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Synthesis and Characterization of Carbon Atom Bridged Heterocyclic Polymers of Specified Conjugation Length. 1. Novel Polyterthiophenes

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ABSTRACT: New polymers containing α-(5,5″-terthiophenediyl) segments separated by an sp^3-carbon atom in the main chain were synthesized by acid-catalyzed polymerization of α-terthienyl with aldehydes and characterized. The polyterthiophenes (PTTs) containing CRH bridging groups are soluble in organic solvents. The methylene-bridged polymer, poly[α-(5,5″-terthienyl)methylene] (PTTM), is highly crystalline whereas the benzylidene-bridged and heptylidene-bridged polymers are largely amorphous. The sp^3-bridged polyterthiophenes exhibit solution optical absorption maxima from 362 to 379 nm, depending on the side group at the bridge carbon, as expected for the nonconjugated polymers. The new heterocyclic polymers represent the first example of main chain polymers containing conjugated segments of precisely defined π-electronic conjugation length. The polymers are useful precursors to multiblock conjugated copolymers, with alternating aromatic α-(5,5″-terthienyl) and α-(5,5″-terthienylquinodimethane) segments in the main chain. They are the first examples of organic semiconductor superlattices and also have excellent third-order nonlinear optical properties.

Introduction

One of the important contemporary problems in polymer science is the design, synthesis, characterization, and processing of new polymeric materials with interesting or useful linear optical, nonlinear optical, electrooptical, electronically conducting, magnetic, or superconducting properties for applications in electronic and photonic technologies. A related perennial problem is the fundamental understanding of the underlying structure–property relationships in the materials. Conjugated polymers, as a class, represent one of the most fertile areas of investigation relative to these problems. Research in the last decade has led to important progress in the experimental and theoretical understanding of electronic and electrical properties in conjugated polymers and achievement of semiconducting to metallic conductivities ($\sim 10^2$ to 10^5 Ω^{-1} cm^{-1}) in doped conjugated polymers.[1-4] More recently, the same conjugated polymers have become of wide interest because they exhibit ultrafast (picosecond or less) and large third-order nonlinear optical properties ($\chi^{(3)} \sim 10^{-12}$–10^{-8} esu).[5-8]

Aromatic heterocyclic conjugated polymers based on the five-membered thiophene, pyrrole, and furan rings (Figure 1, structure III) have been widely investigated by several research groups.[6,8-19] Initial interests on conjugated polypyrroles and polythiophenes stemmed from both the high conductivity ($\sim$10–1000 Ω^{-1} cm^{-1}) and exceptional stability in their doped state.[9,10,14] Recently, synthesis of poly(3-alkyl-2,5-thiophenediyl)[16-18] and poly(3-alkyl-2,5-pyrrolediyl)[19] has led to the solution characterization of properties of these conjugated polymers. An earlier chemical and electrochemical synthesis[20] of poly(1,3-benzo[c]thiophenediyl) or polyisothianaphthene (PITN), whose optical band gap is remarkably small (1.13 eV), demonstrated the significant effect of molecular structure on the intrinsic electronic and optical properties of heterocyclic polymers.

A central idea in the theoretical and experimental understanding of many properties of conjugated polymers[1-28] is the concept of "conjugation length" or "π-electronic delocalization length". Although there is no one universal measure of the π-electronic delocalization length,[21-29] L_d, of a conjugated system, the underlying chemical or physical notion of the extent of sp^2-carbon π-orbital overlap is often clear. Experimentally measurable parameters which have been used as measures of the electronic delocalization length of conjugated systems include the chain length or the number of repeating units in the chain, the number of conjugated double bonds, the wavelength

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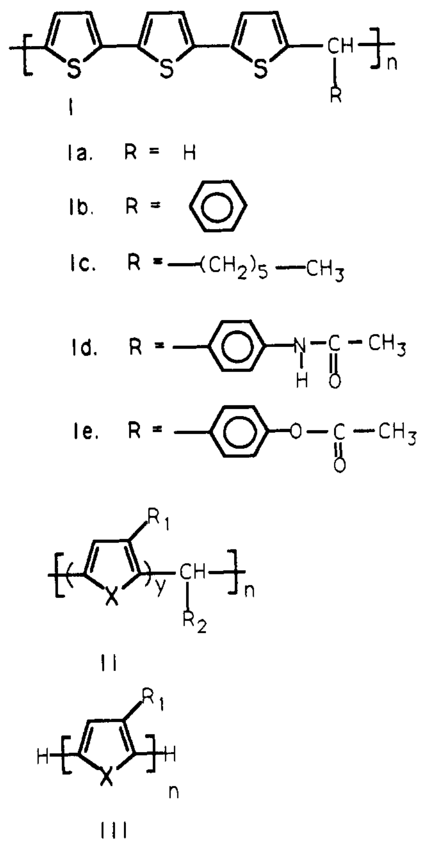


Figure 1. Structures of aromatic heterocyclic polymers.

of the lowest energy $\pi-\pi^*$ absorption maximum (λ_{max}), the band gap E_g, and others. Regardless of how measured, many solid-state and solution properties of conjugated polymers have been correlated with or explained in terms of the conjugation length.[1-29] It has been shown from many studies that both the maximum dc conductivity and the nature of electronic transport in doped conducting polymers depend on the conjugation length.[28,29] It has also been shown theoretically and experimentally that the third-order nonlinear optical properties ($\chi^{(3)}$ and γ) of conjugated polymers scale[6b,25,26] as $L_d{}^m$, where m is between about 5 and 7.

Two possible approaches can be followed in the experimental investigation of the effects of π-electron delocalization length on properties. The classic approach uses oligomers of varying chain length to investigate the desired properties and extrapolate to the high polymer. For example, this approach has been used to correlate the third-order nonlinear optical properties to the chain length of polyenes[25] and of polythiophenes.[6b] Although this approach qualitatively simulates the effects of chain length and π-electron delocalization, its limitations include the neglect of important factors of the polymer structure, e.g., effects of polymer chain configuration, conformation, degree of crystallinity, etc., which can be very different from those of oligomers. The second and more desirable approach is to incorporate segments of varying conjugation length into the polymer backbone. This latter approach has so far been used only in the investigation of the electronic and electrical properties of polyacetylene.[28,29] The so-called segmented polyacetylenes[28,29] have been prepared by reaction of doped polyacetylene with water, deuterated water, or deuterated methanol. Although the total concentration of the resulting sp^3-carbons can be measured and correlated with the achieved maximum conductivity or other physical property, the distribution of the sp^3-carbons, and hence conjugation length, in segmented polyacetylenes is necessarily statistical.[28]

The purpose of our studies being reported here and in a series of forthcoming papers[30] is the synthesis and characterization of new aromatic heterocyclic polymers containing precisely defined conjugated segments separted by single sp^3-carbon atoms in the main chain (Figure 1, structure II). We believe that such a class of polymers offers the potential for a systematic investigation of the effects of polymer structure, particularly π-conjugation length, on electronic structure, intrinsic electronic properties, electrical conductivity, electronic transport mechanisms, and nonlinear optical properties. Our interest in these sp^3-carbon atom bridged heteroaromatic polymers was further stimulated by the discovery that the methylene bridges can be dehydrogenated to yield multiblock conjugated copolymers which can be regarded as organic semiconductor superlattices.[31,32] We have prepared a large number of homopolymers II and related copolymers, with varying conjugated segment chain length y and substituents X, R_1, and R_2. A preliminary account of the synthesis of some members of II was given elsewhere.[33] Also, preliminary accounts of the third-order nonlinear optical properties of some members of II have appeared.[8] Here we describe the synthesis and characteirzation of I (Figure 1). The linear polyterthiophenes (PTTs), I, were prepared by acid-catalyzed condensation of linear α-terthienyl with aldehydes (RCHO). Thus, a large number of possible side groups can be incorporated in these polymers because of the numerous commercially available aldehydes.

Experimental Section

Materials. Pure α-terthienyl (2,2′:5′,2″-terthiophene) synthesized according to the method of Wynberg and Metselaar[34] was purchased from Syncom BV (Groningen, The Netherlands) and used without further purification. Paraformaldehyde (Kodak), *p*-acetamidobenzaldehyde (Kodak), *p*-acetoxybenzaldehyde (99.5%, Kodak), sulfuric acid (Mallinckrodt), *p*-dioxane (Kodak or Burdick & Jackson), and 99.99% argon (Linde Specialty Gases) were used as received. Benzaldehyde (Baker) and heptaldehyde (Kodak) were purifed by distillation.

Polymer Synthesis. Poly[α-(5,5″-terthiophenediyl)methylene] (PTTM, Ia). Into a 500-mL three-necked round-bottom flask fitted with a condenser capped with a gas outlet, a mechanical stirrer, a thermometer, and an argon gas inlet were placed 54 mL of *p*-dioxane solvent, 4.00 g (0.016 mol) of α-terthiophene, 0.5693 g (0.019 mol) of paraformaldehyde, and 0.28 mL (0.005 mol) of concentrated H_2SO_4. The temperature was allowed to rise and was maintained at 86 °C. The reaction ran 18 h in a flowing argon atmosphere. A yellowish product was recovered in 500 mL of MeOH and dried in vacuum oven at 35 °C. The yield was greater than 64%. The polymer was slightly soluble in DMF and partially soluble in *N*-methyl-2-pyrrolidone (NMP). Anal. Calcd for $(C_{13}H_8S_3)_n$: C, 59.96; H, 3.10; S, 36.94. Found: C, 57.75; H, 3.16; S, 36.96. IR: 3100, 3065, 2925, 1628, 1594, 1507, 1425, 1310, 1230, 1190, 1105, 1055, 856, 830, 790, 685, 570, 460 cm^{-1}.

Poly[α-(5,5″-terthiophenediyl)benzylidene] (PTTB, Ib). The polymerization mixture consisted of 56 mL of *p*-dioxane, 8.002 g (0.032 mol) of α-terthiophene, 3.56 mL (0.035 mol) of benzaldehyde, and 0.61 mL (0.011 mol) of concentrated H_2SO_4. The reaction time was 6 h at a temperature of 82 °C. A yellow product was recovered in methanol, redissolved in THF, recovered in methanol, and dried in a vacuum at 35 °C. The yield was greater than 82%. Anal. Calcd for $(C_{19}H_{12}S_3)_n$: C, 67.82; H, 3.59; S, 28.58. Found: C, 64.88; H, 4.10; S, 30.06. IR: 3062, 3024, 2970, 2862, 1751, 1688, 1598, 1514, 1497, 1452, 1366, 1228, 1205, 1067, 1035, 1004, 981, 967, 950, 912, 852, 836, 795, 740, 703, 630, 480 cm^{-1}. ^{1}H NMR: δ 5.95, 6.78, 7.10, 7.20, 7.30, 7.35 ppm (TMS).

Poly[α-(5,5″-terthiophenediyl)heptylidene] (PTTH, Ic). The polymerization mixture was 30 mL of *p*-dioxane, 3.99

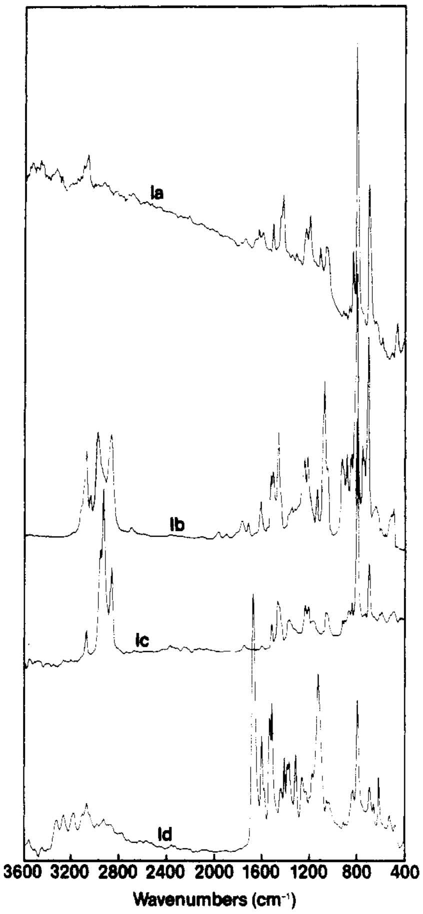


Figure 2. FTIR absorption spectra of films of the PTTs.

g (0.016 mol) of α-terthiophene, 2.7 mL (0.019 mol) of heptaldehyde, and 0.28 mL (0.005 mol) of concentrated H_2SO_4. The reaction time was 18 h at a temperature of 86 °C. A yellowish product was recovered upon quenching in 300 mL of MeOH. Reprecipitation from THF solution/MeOH gave a yellowish polymer which was soluble in several solvents including THF and DMF. The yield was greater than 80%. Anal. Calcd for $(C_{19}H_{20}S_3)_n$: C, 66.23; H, 5.85; S, 27.91. Found: C, 63.23; H, 5.79; S, 27.51. IR: 3065, 2952, 2928, 2854, 1512, 1464, 1364, 1228, 1200, 1054, 864, 836, 790, 690, 576, 480 cm^{-1}.

Poly[α-(5,5''-terthiophenediyl)-*p*-acetamidobenzylidene] (PTTAAB, Id). The polymerization mixture was 38 mL of *p*-dioxane, 4.00 g (0.016 mol) of α-terthiophene, 3.104 g (0.019 mol) of *p*-acetamidobenzaldehyde, and 0.28 mL (0.005 mol) of concentrated H_2SO_4. The reaction time was 6 h at a temperature of 88 °C. A yellow product was recovered in 500 mL of MeOH and reprecipitated. The yield was greater than 51%. The polymer was soluble in several solvents including THF and DMF. Anal. Calcd for $(C_{21}H_{15}S_3NO)_n$: C, 64.09; H, 3.84; S, 24.44; O, 4.06; N, 3.56. Found: C, 60.87; H, 3.82; S, 28.35; O, 4.40; N, 2.48. IR: 3312, 3254, 3172, 3060, 2972, 2912, 2860, 1660, 1592, 1526, 1504, 1429, 1401, 1376, 1359, 1305, 1252, 1165, 1116, 1047, 1028, 828, 788, 686, 646, 608, 520, 470 cm^{-1}. ^{1}H NMR δ 1.92, 5.84, 6.75, 7.00, 7.20, 7.51, 7.63, 9.96 ppm (TMS). ^{13}C NMR: δ 24.0, 47.33, 119.75, 124.20, 125.0, 128.0, 129.12, 136.2, 136.3, 140.0, 148.0 ppm (TMS).

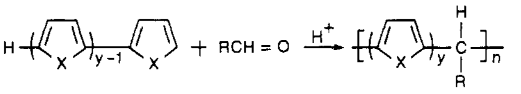
Poly[α-(5,5''-terthiophenediyl)-*p*-acetoxybenzylidene] (PTTAB, Ie). The polymerization mixture was 60 mL of *p*-dioxane, 0.6 g (2.415 mmol) of α-terthiophene, 0.35 mL of (2.49 mmol) *p*-acetoxybenzaldehyde, and 0.05 mL of concentrated H_2SO_4. The temperature was 85 °C, and the reaction time was 24 h. A yellowish solution was poured into 500 mL of stirring hexane. The polymer was dissolved in THF, reprecipitated in hexane, filtered, and dried in a vacuum oven at 40 °C. The yield was 61%. Anal. Calcd for $(C_{21}H_{14}S_3O_2)_n$: C, 63.95; H, 3.58; S, 24.36; O, 8.11. Found: C, 62.80; H, 3.38; S, 27.39; O, 7.46. IR: 3047, 2927, 2851, 1733, 1639, 1604, 1578, 1511, 1436, 1368, 1222, 1171, 1139, 1055, 839, 794, 589, 478 cm^{-1}. ^{1}H NMR: δ 1.42 (3 H), 6.0 (1 H), 6.92 (4 H), 7.24 (4 H), 7.3 (2 H) ppm (TMS).

Characterization. Infrared spectra of polymer thin films cast from THF, DMF, or NMP solutions were recorded in KCl windows at room temperature (23 °C) by using a Digilab Model FTS-14 Fourier transform infrared (FTIR) spectrometer. Optical absorption spectra were obtained at room temperature (23 °C) in the 185–3200-nm-wavelength range with a Perkin-Elmer Lambda 9 UV–vis NIR spectrophotometer and THF, DMF, DMSO, or NMP solutions. Thermal analysis, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) were done on a DuPont Model 1090B thermal analyzer using a flowing nitrogen or air atmosphere. Indium (156.6 °C) and zinc (419.4 °C) DSC standards were used to calibrate the accuracy of measured transition points. Samples (~3–4 mg) were sealed in DSC pans and run from -50 to 400 °C at 20 °C/min. TGA runs were performed at a heating rate of 10 °C/min. Polymer molecular weight was characterized by using a Waters Associate Model 150C gel permeation chromatograph (GPC) at 60 °C. The GPC was packed with 10^5-, 10^4-, 10^3-, and 500-Å ultrastyrogel columns in DMF and operated at a flow rate of 0.9 mL/min. Polystyrene standards were used to estimate weight-average and number-average molecular weights. Elemental analysis was done by Galbraith Laboratories, Inc. (Knoxville, TN).

^{1}H NMR and ^{13}C NMR spectra of some of the polymers were obtained in deuterated DMF solutions by using a Nicolet spectrometer at 300 MHz. X-ray diffraction patterns of samples were obtained by using a Rigaku powder X-ray diffractometer and a computerized diffraction analyzer with sealed tube Cu Kα X-ray radiation at 1.540562-Å wavelength. The 2θ scans were from 3° to 93°, with a step size of 0.02° and 1 s of counting per step. Powdered samples were held on a single-crystal silicon wafer with grease. The silicon wafer was detuned 2° to suppress reflections from the Si crystal.

Results and Discussion

Polymer Structure. The linear polymer structure I (or II) is that anticipated from the synthetic scheme, under protonic acid catalysis:



Thiophene and other five-membered aromatic heterocycles preferentially undergo electrophilic substitution reactions at the α-positions (2,5-positions) rather than at the β-positions (3,4-positions).[35,36] For example, in the trifluoroacetylation of thiophene with trifluoroacetic acid, α/β reactivity ratios of 10^3 or higher are achieved.[35] Even higher preferential α-orientation for electrophilic substitution reactions, such as the present acid-catalyzed condensation polymerization with aldehydes, can be expected in 2,2''-bithiophene, α-terthienyl, and higher linear oligomers. The solubility of the polyterthiophenes (PTTs) in organic solvents suggests absence of any significant branches or cross-linking. The principal direct evidence for the linear polymer structure I is from infrared and NMR spectra, which are discussed below.

Figure 2 shows the infrared absorption spectra of four members of I. The very strong band near 790 cm^{-1} in all four polymers is due to C–H out-of-plane vibration and is characteristic of α-linkages in thiophene rings. The band at 686–703 cm^{-1} in all the polymers has been attributed to C–H vibration and considered evidence for β-substitution or thiophene end groups in polythiophenes.[11,12,37] The 686–703-cm^{-1} band is also present in α-terthiophene.[38] In the case of Ib, the 703-cm^{-1} band is also attributable to a monosubstituted benzene ring. The presence of the sp^3-carbon atom (CRH) bridges is evidenced by the C–H bands in the 2800–3000-cm^{-1} region and in the case of Ib additionally by the ~703-cm^{-1} band. Note the absence of a carbonyl band in the 1650–1750-cm^{-1} region except

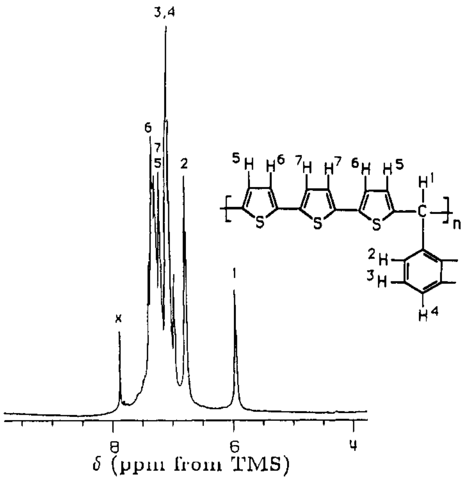


Figure 3. Proton NMR spectrum of PTTB (DMF solvent peak indicated by x).

in Id, where it is part of the acetamido side group, and in Ie, where it is part of the acetoxy side group. The 3312-cm^{-1} band in Id is attributed to the N-H of the acetamido side group. The 3254-cm^{-1} band present in Id is probably due to a N-H stretching vibration due to intermolecular or intramolecular hydrogen bonding involving the amide (NHCO) side group.

^{1}H and ^{13}C NMR spectra of the PTTs as well as the linear thiophene oligomers were obtained to further confirm the polymer structure. Interpretation of the NMR spectra and assignment of chemical shifts were facilitated by the NMR spectra of the oligomers in conjunction with those of poly(2,5-thiophenediyl)[16,37] and polystyrenes[39] in the literature. The ^{1}H NMR spectrum of PTTB (Ib) in deuterated DMF is shown in Figure 3. A characteristic feature of the ^{1}H NMR spectra of I is the singlet resonance at 5.95 ppm (relative to TMS) in PTTB, 6.0 in PTTAB, and 5.84 ppm in PTTAAB due to the bridge methine proton, C(R)H. The ^{13}C NMR spectra showed a resonance at 47–48 ppm (47.33 ppm in PTTAAB) due to the sp^3-carbon atom bridges on the main chain. The NMR spectra confirmed the linear polymer structure I and the absence of β-linkages in the polymers. Secondary evidence for the polymer structure includes electronic absorption spectra, which will be discussed later, and the elemental analysis, which is in fairly good agreement with that theoretically calculated for the polymer repeating unit I.

Molecular Weight and Solution Properties. The PTTs are soluble in some organic solvents, including THF, DMF, or NMP, giving solutions with light-yellow colors. PTTB and PTTH samples were completely soluble in THF, DMF, and NMP. PTTM was insoluble in THF, partially soluble in DMF, and soluble in NMP, giving orange solutions. Hot (~100 °C) clear orange solutions of PTTM in DMF turned cloudy when cooled to room temperature (25 °C). PTTAAB was partially soluble in THF and DMF and soluble in NMP, giving yellowish solutions. Excellent transparent yellowish films of the PTTs, except PTTM, were obtained by casting from solutions. PTTM films cast from DMF or NMP solutions were generally cloudy and of poorer quality compared to the other PTTs due to its higher degree of crystallinity.

The molecular weight distributions of the PTTs revealed by GPC were generally bimodal except PTTH and PTTB, which had single distributions. The presence of oligomers (n < 10) in PTTB was evidence by discrete peaks in its chromatogram. The molecular weight parameters for the PTTs, calculated relative to polystyrene standards, are shown in Table I. The observed dispersity in the polymer samples varies from 1.60 for the high molecular weight fraction of PTTAAB to 2.35 for PTTM. The estimated number-average degree of polymerization, $\overline{\mathrm{DP}}_n$, shown in Table I is probably less than the true value. The estimated degree of polymerization of about 4 in PTTB implies an average of about 15 thiophene rings (counting the one trimer end group) in the main chain, separated by an sp^3-carbon atom every 3 rings. PTTH and low molecular weight PTTAAB similarly have an estimated 27 and 32 thiophene rings per average chain, respectively. In contrast, PTTM has an estimated 5370 rings per average chain. The lower molecular weight of PTTB and PTTH relative to PTTM and PTTAAB arises in part from the polymerization time and the reactivity of the relevant aldehyde.

Table I
Molecular Weight Properties of the PTTs

PTT	M_w	M_n	M_w/M_n	DP_n
PTTM[a]	1095600	466720	2.35	1790
PTTB	2560	1260	2.03	3.7
PTTH	5550	2790	1.99	8.1
PTTAAB	6880	3770	1.83	9.6
	1985600	1243000	1.60	3160

[a] Only the parameters for the high molecular weight fraction of PTTM are given; meaningful parameters for the low molecular weight fraction could not be calculated.

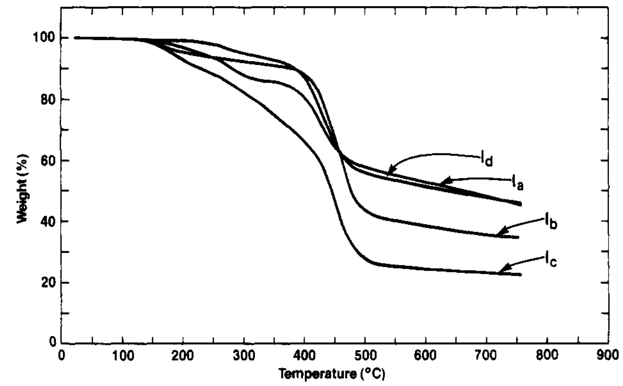


Figure 4. Thermal stability of the PTTs in nitrogen atmosphere at 10 °C/min.

Thermal Properties and Crystallinity. Figure 4 shows the thermal stability of the PTTs in nitrogen atmosphere. It is clear that the polymers show similar decomposition characteristics. Onset of weight loss is in the range ~150–250 °C where polymer decomposition begins. Weight loss prior to 400 °C can be attributed to the loss of low molecular weight fractions in light of the molecular weight data. Note that at 750 °C the weight remaining is about 23–46%, in decreasing order of weight remaining: PTTAAB > PTTM > PTTB > PTTH.

The results of a DSC investigation of possible crystalline melting and glass transition temperatures of the PTTs are shown in Figure 5. The multiple endothermic peaks exhibited by Ia, Ib, and Id in Figure 5 are real and reproducible. PTTM has endothermic transitions at 66, 118, 164, 180, 222, and 324 °C. PTTB has transitions at 79 and 324 °C and PTTH, has a single endotherm at 240 °C. PTTAAB has two major endotherms at 128 and 291 °C and a small transition at 159 °C. In view of the observed nonhomogeneous molecular weight distributions in the polymer samples, the multiple endothermic peaks may be due to melting in different molecular weight fractions. Also, possible side-chain melting phenomena in PTTAAB can result from hydrogen bonding through its side-chain amide group. In the case of PTTM, where

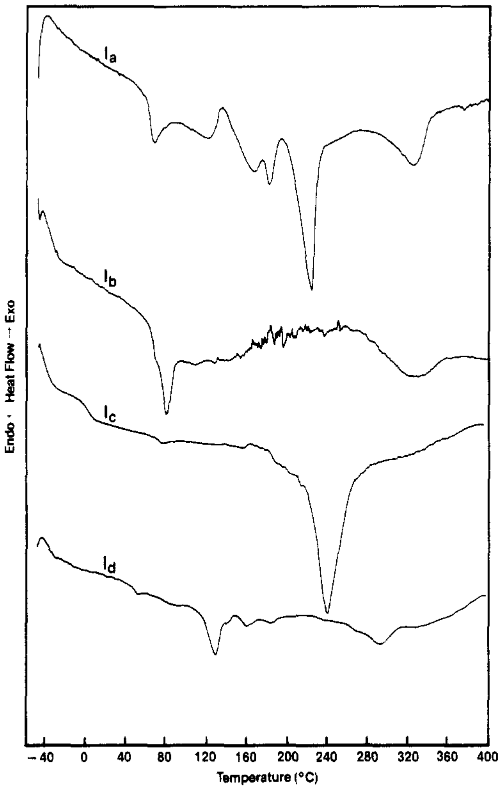


Figure 5. DSC thermograms of the PTTs; the scales of the ordinate are not the same on all four curves.

CH_2 units alternate with rigid rod linear α-terthiophene segments, liquid-crystalline phases may be anticipated. On the basis of the DSC results, solubility behavior of the PTTs, solution cast film properties, and X-ray diffraction patterns, the estimated degree of crystallinity is in the order PTTM > PTTAAB > PTTAB > PTTB > PTTH.

X-ray diffraction patterns (Figure 6) showed that only the methylene-bridged polymer, PTTM, is highly crystalline. As to be expected, substitution of a bulky side group for one of the CH_2 hydrogens dramatically reduces the degree of crystallinity as evidenced by PTTB, PTTH, and PTTAB that are largely amorphous. Such a bulky side group disrupts chain packing and lowers the degree of crystallinity, but it significantly improves the solubility. It should be noted that the crystal structure of the polymer PTTM is different from that of the oligomer α-terthiophene (α-TT) as evidence by the different reflections in their X-ray diffraction patterns (Figure 6).

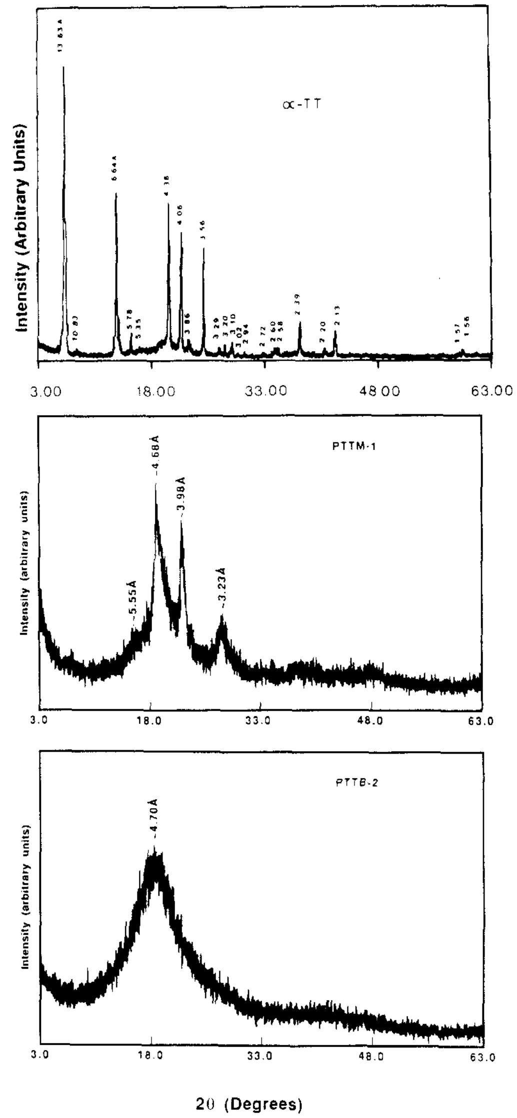


Figure 6. X-ray diffraction patterns of the PTTs and α-terthiophene (α-TT).

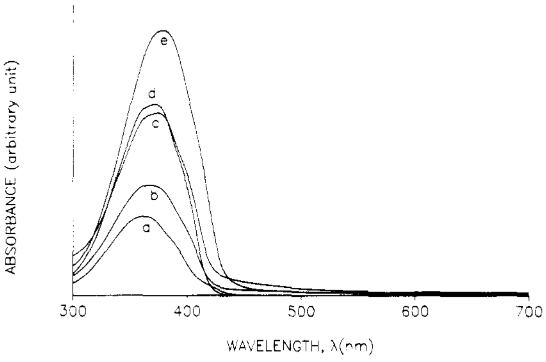


Figure 7. Electronic absorption spectra of PTTs: (a) PTTH/THF; (b) PTTM/NMP; (c) PTTAAB/DMF; (d) PTTB/THF; (e) PTTAB/DMSO.

Electron Absorption Spectra. Figure 7 shows the solution electronic absorption spectra of the PTTs. The optical absorption maximum (λ_{max}) due to the $\pi-\pi^*$ transition is from 362 to 379 nm, and the corresponding molar extinction coefficient ϵ_{max} is about 2×10^4 M^{-1} cm^{-1}: PTTM, λ_{max} = 367 nm (ϵ_{max} = 19 400); PTTH, λ_{max} = 362 nm (29 400); PTTB, λ_{max} = 372 nm (27 700); PTTAAB, λ_{max} = 373 nm (29 300); PTTAB, λ_{max} = 379 nm (21 800). For comparison, the λ_{max} of thiophene oligomers α-terthiophene, α-quaterthiophene, and α-sexithiophene is 350–355, 395, 438 nm, respectively. The high molecular weight parent poly(2,5-thiophenediyl) (PT) has a λ_{max} of 480 nm.[14d] The electronic absorption results show that there is a small red shift when benzylidene groups replace the methylene bridge of PTTM. A small blue shift is observed when the bulky heptylidene replaces the methylene bridge of PTTM. However, the observed λ_{max} in the polyterthiophenes is quite comparable to that of α-terthienyl. Thus, the introduction of an sp^3-carbon between conjugated segments of α-terthienyl in the polymer backbone effectively interrupts conjugation along the chain and consequently isolates the electronic conjugated segments. Although hyperconjugation,[40] whereby the σ-orbital of the bridge C–H bond overlaps with the π-orbital systems of adjacent conjugated segments, is a possible mechanism for extending electronic delocalization along the polymer chain, the results show that this does not occur in polymers I and in fact in all the polymers II.[30] The results also rule our the possibility of self-condensation

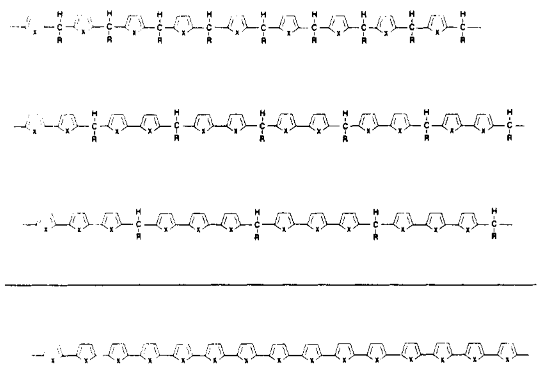


Figure 8. Chain structures of nonconjugated polymers II and conjugated polymers III.

of α-terthiophene during the polymerization with aldehydes. Such a side reaction would have produced conjugated segments with higher λ_{max} that are not observed; sexithienyl has a λ_{max} of 438 nm.

The most important conclusion from the electronic absorption spectra of the present polymers (Figure 1, I) is that they prove the successful preparation of polymers with predetermined conjugation length. As will be reported in forthcoming papers,[30] other polymers with the structure II with different conjugation length or conjugated segment chain length y have similarly been prepared and characterized. It is well-known that the λ_{max} or conjugation length of conjugated polymers increases with the degree of polymerization or repeating unit chain length,[21-24,41] n, until it eventually levels off at some finite chain length n_o that is significantly less than the maximum chain length (n_∞) of the high molecular weight polymer. In poly(2,5-thiophenediyl), structure III of Figure 1, the asymptotic λ_{max} of 480 nm is reached at $n_o \sim$ 10–11. The nonconjugated polymers of structure II, however, were designed to have a conjugation length or λ_{max} that is *independent of degree of polymerization*, as illustrated in Figure 8. However measured (the number of conjugated double bonds, λ_{max}, conjugated segment chain length y, etc.), the conjugation length of the polymers II is precisely specified prior to the reaction rather than by the statistics of the polymerization reaction.

These polymers with specified conjugation length are expected to be ideal model systems for the investigation of the effects of electronic conjugation length on electrical conductivity, electronic transport properties, and third-order optical nonlinearity. Such studies are currently underway in our laboratory. Also, we have found ways to dehydrogenate these nonconjugated polymers II to yield fully conjugated multiblock copolymers consisting of alternating aromatic and quinoid conjugated segments, as will be reported elsewhere.[31c,d]

Conclusions

Novel carbon atom bridged aromatic heterocyclic polymers of precisely specified conjugation length are described and exemplified by polyterthiophenes (PTTs) of structure I prepared by acid-catalyzed polymerization of α-terthiophene with aldehydes. The nonconjugated polymers exhibit electronic absorption spectra characteristic of the electronically isolated conjugated α-terthiophene segments. The polyterthiophenes are soluble in organic solvents and are largely amorphous except for the methylene-bridged polymer (PTTM), which is highly crystalline as evidence by X-ray diffraction and DSC.

The new polymers with well-defined conjugation length are expected to be useful for the investigation of the effects of π-electron delocalization length on polymer physical properties such as electrical conductivity, electronic transport mechanisms, and third-order nonlinear optical response. The PTTs and related polymers with the structure II are also useful precursors to multiblock conjugated copolymers with alternating aromatic and quinoid segments in the main chain.

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Registry No. Ia (SRU), 111791-73-2; Ia (copolymer), 111791-46-9; Ib (SRU), 111791-74-3; Ib (copolymer), 111791-47-0; Ic (SRU), 111791-71-0; Ic (copolymer), 111791-44-7; Id (SRU), 111791-72-1; Id (copolymer), 111791-45-8; Ie (SRU), 126615-65-4; Ie (copolymer), 126615-61-0; H_2SO_4, 7664-93-9.

Poly(aryl ether–benzoxazoles)

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ABSTRACT: A general method for the preparation of poly(aryl ether–benzoxazoles) has been developed where the generation of an ether linkage is the polymer-forming reaction. We found that aryl fluorides para to a 2-benzoxazolyl group were activated toward nucleophilic aromatic substitution with phenoxides. Facile displacement occurred at this position since the benzoxazole ring can stabilize the negative charge developed in the transition state through a Meisenheimer complex, analogous to conventional activating groups (e.g. sulfone or carbonyl). Appropriately substituted dihalo bisbenzoxazoles, 2,2′-bis[2-(4-fluorophenyl)benzoxazol-6-yl]hexafluoropropane, 2,2′-bis(4-fluorophenyl)-6,6′-bibenzoxazole, and 2,2′-(4-fluorophenyl)-5,5′-bibenzoxazole, were prepared and polymerized with bisphenols in *N*-methyl-2-pyrrolidone in the presence of K_2CO_3. High molecular weight polymers were obtained, with glass transition temperatures ranging from 213 to 300 °C. The resulting polymers were processable from solution or the melt and showed excellent thermal stability and mechanical properties. This synthetic route affords the poly(benzoxazole) analogue of poly(ether–imide) and shows many of the same desirable characteristics.

Introduction

Aromatic poly(benzoxazoles) (PBO) are a class of high-temperature heterocyclic polymers that show excellent thermal stability.[1-5] PBO's are generally prepared by step-growth polymerization of aromatic bis(*o*-aminophenols) with aromatic diacid derivatives.[1-5] The use of PBO's has been limited since they are soluble only in strong acids and cannot be processed from organic solvents. Recently, a novel synthetic route for the synthesis of PBO's was reported that involved the polymerization of silylated bis(*o*-aminophenols) with aromatic diacid chlorides.[6] Monomers containing flexible hexafluoroisopropylidene linkages afforded PBO's that were soluble in

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