Synthesis and Processing of Heterocyclic Polymers as Electronic, Optoelectronic, and Nonlinear Optical Materials. 3. New Conjugated Polyquinolines with Electron-Donor or -Acceptor Side Groups

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We report the synthesis, characterization, and preparation of thin films and optical properties of five new polymers containing electron-donor or -acceptor side groups in the class of conjugated polyquinolines. It is found that the electronic structure and linear optical properties of the new phenylated polyquinolines with or without methoxy or fluoro substitutions on the phenyl side group were very similar: a λ_{max} of about 450 nm and a bandgap of ~2.36 eV. The absence of any significant effect of the donor or acceptor side group on the intrinsic electronic and optical properties of the phenylated polyquinolines is explained by the dominant conformational effects of the bulky side group on the π-electron delocalization. The new conjugated polyquinolines with donor or acceptor side-group substituents, by virtue of their asymmetric structure, may prove to be interesting electronic, optoelectronic, and nonlinear optical materials.

Introduction

In our continuing effort to investigate the effects of molecular structure on the electronic, nonlinear optical,[1,2] and optoelectronic properties[3] of conjugated polymers, we have designed and synthesized diverse new polymer structures. The synthesis, characterization, and processing of these polymers are being reported in this series of papers. In part one,[4] the synthesis, processing, and characterization of new conjugated rigid-rod poly(benzobisthiazolevinylenes) were reported. In part two,[5] we presented a series of new polyquinolines and polyanthrazolines with improved intrinsic electronic and optical properties compared with those of the well-known polyquinolines.[6] The present article describes the synthesis and characterization of a new series of conjugated polyquinolines with donor–acceptor side groups.

In an earlier study,[5] we modified the backbone of the polyquinolines in a very systematic way in order to increase as well as tune the π-electron delocalization and electron density along the polymer backbone. Steric hindrances between the various segments of the polymer backbone were reduced or eliminated by introducing conjugated spaces or by fusing the segments together.[5,7] In another approach,[5,8] replacement of the phenylene moieties in the phenylene-linked polyquinolines with thiophene moieties was shown to have substantial and beneficial effect on the electronic and optical properties of the polymers. Compared to the phenylene-linked polyquinolines, the thiophene-linked polymers exhibited a dramatic red shift of the optical absorption spectra, reduction in the bandgap by 0.3–0.5 eV, and a significant increase in the oscillator strength of the lowest energy absorption band. Thus, bithiophene-linked polyquinolines and polyanthrazolines that combine bandgaps of as small as 2.0 eV with good mechanical and thermal properties were realized. These electronic, optical, and structural features of the new polyquinolines and polyanthrazolines render them a potentially important class of electronic and optoelectronic materials.

One of the important structural features which needs investigation in any class of conjugated polymers is the effect of donor–acceptor side groups on its electronic structure and properties. When substituted with electron-donating side groups such as alkoxy (methoxy, ethoxy etc.) substituents, conjugated polymers such as polythiophene,[9] poly(*p*-phenylenevinylene) (PPV),[12a] and polyazomethines[2f] show a significant reduction in the optical bandgap. Copolymerization of unsubstituted and substituted derivatives of conjugated polymers has also been used to fine tune the spectral properties of these materials.

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Recently, it was shown that copolymers of methoxy-PPV and PPV have better electroluminescent properties than the PPV homopolymer alone.[10] Furthermore, theoretical calculations of Garito et al.[11] have shown that by reducing the symmetry of a conjugated polymer structure, donor–acceptor substitutions on a conjugated molecule may enhance its third-order nonlinear optical response. Methoxy derivatives of PPV[12a] and polyazomethines[2f] have been shown to have larger third-order optical nonlinearity than their unsubstituted basic polymers. Also, it has recently been reported that donor–acceptor side-group substitution on conjugated polymers can lead to a large second-order optical nonlinearity with good thermal stability.[12b] Consequently, an investigation of the effects of donor or acceptor side group substitution on the properties of conjugated polyquinolines is of interest and is described in this paper.

Experimental Section

Monomer Synthesis. 5,5′-Diacetyl-2,2′-bithiophene[5,8] and 3,3′-dibenzoylbenzidine[13] were synthesized as described earlier. Di-*m*-cresyl phosphate was prepared according to the literature method[14] and used with freshly distilled *m*-cresol as the reaction medium for polymerization.

5-Bromo-2-(trifluoroacetamido)benzophenone (1). To a solution of 17 g (61.6 mmol) of 2-amino-5-bromobenzophenone[13] in 556 mL of diethyl ether (anhydrous) was added 64.3 g (0.61 mol) of anhydrous sodium carbonate. The mixture was cooled in an ice bath, and trifluoroacetic anhydride was added dropwise as rapidly as possible to maintain at the most a gentle reflux. The reaction mixture was removed from the ice bath and stirred for 30 min at room temperature. The white slurry was separated between 700 mL of water and 700 mL of methylene chloride. After removal of the aqueous phase, the organic phase was washed twice with water and dried over $MgSO_4$. Removal of the solvent gave 22.3 g (97.4%) of an off-white solid; mp 138 °C (lit. 136–138 °C);[15] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.54–7.59 (m, 2 H), 7.66–7.80 (m, 5 H), 8.55 (d, 1 H), 11.89 (br s, 1 H).

1,2-Bis(trifluoroacetamido)-3,3′-dibenzoyldiphenyl-1,1′-acetylene (2). To a mixture of 22 g (59.1 mmol) of **1** in 220 mL of dry toluene was added a mixture of 1 g of tetrakis(triphenylphosphine)palladium(0) in 50 mL of dry toluene under argon. The light brown solution so obtained was heated to reflux, and to this solution was added dropwise a solution of 17.9 g (29.6 mmol) of bis(tri-*n*-butylstannyl)acetylene in 92 mL of dry toluene. On completion of the addition, the reaction was refluxed for an additional 10 h. The reaction was cooled to −5 °C, and a yellow product isolated by suction filtration, followed by drying. The crude yield was 14.5 g (80%). The product was purified by recrystallization from 300 mL of tetrahydrofuran; yield 13.2 g (73%); mp 253.8 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.53–7.58 (m, 4 H), 7.66–7.81 (m, 10 H), 8.65 (d, 2 H), 12.04 (br s, 2 H). Anal. Calcd for $C_{32}H_{18}N_2O_4F_6$: C, 63.16; H, 2.98; N, 4.60. Found: C, 62.84; H, 2.79; N, 4.55.

4,4′-Diamino-3,3′-dibenzoyldiphenyl-1,1′-acetylene (3). A mixture of 13 g (21.4 mmol) of **2**, 425 mL of degassed ethanol, 105.3 mL of water, and 19.15 g (0.181 mol) of anhydrous sodium carbonate was refluxed for 72 h. The yellow slurry was cooled to room temperature, and the product was separated by filtration. After the product was washed twice with water and then with a little methanol, it was dried in vacuum at 70 °C for 24 h. The crude yield was 8.66 g (97.3%). The product was purified by continuously extracting it in dioxane using a Soxhlet apparatus (with a double-thickness thimble lined with Whatman 42 filter paper) till all of the product was dissolved and recrystallized in the boiling flask. The pure product was recovered by suction filtration, washed with hexane and methanol, and dried in vacuum at 60 °C for 24 h; yield 7.5 g (84%); mp 310.1 °C; ^{1}H NMR (dioxane-d_6, 300 MHz) δ 6.65 (d, 2 H), 6.8 (br s, 4 NH), 7.3 (d, 2 H), 7.4–7.65 (m, 12 H); FT-IR (KBr, cm^{-1}) 3457, 3338, 1630, 1619, 1578, 1545, 1488, 1445, 1417, 1381, 1326, 1306, 1290, 1245, 1170, 1135, 975, 911, 880, 831, 807, 758, 712, 706, 659, 552. Anal. Calcd for $C_{28}H_{20}N_2O_2$: C, 80.75; H, 4.84; N, 6.73. Found: C, 80.53; H, 4.71; N, 6.46.

3-(*p*-Methoxyphenyl)-5-bromo-2,1-benzisoxazole (4). To a solution of 148 g of potassium hydroxide in 300 mL of anhydrous methanol at 0 °C was added 21.3 g (0.145 mole) of 4-methoxyphenylacetonitrile. The mixture was stirred at 0 °C for 10 min, and then a solution of 25.4 g (0.126 mol) of *p*-bromonitrobenzene in 300 mL of tetrahydrofuran and methanol (1:2) was slowly added over 1 h. The deep purple mixture was continuously stirred and maintained at 0–5 °C during addition. The temperature was then raised to 55 °C using a hot water bath and the reaction mixture was stirred for another 3 h. On cooling, the reaction mixture was poured into 1500 mL of water, and the brown precipitate was separated by suction filtration. The product was washed twice with water followed by cold methanol. The yellow solid so obtained was recrystallized twice from methanol to give needle like light yellow crystals; yield 19.5 g (51%); mp 137.1 °C. Anal. Calcd for $C_{14}H_{10}NO_2Br$: C, 55.29; H, 3.31; N, 4.61. Found: C, 54.99; H, 3.14; N, 4.62.

2-Amino-5-bromo-4′-methoxybenzophenone (5). To a solution of 19.3 g of **4** in 193 mL of acetic acid (glacial) at 95 °C was added 28.95 g of iron filings and 63 mL of water in 12 equal portions over 3 h. The reaction was allowed to run for an additional 20 min, after which it was cooled down to room temperature. This step gave a green slurry which was diluted with 1500 mL of water. A yellow product was extracted from this mixture in ethyl ether and was then washed with sodium carbonate solution followed by water and dried over $MgSO_4$. Removal of solvent gave a yellow solid product which was recrystallized from methanol to give a yield of 16.6 g (85.4%); mp 120.4 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.9 (s, 3 H), 5.87 (br s, 2 H), 6.64 (d, 1 H); 6.96 (d, 2 H), 7.32–7.4 (m, 1 H), 7.57 (d, 1 H), 7.65–7.75 (d, 2 H). Anal. Calcd for $C_{14}H_{12}NO_2Br$: C, 54.92; H, 3.95; N, 4.57. Found: C, 54.70; H, 3.74; N, 4.56.

5-Bromo-4′-methoxy-2-(trifluoroacetamido)benzophenone (6). To a solution of 16 g (52.3 mmol) of **5** in 368 g of ethyl ether (dry) was added 54 g (0.515 mol) of sodium carbonate (anhydrous). The slurry was cooled in an ice bath, and 37.2 mL (0.263 mol) of trifluoroacetic anhydride was added dropwise as rapidly as possible to maintain at most a gentle reflux. The thick white slurry so obtained was stirred at room temperature for another 45 min and then phase separated into two layers, 500 mL of methylene chloride and 500 mL of water. The aqueous layer was removed, and the organic layer was washed twice with water before drying it over $MgSO_4$. Removal of solvent gave 21.02 g (95.5%) of off-white product; mp 148.9 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.93 (s, 3 H), 7.02 (d, 2 H), 7.75–7.78 (m, 4 H), 8.49 (d, 1 H), 11.66 (br s, 1 H). Anal. Calcd for $C_{16}H_{11}NO_3BrF_3$: C, 47.79; H, 2.76; N, 3.48. Found: C, 47.67; H, 2.70; N, 3.51.

4,4′-Bis(trifluoroacetamido)-3,3′-di-*p*-methoxybenzoyldiphenyl-1,1′-acetylene (7). To a solution of 19.5 g of **6** in 233 mL of dry toluene was added a mixture of 1 g of tetrakis(triphenylphosphine)palladium(0) and 50 mL of dry toluene under argon. The mixture was heated to reflux, and to it was added dropwise a solution of 14.6 g (24.2 mmol) of bis(tri-*n*-butylstannyl)acetylene in 76.5 mL of dry toluene over 2 h. The reaction was refluxed for an additional 10 h during which time part of orange-yellow product precipitated. After cooling the reaction mixture to −5 °C, the product was isolated by suction

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filtration (crude yield 13.03 g, 80%). The product was purified by continuously extracting it in toluene using Soxhlet apparatus (with double-thickness thimble lined with Whatman 42 filter paper) until all of the product was dissolved and collected in the boiling flask. The pure product was recovered by suction filtration of the cold toluene mixture (at −5 °C); yield 11 g (68%); mp 261.2 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.93 (s, 6 H), 7.02 (d, 4 H), 7.75–7.80 (m, 8 H), 8.60 (d, 2 H), 11.82 (br s, 2 H). Anal. Calcd for $C_{34}H_{22}N_2O_6F_6$: C, 61.08; H, 3.32; N, 4.19. Found: C, 60.80; H, 3.20; N, 4.19.

4,4′-Diamino-3,3′-di-*p*-methoxybenzoyldiphenyl-1,1′-acetylene (8). 7 (11 g) was mixed with 350 mL of degassed ethanol, 89 mL of water, and 15 g (0.142 mol) of sodium carbonate. The mixture was refluxed for 84 h. A bright yellow slurry was cooled to room temperature and filtered, and the solid product dried to give a crude yield of 7.7 g. The product was purified by continuously extracting it in dioxane using Soxhlet apparatus (with double thickness thimble lined with Whatman 42 filter paper) until all of the product was dissolved and recrystallized in the boiling flask. The pure product was recovered by suction filtration and dried in vacuum at 60 °C for 24 h. The yield was 6.3 g (80%); mp 235.3 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.90 (s, 6 H), 6.01 (br s, 4 NH), 6.67 (d, 2 H), 6.97 (m, 4 H), 7.37 (d of d, 2 H), 7.60 (d, 2 H), 7.68 (d, 4 H); FT-IR (KBr, cm^{-1}) 3457, 3345, 1624, 1602, 1562, 1570, 1508, 1461, 1441, 1415, 1363, 1305, 1258, 1243, 1172, 1111, 1028, 977, 957, 881, 843, 785, 695, 635, 614. Anal. Calcd for $C_{30}H_{24}N_2O_6$: C, 75.62; H, 5.08; N, 5.88. Found: C, 75.86; H, 5.01; N, 5.78.

5-Bromo-2′-fluoro-2-(trifluoroacetamido)benzophenone (9). To a solution of 12 g of 2-amino-5-bromo-2′-fluorobenzophenone (Lancaster) in 407 mL of dry diethyl ether was added 42.6 of anhydrous sodium carbonate. The reaction mixture was cooled in an ice bath, and 29 mL of trifluoroacetic anhydride was added dropwise as rapidly as possible while maintaining at most a gentle reflux. Thereafter, the ice bath was removed, and the reaction mixture was stirred for 30 min at room temperature. The off-white reaction slurry was phase separated into two layers of a 500 mL of methylene chloride and a 500 mL of water phase. The aqueous layer was removed, and the organic layer was washed twice with water and dried over $MgSO_4$. Filtration and evaporation of the solvent gave 15.7 g (98.5%) of product; mp 132 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.26 (d, 1 H), 7.35 (t, 1 H), 7.50–7.55 (m, 1 H), 7.60–7.67 (m, 1 H), 7.72 (t, 1 H), 7.77–7.81 (d of d, 1 H), 8.62 (d, 1 H), 12.29 (s, 1 NH). Anal. Calcd for $C_{15}H_8NO_2BrF_4$: C, 46.18; H, 2.07; N, 3.59. Found: C, 46.33; H, 1.94; N, 3.68.

4,4′-Bis(trifluoroacetamido)-3,3′-di-*o*-fluorobenzoyldiphenyl-1,1′-acetylene (10). To a solution of 15 g (38.4 mmol) of 9 in 100 mL of dry toluene was added a mixture of 1 g of tetrakis(triphenylphosphine)palladium(0) in 50 mL of dry toluene under argon. The reaction mixture was then heated to reflux, and to this mixture was added dropwise a solution of 11.6 g (19.2 mmol) of bis(tri-*n*-butylstannyl)acetylene in 60 mL of toluene (dry) over 2 h. The reaction was refluxed for additional 10 h after which it was cooled to −5 °C. The yellow crystals of product were isolated by suction filtration followed by washing with hexane. The crude product obtained (12.4 g) was dissolved in excess chloroform, filtered, and then recrystallized from chloroform to give a yield of 7.6 g (61.1%); mp 267.2 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.26 (t, 2 H), 7.35 (t, 2 H), 7.5–7.55 (m, 2 H), 7.59–7.67 (m, 2 H), 7.72 (t, 2 H), 7.76–7.81 (d of d, 2 H), 8.71 (d, 2 H), 12.29 (s, 2 NH). Anal. Calcd for $C_{32}H_{16}N_2O_4F_8$: C, 59.64; H, 2.50; N, 4.35. Found: C, 59.24; H, 2.41; N, 4.33.

4,4′-Diamino-3,3′-di-*o*-fluorodibenzoyldiphenyl-1,1′-acetylene (11). A mixture of 7.35 g (11.5 mmol) of **10**, 10.36 g (98 mmol) of anhydrous sodium carbonate, 57 mL of water, and 230 mL of degassed ethanol was heated at reflux for 72 h. On cooling, the solid product was separated by suction filtration, washed with water (twice), and dried in a vacuum oven. The crude yield was 5.05 g. The product was purified by continuously extracting it in chloroform using a Soxhlet apparatus (with double-thickness thimble layered with Whatman 42 filter paper) until all of the product was dissolved and recrystallized in the boiling flask. Upon cooling, the product was isolated by suction filtration and dried overnight in vacuum oven at 60 °C. The yield was 4.24 g (82%). The product does not show any melting point but an exothermic peak (possibly cross-linking) starts at around 290 °C; ^{1}H NMR (dioxane-d_6, 300 MHz) δ 6.67 (d, 2 H), 7.17 (br s, 4 H), 7.30 (d of d, 4 H), 7.27–7.33 (m, 4 H), 7.38–7.60 (m, 4 H); FT-IR (KBr, cm^{-1}) 3464, 3338, 1638, 1621, 1582, 1545, 1485, 1450, 1420, 1364, 1329, 1307, 1289, 1270, 1245, 1218, 1172, 1138, 976, 887, 830, 817, 757, 648. Anal. Calcd for $C_{28}H_{18}N_2O_2F_2$: C, 74.33; H, 4.01; N, 6.19; F, 8.40. Found: C, 73.98; H, 3.93; N, 6.12; F, 8.46.

Polymer Synthesis. Polymers PBTPQ (**12**) and PBTDA (**13**) were synthesized as described earlier.[5,8] The new polymers were synthesized as follows:

(*i*) *Poly(2,2′-(2,2′-bithiophene)-6,6′-bis(4-phenylquinoline)-acetylene) (PBTPQA, 14).* Equimolar amounts (1.2 mmol each) of both 4,4′-diamino-3,3′-dibenzoyldiphenyl-1,1′-acetylene (**3**) and 5,5′-diacetyl-2,2′-bithiophene were added to a solution of 12 g of di-*m*-cresyl phosphate (DCP) and 15 g of freshly distilled *m*-cresol in a cylindrically 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 90 °C. The reaction was run at this temperature for 24 h and then at 120–130 °C for an additional 10 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 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. The yield was 0.43 g (60.2%). [η] = 0.89 dL/g (25 °C, 0.5 mol % DCP/*m*-cresol); FT-IR (KBr, cm^{-1}): 3050, 2910, 1584, 1542, 1490, 1457, 1438, 1361, 1290, 1229 (w), 1155, 1074, 1030, 873, 835, 797, 767, 700, 619, 584; Anal. Calcd for $(C_{40}H_{22}N_2S_2)_n$: C, 80.78; H, 3.73; N, 4.71. Found: C, 77.5; H, 4.32; N, 3.96.

(*ii*) *Poly(2,2′-(2,2′-bithiophene)-6,6′-bis(4-(p-methoxy)phenylquinoline)acetylene) (PBTPQA-OCH$_3$, 15).* Equimolar amounts (1.2 mmol each) of both 4,4′-diamino-3,3′-di-*p*-methoxybenzoyldiphenyl-1,1′-acetylene (**8**) and 5,5′-diacetyl-2,2′-bithiophene were added to a solution of 12 g of di-*m*-cresyl phosphate (DCP) and 15 g of freshly distilled *m*-cresol in a reaction flask as described in (i). The reactor was purged with argon for 10–15 min before the temperature was raised slowly to 60 °C and then to 90 °C. The reaction was run at 90 °C for 4 h and then at 110 °C for additional 15 h under static argon. The temperature was then raised to 125–130 °C for 5 h and then to 140 °C for 2 h. As the viscosity of the reaction mixture increased with time, additional *m*-cresol was added to the reaction mixture to maintain dilute conditions. Thereafter the reaction was quenched, precipitated, and purified as described above. The yield of polymer was 0.63 g (80%); [η] = 1.1 dL/g (25 °C, 0.5 mol % DCP/*m*-cresol); FT-IR (KBr, cm^{-1}) 3055, 2914, 1649, 1608, 1583, 1541, 1511, 1453, 1439, 1400, 1362, 1291, 1248, 1176, 1031, 832, 798, 573. Anal. Calcd for $(C_{42}H_{26}N_2O_2S_2)_n$: C, 77.04; H, 4.00; N, 4.28. Found: C, 74.27; H, 4.51; N, 3.60.

(*iii*) *Poly(2,2′-(2,2′-bithiophene)-6,6′-bis(4-(o-fluoro)phenylquinoline)acetylene) (PBTPQA-F, 16).* Equimolar amounts (0.663 mmol each) of both 4,4′-diamino-3,3′-di-*o*-fluorodibenzoyldiphenyl-1,1′-acetylene (**11**) and 5,5′-diacetyl-2,2′-bithiophene were reacted as described in (i). The polymer product was collected and purified as usual. The yield was 0.2 g (48%); [η] = 0.65 dL/g (25 °C, 0.5 mol % DCP/*m*-cresol); FT-IR (KBr, cm^{-1}) 1616, 1585, 1543, 1518, 1487, 1447, 1433, 1358, 1290, 1270, 1227 (s), 1156, 1100, 1064, 1032, 877, 835, 799, 758, 619, 589. Anal. Calcd for $(C_{40}H_{20}N_2S_2F_2)_n$: C, 76.17; H, 3.2; N, 4.44. Found: C, 74.66; H, 3.87; N, 3.72.

Copolymer Synthesis. (*iv*) *PBTPQ/PBTPQA-OCH$_3$ (80:20) (17).* 8 (0.255 mmol), 1.02 mmol of 3,3′-dibenzoylbenzidine,[13] and 1.275 mmol of 5,5′-diacetyl-2,2′-bithiophene were mixed together in a reaction medium of 12 g of DCP and 2 g of *m*-cresol. After the reactor was purged with argon for 10–15 min, the temperature was raised slowly to 90 °C. The reaction was run at this temperature for 9 h and then at 110 °C for 15 h followed by 135–140 °C for additional 24 h under static argon. As the viscosity of the reaction mixture increased with time, additional *m*-cresol was added to the reaction mixture to facilitate efficient stirring. Thereafter the reaction was quenched, precipitated, and purified as described in (i). The yield was 0.72 g (96%); [η] = 3.6 dL/g (25 °C, 0.1 mol % DCP/m-cresol); FT-IR (freestanding

film, cm^{-1}) 3062, 2967, 1659, 1606, 1586, 1544, 1513, 1489, 1455, 1441, 1360, 1290, 1248, 1230, 1177, 1150, 1074, 1031, 874, 827, 795, 768, 744, 701, 621, 590, 571.

(*v*) *PBTPQ/PBTPQA-F (80:20)* (*18*). 11 (0.255 mmol), 1.02 mmol of 3,3′-dibenzoylbenzidine,[13] and 1.275 mmol of 5,5′-diacetyl-2,2′-bithiophene were mixed together in a reaction medium of 12 g of DCP and 2 g of *m*-cresol. The reactor was purged with argon for 10–15 min before the temperature was raised slowly to 90 °C. The reaction was run at this temperature for 2 h and then at 100 °C for 3 h followed by 130 °C for additional 25 h under static argon. As the viscosity of the reaction mixture increased with time, additional *m*-cresol was added to the reaction mixture to facilitate efficient stirring. Thereafter the reaction was quenched, precipitated, and purified as described in (i). The yield was 0.69 g (93%); $[\eta]$ = 1.9 dL/g (25 °C, 0.1 mol % DCP/*m*-cresol); FT-IR (freestanding film, cm^{-1}) 3062, 2968, 1587, 1544, 1521, 1488, 1460, 1442, 1360, 1286, 1229, 1075, 826, 794, 766, 701.

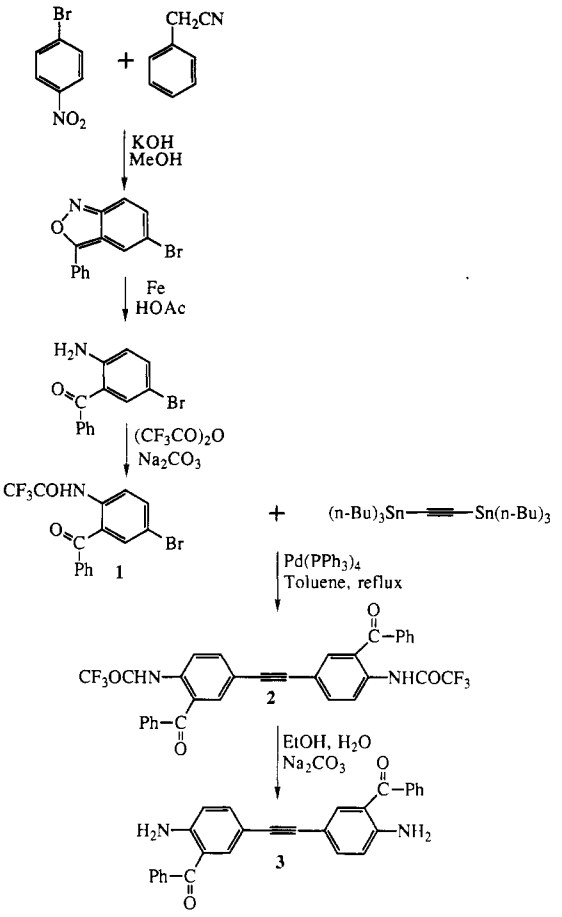
Characterization. Intrinsic viscosity $[\eta]$ of the polymers was measured using dilute solutions in the range 0.5–0.02 g/dL in 0.1–0.5 mol % DCP/*m*-cresol at 25 °C. The FT-IR spectra of freestanding polymer films were recorded on a Nicolet FTIR spectrometer. In the case of polymers where good-quality freestanding 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. (Whitehouse, 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/NIR spectrophotometer (Model Lambda 9). Similarly, solution optical absorption spectra of the polymers were obtained by using dilute solutions of polymers in 0.1 mol % DCP/*m*-cresol solvent. Thermal analysis of pressed polymer powder or films were performed on a du Pont Thermal Analyst 2100 equipped with a Model 951 thermogravimetric analyzer (TGA).

Solubilization and Thin-Film Processing. The polymers were solubilized and processed using the same technique as described earlier for other polyquinolines.[7] 4–5 wt % solutions of polymers were prepared by gently heating a mixture of polymer and diphenyl phosphate (DPP); solid powder at room temperature) for a few hours. This procedure resulted in formation of a polymer–diphenyl phosphate complex which was soluble in excess DPP. The hot viscous solution was used for spin coating thin films of the polymer complex on heated silica substrates. Cooling of the substrates during the spinning process resulted in solid polymer–complex coatings which were regenerated to the pure polymer films by precipitating them in a 10% triethylamine/ethanol nonsolvent system. The films were then washed in methanol and dried in vacuum oven at 80 °C for a few hours. Suitable polymer solutions for preparing films could also be made in 18 wt % $GaCl_3$/nitromethane and di-*m*-cresyl phosphate/organic solvents.[7]

Results and Discussion

Monomer Synthesis. The synthesis of the monomer 4,4′-diamino-3,3′-dibenzoyldiphenyl-1,1′-acetylene (**3**) is described in Scheme I. First, bromobenzisoxazole was prepared by treating *p*-bromonitrobenzene with acetonitrile in basic methanol and tetrahydrofuran.[13] This was then reduced to 2-amino-5-bromobenzophenone using iron and acetic acid and purified by recrystallization from methanol as described in the literature.[13] Before proceeding with the coupling reaction, the amino group in 2-amino-5-bromobenzophenone was protected as trifluoroacetamide.[15] 5-Bromo-2-(trifluoroacetamido)-benzophenone (**1**; 2 mol) was then coupled with 1 mol of bis(tributylstannyl)acetylene in dry toluene using tetra

Scheme I



kis(triphenylphosphine)palladium(0) catalyst. Deprotection of **2** with basic aqueous ethanol and purification of the product by continuous extraction and recrystallization in dioxane gave **3** in an overall yield of 67%.

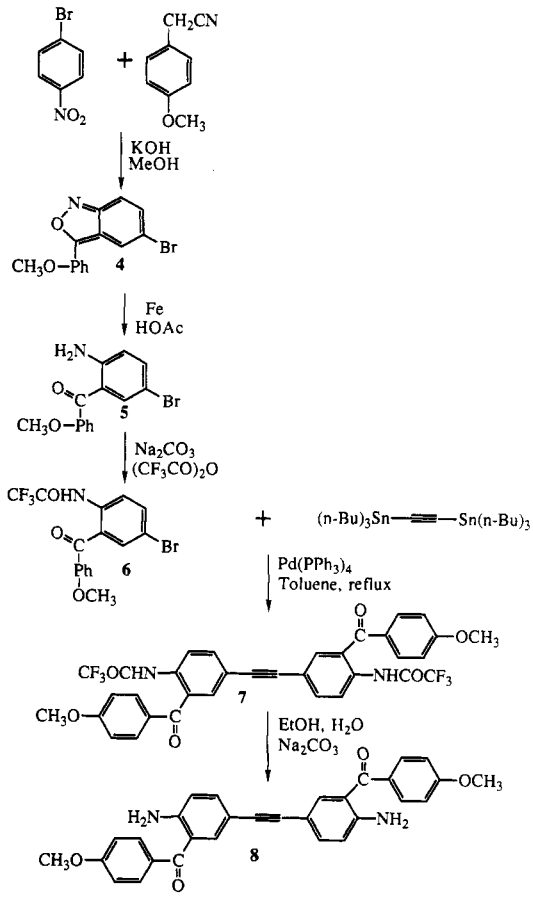
In Scheme II, the synthesis of the monomer 4,4′-diamino-3,3′-di-*p*-methoxybenzoyldiphenyl-1,1′-acetylene (**8**) is described. The procedure is a modification of Scheme I where 4-methoxyphenylacetonitrile instead of phenylacetonitrile was reacted with *p*-bromonitrobenzene to give 3-(*p*-methoxyphenyl)-5-bromo-2,1-benzisoxazole (**4**). Compound **4** was reduced using iron filings and acetic acid to give 2-amino-5-bromo-4′-methoxybenzophenone (**5**). Protection of the amino group of **5** followed by coupling of **5** with bis(tributylstannyl)acetylene using palladium(0) catalyst and then deprotection of amino groups gave the final monomer **8** in a good yield. The product was purified by continuously extracting it in dioxane followed by recrystallization from dioxane. The overall yield was 55%.

The monomer 4,4′-diamino-3,3′-di-*o*-fluorodibenzoyldiphenyl-1,1′-acetylene (**11**) was synthesized in three steps as shown in Scheme III. Procedures similar to those used for the synthesis of **3**, i.e., protection of amino group in 2-amino-5-bromo-2′-fluorobenzophenone by converting it to trifluoroacetamide (**9**), coupling of **9** with bis(tributylstannyl)acetylene to give **10**, and deprotection of amino groups of **10** using basic aqueous ethanol gave **11** in a good yield. The product was purified by extraction and recrystallization from chloroform. The overall yield for the three steps was 50%.

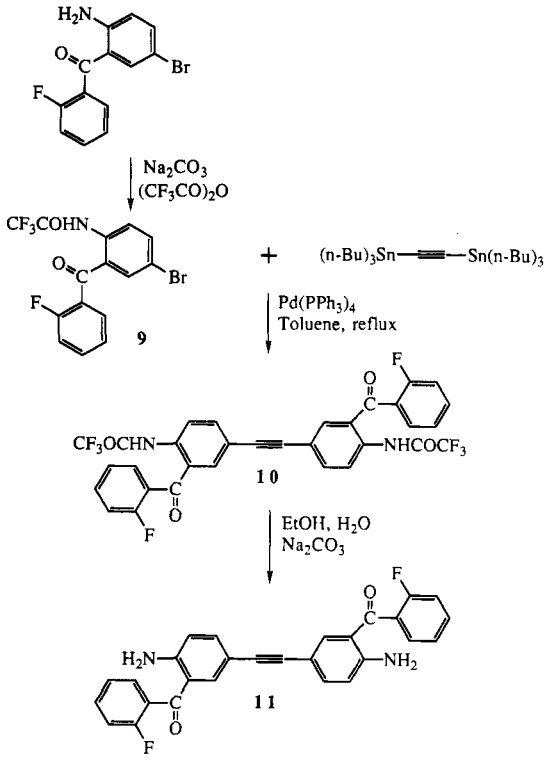
Polymer Synthesis. The acetylene linkages in the new bis(amino ketone) monomers **3**, **8**, and **11** were found to be highly reactive under the normal polymerization

(15) Zimmermann, E. K.; Stille, J. K. *Macromolecules* **1985**, *18*, 321–327.

Scheme II

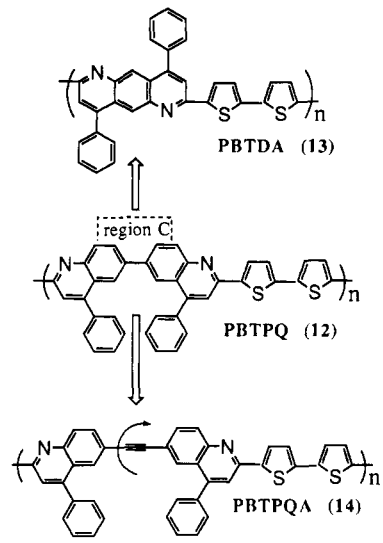


Scheme III



conditions[5] used for the synthesis of high molecular weight polyquinolines. This observed behavior of the new bis(amino ketone) monomers (**3**, **8**, **11**) containing acetylene linkage contrasts sharply with acetylene-containing bis(keto methylene) monomers such as bis(acetylphenyl)-

Chart I

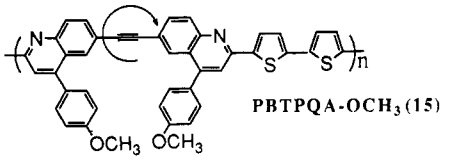


acetylene which we have previously used to achieve *soluble* high molecular weight conjugated polyquinolines.[5] When the polymerization of **3**, **8**, or **11** was carried out at high monomer concentration to achieve high reaction-medium viscosity, the polymers obtained were highly cross-linked and insoluble in the normal solvents.[5] An approach of using imbalanced monomer ratio to achieve low molecular weight soluble polymers was unsuccessful. Therefore, the cross-linking problem was circumvented by polymerization of the acetylene-linked monomers (**3**, **8**, **11**) under extremely dilute conditions and at relatively lower reaction temperatures (see Experimental Section). However, a high temperature (~130–140 °C) was used for a short time (a few hours) at the end of the reaction to ensure complete cyclization. This approach was successful for preparing soluble linear polymers. However, the intrinsic viscosity of the resulting polymers, and hence their molecular weight, was found to be quite low compared to the polyquinolines reported earlier.[5]

Another approach for diluting the concentration of acetylene monomers in a polymerization reaction medium is to use an additional monomer (of the same functionality as the acetylene monomers) in the reaction, i.e., random copolymerization. High molecular weight random copolymers were obtained when two bis(amino ketone) monomers (A–A monomers) **3** (or **8**) and 3,3′-dibenzoylbenzidine (which is not susceptible to cross-linking) were copolymerized with a bis(ketomethylene) monomer (B–B monomer), in this case 5,5′-diacetyl-2,2′-bithiophene. By reducing the mole percentage of acetylene monomer (**3** or **8**) (to 20 mol %) in comparison to that of 3,3′-dibenzoylbenzidine (80%), the effective concentration of the acetylene monomer in the reaction mixture was lowered, thereby, essentially eliminating the chances of cross-linking. This approach of random copolymerization is important as it provides not only a way to incorporate acceptor–donor substitutions in this class of polymers but also a chance to fine tune the electronic, optoelectronic, and nonlinear optical properties of the resultant materials.

The polymers **14**–**18** shown in Charts I–III were characterized by thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), UV/vis spectroscopy, intrinsic viscosity measurement, and elemental analysis. Homopolymers containing acetylene linkages were stable to about 450 °C in nitrogen, whereas the

Chart II



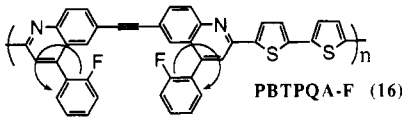
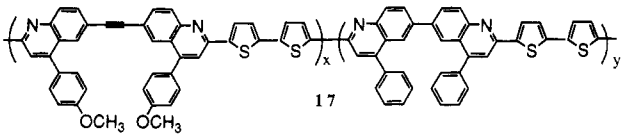
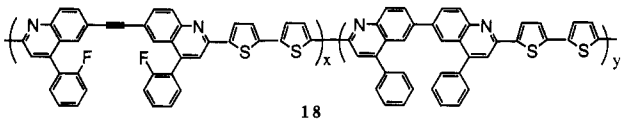


Chart III





copolymers with only 20 mol % of acetylene linkages were stable to a slightly higher temperature (525 °C). This slightly lower thermal stability of the acetylene-linkage polymers compared to the previously reported polyquinolines,[5] such as PBTPQ and PBTDA, is attributable to the lower thermal stability of the acetylene moiety. The IR spectra of the polymers were consistent with the proposed structures shown in Charts I–III. The IR bands characteristic of the functional groups of the monomers, two bands in the regions 3320–3340 and 3443–3460 cm^{-1} corresponding to primary amines and one strong band in the region 1624–1656 cm^{-1} corresponding to the carbonyl group, are absent in the IR spectra of the polymers. The absence of these bands characteristic of the functional groups of the monomers in the IR spectra of the polymers along with the appearance of some new strong bands characteristic of quinolines in the region 1600–1400 cm^{-1} suggest the complete ring closure to form the quinoline units in the polymerization reaction. A strong band at 758 cm^{-1} characteristic of ortho-substituted benzene and another strong band at 1227 cm^{-1} characteristic of monosubstituted aryl fluorides in the IR spectrum of PBTPQA–F confirm the presence of fluorine atoms on the phenyl side groups in the polymer chain. Similarly, in the IR spectrum of PBTPQA–OCH_3, the strong band at 832 cm^{-1} characteristic of para-substituted benzene and a pair of strong bands at 1248 and 1031 cm^{-1} characteristic of, respectively, asymmetric and symmetric stretching of aryl alkyl ether (C–O–CH_3) group confirm the presence of the methoxy substitution on the phenyl side group in the polymer structure (Chart II). The IR spectrum of PBTPQA, which does not have any substitution on the phenyl side group, shows a strong band at 700 cm^{-1} which is characteristic of a monosubstituted benzene.

Solubility and Processing. The polymers were readily solubilized and processed, similar to the other polyquinolines, using the approach of complexation mediated solubilization and processing.[7,16] Di-*m*-cresyl phosphate/*m*-cresol, diphenyl phosphate/*m*-cresol or lewis acids ($GaCl_3$)/nitromethane are some of the solvent systems found to be very effective for obtaining solutions with high polymer concentrations. These solutions were used to prepare thin films on substrates by spin coating or to obtain freestanding films as described earlier.[7] Our attempts to obtain freestanding films of the polymers PBTPQA, PBTPQA-F, and PBTPQA-OCH_3 were unsuccessful owing to their low molecular weights. However, thin films of 1 μm thick or less were easily spin coated onto silica substrates and used for characterizations of various physical properties. As usual, all films were found to be free of complexing or solvent species by spectroscopic techniques.[7]

Optical Properties

Our recent studies[5,7] on polyquinolines such as PBTPQ and other derivatives have shown that the hydrogen atoms ortho to the bond between the two quinoline units in polyquinolines provide steric hindrance (region C, Chart I). This hindrance forces the two rings to be noncoplanar to each other and, hence, limits π-electron delocalization along the polymer backbone. We have shown in our previous studies that this steric hindrance in region C can be eliminated by replacing the two quinoline units of polyquinolines with a single three fused ring moiety, anthrazoline (as in PBTDA, Chart I). This modification resulted in a substantial increase in the π-electron delocalization of the anthrazoline polymers (for example, PBTDA) as evidenced by their smaller bandgap and larger λ_{max} (Table I) compared to those of bis(quinoline) polymers (for example PBTPQ). On the basis of those observations, one can expect that if the two quinoline rings of a polyquinoline are pushed apart by introducing a conjugated spacer (for example, an acetylene linkage), the resulting polyquinoline may have a reduced degree of steric hindrance and hence may show improved π-electron delocalization compared to that without the spacer.

PBTPQA was designed to introduce an acetylene linkage between its two quinoline units. The structure of PBTPQA in all other aspects was kept equivalent to that of PBTPQ (Chart I). Figure 1 shows the linear optical absorption spectra of the thin films of PBTPQA and PBTPQ along with the other new polyquinolines. As can be seen from Figure 1, the spectrum of PBTPQA is slightly blue shifted compared to that of PBTPQ, i.e., PBTPQA has a λ_{max} of 448 nm and a bandgap of 2.36 eV, whereas PBTPQ has a higher λ_{max} of 468 nm with a slightly smaller bandgap of 2.33 eV (Table I). These results are contrary to expectations. Although introduction of a conjugated spacer between the two quinoline rings has removed the above-mentioned steric hindrance, it seems that it has provided a higher degree of mobility (higher rotational freedom) to the quinoline segments of the PBTPQA compared to PBTPQ. Because of this additional rotational freedom, the bulky phenyl-substituted quinoline units may now prefer a highly noncoplanar conformation. This inference is supported by the fact that as the size of the bulky phenylquinoline is increased by a methoxy substituent at the para position of the phenyl side group in

(16) (a) Jenekhe, S. A.; Johnson, P. O.; Agrawal, A. K. *Macromolecules* **1989**, *22*, 3216–3222. (b) Jenekhe, S. A.; Johnson, P. O. *Macromolecules* **1990**, *23*, 4419–4429. (c) Roberts, M. F.; Jenekhe, S. A. *Polym. Commun.* **1990**, *31*, 215–217.

Table I. Properties of Conjugated Polyquinolines

	polymer	[η] (dL/g)	thermal stability[b] (°C)	λ_{max} (film) (nm)	E_g (film) (eV)	λ_{max} (soln)[a] (nm)	log ϵ^a
12	PBTPQ	11.5	590	468	2.33	546	5.06
13	PBTDA	2.30	600	520	2.07	659	4.90
14	PBTPQA	0.89	470	448	2.36	543	4.81
15	PBTPQA-OCH_3	1.10	465	444	2.36	537	4.70
16	PBTPQA-F	0.65	465	455	2.33	554	4.76
17	PBTPQ/PBTPQA-OCH_3 (80:20)	3.6	525	459	2.36	543	5.07
18	PBTPQ/PBTPQA-F (80:20)	1.90	530	462	2.33	545	4.94

[a] Solutions made in 0.1 mol % DCP/m-cresol. [b] Decomposition temperature determined by TGA at 10 °C/min under N_2.

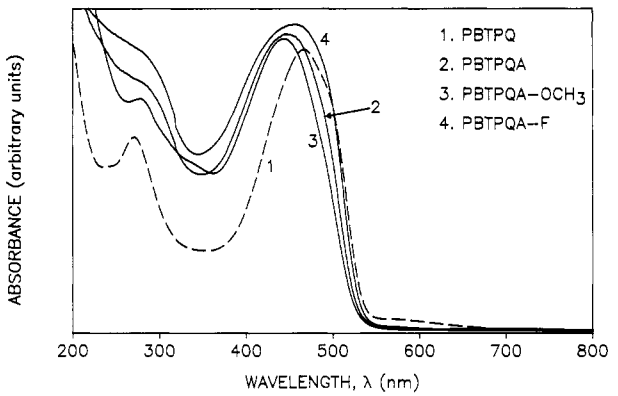


Figure 1. Optical absorption spectra of thin films of PBTPQ, PBTPQA, PBTPQA-OCH_3, and PBTPQA-F.

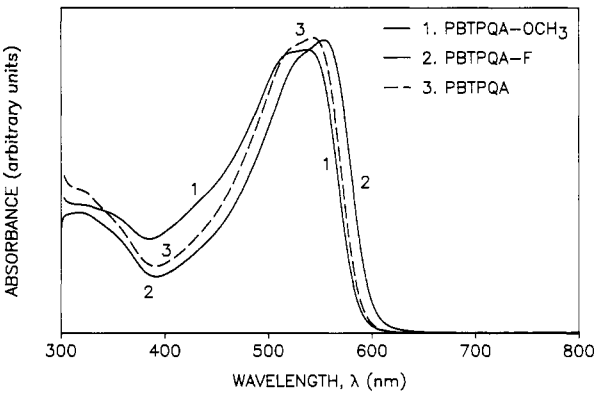


Figure 2. Solution optical absorption spectra of PBTPQA, PBTPQA-OCH_3, and PBTPQA-F in 0.1 mol % DCP/*m*-cresol.

PBTPQA-OCH_3, the π-electron delocalization of the polymer (PBTPQA-OCH_3 compared to PBTPQA) is further reduced. Considering the electron-donating nature of the methoxy substitution, the blue shift of the λ_{max} of PBTPQA-OCH_3 compared to that of PBTPQA (Table I) is significant.

When we compare the optical absorption spectra of PBTPQA-F with PBTPQA, we observe a small red shift of the λ_{max} of the PBTPQA-F (455 versus 448 nm). The result does not seem to be in accord with the expected electron-withdrawing effect of the fluoro side group. Since fluorine is at the ortho position of the phenyl side group, it may provide severe steric hindrance between itself and the hydrogen atoms of the quinoline ring. This hindrance, by forcing the fluorine-substituted phenyl group to rotate out of the plane of the polymer backbone (Chart II), may limit the degree of π-electron overlap between the quinoline unit and the phenyl side group. Consequently, the electron-withdrawing effect of both the phenyl side group (resonance effect) and fluorine atom (induction effect) is expected to be highly reduced or absent in PBTPQA-F. This lower electron-withdrawing power of the phenyl side group in PBTPQA-F compared to that in PBTPQA results in a higher π-electron density in the conjugated backbone of PBTPQA-F, and hence the red shift of its λ_{max} from that of PBTPQA.

The solution optical absorption spectra of the three polymers (PBTPQA, PBTPQA-OCH_3, PBTPQA-F) in 0.1 mol % di-*m*-cresyl phosphate/*m*-cresol are shown in Figure 2. Since the effects of intermolecular interactions on the polymer chain conformations are negligible in solution, the effects of the side-group substitutions were expected to be more evident in the solution spectra than in the thin-film spectra. Table I lists the values for the λ_{max} in the solution spectra for all the polymers. As can be seen from Figure 2 and Table I, the order of increasing λ_{max} and, hence, the order of increasing π-electron delocalization is PBTPQA-OCH_3 < PBTPQA < PBTPQA-F, which is the same order as that observed in the solid state spectra. The close values of the λ_{max} of PBTPQ and PBTPQA in the solution spectra suggest that the two polymers possess a similar conformation in solution. Compared to the solid-state spectra of all the polymers, their respective solution spectra show a huge red shift by about 100 nm. This strong bathochromic shift is a consequence of the complexation reaction between the weekly acidic di-*m*-cresyl phosphate molecule and the basic nitrogen atoms of the polyquinolines. The effect is similar to that seen in other polyquinolines[5,7] and some other classes of heterochain conjugated polymers[17] and arises from the more planar conformation of the protonated polymers.

We have investigated two random copolymers of PBTPQ with PBTPQA-F and with PBTPQA-OCH_3, respectively. The optical absorption maximum (λ_{max}) of the copolymers lies between those of the constituent homopolymers, i.e., the λ_{max} of the copolymers is a molar average of those of the constituent homopolymers (Figure 3). This result shows that random copolymer structures can be used to tune the spectral features of the polyquinolines and at the same time to increase the asymmetry in the polymer chain structures.

Overall, the present results on the optical absorption spectra of donor- and acceptor-substituted *phenylated* polyquinolines show that, contrary to expectations, there was no significant effect of the methoxy or fluoro side groups on the intrinsic electronic and linear optical properties of this class of conjugated polymers. The likely reason for these results is that the conformational effects of the bulky phenylated side groups on the π-electron delocalization of the polymer backbone are dominant over the expected effects of backbone electron density modulation by the methoxy or fluoro substituents on the phenyl

(17) (a) Yang, C.-J.; Jenekhe, S. A. *Chem. Mater.* **1991**, *3*, 878–887. (b) Yang, C.-J.; Jenekhe, S. A., In *Macromolecular Host–Guest Complexes: Optical, Optoelectronic, and Photorefractive Properties and Applications*; Jenekhe, S. A., Ed.; Materials Research Society Proceedings, Materials Research Society: Pittsburgh, PA, 1992; Vol. 277, pp 197–204.

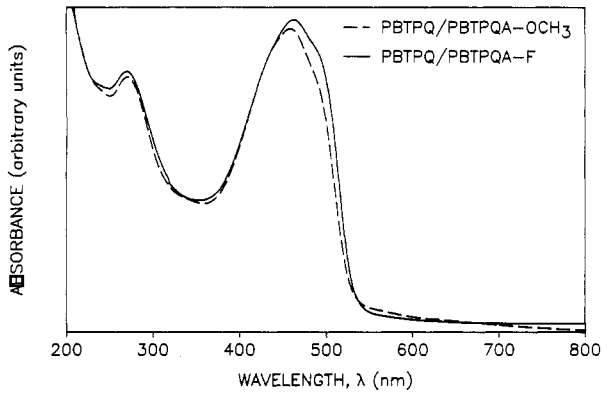


Figure 3. Optical absorption spectra of thin films of copolymers PBTPQ/PBTPQA-OCH_3 (80:20) and PBTPQ/PBTPQA-F (80:20).

side group. It now appears that the well-known effects of donor or acceptor side groups on the electronic and optical properties of conjugated polymers,[2f,9,10,12] are realized if the electron-donating or -withdrawing groups are attached directly on the polymer backbone rather than through a bulky side group such as a phenyl. It would be interesting to confirm this by a future investigation of *nonphenylated* polyquinolines with and without donor and acceptor side groups. It is noteworthy that although the possible role of the electron-deficient nature of the quinoline ring on the electronic structure and properties of the conjugated polyquinolines, and hence the present results, is unclear, the electrochemical reduction and oxidation potentials, ionization potential and electron affinity are also unaffected by the donor/acceptor side group substitutions.[18] The present results also sugest that the bulky phenyl side group in *phenylated* polyquinolines allows π-electron delocalization in two dimensions, thereby reducing the π-electron density on the polymer backbone, as well as increases the interchain distance. These later features can be used to tune not only the intrinsic electronic and optical properties of conjugated polymers but also the nature of the photogenerated charge transport in the materials.[3,19]

Although the substitution of electron-donating or electron-withdrawing side groups in phenylated polyquinolines does not result in a significant effect on the electronic structure as evidenced by the optical absorption spectra, such donor or acceptor groups may still have a significant effect on the detailed electronic excited state and nonlinear optical properties of this class of materials. According to the predictions of Garito et al.[11] for noncentrosymmetric conjugated polymers, it can be expected that polyquinolines with electron-donating or -accepting side groups may have larger nonresonant third-order optical nonlinearity than polyquinolines with centrosymmetric structures.[1] In addition, these new materials may have improved optoelectronic properties.[3] In any case, the polyquinolines presented here and the recently reported polyquinolines[5,7] together constitute excellent model systems for investigation of structure–property relationships with respect to the electronic, optoelectronic, and nonlinear optical properties of conjugated polymers.

Conclusions

A series of new monomers and new conjugated phenylated polyquinolines with electron-donating methoxy side group and electron-withdrawing fluoro side group have been synthesized by the acid-catalyzed Friedlander reaction. Since the acetylene moiety in the polymers was found to be highly susceptible to cross-linking under high reactant concentrations and high temperatures, modified reaction conditions, such as dilute polymer concentration in the reaction medium and lower reaction temperature, were employed to obtain linear polymers. The polymers were easily processable to thin films by using the approach of reversible complexation-mediated solubilization in organic solvents.

The linear optical properties of the new conjugated polyquinolines with or without methoxy or fluoro substitutions on the phenyl side group were found to be very similar: λ_{max} of $\sim$450 nm and an optical bandgap of $\sim$2.36 eV. The lack of any significant effect of the donor or acceptor side groups on the intrinsic electronic properties of the phenylated polyquinolines is attributed to the dominant conformational effects of the bulky phenylated side groups on the π-electron delocalization of the polymer backbone. Although no significant effect of donor or acceptor side groups on the linear optical properties of the phenylated polyquinolines was found, the third-order nonlinear optical and optoelectronic properties of the materials may still be enchanted due to their noncentrosymmetric structures. The present polymers along with the previously reported polyquinolines are excellent model systems for the investigation of structure–property relationships with respect to the electronic, optoelectronic, and nonlinear optical properties of conjugated polymers.

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