Synthesis and Processing of Heterocyclic Polymers as Electronic, Optoelectronic, and Nonlinear Optical Materials. 2. New Series of Conjugated Rigid-Rod Polyquinolines and Polyanthrazolines

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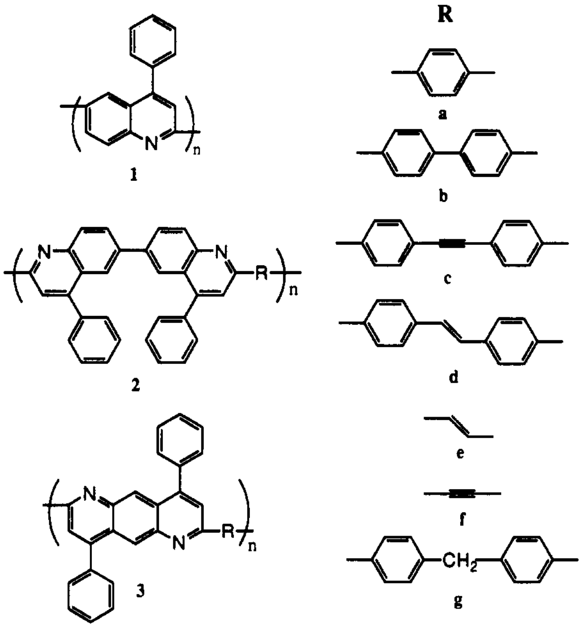
ABSTRACT: A series of 13 new homopolymers and three new copolymers along with six previously known polymers were synthesized and characterized in the class of conjugated polyquinolines and polyanthrazolines. The polymers were designed to systematically vary the π-electron delocalization along the conjugated polymer backbone and, thereby, to tune the electronic structure and properties in a controlled fashion. The solid polymers, which exhibit a range of light yellow to deep red color in transmitted light, were obtained in high yield, with high intrinsic viscosity and high thermal stability. As a result of the rigid-rod nature of the polymer chains, lyotropic liquid crystalline phases were observed at high concentrations of the polymers in di-*m*-cresyl phosphate/*m*-cresol (1:3) solvent. An investigation of the electronic structure of the polymers by optical absorption spectroscopy of the polymer thin films revealed that the structural modifications in the polymers can vary the optical band gap by about 1.0 eV. For example, compared to the biphenyldiyl linked polyquinoline (PBPQ, **2b**) which has a band gap (E_g) of 2.81 eV, the dithienylvinylene linked polyanthrazoline (PBVDA, **3k**) exhibited a drastically lower band gap of 2.0 eV. In general, replacement of a phenylene linkage by a thiophene linkage in the polyquinoline or polyanthrazoline backbone produced a significant red shift of λ_{max} by 64–106 nm and a reduction of band gap by 0.3–0.5 eV. The new polymers are expected to have improved electronic, photoelectronic, and nonlinear optical properties for applications and serve as model systems for investigating structure–property relationships in conjugated polymers.

Introduction

The growing interest in the synthesis, processing, and investigation of polymers with useful electronic, photoconductive, optoelectronic, nonlinear optical, or photorefractive properties for diverse technological applications[1-3] has motivated our studies being reported in this series. In part one of the series,[4] the synthesis, processing, and characterization of new conjugated rigid-rod benzobis(thiazole) polymers, including poly(benzobis(thiazole)–vinylene and poly(benzobis(thiazole)-*trans,trans*-butadiene), were reported. Also, we pointed out that the often difficult problem of *processability* of conjugated polymers has a natural solution intrinsic to *heterocyclic* or *heteroaromatic* polymers through their recently discovered *organic solvent soluble coordination complexes.*[4,5] The present report will focus on another class of conjugated heterocyclic polymers, polyquinolines and polyanthrazolines.

Phenylated polyquinolines and polyanthrazolines, first synthesized by Stille and co-workers,[6-11,13-15b] have proven to be mechanically strong and thermally stable polymers. These polymers are synthesized by using a condensation scheme based on the acid-catalyzed Friedlander reaction.[7] Two monomers consisting of bis(amino ketone) (A-A) and bis(ketomethylene) (B-B) functional moieties, respectively, are reacted in an acidic medium of di-*m*-cresyl phosphate and *m*-cresol at 140 °C under an inert atmosphere to give high molecular weight polyquinoline or polyanthrazoline in quantitative yield. This reaction scheme provides a high degree of flexibility in introducing varied structural features to the backbone of a polymer. Many conjugated, nonconjugated, and cross-linked polyquinolines were synthesized in the past to modify the mechanical, thermal, and solution properties of this class of polymers.[7,8] Conjugated rigid-rod polyquinolines were originally synthesized to achieve highly crystalline and thermally stable materials.[9] Chart I shows the structures of some of the known conjugated rigid-rod polyquinolines and polyanthrazolines (**1**, **2a**, **2b**, **2d**, **3a**, and **3b**).

Chart I



1 = PPQ ref. 9
2a = PPPQ ref. 9
2b = PBPQ ref. 9,10
2c = PBAPQ
2d = PSPQ ref. 13
2e = PVPQ
2f = PAPQ
2g = PDMPQ

3a = PPDA ref. 11
3b = PBDA ref. 11
3c = PBADA
3d = PSDA
3e = PVDA
3f = PADA
3g = PDMDA

Electrical conductivity of many of these polymers has been investigated by n-type chemical and electrochemical doping.[15,16] High conductivities of the order of 1–10 S/cm were realized by n-type chemical doping of PPQ (**1**), PBPQ (**2b**), and PSPQ (**2d**). However, the doped polymers were found to be highly sensitive to ambient atmosphere. Also, these polymers were difficult to oxidize or p-type dope.

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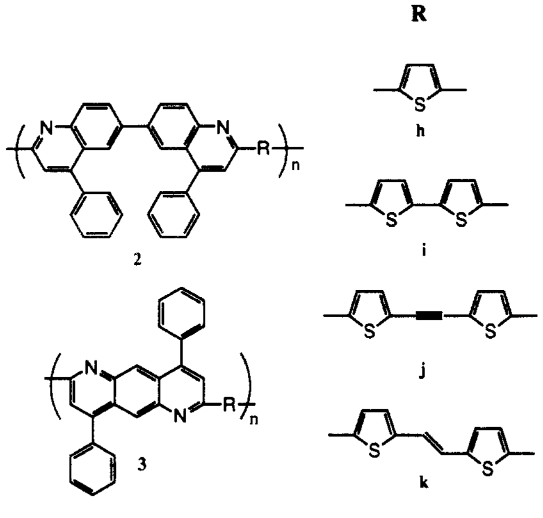
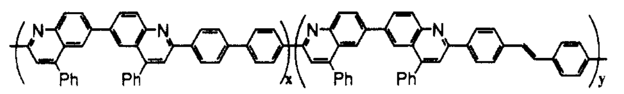
Chart II

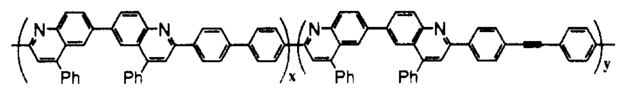


2h = PTPQ 3h = PTDA
2i = PBTPQ 3i = PBTDA
2j = PBTAPQ 3j = PBTADA
2k = PBTVPQ 3k = PBTVDA

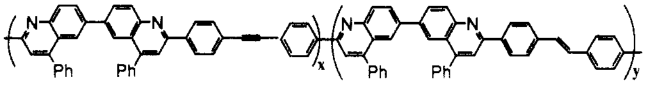
Chart III



4 PBPQ/PSPQ (50:50)



5 PBPQ/PBAPQ (50:50)



6 PBAPQ/PSPQ (50:50)

Theoretical calculations[15c] of the electronic structure of PPQ (1) and its derivatives showed high ionization potential (6.0 eV), large electron affinity (2.8 eV), and small band width (0.5–0.7 eV), which supported the experimental observations on doping of these polymers. Furthermore, our recent studies[17-20] of the optical, photoelectronic, and nonlinear optical properties of conjugated rigid-rod polyquinolines have shown promising results. In addition to the promising results on the linear optical, photoconductive, electrical conductivity, and nonlinear optical properties of the polyquinolines and polyanthrazolines reported to date,[15-20] we believe that this class of polymers holds promise for further systematic investigation and development as electronic, optoelectronic, and nonlinear optical materials. One of the reasons is that the polyquinolines and polyanthrazolines have the attractive combination of excellent mechanical and thermal properties, ease of solution processability, and synthetic flexibility to generate structurally diverse conjugated polymers. Availability of such architecturally diverse π-conjugated structures in high molecular weight polymers makes tuning and optimization of solid-state properties possible as well as provides a basis to establish structure–property relationships.

In this article, we report the synthesis and characterization of new monomers (**15–17**) and a systematic series of polyquinolines and polyanthrazolines represented by the structures in Charts I–III. The polymers with structures **2c**, **2g**, **3c**, **3d**, and **3g** in Chart I, **2h–2k** and **3h–3k** in Chart II, and **4–6** in Chart III are new materials. Two of the thiophene-linked polyanthrazolines PBTDA and PBTADA (**3i**,**3j**), which showed significantly improved intrinsic electronic properties compared to the known phenylene-linked polyanthrazoline PBDA (**3a**), were recently reported by us in a communication.[21] In another study,[17] we have demonstrated new and improved methods of processing polyquinolines and polyanthrazolines into uniform thin coatings and free standing films. The linear optical properties and third-order nonlinear optical properties of polymers **1**, **2a–2d**, **3a–3d**, and **4–6** have been studied in detail and are reported elsewhere.[17-19] A detailed investigation of the electrochemical properties of the polyquinolines and polyanthrazolines is currently in progress, and the results will be reported in a forthcoming paper.

Experimental Section

Monomers. The following monomers were synthesized according to the methods reported in the literature: 3,3′-dibenzoylbenzidine (**18**),[9,10] 2,5-dibenzoyl-1,4-phenylenediamine (**19**),[11] 5-acetyl-2-aminobenzophenone,[12] diacetylstilbene (**10**),[13] bis(acetylphenyl)acetylene (**9**),[14] hex-3-ene-2,5-dione (**13**),[22] hex-3-yne-2,5-dione (**12**),[23] 1,5-diacetylthiophene (**14**).[24] 4,4′-Diacetyl-1,1′-biphenylene (**8**) (methanol), 1,4-diacetylbenzene (**7**) (benzene), and bis(4-acetylphenyl)methane (**11**) (toluene) were obtained commercially and purified by recrystallization. Di-*m*-cresyl phosphate was prepared according to the method of Beever and Stille.[6b]

1,2-Bis(5-acetyl-2-thienyl)ethylene (BATE) (17). To a slurry of 1 g of tetrakis(triphenylphosphine)palladium(0) in 30 mL of dry toluene was added a solution of 6.6 g (32.2 mmol) of 2-acetyl-5-bromothiophene in 30 mL of dry toluene under argon. The light brown solution so obtained was heated to reflux. To this solution was added dropwise a solution of 9.8 g (16.1 mmol) of (*E*)-1,2-bis(tri-*n*-butylstannyl)ethylene[25] in 50 mL of toluene (dry) over a period of 1.5 h. After the reaction mixture was refluxed for another 5.5 h., it was slowly cooled down to −5 °C, and the yellow product was isolated by suction filtration. The product was washed with hexane to remove most of the tri-*n*-butyltin bromide and dried before it was recrystallized from chloroform. On drying in a vacuum oven at 60 °C for 24 h, a yield of 3.23 g (72.6%) was obtained. Mp: 247.6 °C. UV/vis, λ_{max} (nm) ($CHCl_3$): 413 (log ϵ = 4.54), 392 (4.66). FT-IR (KBr, cm^{-1}): 3070, 3014, 1655, 1646, 1528, 1459, 1423, 1363, 1276, 1263, 1224, 1075, 1032, 983, 929, 805, 747, 714, 655, 612, 592, 578, 500, 480. ^1H NMR (CD_2Cl_2, 300 MHz, TMS): δ 2.53 (s, 6 H), 7.15 (d, 2 H), 7.21 (s, 2 H), 7.60 (d, 2 H). Anal. Calcd for $C_{14}H_{12}S_2O_2$: C, 60.84; H, 4.38; N, 0.0. Found: C, 60.55; H, 4.22; N, 0.0.

5,5′-Diacetyl-2,2′-bithiophene (15). To a slurry of 1 g of tetrakis(triphenylphosphine)palladium(0) in 30 mL of dry toluene was added a solution of 6.26 g (30.5 mmol) of 2-acetyl-5-bromothiophene in 30 mL of dry toluene under argon. The reaction was heated to reflux, and to this solution was added dropwise a solution of 5 g (15.26 mmol) of hexamethylditin (99%) in 50 mL of toluene (dry) over a period of 1$^1/_2$ h. The reaction mixture was refluxed for another 6 h and then cooled down to −5 °C. Light yellow crystals of the product were isolated by suction filtration and washed with hexane. The product was then continuously extracted through Whatman filter paper No. 42 with dioxane using a Soxhlet apparatus until all of the product was dissolved and collected in the boiling flask. Slow cooling of the dioxane solution resulted in needle-shaped light yellow crystals of the monomer which were separated by suction filtration and dried in vacuum. Yield: 2.56 g (67%). Mp: 235 °C (lit. mp 233.5–234 °C). UV/vis, λ_{max} (nm) ($CHCl_3$): 367 (log ϵ = 4.19), 262 (3.57). FT-IR (KBr, cm^{-1}): 3070, 1797, 1656, 1611, 1511, 1433, 1361, 1302, 1270, 1089, 1036, 1020, 937, 897, 881, 792, 745, 673, 611, 593, 555, 463, 442. ^1H NMR ($CDCl_3$ 300 MHz, TMS): δ 2.58 (s, 6 H), 7.30 (d, 2 H), 7.62 (d, 2 H). Anal. Calcd for $C_{12}H_{10}S_2O_2$: C, 57.58; H, 4.03; N, 0.0. Found: C, 57.48; H, 3.87; N, 0.0.

Improved Synthesis of 1,2-Bis(5-acetyl-2-thienyl)acetylene (BATA) (16). To a slurry of 1 g of tetrakis(triphenylphosphine)palladium(0) in 30 mL of dry toluene was added a solution of 6.6 g (32.2 mmol) of 2-acetyl-5-bromothiophene in 30 mL of dry toluene under argon. The light brown solution so obtained was heated to reflux. To this solution was added dropwise a solution of 9.8 g (16.1 mmol) of 1,2-bis(tri-*n*-butylstannyl)acetylene in 50 mL of toluene (dry) over a period of 2 h. After the reaction medium was refluxed for another 6 h, it was cooled down to −5 °C, and the yellow product was isolated by suction filtration. The product was washed with hexane to remove most of the tri-*n*-butyltin bromide. The product was then continuously extracted through Whatman filter paper No. 42 with dioxane using a Soxhlet apparatus until all of the product was dissolved and collected in the boiling flask. Slow cooling of the dioxane solution resulted in needle-shaped light yellow crystals of the monomer which were separated by suction filtration and dried in vacuum at 60 °C for 24 h. Yield: 2.56 g (65%). Mp: 214 °C. UV/vis, λ_{max} (nm) ($CHCl_3$): 387 (log $\epsilon = 4.25$), 362 (4.31), 2.81 (3.78). IR (Nujol, cm^{-1}): 3070, 1670, 1390, 1295, 1260, 1045, 945, 910, 820. ^1H NMR (CD_2Cl_2, 300 MHz, TMS): δ 7.60 (d, 2 H), 7.33 (d, 2 H), 2.55 (s, 6 H).

Polymer Synthesis. Polymers 1, 2a, 2b, 2d, 3a, and 3b were synthesized according to the literature procedures.[9,11,13] However, DCP/*m*-cresol was used as the reaction medium for the synthesis of 3a and 3b to obtain polymers with high intrinsic viscosity. New polymers were synthesized as described below.

(i) Poly(2,2′-(*p,p*′-diphenylacetylene)-6,6′-bis(4-phenylquinoline)) (PBAPQ, 2c). Equimolar amounts (3.82 mmol each) of both 3,3′-dibenzoylbenzidine (18) and bis(acetylphenyl)acetylene (9) were added to a solution of 25 g of di-*m*-cresyl phosphate (DCP) and 9 g of freshly distilled *m*-cresol in a cylindrical-shaped reaction flask (glass) fitted with a mechanical stirrer, two gas inlets, and a side arm. The reactor was purged with argon for 10–15 min before the temperature was raised slowly to 140–142 °C in 2–3 h. As the viscosity of the reaction mixture increased with time, small amounts of *m*-cresol were added to the reaction mixture to facilitate efficient stirring. The reaction was maintained at this temperature for 48 h under static argon. Thereafter the reaction was quenched by cooling it down to room temperature under argon and precipitating it in 500 mL of 10% triethylamine/ethanol mixture. The precipitated polymer was then chopped in a blender and collected by suction filtration. The polymer was purified by continuous extraction in a Soxhlet apparatus with 20% triethylamine/ethanol solution for 36 h and was dried in vacuum at 80 °C for 24 h. [η] = 8.9 dL/g (25 °C, 0.1 mol % DCP/*m*-cresol). FT-IR (free-standing film, cm^{-1}): 3057, 3036, 1586, 1575, 1538, 1519, 1488, 1455, 1410, 1358, 1234, 1181, 1153, 1110, 1065, 1016, 874, 840, 828, 786, 771, 735, 701, 622, 588. Anal. Calcd for $(C_{44}H_{28}N_2)_n$: C, 90.70; H, 4.50; N, 4.84. Found: C, 88.87; H, 4.49; N, 4.69.

(ii) Poly(2,2′-(4,4′-diphenylmethylene)-6,6′-bis(4-phenylquinoline)) (PDMPQ, 2g). It was synthesized using a similar procedure as described in (i) using equimolar amounts (1.78 mmol each) of 3,3′-dibenzoylbenzidine (18) and bis(4-acetylphenyl)methane (11) as the two monomers. Diphenyl phosphate (15 g) with 8 g of *m*-cresol was used as the reaction medium instead of DCP/*m*-cresol. [η] = 9.3 dL/g (25 °C, 0.1 mol % DCP/*m*-cresol). FT-IR (free-standing film, cm^{-1}): 3056, 3028, 1585, 1572, 1541, 1486, 1427, 1353, 1230, 1182, 1152, 1065, 1017, 910, 826, 761, 700, 587. Anal. Calcd for $(C_{43}H_{28}N_2)_n$: C, 90.18; H, 4.93; N, 4.89. Found: C, 85.34; H, 4.51; N, 4.58.

(iii) Poly(2,7-(*p,p*′-diphenylacetylene)-4,9-diphenyl-1,6-anthrazoline) (PBADA, 3c). Equimolar amounts (2.21 mmol each) of 2,5-dibenzoyl-1,4-phenylenediamine (19) and bis(acetylphenyl)acetylene (9) were added to a mixture of 15 g of DCP and 8 g of *m*-cresol and reacted with a procedure similar to that described in (i). The polymer obtained was worked up as usual. [η] = 7.65 dL/g (25 °C, 0.1 mol % DCP/*m*-cresol). FT-IR (free-standing film, cm^{-1}): 3037, 2967, 1590, 1558, 1519, 1492, 1453, 1408, 1351, 1288, 1238, 1181, 1052, 1016, 970, 894, 840, 765, 699, 539. Anal. Calcd for $(C_{38}H_{22}N_2)_n$: C, 90.09; H, 4.38; N, 5.53. Found: C, 86.92; H, 4.20; N, 5.23.

(iv) Poly(2,7-(*p,p*′-diphenylethylene)-4,9-diphenyl-1,6-anthrazoline) (PSDA, 3d). Equimolar amounts (2.21 mmol each) of 2,5-dibenzoyl-1,4-phenylenediamine (19) and diacetylstilbene (10) were reacted with a procedure similar to that described in (iii). The polymer obtained was worked up as usual. [η] = 30.3 dL/g (25 °C, 0.1 mol % DCP/*m*-cresol). FT-IR (free-standing film, cm^{-1}): 3028, 2966, 1733, 1590, 1572, 1492, 1453, 1415, 1349, 1238, 1181, 1148, 1053, 1015, 969, 894, 840, 765, 699, 533. Anal. Calcd for $(C_{38}H_{24}N_2)_n$: C, 89.74; H, 4.76; N, 5.51. Found: C, 85.66; H, 4.55; N, 5.32.

(v) Poly(2,7-(4,4′-diphenylmethylene)-4,9-diphenyl-1,6-anthrazoline) (PDMDA, 3g). Equimolar amounts (2.21 mmol each) of 2,5-dibenzoyl-1,4-phenylenediamine (19) and bis(4-acetylphenyl)methane (11) were reacted in a reaction medium of 15 g of DPP and 11.5 g of *m*-cresol with a procedure similar to that described in (i). The polymer obtained was worked up as usual. [η] = 0.87 dL/g (25 °C, 0.1 mol % DCP/*m*-cresol). FT-IR (free-standing film, cm^{-1}): 3027, 1588, 1566, 1528, 1510, 1490, 1451, 1433, 1412, 1363, 1344, 1276, 1234, 1180, 1147, 1110, 1074, 1051, 1030, 1016, 969, 893, 816, 761, 697. Anal. Calcd for $(C_{37}H_{24}N_2)_n$: C, 89.49, H, 4.87; N, 5.64. Found: C, 87.34; H, 4.68; N, 5.40.

(vi) Poly(2,2′-(2,2′-bithiopheneyl)-6,6′-bis(4-phenylquinoline)) (PBTPQ, 2i). Equimolar amounts (1.27 mmol each) of 3,3′-dibenzoylbenzidine (18) and 5,5′-diacetyl-2,2′-bithiophene (15) were mixed with 12 g of DCP and 2 g of *m*-cresol and reacted with a procedure similar to that described in (i). The polymer obtained was worked up as usual. [η] = 11.5 dL/g (25 °C, 0.1 mol % DCP/*m*-cresol). FT-IR (free-standing film, cm^{-1}): 3063, 2967, 1586, 1543, 1519, 1489, 1454, 1442, 1360, 1282, 1225, 1076, 871, 823, 787, 767, 701, 621, 590. Anal. Calcd for $(C_{38}H_{22}N_2S_2)_n$: C, 79.97; H, 3.89; N, 4.91. Found: C, 78.27; H, 3.89; N, 4.77.

(vii) Poly(2,2′-(5-(2-thien-2-ylethynyl)thien-2-yl)-6,6′-bis(4-phenylquinoline)) (PBTAPQ, 2j). Equimolar amounts (1.27 mmol each) of 3,3′-dibenzoylbenzidine (18) and 1,2-bis(5-acetyl-2-thienyl)acetylene (16) were mixed with 12 g of DCP and 2 g of *m*-cresol and reacted with a procedure similar to that described in (i). The polymer obtained was worked up as usual. A small amount of the polymer received was found to be insoluble in any solvent system; therefore, its intrinsic viscosity could not be determined. FT-IR (free-standing film, cm^{-1}): 3059, 2969, 1740, 1590, 1544, 1489, 1465, 1359, 1304, 1243, 1149, 1069, 1030, 970, 874, 825, 768, 701, 585. Anal. Calcd for $(C_{40}H_{22}N_2S_2)_n$: C, 80.78; H, 3.73; N, 4.71. Found: C, 77.04; H, 4.12; N, 4.13.

(viii) Poly(2,2′-(5-(2-thien-2-ylethenyl)thien-2-yl)-6,6′-bis(4-phenylquinoline)) (PBTVPQ, 2k). Equimolar amounts (1.27 mmol each) of 3,3′-dibenzoylbenzidine (18) and 1,2-bis(5-acetyl-2-thienyl)ethylene (17) were mixed with 12 g of DCP and 2 g of *m*-cresol and reacted with a procedure similar to that described in (i). The polymer obtained was worked up as usual. [η] = 6.2 dL/g (25 °C, 0.1 mol % DCP/*m*-cresol). FT-IR (free-standing film, cm^{-1}): 3060, 2968, 1586, 1473, 1360, 1259, 1238, 1066, 1029, 932, 874, 825, 768, 701, 621, 586. Anal. Calcd for $(C_{40}H_{24}N_2S_2)_n$: C, 80.51; H, 4.05; N, 4.69. Found: C, 78.02; H, 4.22; N, 4.71.

(ix) Poly(2,2′-(2,5-thiopheneyl)-6,6′-bis(4-phenylquinoline)) (PTPQ, 2h). Equimolar amounts (1.78 mmol each) of 3,3′-dibenzoylbenzidine (18) and 2,5-diacetylthiophene (14) were reacted in 16.5 g of DCP and 2 g of *m*-cresol with a procedure similar to that described in (i). The polymer obtained was worked up as usual. [η] = 10.5 dL/g (25 °C, 0.1 mol % DCP/*m*-cresol). FT-IR (free-standing film, cm^{-1}): 3057, 2967, 1586, 1544, 1489, 1451, 1362, 1235, 1150, 1075, 1030, 872, 846, 824, 767, 701, 623, 570. Anal. Calcd for $(C_{34}H_{20}N_2S_1)_n$: C, 83.58; H, 4.13; N, 5.73. Found: C, 81.31; H, 4.02; N, 5.55.

(x) Poly(2,7-(2,2′-bithiopheneyl)-4,9-diphenyl-1,6-anthrazoline) (PBTDA, 3i) and Poly(2,7-(5-(2-thien-2-ylethynyl)thien-2-yl)-4,9-diphenyl-1,6-anthrazoline) (PBTADA, 3j). The synthesis and characterization of these polymers are described in ref 21.

(xi) Poly(2,7-(5-(2-thien-2-ylethenyl)thien-2-yl)-4,9-diphenyl-1,6-anthrazoline) (PBTVDA, 3k). Equimolar amounts (1.58 mmol each) of 2,5-dibenzoyl-1,4-phenylenediamine (19) and 1,2-bis(5-acetyl-2-thienyl)ethylene (17) were reacted in 12 g of DCP and 2.5 g of *m*-cresol with a procedure similar to that described in (i). The polymer obtained was worked up as usual. [η] = 4.4 dL/g (25 °C, 0.1 mol % DCP/*m*-cresol). IR (free-standing film, cm^{-1}): 3060, 2968, 1588, 1574, 1532, 1492, 1475, 1357, 1289, 1259, 1239, 1146, 1061, 1030, 959, 934, 895, 796, 765, 748, 702, 616, 545. Anal. Calcd for $(C_{34}H_{20}N_2S_2)_n$: C, 78.43; H, 3.87; N, 5.38. Found: C, 77.38; H, 3.83; N, 5.09.

(xii) Poly(2,7-(2,5-thiopheneyl)-4,9-diphenyl-1,6-anthrazoline) (PTDA, 3h). Equimolar amounts (1.58 mmol each) of 2,5-dibenzoyl-1,4-phenylenediamine (**19**) and 2,5-diacetylthiophene (**14**) were reacted with a procedure similar to that described in (xi). The polymer obtained was worked up as usual. [η] = 1.2 dL/g (25 °C, 0.1 mol % DCP/*m*-cresol). FT-IR (free-standing film, cm^{-1}): 3056, 3028, 1586, 1571, 1529, 1491, 1432, 1354, 1234, 1042, 1030, 892, 851, 805, 763, 698, 616, 587. Anal. Calcd for $(C_{28}H_{16}N_2S_1)_n$: C, 81.53; H, 3.91; N, 6.79. Found: C, 78.68; H, 3.83; N, 6.29.

(xiii) PSPQ/PBPQ (4). Diacetylstilbene (**10**) (1.27 mmol), 1.27 mmol of diacetylbiphenylene (**8**), and 2.55 mmol of 3,3′-dibenzoylbenzidine (**18**) were mixed together in a reaction medium of 17 g of DCP and 16 g of *m*-cresol. The reaction was carried out as described in (i). The polymer obtained was worked up as usual. [η] = 22.6 dL/g (25 °C, 0.1 mol % DCP/*m*-cresol). FT-IR (free-standing film, cm^{-1}): 3057, 3029, 2960, 1586, 1574, 1540, 1488, 1457, 1357, 1234, 1182, 1068, 1004, 870, 827, 772, 743, 701, 590.

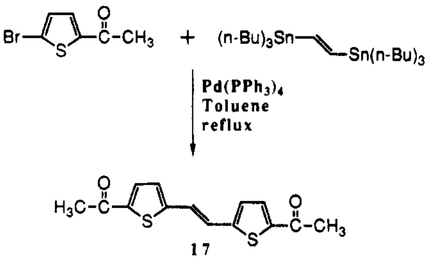
(xiv) PBPQ/PBAPQ (5). Bis(acetylphenyl)acetylene (**9**) (1.27 mmol), 1.27 mmol of diacetylbiphenylene (**8**), and 2.55 mmol of 3,3′-dibenzoylbenzidine (**18**) were mixed together in a reaction medium of DCP/*m*-cresol. The reaction was carried out as described in (xiii). The polymer obtained was worked up as usual. [η] = 25 dL/g (25 °C, 0.1 mol % DCP/*m*-cresol). FT-IR (free-standing, cm^{-1}): 3057, 3033, 2960, 1586, 1539, 1488, 1457, 1357, 1233, 1151, 1068, 1016, 1004, 872, 827, 771, 701, 623, 590.

(xv) PSPQ/PBAPQ (6). Diacetylstilbene (**10**) (1.27 mmol), 1.27 mmol of bis(acetylphenyl)acetylene (**9**), and 2.55 mmol of 3,3′-dibenzoylbenzidine (**18**) were mixed together in a reaction medium of 17 g of DPP and 15 g of *m*-cresol. The reaction was carried out as described in (i). The polymer obtained was worked up as usual. [η] = 14.3 dL/g (25 °C, 0.1 mol % DCP/*m*-cresol). FT-IR (free-standing film, cm^{-1}): 3057, 3030, 2960, 1586, 1575, 1539, 1488, 1460, 1357, 1235, 1181, 1065, 1015, 828, 771, 701, 588.

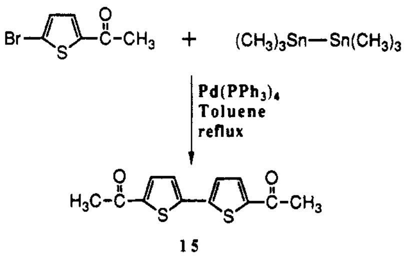
Attempted Polymerizations. (xvi) Poly(2,2′-(1,2-acetylene)-6,6′-bis(4-phenylquinoline)) (PAPQ, 2f), Poly(2,2′-(1,2-vinylene)-6,6′-bis(4-phenylquinoline)) (PVPQ, 2e), Poly(2,7-(1,2-acetylene)-4,9-diphenyl-1,6-anthrazoline) (PADA, 3f), and Poly(2,7-(1,2-vinylene)-4,9-diphenyl-1,6-anthrazoline) (PVDA, 3e). Equimolar amounts (1.27 mmol each) of appropriate bis(amino ketone) and bis(ketomethylene) monomers were dissolved separately in 5 g of *m*-cresol and added to the reaction medium containing 12 g of DCP. The reaction was purged with argon and stirred for 15 min at room temperature before raising the temperature in steps to 140 °C. Thereafter the procedure was followed as described in (i).

Characterization. Intrinsic viscosity of the polymers was measured using dilute solutions in the range 0.05–0.2 g/dL in 0.1 mol % DCP/*m*-cresol at 25 °C. The FT-IR spectra of the free-standing polymer films were recorded on a Nicolet FTIR spectrometer. In the case of polymers where good quality free-standing films could not be fabricated (i.e. polymers with low intrinsic viscosity), they were powdered and blended with KBr to make compressed pellets which were then used to obtain FT-IR spectra. ^{1}H NMR spectra were obtained on a GE 300-MHz NMR spectrometer. Elemental analyses of the monomers and polymers were done by Quantitative Technologies, Inc. (White House, NJ). Optical absorption spectra of the polymer thin films were obtained from thin coatings of the polymers on fused-silica substrate on a Perkin-Elmer UV/vis/near-IR spectrophotometer (Model Lambda 9). Similarly, solution spectra of polymers were obtained by using dilute solutions of polymers in 0.1 mol % DCP/*m*-cresol solvent. Thermal analyses of pressed polymer powder or films were performed on a du Pont Thermal Analyst 2100 equipped with a 951 thermogravimetric analyzer (TGA). Liquid crystalline phases in polymer solutions were determined by viewing a thin film of solution sheared between a microscope glass slide and a cover slip under a cross-polarized Olympus optical microscope (Model BHS) fitted with a Polaroid camera. Concentrated solutions of polymers (>5 wt %) in DCP/*m*-cresol (1:3) were obtained by heating the polymer–solvent mixture in an oil bath at 135 °C for 4–6 h. The solutions were occasionally stirred during heating to obtain a homogeneous polymer concentration throughout the solution.

Scheme I



Scheme II

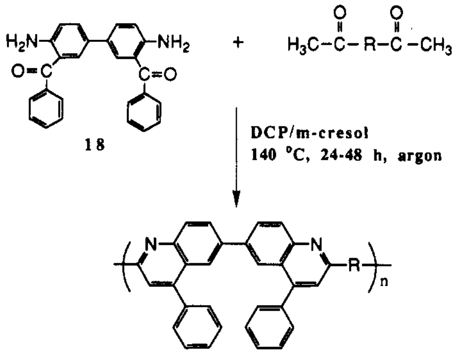


Results and Discussion

Monomer Synthesis. Thiophene-containing monomers, 5,5′-diacetyl-2,2′-bithiophene (**15**), 1,2-bis(5-acetyl-2-thienyl)acetylene (**16**), and 1,2-bis(5-acetyl-2-thienyl)ethylene (**17**), were prepared using a coupling chemistry based on tetrakis(triphenylphosphine)palladium(0) catalyst.[10,13,14] The coupling was carried out between 2-acetyl-5-bromothiophene and an appropriate hexaalkylditin compound. In the case of 1,2-bis(5-acetyl-2-thienyl)ethylene (**17**), 1 mol of bis(tri-*n*-butylstannyl)vinylene[25] was coupled with 2 mol of 2-acetyl-5-bromothiophene in dry toluene (Scheme I). 5,5′-Diacetyl-2,2′-bithiophene (**15**) was synthesized by coupling 2 mol of 2-acetyl-5-bromothiophene with 1 mol of hexamethylditin (Scheme II). Compared to the reported method in the literature[26] for the preparation of 5,5′-diacetyl-2,2′-bithiophene, the coupling Scheme II gave the pure product in higher yield (67% versus 55%) in our hands. Also, the product so received was much easier to purify to monomer grade than the literature method. Synthesis of 1,2-bis(5-acetyl-2-thienyl)acetylene (**16**) has been described earlier.[21] However, the yield was improved from 22% to 65% by using an improved procedure. In this synthesis, toluene was used as the reaction medium instead of tetrahydrofuran and a solution of bis(tri-*n*-butylstannyl)acetylene in toluene was added dropwise to a refluxing reaction mixture consisting of a solution of 2-acetyl-5-bromothiophene and palladium(0) catalyst in toluene. It was found that a reaction time of less than 8 h was sufficient to complete the coupling in all of the above reactions. In general, no efforts were made to optimize the reaction conditions for better yields. 2,5-Diacetylthiophene (**14**) was synthesized using the method of Potts et al.[24] The product was purified to monomer grade using active charcoal treatment followed by recrystallization.

Hex-3-ene-2,5-dione (**13**) was synthesized using the method of Levisalles.[22] The crude product was purified by treating its solution in boiling cyclohexane with active charcoal followed by recrystallization from cyclohexane. Hex-3-yne-2,5-dione (**12**) was synthesized using the improved method of Dunn and Rees.[23] The product was recovered by distillation at 85 °C/10 mmHg from the mixture of side products and reactants and was found to be highly sensitive to temperature and air. When left at room temperature, it changed rapidly from a colorless liquid to a thick brown gel.

Scheme III



Scheme IV

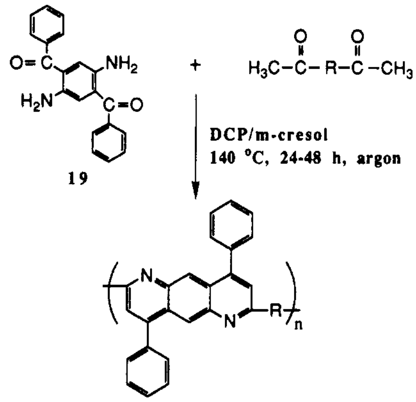
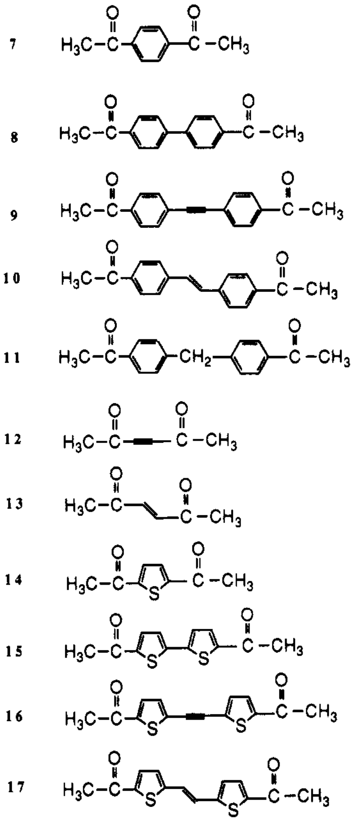


Chart IV



Polymer Synthesis. A reaction scheme similar to the one described in the literature[6,7] for phenylated polyquinolines and polyanthrazolines was used to synthesize the new polymers. This synthetic approach, which is depicted by Schemes III and IV, allows facile modification of the π-conjugated polymer backbone with a proper choice of monomers. Since the functional groups ketomethylene (B) and aminoketone (A) of the monomers used in the polymerization condense to form a quinoline (or an anthrazoline) unit, the structural differences from one monomer to another appear as the variations in the linking groups between the quinoline (or anthrazoline) units in the polymer chain. This flexibility facilitates a systematic investigation of the structure–property relationships within the confinements of a single class of polymer. A systematic series of polyquinolines (**2**) was synthesized using Scheme III, where a series of bis(ketomethylene) (B-B) monomers (Chart IV) was polymerized one by one with 3,3′-dibenzoylbenzidine (**18**) to structurally vary the linking group between quinoline units of the polymers. Similarly, polyanthrazolines were synthesized using Scheme IV where the same set of bis(ketomethylene) (B-B) monomers (Chart IV) was used to generate another systematic series of polyanthrazolines (**3**). The polymers shown in Chart I have been designed to vary the conformation of the conjugated polymer backbone in a controlled and predictable manner. Due to the expected varying degree of planarity of these structures, the π-electron delocalization and hence the electronic properties are also expected to vary in a predictable way. Results of the investigation of the linear optical properties of this series of polymers agree well with these intuitive expectations. For example, a bathochromic shift of 64 nm in λ_{max} and a reduction of ~0.35 eV in band gap (E_g) was observed while going from PBPQ (**2a**) to PSDA (**3d**). A detailed description of the linear optical properties of the polymers in Chart I has been reported earlier.[17]

The polymers in Chart II are thiophene-linked polyquinolines and polyanthrazolines. Within the series, structures are again designed to produce a varying degree of π-electron delocalization. However, the polymers in Chart II were also synthesized in order to study the effects of thiophene linkages (**2h**–**2k**, **3h**–**3k**) in comparison to phenylene linkages (polymers in Chart I: **2a**–**2d**, **3a**–**3d**) in conjugated polymer chains. The optical properties of the thiophene-linked polymers will be discussed in detail under a separate section.

Random copolymerization provides a unique way of modifying the structure, morphology, and properties of a polymer system. Three random copolymers (**4**–**6**) were synthesized by reacting 0.5 mol each of two bis(ketomethylene) (B-B) monomers with 1 mol of bis(amino ketone) (A-A) monomer. Since all of the polymers were obtained in essentially quantitative yield (>95%), the molar ratio of the two polymer segments in the copolymers is expected to be 1:1, which is the same as the ratio of the two bis(ketomethylene) (B-B) monomers used in the polymerization.

All the polymers were obtained with high intrinsic viscosity except for a few polymers, for example PPQ (**1**), PDMDA (**3g**), and PTDA (**3h**). The intrinsic viscosity of the polymers in Charts I and III was in the range of 0.87–31.3 dL/g and that of the polymers in Chart II was 1.2–11.5 dL/g (Table I). The low intrinsic viscosity of PPQ, PDMDA, and PTDA is the result of either low monomer purity or unsuitable reaction conditions used in their polymerization. Since Mark–Houwink coefficients for conjugated rigid-rod polyquinolines or polyanthrazolines are not available, we are unable to provide estimates for the molecular weight of these polymers. However, light-scattering experiments done on one of the phenylene-linked polyquinolines PBPQ (**2b**) gave a molecular weight of 370 000 for an intrinsic viscosity of 20 dL/g.[27] Therefore, the high intrinsic viscosity values obtained for the polyquinolines and polyanthrazolines suggest that the polymers are of high molecular weight. The relatively lower intrinsic viscosity of thiophene-linked polymers does

Table I
Properties of the Polyquinolines and Polyanthrazolines

	polymer	$[\eta]^a$ (dL/g)	thermal stability^b (°C)	λ_{max} (film) (nm)	E_g (film) (eV)	λ_{max} (soln)^a (nm)	log ϵ^a
1	PPQ	0.95	580	410	2.65	389	4.16
2a	PPPQ	18.5	590	398	2.78	405	4.63
2b	PBPQ	8.5	600	394	2.81	429	4.83
2c	PBAPQ	8.9	600	399	2.72	436	4.86
2d	PSPQ	31.3	580	408	2.65	467	4.88
2g	PDMPQ	9.3	575	370	3.01	389	4.68
3a	PPDA	3.05	590	443	2.47	442	4.49
3b	PBDA	6.85	600	414	2.56	484	4.67
3c	PBADA	7.65	590	426	2.57	490	4.65
3d	PSDA	30.3	585	448	2.46	547	4.78
3g	PDMDA	0.87	560	404	2.7	431	4.62
2h	PTPQ	10.5	590	441	2.49	493	4.78
2i	PBTPQ	11.5	590	468	2.33	546	5.06
2j	PBTAPQ	c	415	469	2.26	567	c
2k	PBTVPQ	6.2	515	484	2.23	578	5.00
3h	PTDA	1.2	565	498	2.17	572	4.49
3i	PBTDA	2.3	600	520	2.07	659	4.90
3j	PBTADA	4.4	415	525	2.0	709	4.72
3k	PBTVDA	4.4	510	532	2.0	694	4.85

[a] Solutions made in 0.1 mol % DCP/*m*-cresol. [b] Decomposition temperature determined by TGA at 10 °C/min under N_2. [c] Polymer not completely soluble.

not mean that these polymers are of lower molecular weight than the phenylene-linked polymers. Since thiophene linkages are expected to be more flexible compared to phenylene linkages, high molecular weight thiophene-linked polymers may show lower intrinsic viscosity than phenylene-linked polymers of similar molecular weight.

The synthesis of six polymers (**1**, **2a**, **2b**, **2d**, **3a**, **3b**) in Chart I has been previously reported in the literature.[9,11,13] These polymers were also synthesized for the present study. Most of these polymers were obtained with higher intrinsic viscosity than reported earlier.[7,9,11,13] The higher intrinsic viscosity of these polymers than those reported in the literature may be in part due to the higher purity of monomers used in their polymerization in our hand. The synthesis of the polyanthrazolines PPDA and PBDA (**3a**, **3b**) was modified by using di-*m*-cresyl phosphate/*m*-cresol as the polymerization medium. This modification, which was also suggested but not experimentally carried out by Stille,[7] resulted in a significant increase in the molecular weight of these polyanthrazolines. Compared to previous results,[11] the intrinsic viscosity of PPDA and PBDA increased from 0.37 to 3.05 dL/g and 1.24 to 6.85 dL/g, respectively. In our study, all polyanthrazolines synthesized in DCP/*m*-cresol or DPP/*m*-cresol, in contrast to those reported in the literature, were obtained with much higher intrinsic viscosity.

In some cases, for example the synthesis of PPPQ, PPDA, PDMPQ, PDMDA, PSPQ/PBAPQ, and PBTDA, diphenyl phosphate (DPP)/*m*-cresol was used successfully in place of di-*m*-cresyl phosphate (DCP)/*m*-cresol as the polymerization medium. The high yields and high intrinsic viscosities obtained for these polymers suggest that catalytic activity of DPP is similar to that of DCP. For example, polymerization of PPPQ in DPP/*m*-cresol gave an intrinsic viscosity of 18.5 dL/g, which is comparable to that reported for PPPQ synthesized in DCP/*m*-cresol. The commercial availability of DPP makes it an attractive alternative to DCP as the polymerization medium for the synthesis of polyquinolines and polyanthrazolines. Polymers with phenylene linkages (Charts I and III), whether synthesized in DPP/*m*-cresol or DCP/*m*-cresol, were all received with high molecular weight. However, thiophene-linked polymers (Chart II) were obtained with higher intrinsic viscosities when synthesized in DCP/*m*-cresol compared to DPP/*m*-cresol.

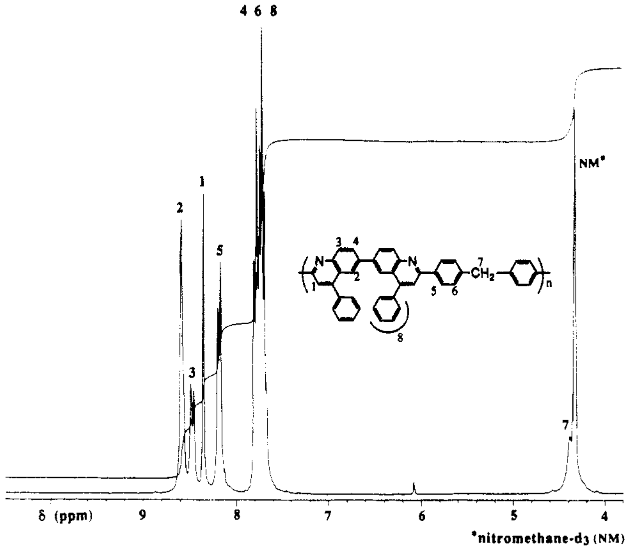


Figure 1. ^{1}H NMR spectrum of PDMPQ (**2g**) in $GaCl_3$/nitromethane-d_3.

The new polymers were characterized by Fourier transform infrared (FT-IR) spectroscopy, elemental analysis, and thermogravimetric analysis. The complete disappearance of bands characteristic of the carbonyl groups of the monomers and appearance of new strong bands between 1400 and 1600 cm^{-1} in the FT-IR spectra of the polymers confirmed completion of the cyclization reaction forming quinoline or anthrazoline rings. A listing of the main IR bands of the new polymers and the results of the elemental analyses are reported in the Experimental Section. The FT-IR spectra were consistent with the proposed polymer structures. The analytical results were also consistent with the structure. However, a small difference in carbon content was observed in the elemental analysis of all samples and is similar to that seen for other polyquinolines and polyanthrazolines reported in the literature.[6-11,13-15b] It is characteristic of thermally stable polymers with high carbon content to give lower experimental values by 2–3 wt %.

In order to unambiguously verify the polymer structures shown in Charts I–III, diphenylmethane-linked polymers PDMPQ and PDMDA were characterized by NMR spectroscopy. Figures 1 and 2, respectively, show the ^{1}H NMR spectra of 1–1.3 wt % of PDMPQ and PDMDA in $GaCl_3$/nitromethane-d_3 from a 300-MHz spectrometer. The ^{13}C NMR spectra chemical shifts of the same polymers are presented in Table II. Surprisingly, excellent proton resonances and splittings and their correct integration signals can be observed in the ^{1}H NMR spectra for all the protons in the polymer repeat units shown in Chart I. When an assignment of signals (Figures 1 and 2 and Table II) was made by empirically estimating[28] the values of proton and carbon shifts, an excellent agreement was found between the calculated and the observed values which further confirmed the proposed structures (Chart I) of PDMPQ and PDMDA. The somewhat larger difference between some of the calculated and experimental ^{13}C shifts of PDMDA is because of the errors incurred in calculating ^{13}C shifts of an anthrazoline ring. Since we could not find any ^{13}C NMR spectrum of anthrazoline in the literature, the ^{13}C shifts of an anthrazoline ring were estimated by adding the effect of nitrogen to the experimental values for an anthracene ring, and the effect of nitrogen was

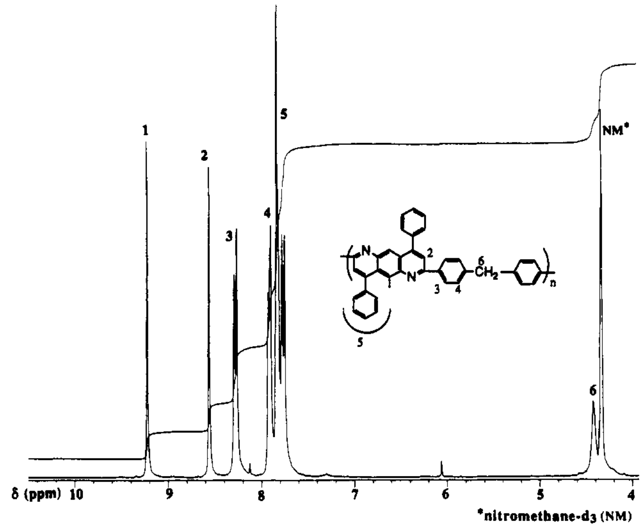
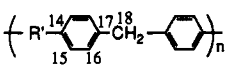
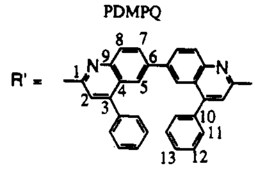


Figure 2. ^{1}H NMR spectrum of PDMPA (**3g**) in GaCl$_3$/nitromethane-d_3.

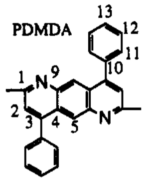
Table II
Carbon-13 Shifts for PDMPQ and PDMDA



PDMPQ



PDMDA



carbon	calcd	obsd	carbon	calcd	obsd
1	163.8	160.6	1	163.3	160.3
2	118.8	122.2	2	118.3	123.4
3	149.5	153.9	3	149.8	157.8
4	126.4	126.3	4	127.8	129.6
5	126.6	126.4	5	127.9	129.9
6	139.6	138.2			
7	128.3	129.5			
8	129.8	134.6			
9	147.9	153.8	9	147.6	148.6
10	141.6	140.0	10	141.6	134.4
11	129.6	131.0	11	129.6	131.2
12	128.9	129.9	12	128.9	130.0
13	129.7	131.1	13	129.7	131.2
14	141.6+	147.3	14	141.6+	135.4
15	127.6	129.0	15	127.6	128.6
16	126.9	128.9	16	126.9	128.1
17	136.8	135.2	17	136.8	131.8
18		121.7	18		121.4

calculated by comparing the experimental ^{13}C shifts for a quinoline ring with that of a naphthalene ring. The carbon shift for $-CH_2-$ in ^{13}C NMR of both polymers has been assigned at ~121 ppm (Table II). The solution optical absorption spectra of PDMPQ and PDMDA suggest that the polymers are quite coplanar in solution and have a reasonable degree of π-electron delocalization. This delocalization may give single bonds connecting $-CH_2-$ some degree of double bond character which may result in a downfield shift of the carbon resonance. Also, unlike the spectra of diphenylmethane, we do not observe any signal at around 42.1 ppm. Therefore, the additional signal seen at ~121 ppm, which corresponds to the chemical shifts shown by alkene carbons, is likely to be due to the $-CH_2-$ carbon.

The monomers hex-3-ene-2,5-dione (**13**) and hex-3-yne-2,5-dione (**12**) could not be polymerized with any of the bis(amino ketone) (A-A) monomers using the above polymerization schemes. These monomers were found to be unstable in the polymerization medium even at room temperature and appeared to undergo self-condensation. Attempted polymerization of these monomers with 3,3′-dibenzoylbenzidine (**18**) or 2,5-dibenzoyl-1,4-phenylenediamine (**19**) did not give any product on precipitation of the polymerization dope in the usual nonsolvent mixture. Thus, all attempts of obtaining polymers **2e**, **2f**, **3e**, and **3f** in Chart I proved unsuccessful.

Thermal Properties. Polyquinolines and polyanthrazolines are highly thermally stable polymers with thermal transitions (glass transition and melting point) occurring at temperatures greater than 250 °C.[7-9] The decomposition temperature as determined by thermogravimetric analysis of the polymers under nitrogen at 10 °C/min was found to be generally greater than 550 °C (Table I). Surprisingly, the diphenylmethane-linked nonconjugated polymers, PDMPQ and PDMDA, were also found to be stable above 550 °C. However, a lower thermal stability (415–500 °C) was exhibited by polymers containing dithienylacetylene or dithienylvinylene linkages. The polymers with dithienylvinylene linkage (PBTVPQ and PBTVDA) showed an onset of decomposition at about 510 °C and the polymers with dithienylacetylene linkage (PBTAPQ and PBTADA) started decomposing at about 415 °C. The lower decomposition temperature of these polymers is attributable to the lower thermal stability of the dithienylvinylene or dithienylacetylene linkages in them. However, their thermal stability is still sufficiently high for their use as thermally stable materials.

Solubilization and Solution Processing. Solutions of polyquinolines and polyanthrazolines (Charts I–III) were easily obtained in organic solvents by using the approach of complexation–mediated solubilization.[5,17] Pure DPP (melt), DCP/*m*-cresol, DPP/*m*-cresol, GaCl$_3$/nitromethane, and DPP/nitromethane are some of the solvent systems successfully used to obtain solutions with a wide range of polymer concentations. Some other combinations of complexing agents and organic solvents have also been studied and found effective in dissolving many of the polyquinolines.[17] Polymer concentrations in excess of 15 wt % could be readily dissolved in 25% (w/w) DCP (or DPP)/*m*-cresol by heating the polymer–solvent mixture at 135 °C for 4–5 h and then cooling it to room temperature. At such high concentrations, most of these conjugated polyquinolines and polyanthrazolines exhibit lyotropic liquid crystalline phases, and hence are categorized as rigid-rod polymers. As an example, Figure 3a shows a photograph of a liquid crystalline phase in a 15 wt % solution of PTPQ in DCP/*m*-cresol (1:3) seen under a cross-polarized microscope at a magnification of 370×. Another photograph in Figure 3b shows the liquid crystalline phase in a 14.4 wt % solution of PSDA in DCP/*m*-cresol (1:3) under similar conditions. The liquid crystalline phases appeared as opaque regions in thin films of the polymer solutions sheared between two glass plates. These mesophase regions disappeared as the thin films of the solutions were heated on a hot plate and reappeared when cooled down. The photographs were taken only when the liquid crystalline regions were found to reappear after a thermal treatment, as described above. This procedure ensured that the textures (Figure 3) seen under the cross-polarizers of an optical microscope were in fact due to lyotropic liquid crystalline phases and not because of shear-induced polymer chain alignment. Some much weaker textures were observed when the polymer chains were aligned by shearing. However, such textures disappeared when polymer chains were allowed to relax either by heat-

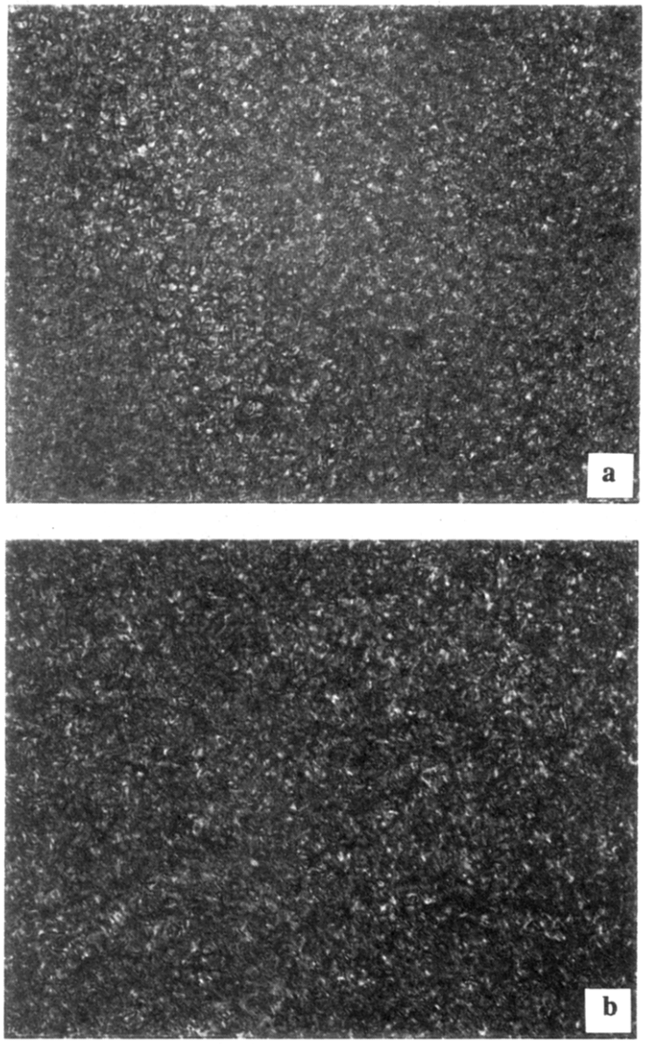


Figure 3. (a) Optical micrograph of the liquid crystalline phase in a 15 wt % PTPQ in DCP/*m*-cresol (1:3) as seen under a cross-polarized microscope at a magnification of 370×. (b) Optical micrograph of liquid crystalline phase in a 14.4 wt % PSDA in DCP/*m*-cresol (1:3) as seen under a cross-polarized microscope at a magnification of 370×.

ing the solution films or by letting them stand overnight.

Dilute solutions of polyquinolines and polyanthrazolines were used to spin coat thin films on substrates or to cast free-standing uniform films on a variety of frames. The coatings of polymer–complex solutions were vacuum dried and then regenerated to the pure polymer films by precipitating them in a mixture of a weak base and a nonsolvent (e.g. 10% (v/v) triethylamine–ethanol). The methods of preparing polymer solutions and their processing into uniform, good quality films have been described in detail elsewhere.[17] The films of the pure polymers were shown to be free of complexing agents by various spectroscopic techniques, for e.g., UV/vis spectroscopy, FT-IR spectroscopy, and thermogravimetric analysis.

Optical Properties. The optical absorption spectra of thin films of the thiophene-linked polymers (Chart II) are shown in Figures 4–7 in comparison to the phenylene-linked polymers. It should be noted that the optical properties of the polymers shown in Charts I and III have been discussed in detail in a recent article.[17] Therefore, optical absorption spectra of thin films of only PBPQ and PBDA in addition to those of thiophene-linked polymers have been included in Figures 4 and 5, respectively, to facilitate comparison between phenylene-linked and thiophene-linked polymers. However, some of the important optical properties of all the homopolymers are compiled in Table I for easy comparison. As can be seen from Figures 4 and 5, replacement of the biphenyldiyl linkage with bithiophene linkage has resulted in a significant red shift of the absorption spectra (λ_{max}) of the polymers. The λ_{max} has increased by about 74 nm from PBPQ to PBTPQ. Similarly, a red shift of about 106 nm in λ_{max} can be observed in PBTDA compared to PBDA. In both cases, when the biphenyldiyl linkage is replaced by the bithiophene linkage, the band gap is reduced by about 0.5 eV (Table I). Compared to the phenylene-linked polymers PPPQ and PPDA, the single thiophene-linked polymers PTPQ and PTDA have higher λ_{max} values by about 45 nm and smaller band gaps by ~0.3 eV (Figures 6 and 7), respectively. Another difference between the optical absorption spectra of the two types of polymer series is the ratio of oscillator strength of the lowest energy

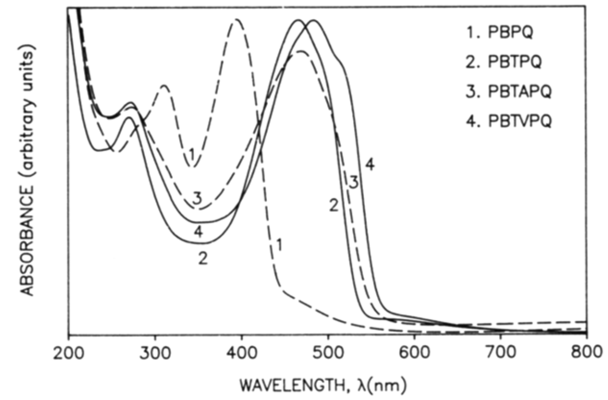


Figure 4. Optical absorption spectra of thin films of PBPQ (**2b**), PBTPQ (**2i**), PBTAPQ (**2j**), and PBTVPQ (**2k**).

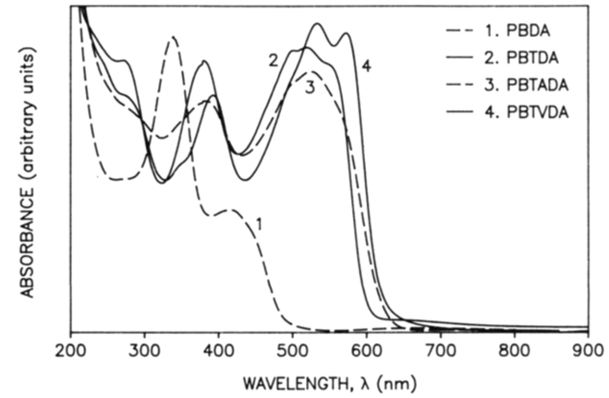


Figure 5. Optical absorption spectra of thin films of PBDA (**3b**), PBTDA (**3i**), PBTADA (**3j**), and PBTVDA (**3k**).

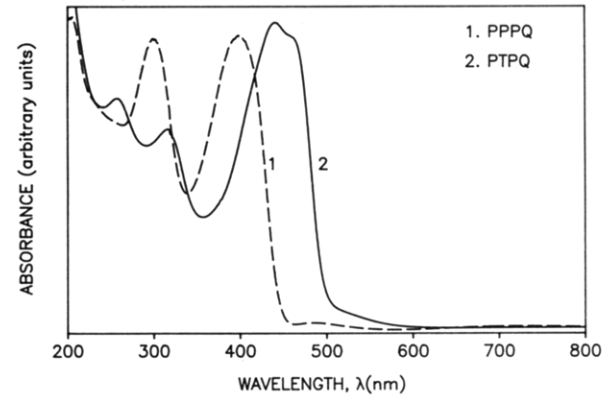


Figure 6. Optical absorption spectra of thin films of PPPQ (**2a**) and PTPQ (**2h**).

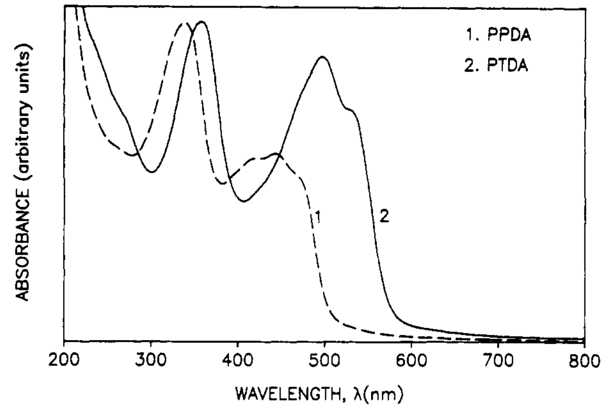


Figure 7. Optical absorption spectra of thin films of PPDA (**3a**) and PTDA (**3h**).

transition to that of the higher energy transitions. In thiophene-linked polymers, this ratio is significantly higher compared to that seen in phenylene-linked polymers. These results clearly demonstrate that by reducing steric hindrance, the thiophene linkage provides a very planar-conjugated backbone in the polymers. Also, the possible delocalization of the lone pair electrons of the sulfur atom in a thiophene ring might contribute to a higher π-electron density in the thiophene-linked conjugated polymers of Chart II.

Similar to the case of biphenyldiyl linked polymers[17] (Chart I), the introduction of an acetylene or vinylene group between the two thiophene units of a dithiophene-linked polymer was expected to facilitate further the π-electron delocalization. As can be seen from Figures 4 and 5 and Table I, the value of λ_{max} is in the order PBTPQ < PBTAPQ < PBTVPQ < PBTDA < PBTADA < PBTVDA and the band gap is in the order PBTPQ > PBTAPQ > PBTVPQ > PBTDA > PBTADA > PBTVDA in support of the above expectations. Another noteworthy point is the effect of the anthrazoline unit in polyanthrazolines versus the bis(quinoline) unit in polyquinolines. Steric hindrance provided by the ortho hydrogens adjacent to the single bond connecting the two quinoline rings in a bis(quinoline) unit forces the polymer segments to be noncoplanar, thereby significantly reducing π-electron delocalization along the conjugated backbone. However, due to the three fused ring structure of anthrazoline, the steric hindrance in this region is eliminated in the polyanthrazolines. Therefore, compared to the polyquinolines (PQ series), polyanthrazolines (DA series) with the same linking group show higher λ_{max} and smaller band gap.

If thiophene-linked polyquinolines are considered as alternating copolymers of the basic polyquinoline PPQ (1) and poly(2,5-thiophenediyl) (PT), the optical properties of the thiophene-linked polyquinolines may be expected to be the molar average of the properties of the constituent homopolymers PPQ and poly(2,5-thiophenediyl). One test of this hypothesis is that the λ_{max} (or optical band gap) should scale linearly (or inversely) with the mole fraction of thiophene moieties in the π-conjugated repeat unit of the polymers. For example, λ_{max} should increase linearly from PPQ through PTPQ and PBTPQ to the pure poly(2,5-thiophenediyl)[29] ($\lambda_{max} \sim 480$ nm). However, the plot in Figure 8 suggests otherwise. The λ_{max} values for PTPQ and PBTPQ deviate significantly from the straight line joining the λ_{max} of the constituent homopolymers PPQ and PT. This observation suggests that the electronic properties of a *block copolymer* such as PTPQ, PBTPQ, and others in Charts I and II cannot be estimated by a simple mathematical interpolation of the properties of the constituent homopolymers. The main reason for this is that *chain microstructure* such as shown in a block copolymer can completely alter the electronic structure of the materials from those of its constituent homopolymers. The results of the λ_{max} and band gap values of the thiophene-linked polyanthrazolines (Table I) also show that the optical properties of the block copolymers can be as good or better than those of the best homopolymers, in this case polythiophene. It has been suggested from theoretical calculations on periodic conjugated block copolymers that the band gap and electronic states of such copolymers are controlled more by the contributions from the moieties of the lower band gap homopolymer than the one with the higher band gap.[30] Our experimental results seem to support such a theoretical argument.

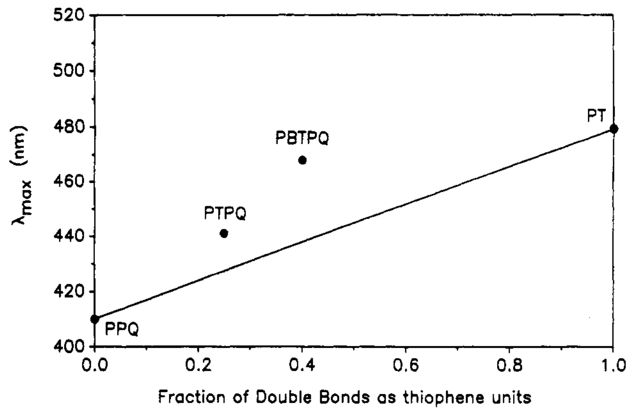


Figure 8. Plot of λ_{max} versus the fraction of double bonds present as thiophene units in a polymer repeat unit of PPQ (**1**), PTPQ (**2h**), PBTPQ (**2i**), and poly(thiophene-2,5-diyl) (PT).

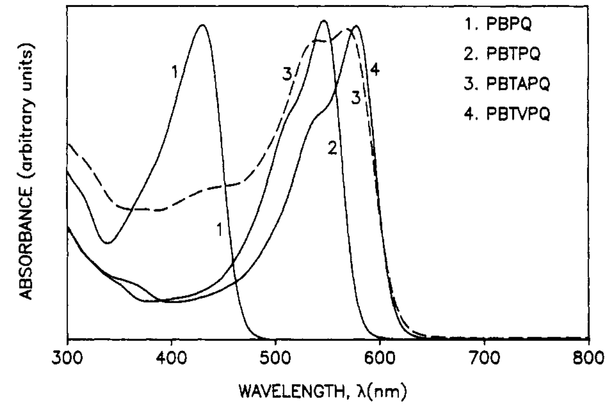


Figure 9. Solution optical absorption spectra of PBPQ (**2b**), PBTPQ (**2i**), PBTAPQ (**2j**), and PBTVPQ (**2k**) in 0.1 mol % DCP/*m*-cresol.

The solution optical absorption spectra of the polyquinolines and polyanthrazolines in 0.1 mol % DCP/*m*-cresol are presented in Figures 9 and 10. Again, compared to the phenylene-linked polymers (PBPQ, PBDA, PPPQ, and PPDA), the thiophene-linked polymers (PBTPQ, PBTDA, PTPQ, and PTDA) exhibit a dramatic red shift of the λ_{max}. For the same set of polymers, these bathochromic shifts are stronger in solutions than in solid-state films. Also, compared to the thin films of the polymers, their solutions in DCP/*m*-cresol show a much higher λ_{max}. The explanation lies in the fact that in solution, the nitrogen atom of the heterocyclic ring forms an acid–base complex with di-*m*-cresyl phosphate, i.e. by protonation, giving a more planar polymer backbone conformation.[17,31] These solution optical spectra also confirm the systematic trends seen in the variation of thin film optical spectra with molecular structure.

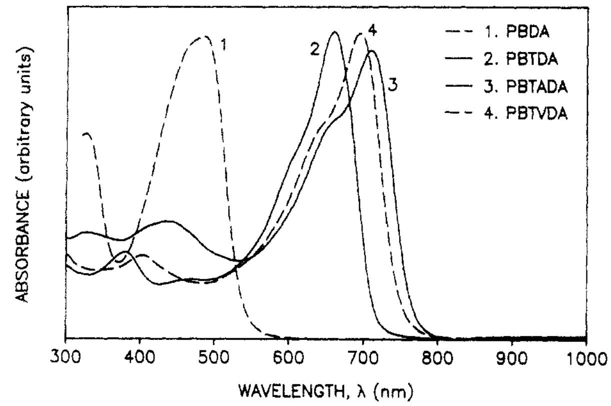


Figure 10. Solution optical absorption spectra of PBDA (**3b**), PBTDA (**3i**), PBTADA (**3j**), and PBTVDA (**3k**) in 0.1 mol % DCP/*m*-cresol.

Conclusions

A series of new conjugated rigid-rod polyquinolines and polyanthrazolines have been synthesized by using a synthetic scheme based on the acid-catalyzed Friedlander reaction. Of particular significance is the result that, compared to the literature method, the polymerization of polyanthrazolines in diaryl phosphate/*m*-cresol gave polymers with significantly higher intrinsic viscosity. Also, it was found that the commercially available diphenyl phosphate (DPP) can be used as the polymerization medium for the synthesis of conjugated polyquinolines and polyanthrazolines instead of di-*m*-cresyl phosphate (DCP) which was difficult to synthesize and purify. All of the polymers were obtained with high intrinsic viscosity and high thermal stability and were easily processable to free-standing films and coatings by using the approach of reversible complexation–mediated solubilization in organic solvents. The polymers could be dissolved in high enough concentrations (>15 wt %) to exhibit lyotropic liquid crystalline phases. By careful manipulation of the structures of the monomers used in the polymerization reaction, a systematic variation in the polymer backbone structure was obtained. These structural variations, achieved through incorporation of different linking groups between bis(quinoline) or anthrazoline rings in the polymer repeat unit, translated into a varying degree of planar conformation of the polymers, as evidenced by the varying degree of π-electron delocalization. In order to establish and compare the effects of thiophene versus phenylene moieties on the electronic structure of conjugated rigid-rod polymers, both phenylene- and thiophene-linked polymers were synthesized.

A comparative study of the optical absorption spectra of the thiophene-linked polymers (Chart II) and the phenylene-linked polymers (Chart I) showed that the thiophene moieties can, by inducing changes in the chain conformation and density of delocalized π-electrons, significantly improve the π-electron delocalization along the polymer backbone. Thus, by replacment of a phenylene linkage with a thiophene linkage of a similar molecular design, a dramatic red shift of the optical band gap by about 0.3–0.5 eV was observed. The present approach of molecular engineering has therefore allowed us to systematically tune the electronic structure and optical properties of the polyquinolines and polyanthrazolines, producing materials with semiconductor band gaps as small as 2.0 eV. The combination of ease of processability, good mechanical and thermal properties, and improved intrinsic electronic properties now qualifies the polyquinolines and polyanthrazolines as an attractive class of new electronic materials which deserve further investigation and development for electronic, optoelectronic, and nonlinear optical applications. This series of conjugated polyquinolines and polyanthrazolines also constitute excellent model systems for investigating structure–property relationships with respect to the electronic, electrochemical,[32] photoconductive,[20] and nonlinear optical[19] properties of conjugated polymers.

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