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Small-Bandgap Conducting Polymers Based on Conjugated Poly(heteroarylene methines). 1. Precursor Poly(heteroarylene methylenes)

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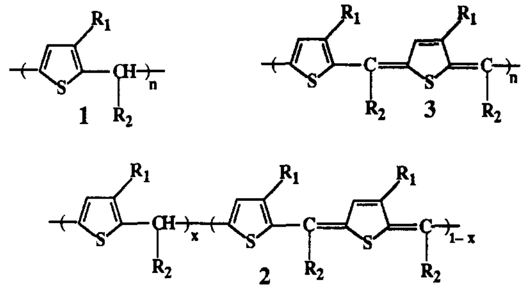
ABSTRACT: A series of 20 new poly(heteroarylene methylenes) containing one to four α-thiophene rings alternating with an sp^3-carbon atom in the main chain were synthesized and characterized. The 11 as-synthesized poly[(2,5-thienylene)methylenes] were found to be highly dehydrogenated, thus resulting in red materials with conjugated segments larger than a single thiophene ring. However, poly[(α-bithienylene)methylenes], poly[(α-terthienylene)methylenes], and poly[(α-quaterthienylene)methylenes] were obtained with optical absorption spectra and π-conjugation lengths characteristic of the isolated thiophene oligomers. The chemical and physical properties of the poly(heteroarylene methylenes) such as the glass transition temperature (T_g) and solubility were significantly modified by the variation of the size of the oligomer in the main chain and by the side group substitution at the bridge carbon. The new polymers are useful precursors to small-bandgap polymers based on poly(heteroarylene methines) and are also useful model systems for the investigation of the effects of π-conjugation length on the electronic and optical properties of conjugated polymers.

Introduction

Conjugated polymers have a range of interesting electronic, optoelectronic, optical, and nonlinear optical properties that vary with their molecular architecture and the extent of π-electron delocalization in the materials.[1−4] One important goal of current studies of conjugated polymers is to understand the structure−property relationships[1−7] that may provide a basis for molecular engineering of polymeric materials for diverse applications in electronics, optoelectronics, and photonics. In a previous paper we reported the synthesis and characterization of several poly[(α-terthien-5,5″-ylene)methylenes] as model polymers with a precisely defined π-electron conjugation length.[7] Such a class of polymers containing well-defined π-conjugated segments of varying length in the backbone provides a more realistic approach to the correlation of polymer physical properties, such as electronic structure, electrical conductivity, charge transport, and nonlinear optical susceptibilities, with conjugation length. Others have also recently reported the synthesis of silicon atom bridged polythiophenes containing one to five thienylene units in the main chain for model studies of electronic properties.[8] In the case of sp^3-carbon atom bridged heteroaromatic polymers, the polymers are also of interest because they can serve as precursors to small-bandgap polymers based on poly(heteroarylene methines)[9] which contain alternating aromatic and quinoid segments in the main chain.

This paper reports the preparation and characterization of a series of 20 new methylene-bridged polythiophenes shown in Charts 1 and 2: poly[(thienylene)methylenes) (**1** and **2**); poly(α-bithienylene)methylenes] (**4**); poly[(α-terthienylene)methylenes] (**5**); and poly[(α-quaterthienylene)methylenes] (**6**). The carbon atom bridged polymers were synthesized by acid-catalyzed polymerization of various aldehydes with 3-alkylthiophenes, α-bithiophene, α-terthiophene, and α-quaterthiophene, respectively. The two poly[(α-terthiophenediyl)methylenes) **5c** and **5d** were prepared for comparison with the other methylene-bridged polythiophenes. The use of different aldehydes allowed us to introduce various substituent side groups at the bridge carbon of the polymers. Unlike the poly(heteroarylene methylenes) of Chart 2, which contain segments having two or more thiophene rings, those containing segments having a thiophene ring (Chart 1) were found to be highly dehydrogenated as prepared. A comprehensive study of the oxidative dehydrogenation of all the present polymers and the characterization of the resulting conjugated poly(heteroarylene methines) will be reported elsewhere.[10] Poly(3-hexylthiophene) (P3HT) was also prepared and characterized for comparison with the present polythiophene derivatives.

Chart 1



2a: R_1=CH_3, R_2=Ph (PMTB)
2b: R_1=CH_3, R_2=$PhOC_7H_{15}$ (PMTHB)
2c: R_1=CH_3, R_2=$PhNO_2$ (PMTNB)
2d: R_1=CH_3, R_2=$PhOCOCH_3$ (PMTAB)
2e: R_1=CH_3, R_2=PhOH (PMTHOB)
2f: R_1=CH_3, R_2=$PhOCH_2Ph$ (PMTBB)
2g: R_1=C_4H_9, R_2=H (PBuTM)
2h: R_1=C_6H_{13}, R_2=H (PHTM)
2i: R_1=C_6H_{13}, R_2=Ph (PHTB)
3a: R_1=H, R_2=Ph (PTBQ)
3b: R_1=H, R_2=$PhNO_2$ (PTNBQ)

Experimental Section

Materials. 3-Methylthiophene (Aldrich, 99+%), thiophene (Aldrich, 99+%), benzaldehyde (Aldrich, 99+%), *p*-acetoxybenzaldehyde (Aldrich, 98%), and *p*-(heptyloxy)benzaldehyde (Chemical Dynamics) were purified by vacuum distillation. α-Bithiophene (Kodak, 99.2%) was purified by recrystallization

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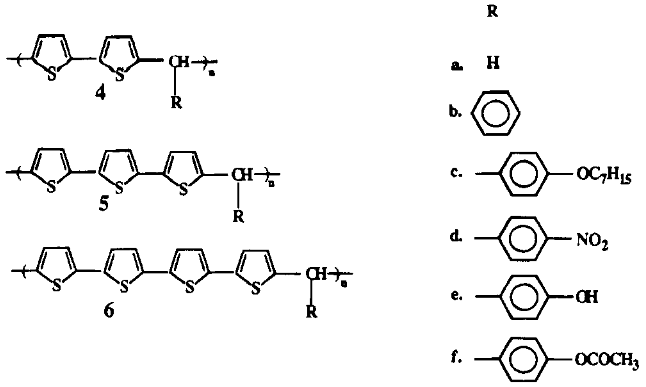
Chart 2



4a: PBTM
4b: PBTB
4c: PBTHB
4d: PBTNB
4e-co-4f: PBTAB-co-PBTHOB
5a: PTTM
5b: PTTB
5c: PTTHB
5d: PTTNB
6b: PQTB
6c: PQTHB

from acetone. Sulfuric acid (Baker), *p*-dioxane (Fisher), *p*-benzoxybenzaldehyde (Chemical Dynamics), *p*-hydroxybenzaldehyde (Chemical Dynamics), *p*-nitrobenzaldehyde (Kodak, 99.5%), paraformaldehyde (Kodak), and ultrapure grade nitrogen (Air Products) were used without further purification. α-Terthiophene and α-quaterthiophene were synthesized by using the method reported by Tamao et al.[11] 3-Butylthiophene and 3-hexylthiophene were synthesized by Grignard reactions of butylmagnesium bromide (Aldrich) and hexylmagnesium bromide (Aldrich), respectively, with 3-bromothiophene (Aldrich) in the presence of NiCl$_2$(dppp) catalyst as reported by Tamao et al.[11] Poly(3-hexylthiophene) (P3HT),[12a] poly[(5,5″-terthiophenediyl)methylene] (PTTM, **5a**),[7] and poly[(5,5″-terthiophenediyl)benzylidene] (PTTB, **5b**)[7] were prepared by the literature methods described by Hotta et al.[12a] and Jenekhe,[7] respectively.

Polymer Synthesis. In general, all polymerizations were carried out in a 250 or 500 mL three-necked round-bottom flask fitted with a condenser and gas inlet and outlet. The reactions were stirred by a magnetic stirring bar, carried out under a flowing nitrogen atmosphere, and thermostated at 80–85 °C with an oil bath.

Poly[(3-methylthiophene-2,5-diyl)benzylidene] (PMTB, 2a). The polymerization mixture was 3-methylthiophene (5.2 mL, 54 mmol), benzaldehyde (6.2 mL, 61 mmol), 60 mL of *p*-dioxane, and 1 mL (18 mmol) of 96% sulfuric acid. The reaction temperature was kept at 85 °C for 24 h. A dark red reaction solution was poured into 1000 mL of stirring methanol. A red product was recovered in methanol, redissolved in THF, recovered in methanol, and dried in a vacuum oven at 40 °C for 24 h. The yield was 60%. Anal. Calcd for $[(C_{12}H_{10}S)_{0.36}(C_{24}H_{18}S_2)_{0.64}]_n$: C, 77.71; H, 4.99; S, 17.3. Found: C, 78.73; H, 5.31; S, 15.54. IR (film on NaCl, cm^{-1}): 3056, 3026, 2918, 2859, 1598, 1492, 1442, 1381, 1260, 1177, 1073, 1001, 838, 735, 697. ^{1}H NMR (δ, ppm, TMS reference); 1.80–2.20 (4.92 H, CH$_3$ on thiophene ring), 5.95 (0.36 H, C(R)H), 7.30 (9.84 H, phenyl and thiophene rings).

Poly[(3-methylthiophene-2,5-diyl)(*p*-(heptyloxy)benzylidene)] (PMTHB, 2b). The polymerization mixture was 3-methylthiophene (3.27 g, 33 mmol), *p*-(heptyloxy)benzaldehyde (8.25 g, 37 mmol), 50 mL of *p*-dioxane, and 0.61 mL (12 mmol) of 96% concentrated sulfuric acid. The reaction temperature was kept at 85 °C for 24 h. A reddish brown reaction solution was precipitated into 500 mL of stirring methanol, recovered, recrystallized from THF/methanol, and dried in a vacuum oven at 40 °C for 12 h. Anal. Calcd for $[(C_{19}H_{24}SO)_{0.38}(C_{38}H_{46}S_2O_2)_{0.62}]_n$: C, 76.15; H, 7.81; S, 10.7; O, 5.34. Found: C, 76.82; H, 8.12; S, 10.67; O, 6.04. IR (film on NaCl, cm^{-1}): 3028, 2952, 2927, 2856, 1605, 1509, 1469, 1376, 1245, 1175, 1109, 1067, 1027, 956, 831, 805, 704. ^{1}H NMR (δ, ppm, TMS reference): 0.92 (4.86 H, CH$_3$ on heptyloxy group), 1.33 (12.96 H, (CH$_2$)$_4$), 1.76 (3.24 H, (CH$_2$), 1.80–2.20 (4.86 H, CH$_3$ on thiophene ring), 3.92 (3.24 H, OCH$_2$), 5.60 (0.38 H, C(R)H), 6.80 (3.24 H, phenylene), 7.10 (4.86 H, phenylene and thiophene rings).

Poly[(3-methylthiophene-2,5-diyl)(*p*-nitrobenzylidene)] (PMTNB, 2c). The polymerization mixture was 3-methylthiophene (4.18 mL, 43 mmol), *p*-nitrobenzaldehyde (7.35 g, 49 mmol), 65 mL of *p*-dioxane, and 0.8 mL (15 mmol) of 96% sulfuric acid. The reaction temperature was kept at 85 °C for 28 h. A red product was recovered in 1000 mL of stirring methanol, redissolved in THF, recovered in methanol, and dried in a vacuum oven at 40 °C for 10 h. The yield was 35%. Anal. Calcd for $[(C_{12}H_9NSO_2)_{0.28}(C_{24}H_{16}N_2S_2O_4)_{0.72}]_n$: C, 62.55; H, 3.54; S, 13.91; O, 13.89; N, 6.08. Found: C, 62.24; H, 3.73; S, 13.75; N, 6.12; O, 13.32. IR (film on NaCl, cm^{-1}): 3074, 2950, 2923, 2863, 1595, 1518, 1445, 1345, 1180, 1109, 1066, 1014, 857, 835, 740, 696. ^{1}H NMR (δ, ppm, TMS reference): 1.80–2.30 (5.16 H, CH$_3$), 5.90 (0.28 H, C(R)H), 7.40 (5.16 H, thiophene and phenylene rings), 8.20 (3.44 H; phenylene).

Poly[(3-methylthiophene-2,5-diyl)(*p*-acetoxybenzylidene)] (PMTAB, 2d). The polymerization mixture was 3-methylthiophene (3.96 mL, 41 mmol), *p*-acetoxybenzaldehyde (6.7 mL, 46 mmol), 60 mL of *p*-dioxane, and 0.76 mL (14 mmol) of 96% sulfuric acid. The reaction temperature was kept at 85 °C. After 15 h, a dark brown solution was poured into 1000 mL of stirring deionized water. A dark red/black product was recovered. For further purification, the product was recrystallized from THF/hexane twice and dried in a vacuum oven at 40 °C for 10 h. The polymer became brown and the yield was 62%. Anal. Calcd for $[(C_{14}H_{12}SO_2)_{0.49}(C_{28}H_{22}S_2O_4)_{0.51}]_n$: C, 69.60; H, 3.91; S, 13.25; O, 13.24. Found: C, 68.01; H, 4.57; S, 13.1; O, 11.77. IR (film on NaCl, cm^{-1}): 3325, 3062, 2970, 2922, 2876, 1762, 1735, 1606, 1514, 1437, 1368, 1268, 1197, 1167, 1103, 1067, 1048, 1016, 968, 916, 837, 667. ^{1}H NMR (δ, ppm, TMS reference): 1.80–2.20 (4.53 H, CH$_3$ on thiophene ring), 2.30 (CH$_3$ on acetoxyphenylene group), 5.90 (0.49 H, (C(R)H), 6.60–7.80 (7.55 H, phenylene and thiophene rings).

Poly[(3-methylthiophene-2,5-diyl)(*p*-hydroxybenzylidene)] (PMTHOB, 2e). The polymerization mixture was 3-methylthiophene (4.77 mL, 49 mmol), *p*-hydroxybenzaldehyde (6.29 g, 52 mmol), 60 mL of *p*-dioxane, and 0.92 mL (17 mmol) of 96% sulfuric acid. The reaction mixture was kept at 85 °C for 24 h. A reddish brown polymer was recovered from 1000 mL of deionized water, recrystallized from DMF/water twice, and dried in a vacuum oven at 65 °C for 24 h. The yield was 95%. Anal. Calcd for $[(C_{12}H_{10}SO)_{0.27}(C_{24}H_{18}S_2O_2)_{0.73}]_n$: C, 71.35; H, 4.86; S, 15.92; O, 7.91. Found: C, 68.64; H, 4.78; S, 12.77; O, 11.62 (moisture sensitive). IR (film on NaCl, cm^{-1}): 3333, 3069, 2972, 2928, 2866, 1658, 1606, 1511, 1437, 1362, 1268, 1236, 1168, 1154, 1035, 1004, 949, 836, 682. ^{1}H NMR (δ, ppm, TMS reference): 1.80–2.20 (5.19 H, CH$_3$), 5.80 (0.28 H, C(R)H), 6.60–7.40 (10.38 H, phenylene and thiophene rings), 9.9 (1.73 H, OH).

Poly[(3-methylthiophene-2,5-(*p*-benzoxybenzylidene)] (PMTBB, 2f). The polymerization mixture consisted of 3-methylthiophene (3.3 mL, 34 mmol), *p*-benzoxybenzaldehyde (7.56 g, 36 mmol), 50 mL of *p*-dioxane, and 0.64 mL (12 mmol) of 96% sulfuric acid. The reaction temperature was kept at 80 °C for 24 h. An orange product was recovered in 1000 mL of stirring methanol, redissolved in THF, recovered in methanol, and dried in a vacuum oven at 40 °C for 12 h. The yield was 35%. Anal. Calcd for $[(C_{19}H_{16}SO)_{0.42}(C_{38}H_{30}S_2O_2)_{0.58}]_n$: C, 78.24; H, 5.27; S, 11.00; O, 5.49. Found: C, 77.91; H, 5.2; S, 10.65; O, 4.85. IR (film on NaCl, cm^{-1}): 3062, 3031, 2917, 2865, 1678, 1604, 1582, 1508, 1454, 1381, 1299, 1242, 1175, 1111, 1082, 1014, 926, 735, 696. ^{1}H NMR (δ, ppm, TMS reference): 1.60–2.20 (4.74 H, CH$_3$ on thiophene ring), 5.1 (3.16 H, CH$_2$), 5.7 (0.42 H, C(R)H), 6.8–7.6 (15.8 H, phenyl, phenylene, and thiophene rings).

Poly[(3-butylthiophene-2,5-diyl)methylene] (PBuTM, 2g). The polymerization mixture was 3-butylthiophene (3.7 g, 26 mmol), paraformaldehyde (0.89 g, 30 mmol), 40 mL of *p*-dioxane, and 0.49 mL (9 mmol) of 96% sulfuric acid. The reaction temperature was kept at 85 °C for 16 h. An orange product was recovered in 500 mL of stirring methanol, redissolved in THF, recovered in methanol, and dried in a vacuum oven at 50 °C for 12 h. The yield was 70%. Anal. Calcd for $[(C_9H_{12}S)_{0.77}(C_{18}H_{22}S_2)_{0.23}]_n$: C, 71.12; H, 7.77; S, 21.11. Found: C, 70.73; H, 7.5; S, 20.93. IR (film on NaCl, cm^{-1}): 3067, 2954, 2928, 2857, 1669, 1553, 1464, 1377, 1298, 1248, 1232, 1181, 1104, 1081, 926, 836, 745, 725. ^1H NMR (δ, ppm, TMS reference): 0.80 (3.69 H, CH_3), 1.28 (7.38 H, $(CH_2)_3$), 2.40 (2.46 H, CH_2 attached at the 3-position of the thiophene ring), 4.00 (1.54 H, CH_2: methylene bridge protons), 6.40–7.10 (1.69 H, thiophene ring and =CH).

Poly[(3-hexylthiophene-2,5-diyl)methylene] (PHTM, 2h). The polymerization mixture was 3-hexylthiophene (2 g, 12 mmol), paraformaldehyde (0.41 g, 14 mmol), 30 mL of *p*-dioxane, and 0.22 mL (4 mmol) of 96% sulfuric acid. The reaction temperature was kept at 85 °C for 23 h. A yellowish brown product was recovered in 500 mL of methanol, redissolved in THF, recovered in methanol, and dried in a vacuum oven at 35 °C for 12 h. The yield was 15%. Anal. Calcd for $[(C_{11}H_{16}S)_{0.62}(C_{22}H_{30}S_2)_{0.38}]_n$: C, 73.50; H, 8.66; S, 17.84. Found: C, 72.7; H, 8.53; S, 18.70. IR (film on NaCl, cm^{-1}): 2954, 2929, 2855, 2655, 1678, 1458, 1302, 1136, 1114, 1012, 840, 721. ^1H NMR (δ, ppm, TMS reference): 0.90 (4.86 H, CH_3), 1.30 (12.96 H, $(CH_2)_4$), 2.50 (3.24 H, CH_2 attached at the 3-position of the thiophene ring), 4.10 (1.24 H, CH_2: carbon bridge protons), 6.50–7.20 (2.14 H, thiophene ring and =CH).

Poly[(3-hexylthiophene-2,5-diyl)benzylidene] (PHTB, 2i). The polymerization mixture was 3-hexylthiophene (6.53 g, 39 mmol), benzaldehyde (4.73 g, 44 mmol), 65 mL of *p*-dioxane, and 0.73 mL (14 mmol) of 96% sulfuric acid. The reaction temperature was kept at 84 °C for 24 h. A red product was recovered in 1000 mL of stirring methanol, redissolved in THF, recovered in methanol, and dried in a vacuum oven at 35 °C for 10 h. The yield was 15%. Anal. Calcd for $[(C_{17}H_{20}S)_{0.48}(C_{34}H_{38}S_2)_{0.52}]_n$: C, 79.85; H, 7.61; S, 12.54. Found: C, 80.20; H, 7.49; S, 11.85. IR (film on NaCl, cm^{-1}); 3059, 3026, 2954, 2927, 2856, 1598, 1522, 1493, 1452, 1377, 1310, 1278, 1200, 1154, 1074, 1030, 878, 840, 734, 697. ^1H NMR (δ, ppm, TMS reference): 0.90 (4.56 H, CH_3), 1.30 (12.16 H, $(CH_2)_4$), 2.40 (3.04 H, CH_2 attached to the thiophene ring), 5.90 (0.48 H, C(R)H), 7.20 (7.60 H, phenyl and thiophene rings).

Poly[(2,5-thiophenediyl)benzylidene(2,5-thiophenequinodimethanediyl)] (PTBQ, 3a). The polymerization mixture was thiophene (15.9 g, 180 mmol), benzaldehyde (21.3 g, 200 mmol), 60 mL of *p*-dioxane, and 3.3 mL (60 mmol) of 96% sulfuric acid. The reaction temperature was kept at 85 °C for 20 h. A red product was recovered in 1000 mL of stirring methanol, redissolved in THF, recovered in methanol, and dried in a vacuum oven at 50 °C for 24 h. The yield was 50%. Anal. Calcd for $(C_{22}H_{14}S_2)_n$: C, 77.16; H, 4.12; S, 18.72. Found: C, 78.63; H, 4.53; S, 15.93. IR (film on NaCl, cm^{-1}): 3027, 1598, 1492, 1443, 1294, 1231, 1176, 1155, 1105, 1073, 1028, 901, 801, 751, 696, 668. ^1H NMR (δ, ppm, TMS reference): 7.25 (14 H, phenyl and thiophene rings).

Poly[(2,5-thiophenediyl)(*p*-nitrobenzylidene)(2,5-thiophenequinodimethanediyl)] (PTNBQ, 3b). The polymerization mixture was thiophene (3.87 g, 46 mmol), *p*-nitrobenzaldehyde (7.82 g, 52 mmol), 50 mL of *p*-dioxane, and 0.85 mL (16 mmol) of 96% sulfuric acid. The reaction temperature was kept at 84 °C for 24 h. A dark red reaction solution was precipitated into 600 mL of stirring methanol, recovered, recrystallized from THF/hexane, and dried in a vacuum oven at 60 °C for 12 h. The yield was 20%. Anal. Calcd for $(C_{22}H_{12}S_2N_2O_4)_n$: C, 61.00; H, 2.80; S, 14.83; N, 6.47; O, 14.8. Found: C, 60.06; H, 2.97; S, 14.72; N, 6.63; O, 14.74. IR (film on NaCl, cm^{-1}): 3106, 3074, 2957, 2844, 2435, 1593, 1518, 1345, 1217, 1140, 1105, 1006, 851, 794, 731, 696. ^1H NMR (δ, ppm, TMS reference): 6.60–7.80 (8 H, phenylene and thiophene rings), 8.00–8.40 (4 H, phenylene ring).

Poly[(α-bithiophene-5,5′-diyl)methylene] (PBTM, 4a). α-Bithiophene (8.03 g (48 mmol), 1.60 g (53 mmol) of paraformaldehyde, and 0.89 mL (16 mmol) of 96% sulfuric acid in 65 mL of *p*-dioxane were reacted at 85 °C in a nitrogen atmosphere for 6 h. A yellowish product was recovered in methanol, extracted with acetone, and dried in a vacuum oven at 60 °C. The yield was 70%. Anal. Calcd for $(C_9H_6S_2)_n$: C, 60.64; H, 3.39; S, 35.97. Found: C, 60.95; H, 3.21; S, 34.51. IR (film on NaCl, cm^{-1}): 3095, 3065, 2968, 2895, 2868, 1530, 1450, 1430, 1335, 1290, 1238, 1202, 1070, 910, 870, 840, 795, 753, 695.

Poly[(α-bithiophene-5,5′-diyl)benzylidene] (PBTB, 4b). α-Bithiophene (8.03 g (48 mmol), 5.41 mL (54 mmol) of benzaldehyde, and 0.89 mL (16 mmol) of 96% sulfuric acid in 75 mL of *p*-dioxane were reacted at 85 °C in a nitrogen atmosphere for 21.5 h. A light yellow/greenish polymerization solution was poured into methanol to recover a polymer. The product was reprecipitated in THF/hexane twice and vacuum dried at 50 °C. The yield was 85%. Anal. Calcd for $[(C_{15}H_{10}S_2)_{0.96}(HSO_4)_{0.04}]_n$: C, 69.72; H, 3.92; S, 25.33. Found: C, 69.68; H, 3.81; S, 24.74. IR (film on NaCl, cm^{-1}): 3060, 3025, 2865, 2858, 1608, 1530, 1500, 1340, 1236, 1210, 1120, 1063, 1025, 908, 870, 795, 735, 695. ^1H NMR (δ, ppm, TMS reference): 6.01 (1 H, C(R)H), 6.82 (2 H, phenyl ring), 7.10 (3 H, phenyl ring), 7.37 (4 H, thiophene ring). ^{13}C NMR (δ, ppm, TMS reference): 47.79 (C(R)H), 124.0 (thiophene ring), 126.0 (phenyl), 128.0 (phenyl), 129.0 (phenyl), 129.2 (phenyl), 137.1 (thiophene ring), 147.2 (phenyl).

Poly[(α-bithiophene-5,5′-diyl)(*p*-(heptyloxy)benzylidene)] (PBTHB, 4c). α-Bithiophene (4.51 g (27 mmol)), 6.69 g (30 mmol) of *p*-(heptyloxy)benzaldehyde, and 0.5 mL (16 mmol) of 96% sulfuric acid in 65 mL of *p*-dioxane were reacted at 80 °C in a nitrogen atmosphere for 21.5 h. A light bluish polymerization solution was poured into methanol to recover a polymer. The product was reprecipitated twice in THF/methanol and vacuum dried at 35 °C. The yield was 80%. Anal. Calcd for $[(C_{22}H_{24}S_2O)_{0.86}(HSO_4)_{0.14}]_n$: C, 68.75; H, 6.34; S, 18.04; O, 6.95. Found: C, 68.68; H, 6.35; S, 18.26; O, 6.85. IR (film on NaCl, cm^{-1}): 3066, 2927, 2855, 1608, 1540, 1508, 1465, 1300, 1246, 1175, 1110, 1026, 835, 797, 688. ^1H NMR (δ, ppm, TMS reference): 0.9 (3 H, CH_3), 1.40 (8 H, $(CH_2)_4$), 1.75 (3.24 H, $OCH_2CH_2^*$), 3.95 (3.24 H, OCH_2), 5.7 (1 H, C(R)H), 6.72 (2 H, phenylene ring), 6.86 (2 H, phenylene ring), 6.97 (2 H, thiophene ring), 7.25 (2 H, thiophene ring).

Poly[(α-bithiophene-5,5′-diyl)(*p*-nitrobenzylidene) (PBTNB, 4d). α-Bithiophene (5.55 g (33 mmol)), 5.68 g (38 mmol) of *p*-nitrobenzaldehyde, and 0.62 mL (12 mmol) of 96% sulfuric acid in 65 mL of *p*-dioxane were reacted at 80 °C in a nitrogen atmosphere for 24 h. A light greenish polymer was recovered from a greenish reaction solution by precipitation into stirring methanol. The product was reprecipitated twice in THF/hexane and vacuum dried at 37 °C. The yield was 83%. Anal. Calcd for $[(C_{15}H_9S_2NO_2)_{0.87}(HSO_4)_{0.13}]_n$: C, 57.40; H, 2.94; S, 21.96; N, 4.46; O, 13.24. Found: C, 57.37; H, 2.98; S, 22.77; N, 4.29; O, 12.82. IR (film on NaCl, cm^{-1}): 3068, 2850, 1520, 1491, 1425, 1346, 1277, 1204, 1109, 1048, 1014, 910, 858, 839, 796, 738, 702, 688. ^1H NMR (δ, ppm, TMS reference): 6.3 (1 H, C(R)H), 6.83 (2 H, thiophene ring), 7.13 (2 H, thiophene ring), 7.60 (2 H, phenylene ring), 8.20 (2 H, phenylene ring).

Poly[(α-bithiophene-5,5′-diyl)(*p*-acetoxybenzylidene))-*co*-(α-bithiophene-5,5′-diyl)(*p*-hydroxybenzylidene)] (PBTAB-*co*-PBTHOB, 4e). α-Bithiophene (8.01 g (48 mmol)), 7 mL (54 mmol) of *p*-acetoxybenzaldehyde, and 0.89 mL (16 mmol) of 96% sulfuric acid in 75 mL of *p*-dioxane were reacted at 85 °C in a nitrogen atmosphere for 21.5 h. A light bluish polymerization solution was poured into 500 mL of stirring methanol, precipitating a polymer. The product was reprecipitated twice in THF/hexane and vacuum dried at 35 °C. The yield was 86%. Anal. Calcd for $[(C_{17}H_{12}S_2O_2)_{0.14}\text{-}(C_{15}H_{10}S_2O)_{0.86}]_n$: C, 66.44; H, 3.75; S, 23.21. Found: C, 64.45; H, 4.66; S, 21.35. IR (film on NaCl, cm^{-1}): 3250, 3065, 2960, 2870, 1660, 1615, 1600, 1520, 1450, 1370, 1320, 1235, 1175, 1105, 1055, 890, 845, 805, 695. ^1H NMR (δ, ppm, TMS reference): 2.30 (0.42 H, CH_3), 5.94 (0.86 H, C(R)H attached to the hydroxyphenyl side group), 6.11 (0.14 H, C(R)H attached to the acetoxyphenyl group), 6.85 (3.44 H, phenylene side group with the hydroxy substituent), 7.10 (2 H, thiophene ring), 7.25 (2 H, thiophene ring), 7.50 (0.56 H, phenylene side group with the acetoxy substituent), 9.85 (0.86 H, OH), ^{13}C NMR (δ, ppm, TMS reference): 26.21 (CH_3), 47.20 (C(R)H), 116.0 (phenylene), 123.52 (thiophene ring), 127.5 (thiophene and phenylene rings), 126.0 (phenyl), 130.0 (phenylene), 134.34

(phenylene), 136.95 (thiophene), 148.1 (phenylene), 157.85 (C=O).

Poly[(α-terthiophene-5,5″-diyl)(*p*-(heptyloxy)benzylidene)] (PTTHB, 5c). α-Terthiophene (5.59 g (22 mmol)), 5.49 g (25 mmol) of *p*-(heptyloxy)benzaldehyde, and 0.4 mL (7.5 mmol) of 96% sulfuric acid in 40 mL of *p*-dioxane were reacted at 85 °C in a nitrogen atmosphere for 24 h. A greenish/yellow polymerization solution was poured into methanol to recover a polymer. The product was purified by reprecipitation in THF/methanol twice and vacuum dried at 35 °C. The yield was 80%. Anal. Calcd for $[(C_{26}H_{26}S_3O)_{0.9}(HSO_4)_{0.1}]_n$: C, 67.67; H, 5.70; S, 21.61; O, 5.02. Found: C, 67.75; H, 5.56; S, 21.44; O, 5.50. IR (film on NaCl, cm^{-1}): 3065, 2951, 2927, 2855, 1609, 1570, 1509, 1467, 1248, 1176, 1055, 1031, 836, 792, 693. ^{1}H NMR (δ, ppm, TMS reference): 0.9 (3 H, CH_3), 1.35 (8 H, $(CH_2)_4$), 1.75 (2 H, OCH_2 CH_2*), 3.95 (2 H, OCH_2), 5.72 (1 H, C(R)H), 6.77 (2 H, phenylene ring), 6.80–6.90 (2 H, phenylene ring), 6.95–7.40 (6 H, thiophene ring).

Poly[(α-terthiophene-5,5″-diyl)(*p*-nitrobenzylidene)] (PTTNB, 5d). The polymerization mixture was 4.5 g (18 mmol) of α-terthiophene, 3.08 g (20 mmol) of *p*-nitrobenzaldehyde, 0.4 mL (7.5 mmol) of 96% sulfuric acid, and 40 mL of *p*-dioxane. The reaction mixture was maintained at 85 °C in a nitrogen atmosphere for 24 h. A yellowish polymerization solution was poured into 500 mL of methanol. The product was purified by reprecipitation in THF/hexane twice, extracted by methanol, and vacuum dried at 50 °C. The yield was 82%. IR (film on NaCl, cm^{-1}): 3063, 2971, 2858, 1596, 1519, 1491, 1436, 1346, 1217, 1189, 1098, 1063, 999, 907, 893, 859, 830, 794, 731, 702. ^{1}H NMR (δ, ppm, TMS reference): 6.30 (1 H, C(R)H), 6.80–7.50 (6 H, thiophene ring), 7.60 (2 H, phenylene ring), 8.20 (2 H, phenylene ring).

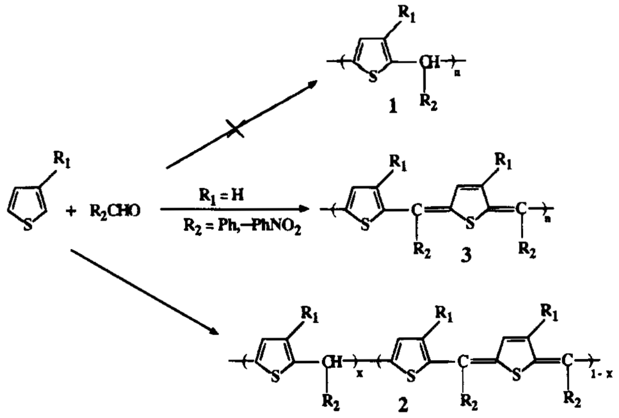
Poly[(α-quaterthiophene-5,5‴-diyl)benzylidene] (PQTB, 6b). A mixture of 0.3 g (0.9 mmol) of α-quaterthiophene, 0.1 mL (1 mmol) of benzaldehyde, and 1 drop of 96% sulfuric acid in 40 mL of *p*-dioxane was reacted at 85 °C for 24 h. A dark red polymerization solution was poured into methanol to recover a reddish brown product. The product was extracted with methanol to remove unreacted α-quaterthiophene and vacuum dried at 50 °C. The yield was 20%. IR (KBr pellet, cm^{-1}): 1640, 1485, 1443, 1412, 1210, 1189, 1140, 1098, 823, 788, 682, 626, 450. The ^{1}H NMR spectrum could not be obtained because of poor solubility.

Poly[(α-quaterthiophene-5,5‴-diyl)(*p*-(heptyloxy)benzylidene)] (PQTHB, 6c). A mixture of 1.5 g (4.5 mmol) of α-quaterthiophene, 1.13 g (5.1 mmol) of *p*-(heptyloxy)benzaldehyde, and 0.08 mL of 96% sulfuric acid in 50 mL of *p*-dioxane was reacted at 85 °C for 48 h. A dark red polymerization solution was poured into methanol to recover a red product. The product was extracted with methanol to remove unreacted α-quaterthiophene and vacuum dried at 50 °C. The yield was 21%. IR (KBr pellet, cm^{-1}): 3055, 2921, 2851, 1654, 1590, 1499, 1477, 1421, 1379, 1351, 1246, 1210, 1168, 1062, 1041, 907, 823, 791, 682. The ^{1}H NMR spectrum could not be obtained because of poor solubility.

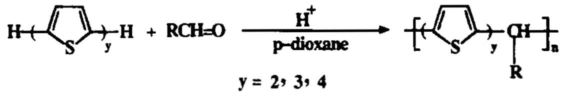
Characterization. Infrared spectra of polymer thin films cast on NaCl windows from THF, DMF, or NMP solutions or samples in KBr pellets were recorded at room temperature using a Nicolet Model 20 SXC FTIR spectrometer. ^{1}H NMR and ^{13}C NMR spectra of polymers were obtained in deuterated DMF, DMSO, or CH_2Cl_2 with a General Electric Model QE300 instrument or a Nicolet spectrometer at 300 MHz. Elemental analysis was done by Galbraith Laboratories, Inc. (Knoxville, TN) or Oneida Research Services, Inc. (Whitesboro, NY).

The molecular weights of PBTM (**4a**), PBTB (**4b**), and PBTAB-*co*-PBTHOB (**4e**) were characterized with a Waters Associates Model 150C gel permeation chromatography (GPC) at 60 °C. This GPC was equipped with 10^5, 10^4, 10^3, and 500 Å Ultrastyragel columns in DMF and operated at a flow rate of 0.9 mL/min. Polystyrene standards were used to estimate the weight-average ($\bar{M}_w$) and number-average $\bar{M}_n$ molecular weights. The molecular weight distributions of the other polymers were measured by size-exclusion chromatography. The chromatograph consisted of a HPLC metering pump (Constametric III, Milton Roy), two PL$_{gel}$ columns in series (500 and 10 000 Å, Hewlett-Packard) housed in a column oven (Jones Chromatography), and a UV differential absorbance detector (UV III Monitor, Milton Roy) set at 254 nm. This latter GPC was operated in THF at 40 °C. The intrinsic viscosities, [η], of all polymers in DMF or NMP were determined at 30 °C using a Cannon-Ubbelohde capillary viscometer and a constant-temperature bath. The intrinsic viscosity values were extracted from the intersection of plots of the reduced viscosity (η_{sp}/C) and inherent viscosity ($\eta_{inh} = [\ln \eta_{rel}]/C$) versus solution concentration.

Scheme 1



Scheme 2



Thermal analysis, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) were performed under flowing nitrogen using a Dupont Model 1090B thermal analyzer or a Dupont Model 2100 thermal analysis system based on an IBM PS/2 Model 60 computer. Indium (156.4 °C) standard was used to calibrate the accuracy of the measured transition points. The samples were sealed in DSC pans and run at 20 °C/min. TGA runs were performed at a heating rate of 10 °C/min. Electronic absorption spectra were obtained at room temperature in the range 185–3200 nm using a Perkin-Elmer Lambda 9 UV–vis–near-IR spectrophotometer. X-ray diffraction patterns of some samples were obtained with a Rigaku powder X-ray diffractometer and a computerized diffraction analyzer (Cu Kα X-ray radiation, 1.540562 Å wavelength). The 2θ scans were from 3 to 93°, with a step size of 0.02° and 1-s counting per step. Powdered samples were held on a single-crystal wafer with grease. The silicon wafer was detuned 2° to suppress reflections from the Si crystal.

Results and Discussion

Polymer Synthesis and Structure. The synthesis of soluble linear poly[(α-terthiophenediyl)methylenes] by acid-catalyzed polymerization of α-terthiophene with aldehydes has previously been demonstrated.[7] However, as shown in Scheme 1, the desired poly[(2,5-thiophenediyl)methylenes] **1** could not be obtained by the analogous acid-catalyzed polymerization of 3-alkylthiophene with aldehydes. Instead of **1**, highly colored partially dehydrogenated polymers **2** and even completely dehydrogenated polymers **3** were obtained. In contrast to this result for the attempted synthesis of **1**, the methylene-bridged polymers of Chart 2, i.e. poly[(α-bithiophenediyl)methylenes] **4**, poly[(α-terthiophenediyl)methylenes] **5**, and poly[(α-quaterthiophenediyl)methylenes] **6**, were successfully synthesized as summarized in Scheme 2.

The structure of all the polymers was investigated primarily by FTIR, ^{1}H NMR, and UV–visible spectra as well as by elemental analysis. The elemental analy-

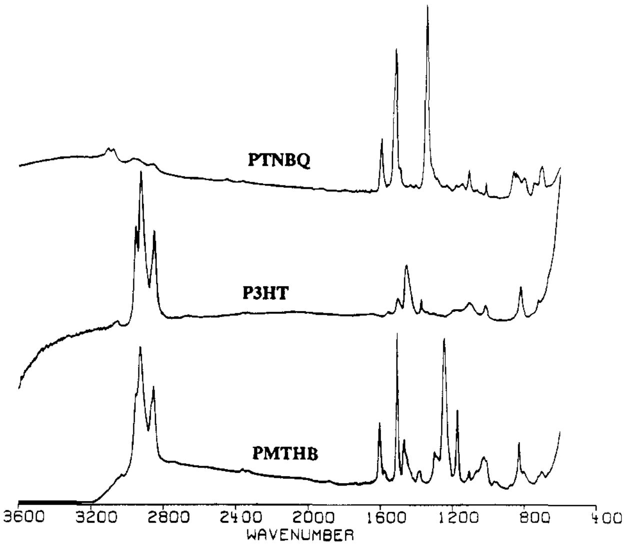


Figure 1. FTIR absorption spectra of P3HT, PTNBQ, and PMTHB.

sis results for most of the polymers **2**–**5** were generally in fair agreement with theoretically calculated compositions. However, the analytical data of some of the polymers (e.g., **3a**) showed a 1–3% difference with the expected carbon or sulfur content. This is due in part to the effects of the end groups (e.g., HSO_4) and low molecular weight. Identification and proof of the polymer structures, therefore, relied more on the spectroscopic characterization than on the elemental analysis.

Figure 1 shows the FTIR absorption spectra of PMTHB (**2b**), PTNBQ (**3b**), and poly(3-hexylthiophene) (P3HT). A distinct peak near 790 cm^{-1} of the spectrum of PTNBQ is due to the C_β–H out-of-plane vibration characteristic of the α-linkage in thiophene rings. The C_β–H out-of-plane vibration bands of P3HT and PMTHB are observed at 822 and 831 cm^{-1}, respectively. The bands between 1420 and 1520 cm^{-1} of Figure 1 are assigned to the C=C symmetric and antisymmetric stretching vibration bands of the thiophene rings. This assignment is based on the reported FTIR spectra of thiophene oligomers and poly(3-alkylthiophenes).[12] The bands in the 3000–3100 cm^{-1} region are the C–H stretching vibration bands of the thiophene ring in the main chain or the phenylene ring in PTNBQ and PMTHB. The absorption bands around 2950–2920 cm^{-1} in the FTIR spectra of P3HT and PMTHB are assigned to the alkyl group C–H vibration or the methine C–H vibration band of PMTHB. The N=O symmetric vibration band of PTNBQ is observed at 1345 cm^{-1}. The rather weak bands at 2844 and 2957 cm^{-1} in PTNBQ (**3b**) are probably due to overtones of the NO_2 band at 1345 cm^{-1}. Similar FTIR vibration bands in the 2840–2960 cm^{-1} region are observed in nitrobenzene.[13] The band at 1245 cm^{-1} in the FTIR spectrum of PMTHB is assigned to the C–O–C stretching vibration band. Other representative FTIR absorption spectra of the polymers in Chart 1 are shown in Figure 2, which includes the spectra of PBuTM (**2g**) and PMTHOB (**2e**). An important feature of the FTIR spectrum of PBuTM is the 1670 cm^{-1} absorption band, which can be assigned to the C=C stretching vibration of the quinoid thiophene ring. A similar absorption band characteristic of the quinoid thiophene ring at 1678 cm^{-1} was observed in the FTIR spectrum of PHTM. These results clearly suggest that the methylene ($-CH_2-$) bridges of PBuTM and PHTM have been partially dehydrogenated to methine bridges (=CH–) during the polymerization. The expected C=C stretching vibration of the quinoid ring near 1670 cm^{-1} in the FTIR spectra of other partially or completely dehydrogenated polymers of Chart 1 could not be unambiguously assigned because of the overlap of the phenyl C=C stretching band in the same region. The OH group vibration band in the FTIR spectrum of PMTHOB was observed as a broad band centered at 3333 cm^{-1}.

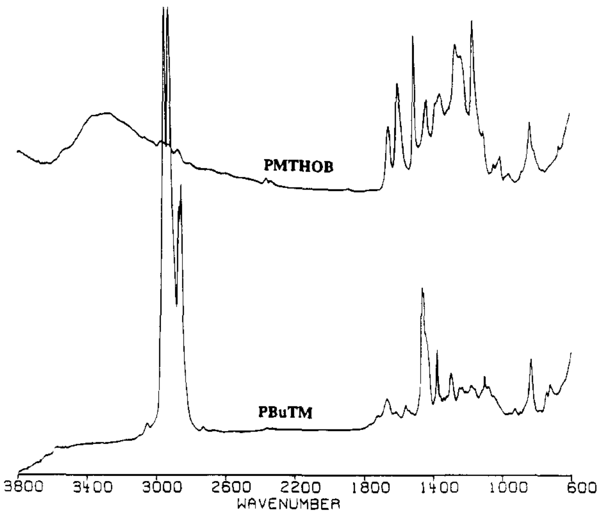


Figure 2. FTIR absorption spectra of PBuTM and PMTHOB.

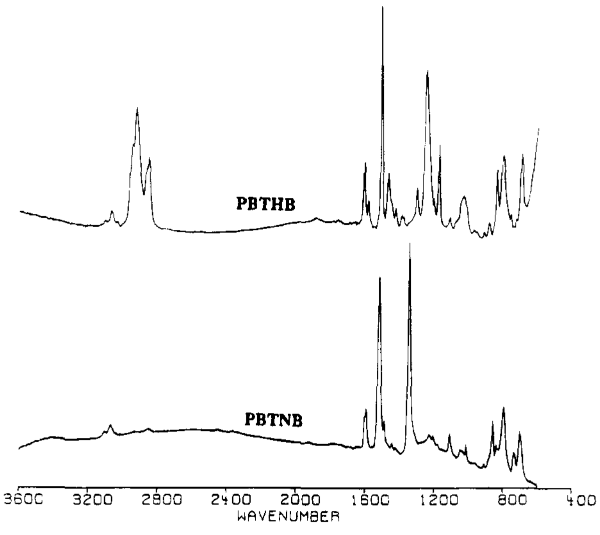


Figure 3. FTIR absorption spectra of PBTHB and PBTNB.

Figure 3 shows the FTIR absorption spectra of PBTHB (**4c**) and PBTNB (**4d**), which are representative of poly[(α-bithiophendiyl)methylenes]. The α-linkage of these polymers is characterized by the strong C_β–H out-of-plane vibration band at 795–805 cm^{-1} in all five polymers containing α-bithienylene moieties. The assignment of some of the main FTIR absorption bands of the polybithiophenes **4** and the other polymers are collected in Table 1. Evidence of partial hydrolysis was found in the FTIR spectrum of PBTAB-*co*-PBTHOB as well as that of PMTAB. In addition to the C=O vibration band at ~1660 cm^{-1} due to the presence of the acetoxy group, a strong broad absorption band at 3250 cm^{-1} due to the OH group was observed. Overall, the FTIR spectra were in very good agreement with the proposed structures.

The ^1H NMR spectra of all the polymers were obtained to further investigate and confirm the proposed

Table 1. Assignment of the FTIR Spectra of Poly(heteroarylene methylenes)

polymer	out-of-plane C−H bending (cm^{-1})	alkyl chain (C−H) or (−C(R)H−) stretching (cm^{-1})	C=C ring stretching[a] (cm^{-1})
PMTB	838	2859, 2918	1442, 1492, 1598
PMTHB	831	2856, 2927, 2952	1469, 1509, 1605
PMTNB	835	2863, 2923, 2950	1445, 1518, 1595
PMTAB	837	2876, 2922, 2970	1437, 1514, 1606
PMTHOB	836	2866, 2928, 2972	1437, 1511, 1606
PMTBB	832	2865, 2917	1454, 1508, 1582, 1604
PBuTM	836	2857, 2928	1464, 1553
PHTM	840	2855, 2929, 2954	1458
PHTB	840	2856, 2927, 2954	1452, 1493, 1522, 1598
PTBQ	801		1443, 1492, 1598
PTNBQ	794		1518, 1593
P3HT	822	2856, 2926, 2955	1457, 1508
PBTM	795	2868, 2895, 2968	1530
PBTB	795	2858, 2965	1455, 1500, 1530, 1608
PBTHB	797	2855, 2927	1465, 1508, 1540, 1608
PBTNB	796	2850	1425, 1491, 1520
PBTAB-*co*-PBTHOB	805	2870, 2960	1450, 1520, 1600
PTTM[b]	790	2925	1425, 1507, 1594
PTTB[b]	792	2866, 2965	1467, 1492, 1513, 1599
PTTHB	792	2855, 2927, 2951	1509, 1570, 1609
PTTNB	794	2858, 2972	1436, 1490, 1519, 1596
PQTB	788		1443, 1485, 1640
PQTHB	791	2851, 2921	1421, 1477, 1490, 1590

[a] The C=C stretching vibration bands of thiophene rings are between 1420 and 1520 cm^{-1} and that of the phenyl ring is near 1590 cm^{-1}. [b] The results of PTTB and PTTM have been reported in ref 7.

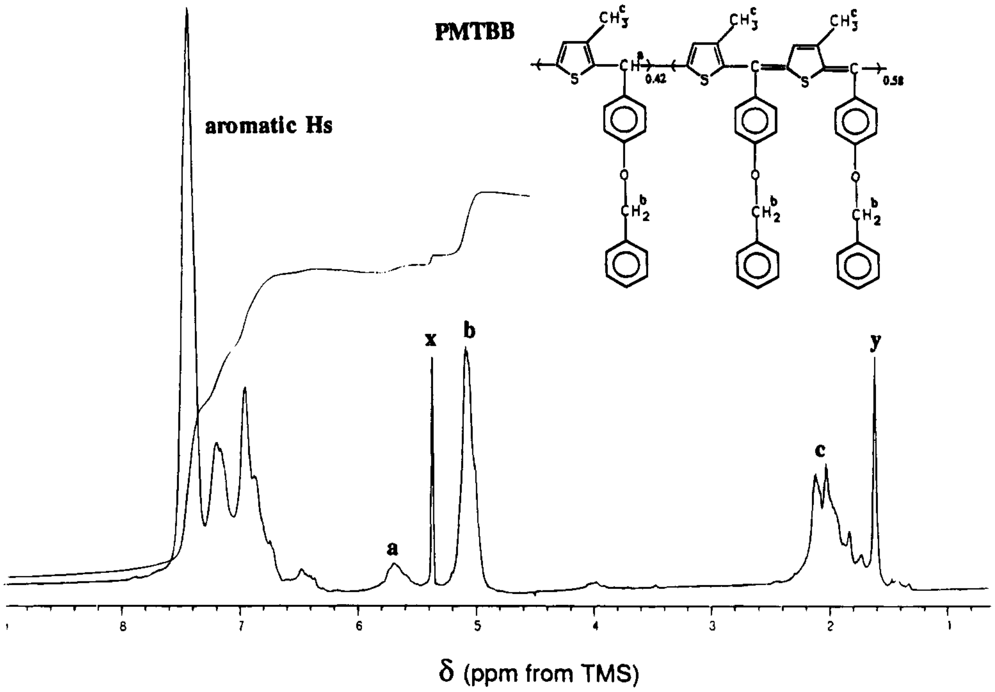


Figure 4. ^{1}H NMR spectrum of PMTBB in deuterated dichloromethane ("x" is CH_2Cl_2 solvent, and "y" is water).

structures (Charts 1 and 2). Figure 4 shows the ^{1}H NMR spectrum of PMTBB (**2f**) in CD_2Cl_2 (solvent peak at $\delta = 5.35$ is marked x, impurity water in CD_2Cl_2 at $\delta = 1.6$ is marked y). Assignment of the resonances is also indicated on Figure 4. An important resonance in the NMR spectrum of Figure 4 that is characteristic of the methylene-bridged polymers **1** and **2** is the methine bridge proton resonance at 5.7 ppm. Integration of this resonance peak gave only 0.42 proton compared to the expected 1.00 proton. This suggests that the as-synthesized PMTBB was partially dehydrogenated; the degree of dehydrogenation estimated from the NMR results was about 58%. The methine proton resonance in the NMR spectra of the different 2,5-thienylene-containing polymers of Chart 1 was at 4.00–4.10 ppm for the CH_2-bridged polymers (PHTM and PBuTM) and at 5.70–5.95 ppm for the others with phenyl or phenylene substituents at the bridge carbon. The ^{1}H NMR spectra provided an accurate estimate of the degree of dehydrogenation, which was in the range of 23% for PBuTM to 100% for PTBQ and PTNBQ as shown in Table 2. The partially dehydrogenated polythiophenes thus contain conjugated segments with alternating aromatic and quinoid thiophene rings. These results are in accord with both the FTIR spectra of the 2,5-thienylene polymers and their highly colored nature; all the single thiophene ring polymers were red. Similar partial dehydrogenation has been observed in the polymerization of furan derivatives such as furfuryl acetate[14a,b] and 2-alkenylfurans.[14c] However, we have found that detectable (NMR, FTIR, elemental analysis) dehydrogenation *does not* accompany the acid-catalyzed

Table 2. Degree of Dehydrogenation of As-Synthesized Poly[(2,5-thienylene)methylenes]

polymer	deg of dehydrog[a] (%)	polymer	deg of dehydrog[a] (%)
PMTB	64	PBuTM	23
PMTHB	62	PHTM	38
PMTNB	72	PHTB	52
PMTAB	51	PTBQ	100
PMTHOB	73	PTNBQ	100
PMTBB	58		

[a] Estimated from ^{1}H NMR spectra.

synthesis of the polymers containing α-bithienylene, α-terthienylene, and α-quaterthienylene (Chart 2).

Representative ^{1}H NMR spectra of the poly[α-bithiopenediyl)methylenes] PBTHB (**4c**) in CD_2Cl_2 and PBTAB-*co*-PBTHOB (**4e**-*co*-**4f**) in DMF-d_8 are shown in Figures 5 and 6, respectively. The characteristic methine proton (C(R)H) resonance was observed at 5.7 ppm in PBTHB and found to vary from 4.2 ppm in PBTM (R = H) to 6.3 ppm in PBTNB (R = *p*-nitrophenyl). Thus, the stronger the electron-withdrawing nature of the substituent R at the bridged carbon, the larger is the downfield shift of δ from that of the methylene (CH_2)-bridged PBTM. Integration of the resonance peak at 2.3 ppm due to CH_3 protons of the acetoxy group gave a total of only 0.42 proton and hence indicated 86% hydrolysis of the acetoxy group during the acid-catalyzed polymerization. The observation of a proton resonance at 9.85 ppm due to a hydroxy group and the splitting of the methine proton resonance near 6 ppm provided further evidence of the hydrolysis of the acetoxy side group. Thus, the resulting polymer is a copolymer (PBTAB-*co*-PBTHOB) with 14% *p*-acetoxyphenyl and 86% *p*-hydroxyphenyl side groups at the bridge carbon. The ^{13}C NMR spectra of PBTB and PBTAB-*co*-PBTHOB showed a resonance at 47.79 and 47.20 ppm, respectively, due to the sp^3-carbon bridges between the α-bithiophene segment in the main chain. The assignments of the ^{1}H NMR and ^{13}C NMR spectra of other polymers are collected in the Experimental Section.

Solution Properties and Molecular Weight. Most of the poly(heteroarylene methylenes) of Charts 1 and 2 were found to be soluble in organic solvents such as tetrahydrofuran (THF), CH_2Cl_2, *N,N*-dimethylformamide (DMF), and sulfolane. Although polymers **2**–**3** (Chart 1) have highly conjugated chains due to the high degree of dehydrogenation, they were very soluble in organic solvents such as THF, giving orange-red solutions of high concentrations. For example, up to 20% (wt/wt) solutions of PMTB, PMTNB, PTBQ, and PTNBQ in organic solvents could be prepared and used for spin-coating deposition of optical-quality films with thickness of 1–10 μm. The very good solubility of polymers **2**–**3** in spite of their high degree of π-conjugation is due largely to the bulky side group (R) at the bridge methine carbon (C(R)H or =C(R)) and also to the low molecular weight to some extent. PMTAB, PMTHOB, and PBTAB-*co*-PBTHOB were completely soluble in DMF and sulfolane but not in CH_2Cl_2 due to their polar side groups. On the other hand, PBuTM, PHTM, and P3HT were soluble in THF and CH_2Cl_2 but were only partially soluble in DMF and DMSO due to their nonpolar alkyl side groups. The methylene-bridged polymers PBTM and PTTM were only partially soluble (<1 wt %) in NMP and not at all in other solvents. Substitution of a bulky side group at the methine carbon in PBTB, PBTHB, PTTB, and PTTHB resulted in solubility in organic solvents. However, PQTB and PQTHB were not completely soluble (<1 wt %) in THF, DMF, DMSO, and NMP in spite of their bulky side groups. This suggests that the increased backbone rigidity of the polymers containing α-quaterthiophene segments outweighs the conformational flexibility introduced by the bulky side group at the bridge carbon. The solubility of polymers **2**–**5** in organic solvents allowed us to characterize their structures by solution spectroscopic techniques and their molecular weights by gel permeation chromatography (GPC) and intrinsic viscosity.

The molecular weights ($\bar{M}_w$, $\bar{M}_n$), molecular weight distributions ($\bar{M}_w/\bar{M}_n$), and number-average degrees of polymerization ($\overline{DP}_n$) of the soluble poly(heteroarylene methylenes) are shown in Table 3. These molecular weight data are based on polystyrene standards and hence are not absolute but mostly of comparative value. The intrinsic viscosity of these polymers, listed in Table 3, also gives an indication of the molecular weight. The intrinsic viscosity values, which are in the range 0.038–0.117 dL/g, indicate that the polymers have mostly low molecular weights. The moderately high molecular weight of P3HT obtained here is comparable to literature reports[12] for the polymer. The observed intrinsic viscosity of 0.445 dL/g for P3HT reflects the high molecular weight and is about a factor of 4–10 times larger than those of the poly(heteroarylene methylenes). The poly(thiophene methylenes) **2** and poly(thiophene methines) **3** were mostly low molecular weight materials with $\overline{DP}_n$ values of 4–7 except PBuTM, which has a $\bar{M}_w$ of 22 000 and $\overline{DP}_n$ of 21.6. The molecular weight distributions of the poly(bithiophene methylenes) PBTM, PBTB, and PBTAB-*co*-PBTHOB were bimodal as revealed by the GPC traces in DMF. However, the proportion of the high molecular weight fraction was small (<~10–20%) and hence will not be discussed separately. The polydispersity ($\bar{M}_w/\bar{M}_n$) in the low molecular weight fractions of polymers **4** varies from 1.46 in PBTM to 3.27 in PBTHB. The estimated number-average degree of polymerization, $\overline{DP}_n$, of the low molecular weight fractions of polymers **4** is in the range of 4–34. For comparison the $\overline{DP}_n$ found by elemental analysis of polymer **4** is 6–24, which is of the same order of magnitude. The number of thiophene rings in each polymer chain is twice the $\overline{DP}_n$ value plus 2 (assuming one 2,2′-bithiophene end group and a hydrogen on the other end). Thus, on average there are about 10–70 thiophene rings per chain even in the low molecular weight fractions of polymers **4**. The molecular weights of these polymers were affected by both the polymerization conditions (time, temperature) and the relative reactivity of the aldehydes. In view of the molecular weight and intrinsic viscosity for polymers **2**–**5**, it appears that the methylene-bridged polymers (e.g., PBuTM and PBTM) have the highest molecular weights and the polymers with the nitrobenzylidene side group have the lowest molecular weights.

Thermal Properties and Crystallinity. Figure 7 shows the TGA curves of PTNBQ, PMTBB, P3HT, PMTB, and PBuTM obtained in a nitrogen atmosphere at a heating rate of 10 °C/min. These polymers show good thermal stability. For example, PMTB has an onset of thermal decomposition of 360 °C, which is comparable to the onset of thermal decomposition of high molecular weight P3HT. The thermal stability of polymers **4** is shown in Figure 8. The onset decomposition temperatures of PBTM, PBTB, and PBTHB are at

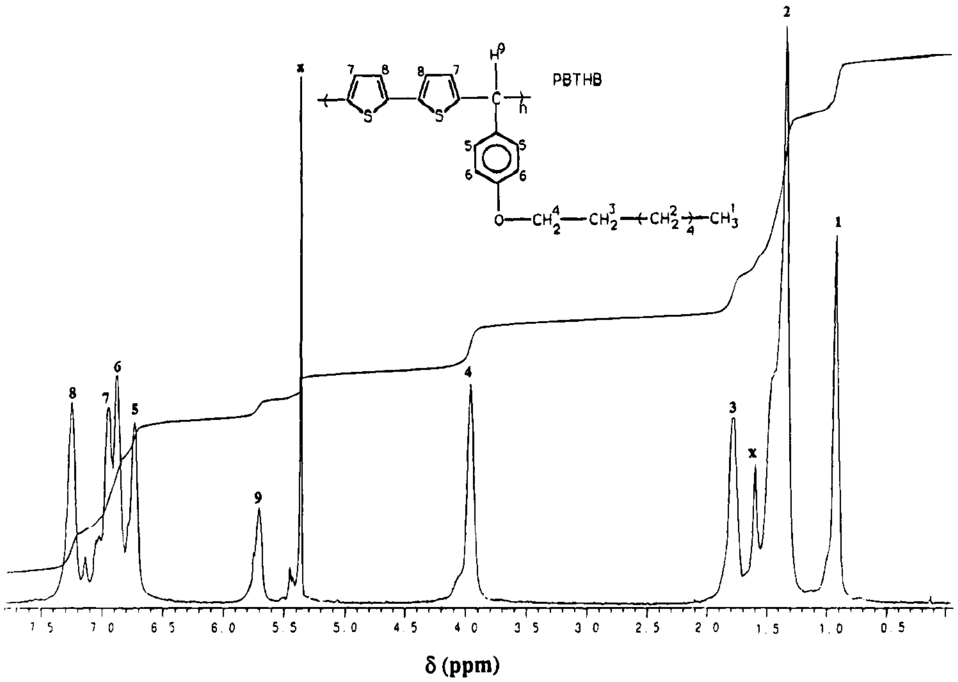


Figure 5. ^{1}H NMR spectrum of PBTHB in deuterated dichloromethane ("x" is CH_2Cl_2 solvent or water contained in the solvent).

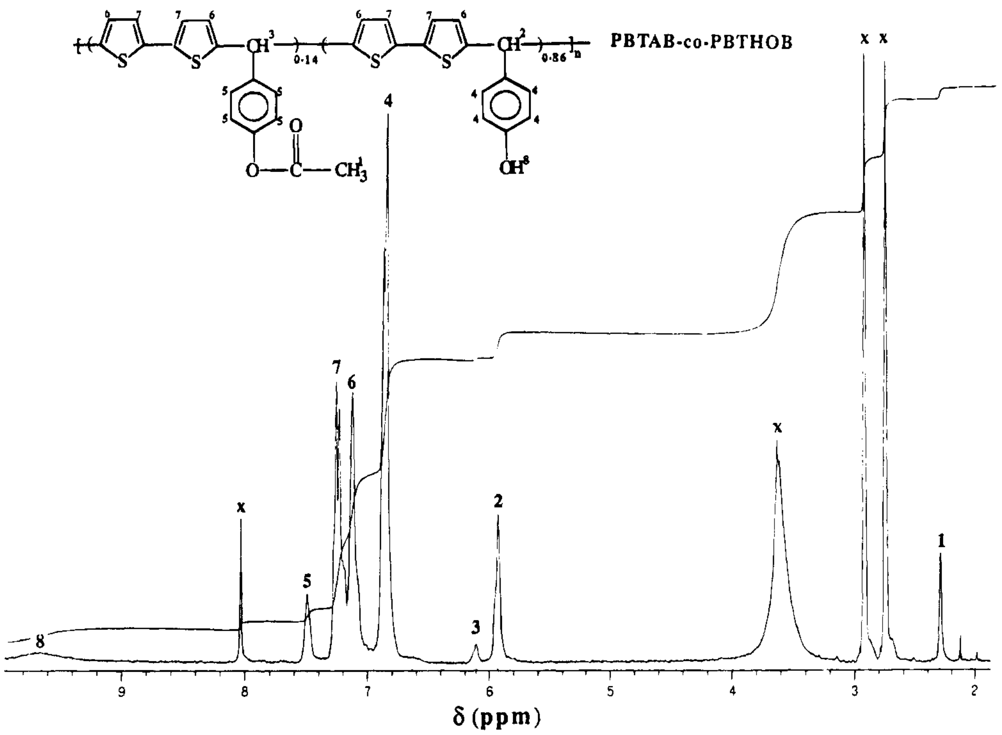


Figure 6. ^{1}H NMR spectrum of PBTAB-*co*-PBTHOB in deuterated DMF ("x" is DMF solvent or water in DMF).

about 400 °C and those of PBTAB-*co*-PBTHOB and PBTNB are about 300 °C. The onsets of thermal decomposition of all of the poly(heteroarylene methylenes) **2**–**6** in a nitrogen atmosphere at a heating rate of 10 °C/min as collected in Table 4.

Figure 9 shows the DSC curves of PTBQ, PHTB, PMTHB, PMTBB, and P3HT obtained in a nitrogen atmosphere at a heating rate of 20 °C/min. The glass transition temperature (T_g) was observed in all five polymers of Figure 9. PTBQ has a T_g of 138 °C. By substituting a long alkyl chain on the 3-position of the thiophene ring of PTBQ or a long alkoxy group or a benzoxy group on the phenyl side group, the T_g decreases to 37 (PHTB), 11 (PMTHB), and 68 °C (PMTBB), respectively. For comparison, the glass transition temperature of P3HT was observed at 19 °C. Polymers **2**–**3** are amorphous materials with T_g values from −18 to +138 °C and they did not show any crystalline melting peaks before decomposition. Figure 10 shows the DSC curves of polymers **4**, the poly[(bithiophenediyl)methylenes]. PBTM does not exhibit any clear thermal transition up to 400 °C. By substituting a phenyl ring at the bridge carbon of PBTM, a T_g was observed at 127 °C for PBTB. A further decrease of the T_g from 127 to 3 °C was observed by substitution of a *p*-heptyloxy group for the hydrogen in the phenyl ring (PBTHB). A similar *p*-nitro group (PBTNB: 135 °C) or a hydroxy group (PBTAB-*co*-PBTHOB: 146 °C) substi-

Table 3. Molecular Weights and Intrinsic Viscosities of Selected Poly(heteroarylene methylenes) and Poly(3-hexylthiophene)

polymer	$\bar{M}_w{}^a$	$\bar{M}_n{}^a$	$\bar{M}_w/\bar{M}_n$	$\bar{D}\bar{P}_n{}^b$	$[\eta]$ (dL/g)
PMTB	1280	1000	1.27	5.3	0.038^e
PMTHOB	1780	1370	1.30	6.7	0.048^e
PMTAB	1395	1295	1.07	5.3	0.044^e
PBuTM	22000	3177	6.92	20.6	0.094^f
PTBQ	1180	970	1.22	5.6	0.046^e
PTNBQ	1050	870	1.21	4.0	0.042^e
P3HT	66780	20570	3.25	123.7	0.445^g
PBTM	5200	3600	1.46	20.2	0.087^h
PBTB	17850	8600	2.08	33.8	0.088^e
	7300^c	2370^c	3.08^c	9.4^c	0.111^g
PBTAB-*co*-PBTHOB	7680	4220	1.85	24.6	0.117^e
PBTHB^d	10400	3100	3.27	8.4	0.089^g
	2800	1400	2.0	3.8	
PBTNB	2400	1460	1.62	4.9	0.050^h
PTTHB	15800	7400	2.14	16.4	0.089^e

[a] Molecular weights of PBTM, PBTB, and PBTAB-*co*-PBTHOB were measured in DMF; other polymers were measured in THF. [b] Based on the corresponding nonconjugated polymer. [c] In THF. [d] From two different polymerizations. [e] In DMF. [f] In *p*-dioxane. [g] In THF. [h] In NMP.

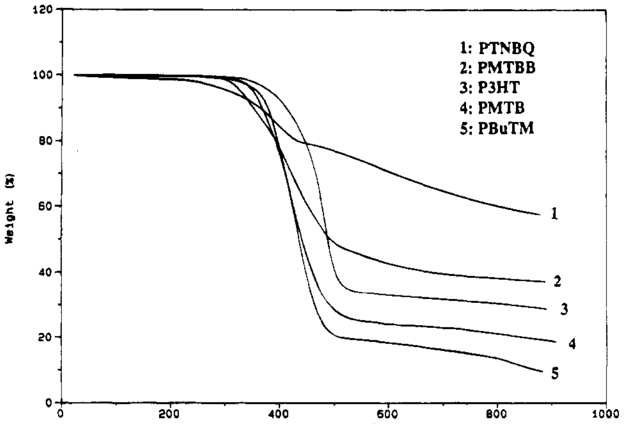


Figure 7. TGA curves of PTNBQ, PMTBB, P3HT, PMTB, and PBuTM obtained in flowing N_2 at a heating rate of 10 °C/min.

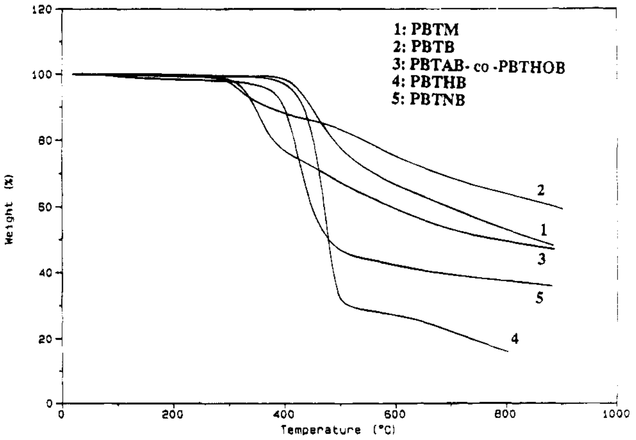


Figure 8. TGA curves of PBTM, PBTB, PBTHB, PBTNB, and PBTAB-*co*-PBTHOB obtained in flowing N_2 at a heating rate of 10 °C/min.

Table 4. Properties of Poly(heteroarylene methylenes)

polymer	$T_d{}^a$ (°C)	T_g (°C)	λ_{max} (nm) (log ϵ_{max})
PMTB	385	133	245 (4.22), 451 (3.74)^b
PMTHB	365		228 (4.40), 450 (3.75)^b
PMTNB	300	125	267 (4.27), 450 (3.71)^b
PMTAB	250		233 (4.18), 457 (3.61)^b
PMTHOB	275		230 (4.19), 457 (3.94)^b
PMTBB	310	68	235 (4.32), 450 (3.62)^b
PBuTM	330		244 (3.90), 366 (2.92)^b
PHTM	348	−18	242 (3.82), 372 (3.00)^c
PHTB	300	37	450 (3.58)^d
PTBQ	375	138	235 (4.14), 366 (3.87), 471 (3.80)^b
PTNBQ	300		271 (4.38), 485 (4.01)^b
P3HT	360	19	435 (3.95)^c
PBTM	420		318 (4.16)^e
PBTB	380	127	324 (4.19)^f
PBTHB	420	3	332 (4.24)^c
PBTNB	300	128	324 (4.23)^e
PBTAB-*co*-PBTHOB	300	146	331 (4.20)^f
PTTB^g	410		372 (4.44)^c
PTTHB	395	44	369 (4.60)^c
PTTNB	300		372 (4.46)^c
PQTB	330		401 (4.39)^f
PQTHB	330		402 (4.48)^f

[a] Onset of thermal decomposition temperature in N_2. [b] Sulfolane. [c] THF. [d] CH_2Cl_2. [e] NMP. [f] DMF. [g] This result for PTTB has been reported in ref 7.

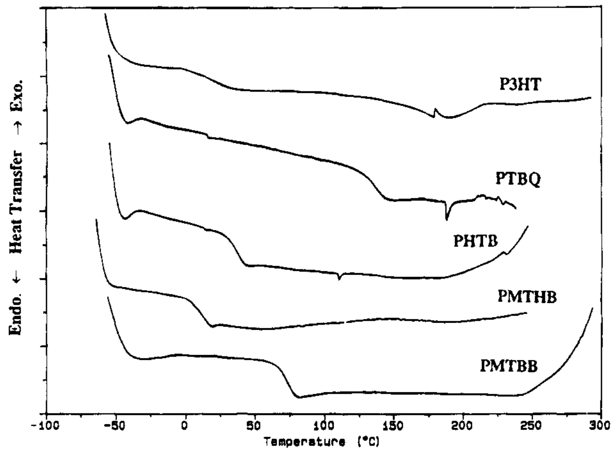


Figure 9. DSC thermograms of P3HT, PTBQ, PMTHB, PMTBB, and PHTB obtained in flowing N_2 at a heating rate of 20 °C/min.

tution does not significantly change the T_g. The effect of the size of the thiophene oligomer in the main chain on the glass transition temperature can be observed from a comparison of PBTHB, PTTHB, and PQTHB, which all have the same *p*-(heptyloxy)phenyl side group. Increase of the thiophene oligomer size in the polymer backbone causes an increase of the T_g from PBTHB (3 °C) to PTTHB (44 °C) and PQTHB (no T_g was observed up to 300 °C). This result indicates that the chain rigidity of this class of polymers increases with the size of the thiophene oligomer in the backbone.

The X-ray powder diffraction patterns of PBTAB-*co*-PBTHOB and other polymers **4** showed that the polymers were largely amorphous. In the case of PBTAB-*co*-PBTHOB, a broad amorphous peak centered at a *d*-spacing of ~4.75 Å was observed. Similar results were obtained with the other polymer samples. These X-ray diffraction results are in accord with the DSC results which showed that the polymers were amorphous.

Optical Absorption Spectra. The solution optical absorption spectra of several members of polymers **2** and **3** along with P3HT are shown in Figure 11. One of the most striking features of the optical absorption spectra of the poly(heteroarylene methylenes) shown in this figure is the strong visible absorptions which clearly rule out structure **1** (Chart 1) in accord with the previously discussed FTIR and ^{1}H NMR results. The optical spectra indicate a high degree of dehydrogenation and incorporation of quinoid 2,5-thienylene rings in poly-

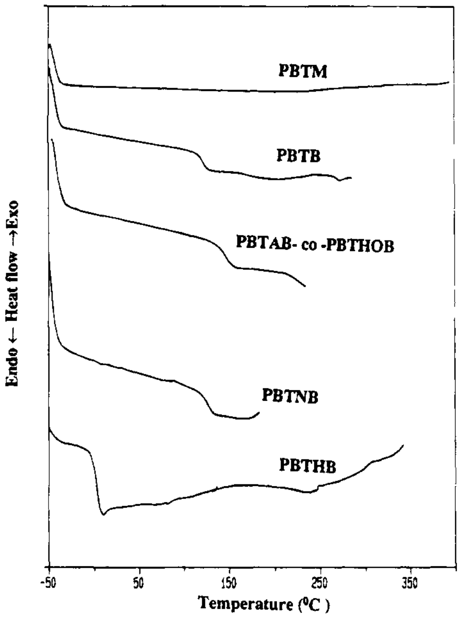


Figure 10. DSC curves of PBTM, PBTB, PBTHB, PBTNB, and PBTAB-*co*-PBTHOB obtained in flowing N_2 at a heating rate of 20 °C/min.

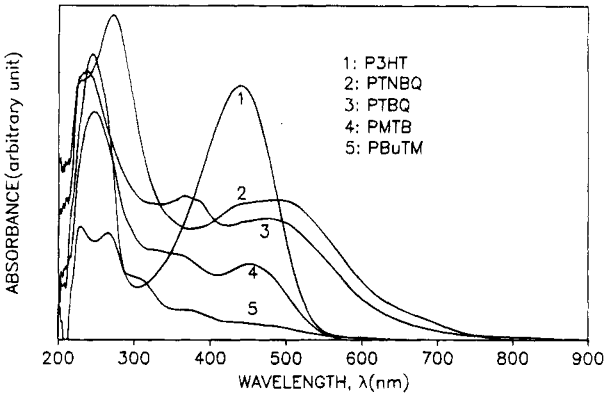


Figure 11. Optical absorption spectra of P3HT (1, in THF), PTNBQ (2, in sulfolane), PTBQ (3, in sulfolane), PMTB (4, in sulfolane), and PBuTM (5, in CH_2Cl_2).

mers **2** and **3** (Chart 1). The methylene- and methine-bridged polythiophenes in Figure 11 are characterized by two main absorption bands, one in the ultraviolet (UV) region and the other in the visible. The UV absorption bands of these polymers except PTNBQ and PMTNB arise from the $\pi-\pi^*$ transition of the aromatic thiophene ring and have λ_{max} from 230 to 245 nm. The UV absorption bands of PTNBQ and PMTNB which are assigned to the $\pi-\pi^*$ transition of the *p*-nitrophenyl side group have a λ_{max} that is about 30 nm larger than that of other polymers **2**–**3**. The visible absorption band of polymers **2**–**3** arises from the $\pi-\pi^*$ bandgap transition and has a λ_{max} from 366 to 485 nm. The λ_{max} of most of the polymers **2**–**3** in Chart 1 and Figure 11 is comparable to that of P3HT (λ_{max} = 435 nm) (see Table 4).

The solution optical absorption spectra of poly(heteroarylene methylenes) **4**–**6** are shown in Figures 12–14, respectively. The λ_{max} is found to vary from 318 to 332 nm for polymers **4**, from 369 to 372 nm for polymers **5**, and from 401 to 402 nm for polymers **6**. The observed λ_{max} for these polymers is to be compared to those of the corresponding thiophene oligomers α-bithiophene, α-terthiophene, and α-quaterthiophene, which have λ_{max} at 305–310, 350–355, and 390–395 nm, respectively, depending on the solvent. Thus, the conjugated bithiophene, terthiophene, and quaterthiophene segments in the main chain and the side group at the carbon bridge are isolated by the sp^3-carbon atom. The side group at the bridged carbon shows a negligible effect on the λ_{max} of the optical absorption spectra of the poly(heteroarylene methylenes) **4**–**6**.

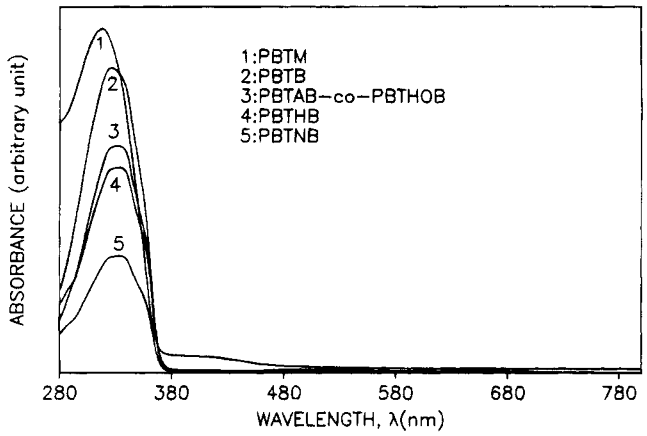


Figure 12. Optical absorption spectra of PBTM (1, in NMP), PBTB (2, in THF), PBTAB-*co*-PBTHOB (3, in THF), PBTHB (4, in CH_2Cl_2), and PBTNB (5, in THF).

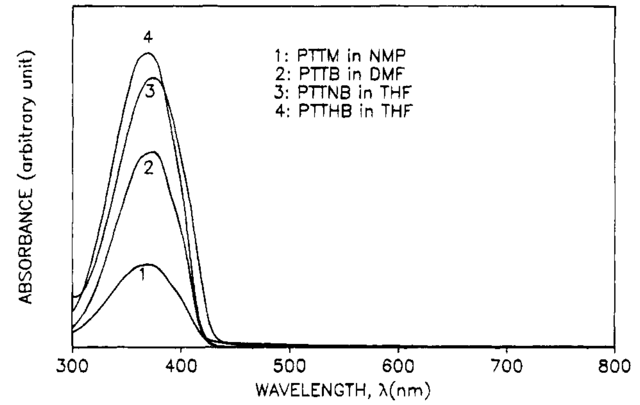


Figure 13. Optical absorption spectra of PTTM (1, in NMP), PTTB (2, in DMF), PTTNB (3, in THF), and PTTHB (4, in THF).

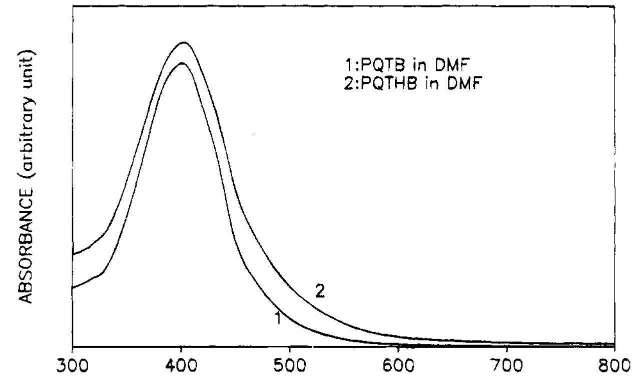


Figure 14. Optical absorption spectra of PQTB (1, in DMF) and PQTHB (2, in DMF).

Conclusions

We have prepared a series of poly(heteroarylene methylenes) by acid-catalyzed polymerization of thiophene oligomers (n = 1–4) with aldehydes. The as-prepared poly[(α-bithiophenediyl)methylenes], poly[(α-terthiophenediyl)methylenes], and poly[(α-quaterthiophenediyl)methylenes] were obtained as nonconjugated polymers with π-conjugated moieties identical with the corresponding oligomers. However, the as-prepared poly[(2,5-thienylene)methylenes] were found to be highly dehydrogenated (23–100%) and consequently have solution optical absorption bands in the visible that are comparable to those of poly(3-hexylthiophene). The chemical and physical properties of the poly(heteroarylene methylenes), such as solubility and T_g, were significantly modified by the variation of the side group substituent at the sp^3-carbon atom bridge and by the size of the thiophene oligomer in the main chain.

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