of 3,3'-dibenzoylbenzidine (**6**), 0.572 482 g (1.971 55 mmol) of 2,6-diacetyl-9,10-dihydro-9,10-ethanoanthracene (**4**), 11.8 g (47.7 mmol) of diphenyl phosphate, and 4.4 mL of freshly distilled *m*-cresol was placed in a three-necked polymerization flask equipped with an argon inlet, an overhead stirrer, and an argon outlet. The reaction mixture was flushed with argon for about 5 min and then heated in an oil bath from room temperature to 135–140 °C in about 30 min. It was maintained at this temperature for 48 h under a static argon atmosphere. An additional 10 mL of *m*-cresol was added after 12 h to ensure efficient stirring. The resulting clear, highly viscous, red-orange solution was poured slowly into a stirred solution of 500 mL of ethanol containing 50 mL of triethylamine to yield a yellowish fibrous material. This fibrous polymer was suspended in a small amount (about 15 mL) of ethanol containing 10% v/v of triethylamine, chopped in a blender, and collected by filtration. The polymer was continuously extracted for 48 h in a Sohxlet apparatus with ethanol containing 10% v/v of triethylamine. It was air-dried and then further dried at 100 °C under reduced pressure for 18 h. The polymer was redissolved in 40 mL of chloroform and reprecipitated by slow addition to a stirred solution of 500 mL of ethanol containing 50 mL of triethylamine. The precipitated fibrous polymer was suspended in about 15 mL of ethanol containing 10% v/v of triethylamine, chopped in a blender, air-dried, and then further dried at 100 °C under reduced pressure for 24 h to afford an off-white fibrous polymer. $[\eta]$ = 8 ($CHCl_3$), 5.5 ($CHCl_2CHCl_2$), 10.1 (CF_3SO_3H). IR (film): 3057, 2943, 2868, 1586, 1545, 1484, 1349, 1133, 882, 828, 788, 766, 701, 558 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.81 (s, 4 H), 4.58 (s, 2 H), 7.55 (m, 10 H), 7.82 (m, 2 H), 7.91 (m, 4 H), 8.14 (m, 2 H), 8.25 (m, 4 H). Anal. Calcd for $C_{46}H_{30}N_2$: C, 90.54; H, 4.91; N, 4.58. Found: C, 89.31; H, 4.90; N, 4.52.

Poly[2,2'-(2,6-anthracenyl)-6,6'-oxybis(4-phenylquinoline)] (9). Film and powder samples of (**7**) were heated under argon at 200 °C for 6 h and then at 300 °C for 2 h. Reddish brown films and powders were obtained in quantitative yield. IR (film): 3059, 1606, 1552, 1484, 1389, 1356, 1228, 1158, 988, 956, 924, 833, 766, 702, 635 cm^{-1}. Anal. Calcd for $C_{44}H_{26}N_2O$: C, 88.27; H, 4.34; N, 4.67. Found: C, 87.05; H, 4.32; N, 4.61.

Poly[2,2'-(2,6-anthracenyl)-6,6'-bis(4-phenylquinoline)] (10). Film and powder samples of **8** were heated under argon at 200 °C for 6 h and then at 300 °C for 2 h. Reddish brown films and yellowish brown powders were obtained in quantitative yields. IR (film): 3057, 1674, 1588, 1548, 1489, 1360, 1294, 1214, 1150, 889, 827, 771, 701, 636, 624, 592, 466 cm^{-1}. Anal. Calcd for $C_{44}H_{26}N_2$: C, 90.69; H, 4.46; N, 4.81. Found: C, 89.95; H, 4.48; N, 4.76.

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Registry No. 2, 79375-66-9; 3, 124921-93-3; 4, 80683-59-6; 6, 71713-10-5; 7 (copolymer), 124922-07-2; 7 (SRU), 124921-95-5; 8 (copolymer), 124922-08-3; 8 (SRU), 124942-75-2; CH_2=C(OEt)$SnMe_3$, 115880-62-1; trifluoromethanesulfonic anhydride, 358-23-6; 5-bromo-2-(trifluoroacetamido)benzophenone, 94752-10-0; *N,N'*-bis(trifluoroacetyl)-3,3'-dibenzoylbenzidine, 124921-94-4.