

Functional Polythiophene Bearing Hydroxyethyl Groups and Their Derivatives

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Abstract: Poly(3-(2-hydroxyethyl)thiophene) (P3HET) was synthesized using oxidative coupling polymerization that involved the protecting and deprotecting of hydroxyl groups but not the chlorine substitution or oxidative decomposition of the hydroxyl groups. The resulting P3HET exhibited good solubility in aprotic solvents, in contrast to the insoluble polymer product synthesized directly from the monomer, 3-(2-hydroxyethyl)thiophene (3HET). P3HET had low conductivity due to the strong hydrogen bonding of its hydroxyl groups. The ester-functionalized poly(3-(2-acetoxyethyl)thiophene) and poly(3-(4-pentylbenzoateethyl)thiophene) were also prepared with reasonably high molecular weights in order to examine how this functionalization modified the physical and chemical properties of P3HET. These polymers exhibited better solubility in common solvents and higher conductivity than P3HET. All these polymers exhibited bathochromic shifts of their film state absorption maxima with respect to those found in the UV-visible spectra of their solution phases. The extent of the bathochromic shift was found to vary with the lengths of the side chains of the ester-functionalized polymers.

Keywords: 3-substituted polythiophene, conjugated polymer, conductivity, bathochromic shift.

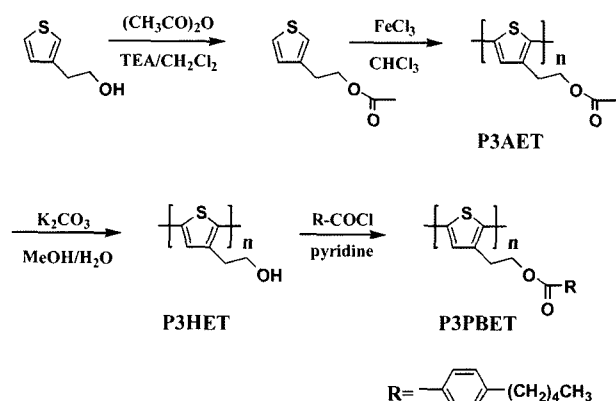
Introduction

Conjugated polymers such as polyaniline, polypyrrole and polythiophene have been receiving a great deal of attention for more than two decades because of their potential applications in electro-chemical and electro-optical devices.¹⁻⁹ However, the characterization and processing of conjugated polymers have been limited by their inherent infusibility and insolubility in common solvents. The combination of their rigid-rod structure and strong inter-chain interactions prevents the melting of these materials and their dissolution in common organic solvents. It is well known that the incorporation of relatively long and flexible pendants onto the stiff backbones of these polymers improves their solubility and processability.¹⁰⁻¹³ Using this approach, a number of 3-substituted polythiophenes such as poly(3-alkylthiophene)s, poly(3-alkoxythiophene)s, and poly(3-alkylesterthiophene)s have been synthesized with the aim of improving their processability in industrial applications and modifying their electronic properties.¹⁴⁻¹⁷ Short pendant groups have also been introduced into synthesized heteroaromatic monomers in order to produce both solution- and melt-processable poly-

thiophenes.¹⁸⁻²²

Of short pendant incorporated thiophene monomers, 3-(2-hydroxyethyl)thiophene (3HET) has particularly gained great attention because of its commercial availability and potential to produce soluble polythiophene derivative which can be used as a reactive polymer intermediate.^{21,22} For these potential advantages, Andreani *et al.*²¹ and Della Casa *et al.*²² have attempted to synthesize poly(3-(2-hydroxyethyl)thiophene) (P3HET) by oxidative homopolymerization of the monomer in nitro-methane using ferric chloride. However, they obtained only insoluble products, rather than soluble P3HET. Due to the insolubility, they conducted very limited characterizations, such as infrared spectroscopy and elemental analysis, on the obtained products, and then found that the polymer products own chloroethyl pendant groups in addition to the hydroxyethyl pendant groups originated from the 3HET monomer.²² This result suggests that the ferric chloride agent used in the homopolymerization induces chlorination of the hydroxy end group in the pendant of the monomer in addition to the oxidative homopolymerization of the monomer. Even taking this result into account, in the polymerization the products were obtained as a copolymer containing hydroxyethyl and chloroethyl pendants, rather than a homopolymer bearing only hydroxyethyl pendant. Even taking into con-

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Scheme I. Synthesis of P3HET and its derivatives.

sideration the copolymer composition, the products may be soluble. However, the result is opposite to this expectation based on the copolymer composition. Collectively from these results it is speculated that in addition to the chlorination, crosslinking reaction in some degree takes place between hydroxy end groups in the pendant groups of the monomers which undergo polymerization in the reaction. It turns out that more research work still is demanded to obtain soluble P3HET from the 3HET monomer.

In this study, we report a synthetic route of soluble P3HET that avoids both the partial substitution of hydroxyl groups with chlorine and oxidative decomposition during the oxidative coupling polymerization of 3HET (see Scheme I). In addition, ester-functionalized polythiophenes with different side chain lengths were synthesized from P3HET, and their physical and chemical properties were found to be dependent on the side chain length.

Experimental

Materials and Instruments. All chemicals and reagents were purchased from Aldrich Chemical Company and used as received. The molecular weights of the products were determined by gel permeation chromatography (GPC), using a Wyatt Technology chromatography system equipped with a UV detector; a set of two PL mix columns was used and tetrahydrofuran (THF; HPLC grade) was used as eluent. Calibration was performed with polystyrene standards. The Fourier-transformed infrared (FTIR) spectra were recorded on a Research Series IR spectrophotometer (Mattson Co.) and reported in wavenumbers (cm^{-1}). Nuclear magnetic resonance (NMR) spectra were obtained for solutions of the polymers in CDCl_3 or dimethyl- d_6 sulfoxide ($\text{DMSO}-d_6$) using a Bruker NMR spectrometer (model Aspect 3000 FT-300 MHz). The thermal stability of the polymers in the range 50–800 °C was measured using a Seiko thermogravimeter (TG/DTA6300). Nitrogen gas was used for purging with a flow rate of 100 cc/min, and a ramping rate of 10.0 °C/min

was employed. Ultraviolet-visible (UV-Vis) spectra of the polymers in dilute NMP solutions and in thin films on quartz plates were obtained using a Hewlett-Packard Spectrometer.

Monomer Synthesis and Polymerization.

3-(2-Acetoxyethyl)thiophene: Triethylamine (1.8 mL) was added dropwise to a solution of 2-(3-thienyl)ethanol (1 mL) and acetic anhydride (1.5 mL) in 30 mL of dry methylene chloride at 0 °C. After the addition was complete, the mixture was allowed to warm to 25 °C and then stirred for 6 h. The mixture was then washed with 100 mL of water. The aqueous layer was extracted with an additional 50 mL of methylene chloride. The combined organic layers were dried over MgSO_4 , filtered, and concentrated in a rotary evaporator to afford 3.8 g of liquid product. ^1H NMR (δ , CDCl_3): 7.30–7.27 (m, 1H, Ph-*H*), 7.06–7.05 (m, 1H, Ph-*H*), 7.01–6.99 (m, 1H, Ph-*H*), 4.33–4.28 (t, 2H, methylene), 3.01–2.97 (t, 2H, methylene), 2.07 (s, 3H, methyl); ^{13}C NMR (δ , CDCl_3): 171, 137, 129.5, 125.7, 69.5, 29.7, 17.3.

Poly(3-(2-acetoxyethyl)thiophene) (P3AET): 3-(2-acetoxyethyl)thiophene (2.7 g, 15.6 mmol) was chemically polymerized using a FeCl_3 (49.9 mmol) suspension in dry chloroform, according to the oxidative method generally used for the preparation of poly(3-alkylthiophenes).²³ The mixture was added to a large excess of methanol. Red to blackish solids were isolated. After washing the recovered polymer several times with hot methanol, it was subjected to Soxhlet extraction for 2 days using methanol in order to remove any inorganic impurities, then dried in vacuum at 65 °C for 20 h, resulting in 2.4 g of dried product. ^1H NMR (δ , CDCl_3): 7.14–7.07 (m, 1H, Ph-*H*), 4.38–4.29 (t, 2H, methylene), 3.17–2.95 (t, 2H, methylene), 2.08–2.07 (d, 3H, methyl).

Poly(3-(2-hydroxyethyl)thiophene) (P3HET): To a room temperature solution of P3AET (2 g) in 50 mL of a mixture of methanol and water (1:1 volume ratio), excess K_2CO_3 (3 g) was added. The reaction was allowed to proceed for 5 days. The resulting mixture was neutralized with 1 M HCl. The precipitates were filtered, then washed with water and hot methanol. The product was dried in vacuum at 65 °C for 24 h, resulting in 1.1 g of dried product. ^1H NMR (δ , DMSO): 7.41–7.36 (d, 1H, Ph-*H*), 4.96–4.86 (d, 1H, hydroxy), 3.82–3.71 (d, 2H, methylene), 3.05–2.81 (d, 2H, methylene).

Poly(3-(4-pentylbenzoateethyl)thiophene) (P3PBET): P3HET (0.5 g) was dissolved in pyridine (10 mL) under an atmosphere of nitrogen. This solution was stirred at room temperature for 30 min and then warmed to 60 °C. Excess pentylbenzoylchloride was added dropwise to the P3HET solution. After the reaction was complete, the mixture was added to excess methanol. The precipitates were filtered, then washed with 1 M HCl solution to remove pyridine. The product was dried in vacuum at 65 °C for 24 h, resulting in 1.3 g of dried product. ^1H NMR (δ , CDCl_3): 7.96–7.94 (d, 2H, Ph-*H*), 7.27–7.15 (m, 4H, Ph-*H*), 4.57–4.54 (d, 2H, methylene), 3.28–3.10 (d, 2H, methylene), 2.63 (s, 2H, methylene), 1.30

(s, 6H, methylene), 0.89-0.85 (t, 3H, methyl).

Results and Discussion

P3AET was synthesized in reasonably high yield via an oxidative coupling polymerization of 3-(2-acetoxyethyl)thiophene in dry chloroform using FeCl_3 as the oxidant at room temperature. A dark red product was obtained after Soxhlet extraction with methanol. The low conductivity of this product indicates that P3AET was almost dedoped of FeCl_3 during the polymer synthesis (see Table I). After this treatment, P3AET was hydrolyzed using base conditions and P3HET was successfully prepared. In addition, P3PBET which has an ester-functionalized side chain was synthesized from P3HET and pentylbenzoylchloride. In contrast to previous reports, which concluded that P3HET is insoluble in solvents,^{21,22} we found that P3HET synthesized in the present study is soluble in aprotic solvents such as DMSO, *N*-methyl-2-pyrrolidinone, and *N,N*-dimethylformamide. Moreover, the ester-functionalized P3AET and P3PBET were found to exhibit good solubility in a variety of common solvents, including chloroform, THF and methylene chloride, as well as in aprotic solvents.

We also determined their molecular weights using gel-permeation chromatography. The weight-average molecular weight (\overline{M}_w) and polydispersity were found to be 52,000 g/mol and 4.06 for P3AET and 86,000 g/mol and 3.91 for P3PBET, respectively. The (\overline{M}_w) of the synthesized P3HET could not be obtained because of its poor solubility in THF that is the eluent for the GPC measurements. However, P3HET has been obtained by the deprotection of acetyl end groups of the pendants of P3AET. Taking this point into account, (\overline{M}_w) of P3HET is estimated to be 39,000 g/mol from that of P3AET using the ratio of the molecular weights of the repeat units of P3HET and P3AET.

The chemical structures of the polymer products were characterized using FTIR and ^1H NMR spectroscopy. Figure 1 shows the FTIR spectra of the three polymers. All the polymers exhibit adsorption due to ring vibration at 1463 cm^{-1} . In addition, we attribute the band at 830 cm^{-1} to the C-H_α out of plane deformation mode of the 2,3,5-trisubstituted thiophene rings, which indicates that the poly(3-alkyl-2,5-thienylene) chain structure is linear. The presence of the pendant groups was confirmed by the observation of adsorption bands due

to aliphatic C-H stretching at 2860 and 2955 cm^{-1} . For the ester-functionalized polymers, C=O stretching bands are seen at 1743 cm^{-1} for P3AET and at 1723 cm^{-1} for P3PBET. The O-H stretching vibration of P3HET results in a broad absorption in the 3388 cm^{-1} region of the spectrum.

Figure 2 shows the ^1H -NMR spectrum of P3HET in $\text{DMSO-}d_6$. As mentioned above, it was previously reported that the chemical polymerization with ferric chloride of 2-(3-thienyl) ethanol results in an insoluble polymer because of the partial nucleophilic substitution of hydroxyl groups by chlorine^{21,22} and the possible crosslink reaction of hydroxyl groups in the pendants. To prevent this partial substitution of hydroxyl groups by chlorine and oxidative decomposition during the oxidative coupling polymerization, we protected the hydroxyl group of 2-(3-thienyl)ethanol with an acetoxy group. The deprotecting reaction for P3AET was then performed for 5 days because of its low wettability by water. After hydrolysis, the characteristic signal of a hydroxyl proton bonded to a $\beta(2)$ -methylene group appeared at 4.9 ppm. Judging from the integral ratio of this peak to the peak of the characteristic

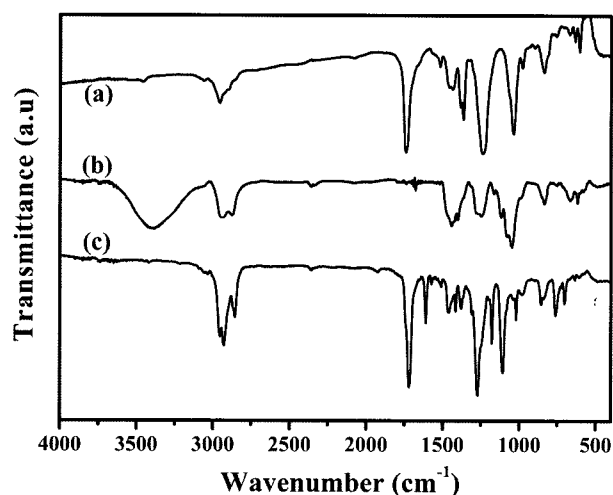


Figure 1. FTIR spectra of the polymers: (a) P3AET, (b) P3HET, and (c) P3PBET.

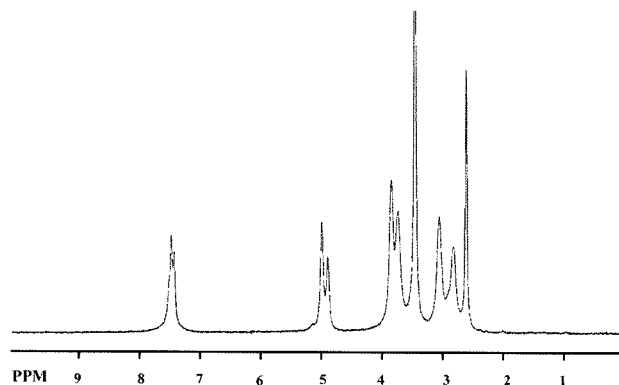


Figure 2. ^1H NMR spectrum of P3HET.

Table I. Electrical Conductivities of Films of the Three Polymers

Polymer	Conductivity (S/cm)	
	Undoped State	Doped State
P3HET	1.0×10^{-11}	2.9×10^{-6}
P3AET	2.1×10^{-10}	7.2×10^{-3}
P3PBET	1.6×10^{-10}	3.7×10^{-2}

signal of the 4-position protons of thiophene rings at 7.4 ppm, a nearly complete degree of hydrolysis was achieved without chlorine substitution. Hence, the ^1H NMR spectrum of P3HET agrees with its expected structure; ^1H NMR (δ , DMSO): 7.41-7.37 ppm (m, thiophene ring proton, 1H), 4.96-4.86 ppm (d, -OH, 1H), 3.82-3.71 (m, hydroxyl -CH₂-, 2H), 3.04-2.81 ppm (m, thiophene ring -CH₂-, 2H). It is well documented that proton peaks in ^1H NMR spectra associated with the α -methylene groups of poly(3-alkylthiophenes) are split because polymerization of asymmetric 3-alkylthiophenes results in dyad structures which are either head-to-tail (HT) or head-to-head (HH) linkages. Similar splitting patterns were observed for the α -methylene peaks of P3HET (δ = 3.09 and 2.80); the low field (δ =3.09) peak was assigned to HT linkages.²⁴ From the integral ratio of the split peaks corresponding to α -methylene protons, we determined that the P3HET produced in this work has a 55% HT-HT coupling structure.

Figure 3 shows the thermal stabilities of the three polymers. Though the weight loss steps are unclear, the decompositions of these polymers exhibit two major steps in the temperature scan region. The P3AET polymer starts to decompose at 230°C and continues this first step decomposition up to 570°C, which corresponds to the decomposition of its 2-acetoxyethyl side groups. The second weight loss step occurs very slowly above 570°C, and corresponds to the degradation of the polymer backbone. The P3HET polymer also starts to decompose at 156°C but continues the first step decomposition until 400°C, which is attributed to the decomposition of its 2-hydroxyethyl side groups. Above 400°C this polymer undergoes very slowly the second weight loss step, which is due to the degradation of the polymer backbone. On the other hand, the P3PBET polymer begins decomposition at 156°C and continues the first step decomposition associated with 4-pentylbenzoyloxyethyl side groups until 400°C. Thereafter the polymer undergoes the degradation of the polymer back-

bone as the second step weight loss. These results collectively indicate that the thermal stabilities of the P3HET derivatives in our study are strongly dependent on the capping moieties of the 2-hydroxyethyl side group. The stability of the P3HET polymer was enhanced by acetyl capping but degraded by 4-pentylbenzoyl capping. The difference in these capping effects might be attributed to the leaving abilities of the capping groups in the decomposition process. Both P3AET and P3PBET have ester unit in the side group (see Scheme I); the ester unit of the P3AET polymer is composed of aliphatic acetyl capping group and β -hydrogen containing ethylenyl unit while that of the P3PBET polymer consists of aromatic 4-pentylbenzoyl capping group and β -hydrogen containing ethylenyl unit. Such ester units containing β -hydrogen are easily decomposed to carboxylic acid and double-bonded carbon unit. In this case, aromatic ester unit can more easily undergo this decomposition reaction than aliphatic ester unit because the aromatic ester is a better leaving group, compared to the aliphatic ester. Taking these facts into account, the relatively lower onset temperature of thermal decomposition observed in the P3PBET polymer resulted from the relatively leaving ability of the aromatic capping group connected to the ethylenyl side group via an ester unit.

The UV-Vis spectra of the solutions and films of these polymers are shown in Figures 4 and 5 respectively. P3AET has maximum absorption bands at 429 nm in NMP solution and at 440 nm in the film state. This indicates that the packing of polymer chains in the film favors a coplanar arrangement with respect to adjacent thiophene rings, which results in a bathochromic shift in the absorption maximum with respect to that of the solution phase polymer. The absorption maximum of P3HET in NMP solution arises at a higher wavelength than those of P3AET and P3PBET, which is perhaps due to differences in their solvent-polymer interactions. In contrast, the absorption bands of the films of these polymers arise at almost the same wavelength because there are no

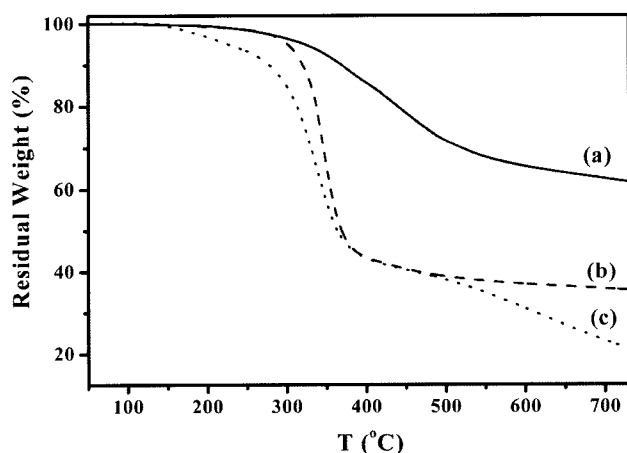


Figure 3. Thermogravimetry thermograms of the polymers: (a) P3AET, (b) P3HET, and (c) P3PBET.

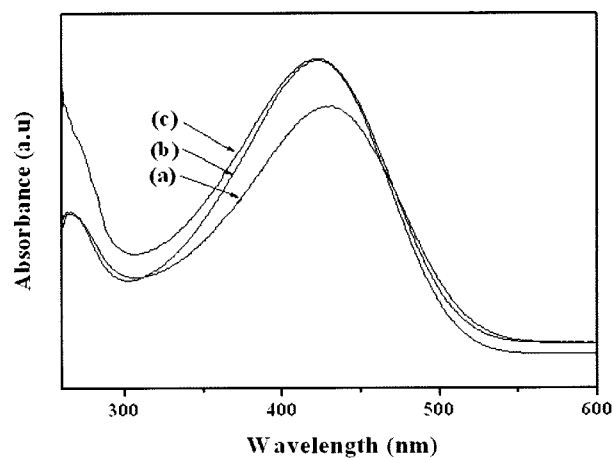


Figure 4. UV-Vis spectra of NMP solutions of the polymers: (a) P3HET, (b) P3AET, and (c) P3PBET.

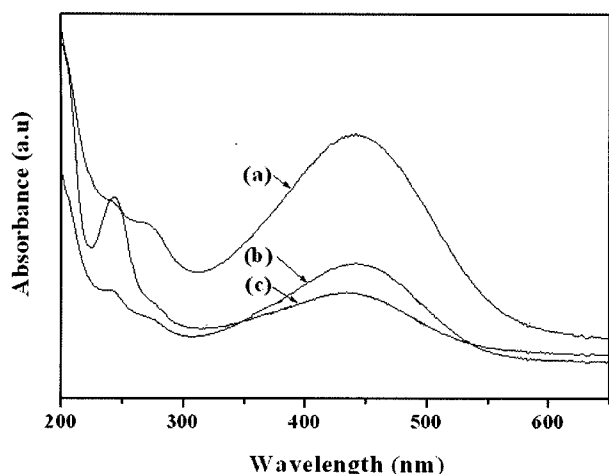


Figure 5. UV-Vis spectra of films of the polymers: (a) P3HET, (b) P3AET, and (c) P3PBET.

solvent-polymer interactions in the film state. The ester-functionalized P3AET and P3PBET also exhibit bathochromic shifts of their film state absorption maxima. The maximum absorption bands of these two polymers in solution arise at the same wavelength, but occur at different wavelengths in the spectra of the polymer films. The larger side chain length of P3PBET means that the film state absorption band is slightly shifted to a lower wavelength than that of P3AET. This observation suggests that the side chains of P3PBET interfere with the packing of polymer chains and thus lead to a decrease in the conjugation length.

The free-standing films of the three polymers were doped with I_2 vapor for 4 h, and their color changed from light red to dark red. After doping, the electrical conductivity of both the neutral free standing and I_2 -doped films was measured in air using the four-probe method. The conductivities of the polymers are reported in Table I. The undoped polymers are insulators in the range 1.6×10^{-10} to 1.0×10^{-11} S/cm, but the doped ones exhibit semiconductivity. From these results, we conclude that the conductivity of P3HET is low due to the strong hydrogen bonding by hydroxyl groups and that P3PBET has higher conductivity because its alkylester unit is longer than that of P3AET.

Conclusions

Soluble poly(3-(hydroxyethyl)thiophene) (P3HET) was successfully synthesized in reasonably high molecular weight via a synthetic pathway which can prevent chlorine substitution and/or oxidative decomposition of hydroxyl groups, and was found to exhibit solubility in aprotic solvents. P3HET reveals low conductivity due to the strong hydrogen bonding of its hydroxyl groups. In addition, the ester-functionalized polymers P3AET and P3PBET were prepared with reasonably high molecular weights in order to examine

how this functionalization modifies the physical and chemical properties of P3HET. Both polymers have good solubility in common solvents and a higher conductivity than P3HET. The UV-visible spectra of the three polymers indicate that there are bathochromic shifts of the film state absorption maxima with respect to those found for the solution phase. The extent of the bathochromic shift is affected by the size of the side chains in the cases of the ester-functionalized P3AET and P3PBET.

In summary, the solubility and the reactive hydroxy end groups in the pendants of this P3HET make it a promising candidate intermediate for developing highly functional polythiophene derivatives with high performance. The P3HET derivatives (P3AET and P3PBET) revealing good solubility and properties are additionally considered as potential candidate materials for the fabrication of electro-chemical and electro-optical devices.

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