Soluble Regioregular Polythiophene Derivatives as Semiconducting Materials for Field-Effect Transistors

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Soluble regioregular polythiophene derivatives with chiral alkyl side chains, bulky side chains, and carboxylic side chains have been synthesized. Their thin-film field-effect transistor performance and structural characteristics have been investigated. The above properties were found to be strongly affected by the nature of the side chains. Poor molecular ordering and low crystallinity were found for regioregular polythiophenes with bulky or carboxylic-substituted side chains, and their resulting transistor devices showed poor field-effect mobilities (less than $10^{-5}-10^{-4}$ cm^2/(V s)). A chiral alkyl-substituted regioregular polythiophene showed high crystallinity. However, its $\pi-\pi$ overlap distance between the polythiophene backbones increase substantially (i.e., to ∼4.3 vs 3.8 Å for regioregular poly(3-hexylthiophene) (PHT)) through the introduction of methyl branches in the side chains. The field-effect mobility of this polymer is reasonably high for solution-processable conjugated polymers (i.e., of the order of 10^{-3} cm^2/(Vs)), but is still an order of magnitude lower than for regioregular PHT. These studies provide an initial basis for further structural design and molecular engineering of soluble regioregular polythiophenes with potentially improved transistor performance.

Introduction

There has been great interest recently in the development of electronic circuits and displays using fabrication methods such as screen printing and ink-jet printing.[1−11] This trend is driven by the demand for low-cost, flexible, and lightweight devices. We have previously demonstrated printed polymer light-emitting diodes and all-printed polymer thin-film field-effect transistors (FETs).[2,4,5,11] The demonstration of those devices relies heavily on high-performance solution-processable materials. For all-printed polymer FETs (schematic structure shown in Figure 1), various kinds of soluble polymers (from conducting, semiconducting to insulating) are required. For conducting polymers, polyaniline, poly(ethylene dioxide thiophene), and metal or graphite colloid particle-based inks can be used as the electrodes. A number of polymer dielectric materials (such as polyimide, PMMA, etc.) have been shown to have reasonable performance, although further evaluation is needed. The availability of soluble semiconducting polymers remains limited. An alternative is to use the dilute solutions of low-solubility conjugated oligomers;[12−14] however, reliable high performance over a large area (i.e., over 1 cm^2) is to be demonstrated.

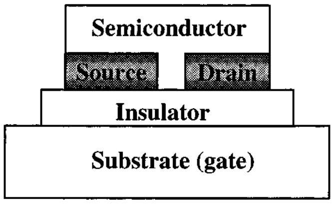

Figure 1. Schematic structure of a thin-film field-effect transistor.

Regioregular poly(3-hexylthiophene) has been found to have high field-effect mobility (∼0.01−0.1 cm^2/(V s)) and reasonable on/off ratios (>100 in air and 10^6 in a vacuum or argon atmosphere).[15,16] Its high solubility in various organic solvents and good film-forming properties make it attractive as a printable semiconducting polymer. We have shown that high regioregularity is required for formation of highly ordered thin films and that it results in high transistor performance.[15] However, there has been no study of how the nature of the side chains affects the FET performance of the resulting polymer. We report here the synthesis of several soluble

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regioregular poly(3-substituted thiophene) derivatives and their FET and structural characterizations.

Experimental Section

All chemicals were purchased from Aldrich Chemical Co. and used as received. The synthetic procedures for all monomers and polymers were similar to those reported previously.[17-19] The purification involved dissolving the polymer in toluene and precipitating from hexane followed by filtration. The same procedure was repeated using acetone instead of hexane. Finally, the polymer was Soxhlet extracted with hexane and then acetone until the condensed solvent was colorless.

Polymer 1: ^{1}H NMR (CDCl$_3$) 6.95 (s, 1H), 2.78 (m, 1H), 2.60 (m, 1H), 1.77 (m, 1H), 1.50 (m, 2H), 1.25 (m, 1H), 0.94 (t, 6H); ^{13}C NMR (CDCl$_3$) 138.9, 133.6, 131.1, 129.5, 36.5, 35.9, 29.4, 19.2, 11.4; GPC (THF, 45 °C) M_n 7200, M_w 15 800; polydispersity 2.20. Anal. Calcd for $C_9H_{12}S$: C, 71.00, H, 7.94; Found: C, 69.45, H, 7.25.

Polymer 2: ^{1}H NMR (CDCl$_3$) 7.02 (s, 1H), 3.91, (s, 2H), 3.10 (t, 7.5 Hz, 2H), 2.60 (t, 7.5 Hz, 2H), 1.25, (s, 6H); ^{13}C NMR (CDCl$_3$) 164.8, 137.8, 133.5, 131.5, 128.9, 79.1, 67.0, 28.9, 28.5, 25.7; GPC (NMP, 85 °C) M_n 6200, M_w 8000; polydispersity 1.31. Anal. Calcd for $C_{11}H_{13}ONS$: C, 63.74, H, 6.32, N, 6.76; Found: C, 56.79, H, 5.67, N, 5.49.

Polymer 3: ^{1}H NMR (DMSO-d_6) 6.28 (s, 1H), 2.03 (broad, 2H), 1.68 (broad, 2H). Anal. Calcd for $C_7H_6O_2S$: C, 54.53, H, 3.92; Found: C, 52.60, H, 3.96, N <0.02.

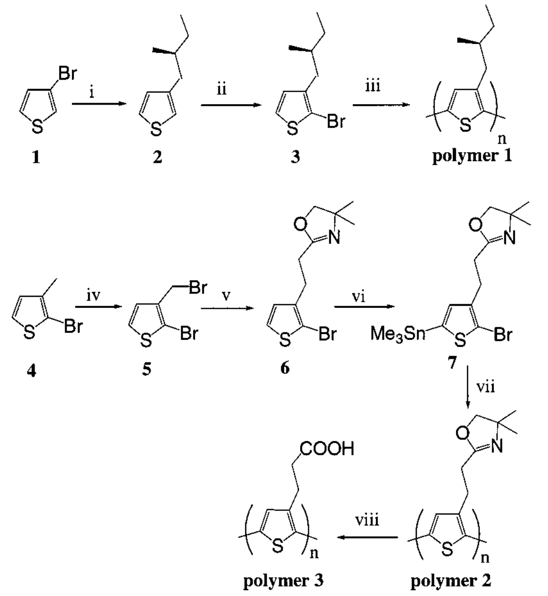
Gel permeation chromatography (GPC) measurements were performed by Lark Enterprises, Inc., using chloroform at 45 °C (for polymer 1) and *N*-methylpyrrolidinone (NMP) at 85 °C (for polymer 2) as solvents and calibrated with polystyrene standards. The ^{1}H NMR and ^{13}C NMR spectra were collected on a Bruker 360 MHz FT-NMR spectrometer. UV–vis spectroscopy was performed on an HP-8453 spectrometer. Elemental analysis was carried out by Robertson Microlit Laboratories, Inc.

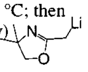
For structural characterizations, the materials were deposited onto carbon-coated electron microscope grids and Si/SiO$_2$ chips simultaneously with the TFTs. X-ray diffraction studies were done using the films on the Si/SiO$_2$ chips in the reflection mode at 40 kV and 25 mA. A 2-kW Rigaku X-ray generator was used as a source of Ni-filtered Cu Kα radiation. The films on the grids for electron microscopy were shadowed with Pt/C at $\tan^{-1}$ 0.5 and lightly carbon-coated in a vacuum evaporator before examination in a JEOL transmission electron microscope operated at 100 kV.

The transistor substrates are n-doped Si substrates, with a gold contact functioning as the gate and an oxide layer of 3000 Å as the gate dielectric having a capacitance per unit area of 10 nF/cm^2. The drain and source electrodes have widths W = 250 μm and channel lengths L = 1.5, 4, 12, and 25 μm. Polymer thin films were prepared by solution casting with their thicknesses ranging from a few hundred angstroms to several micrometers as adjusted by solution concentration. All solutions were filtered through a 0.20 μm pore size PTFE membrane syringe filter before use. The electric characteristics of these devices were measured in air. The current–voltage characteristics were obtained with a Hewlett-Packard (HP) 4145B parameter analyzer.

Results and Discussions

Synthesis. Three types of regioregular polythiophenes as shown in Figure 2 were investigated. Polymer 1 is substituted with optically active and slightly branched side chains. Polymer 2 is the precursor polymer for polymer 3, and its bulky protecting group can be used to investigate the effect of side-chain bulkiness on device performance. Polymer 3 is substituted with carboxylic acid side chains, which can form H-bonds and may help promote self-assembly of the polymer on polar substrates. In all three polymers, the side chains are connected to the polymer backbone through methylene (–CH$_2$–) linkages so that the electronic properties of the polymer backbones are not chemically changed; thus, morphological effects should be the major factor affecting electronic properties.



(i) C_4H_9MgBr, Ni(dpp)$_2$Cl$_2$, ether, reflux; (ii) NBS, CHCl$_3$; (iii) LDA -78 °C; then Mg(OEt)$_2$Br$_2$, -78 °C; then Ni(dpp)$_2$Cl$_2$; (iv) NBS, AIBN, CCl$_4$, reflux; (v) 

(vi) LDA, then Me$_3$SnCl; (vii) Pd(PPh$_3$)$_4$, THF; (viii) 3M aq. HCl

Figure 2. Synthetic schemes for regioregular polythiophene derivatives.

The above polymers were synthesized according to literature procedures.[17-19] The synthetic schemes are outlined in Figure 2. Polymer 1 was synthesized using the McCullough method and polymer 2 was prepared using the Stille coupling reaction.[17,20-21] The elemental analysis results for polymer 2 had a relatively large deviation from the calculated values, possibly due to its relatively low molecular weight and the high molecular weight of trimethylstannyl end groups. However, the molecular weight obtained here is similar to that reported in the literature using the same polymerization method.[17,21] Polymer 3 was obtained by refluxing polymer 2 in 3 M aqueous solution of HCl and is soluble in polar solvents such as *N*,*N*-dimethylforamide (DMF), NMP, and aqueous base solutions. The deprotection reaction of polymer 2 appears to be almost quantitative since no trace of nitrogen has been found in the elemental analysis.

Both polymers 1 and 2 are soluble in common organic solvents such as chloroform, tetrahydrofuran (THF), and DMF. The regioregularity of the polymers has been examined by ^{1}H NMR and ^{13}C NMR. For all polymers, only one kind of aromatic proton and four kinds of

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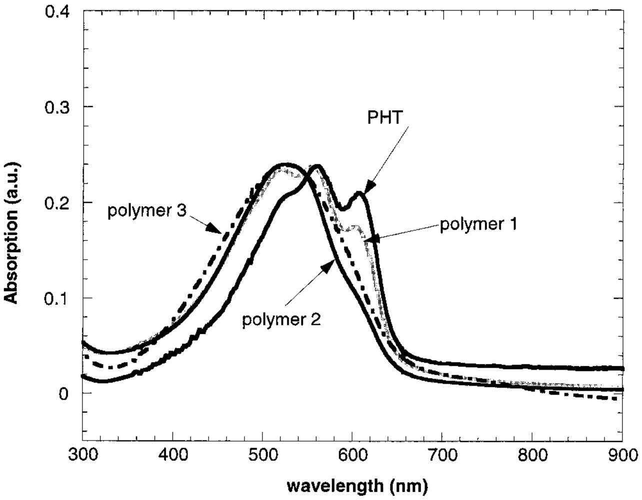

Figure 3. UV−vis spectra of polymer films: polymer 1, cast from chloroform solution at room temperature; polymer 2, cast from chloroform solution at room temperature; polymer 3, cast from DMSO solution and solvent was slowly evaporated by covering the substrate and solution with a peri dish at 50 °C; and PHT, cast from chloroform solution at room temperature.

thiophene carbons were detected, indicating that the regioregularity is greater than 95%.

Electronic properties. The UV−vis spectra of thin films prepared from all polymers are shown in Figure 3. Polymer 1 showed a three-peak structure at 514, 540, and 600 nm, which is also observed with other highly regioregular poly(3-alkylthiophene)s.[22,23] The well-resolved peak at 600 nm is assigned to the lowest singlet (^{1}Bu) exciton transition and the others are its vibronic sidebands.[22,23] Polymers with structures similar to polymer 1 have also been found to be optically active as a result of optically active side chains.[24] The UV−vis spectrum of regioregular PHT, which had been prepared using a similar synthetic method as reported for polymer 1 is also shown in Figure 3. It is noted that the peak positions of polymer 1 and regioregular PHT are almost identical. The vibrational structure in the solid-state optical spectra of polymers is a typical manifestation of the electron−lattice coupling.[25] The lowest energy transition (0−0 transition) is inversely proportional to the conjugation length. Despite its lower molecular weight compared to regioregular PHT (M_n = 12 000 kD, polydispersity = 2.5), polymer 1 appears to have similar average conjugation length as the well-ordered regioregular PHT, indicating that polymer 1 film is also highly ordered, which is consistent with the X-ray diffraction measurements discussed later. In polymer 2, there is an indication of a vibronic structure even though the position of maximal absorption is shifted to a lower wavelength. Polymer 3 does not show any vibronic structure, but has a similar peak absorption position as polymer 2, and they are both blue-shifted compared to those of polymer 1 and regioregular PHT. Several other solvents have been used to prepare films of polymers 2 and 3, and they all produced similar characteristics to those shown in Figure 3. Many factors may contribute to this blue shift, such as lower degrees of polymerization, steric hindrance in polymer 2, and random H-bonding formation causing chain twisting in polymer 3. Despite their blue shifts, polymers 2 and 3 are significantly red-shifted compared to regiorandom PHT with about 70% head-to-tail ratio (λ_{max} = 460 nm). Films of polymers 2 and 3 still appear blue-purple (similarly color to regioregular PHT films), while films of regiorenadom PHT appear yellow-orange.

Table 1. Transistor Performance of Regioregular Polythiophene Derivatives

entry	polymer	solvent	mobility ($cm^2/(V\ s)$)	on/off ratio
1	polymer 1	$CHCl_3$, room temperature	1.0×10^{-3}	15−60
2		chlorobenzene, vacuum (25 Torr), 80 °C	3.7×10^{-4}	10−20
3		$CHCl_3$, substrate HMDS treated	6.3×10^{-4}	15−20
4	polymer 2	$CHCl_3$, room temperature	2.8×10^{-5}	2
5		NMP, vacuum (25 Torr), 80 °C	(−)[a]	(−)[a]
6	polymer 3	DMF, vacuum (25 Torr), 80 °C	2.9×10^{-4}	2−5
7		NMP, vacuum (25 Torr), 80 °C	(−)[a]	(−)[a]
8		DMSO, vacuum (25 Torr), 80 °C	(−)[a]	(−)[a]
9		DMSO, solution covered with a Petri dish, 50 °C	8.0×10^{-5}	1.3

[a] (−), no field-effect transistor activity.

Thin-film FETs have been fabricated with the three types of regioregular polythiophenes. The transistor device structure is shown in Figure 1. The n-doped Si substrate with gold contact functions as the gate, while an oxide layer of 3000 Å is the gate dielectric having a capacitance per unit area of 10 nF/cm^2. The drain and source electrodes define channel widths W = 250 μm and channel lengths L = 1.5, 4, 12, and 25 μm. Table 1 summarizes the field-effect mobility and on/off ratio for FETs prepared under various conditions based on polymers 1−3. All polymers functioned as p-channel FET devices operating in the accumulation mode in which the drain−source currents (I_{DS}) of negative signs scale-up with negative gate voltages (V_G). Their typical current−voltage characteristics are shown in Figure 4. A plot of $I_{DS}{}^{1/2}$ vs V_G can be used to obtain V_0 , the extrapolated threshold voltage, after extrapolation to the V_G axis. At the saturated region, I_{DS} can be described using eq 1, where μ is the field-effect mobility, W is the channel width, L is the channel length, and C_i is the capacitance per unit area of the insulating layer (SiO_2, 3000 Å, C_i = 10 nF/cm^2). The field-effect mobility calculated using this method is shown in Table 1. The on/off ratio is calculated by using I_{DS} ($V_{DS} = -100$ V) at $V_G = -100$ V vs that at $V_G = 0$ V. Both the field-effect mobilities and on/off ratios for these regioregular polythiophene derivatives are smaller than for the regioregular poly(3-hexylthiophene) itself synthesized using similar polymerization and purification methods. However, the mobility for polymer 1, which has chiral side chains, is still relatively high for solution processable polymeric semiconductors. Most soluble conjugated polymers, such as poly(2,5-dialkoxyphenylene-*co*-thiophene)s or poly(2,5-dialkoxyphenylene vinylene)s, have mobilities in the range of 10^{-7}−10^{-5} cm^2/(V s).[26,27] The on/off ratios reported here are low since these devices were prepared in air or under low vacuum, and all tests were performed in air. An increase in on/off ratio by 10 to 1000 has previously been realized with regioregular poly(3-hexylthiophene) when it is handled and measured in a drybox environment.[16]

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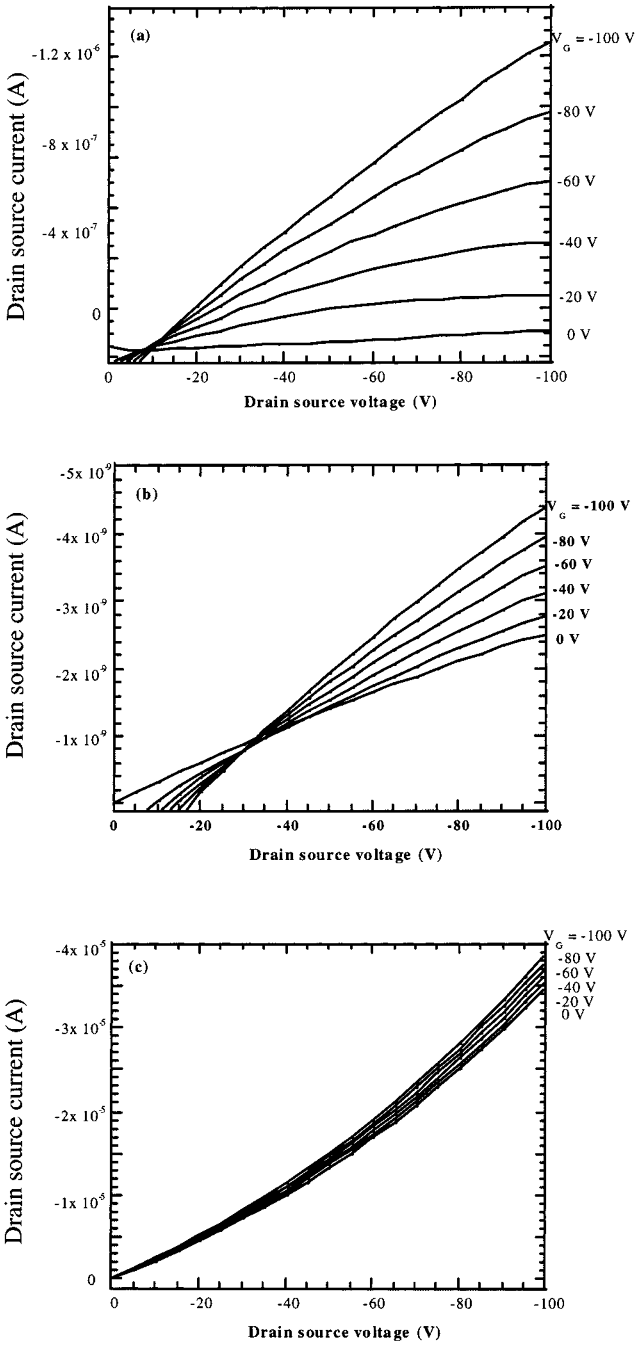

Figure 4. Current–voltage characteristics of regioregular polythiophene derivatives: (a) polymer 1, cast from chloroform solution at room temperature; (b) polymer 2, cast from chloroform solution at room temperature; and (c) polymer 3, cast from DMF under vacuum (25 Torr) at 80 °C.

$$I_{DS} = \frac{WC_i}{2L}\mu(V_G - V_o)^2 \qquad (1)$$

The large difference in the transistor performance may be a result of several factors. First, the electronic states of polymers 2 and 3 may be slightly different from those of polymer 1 and regioregular PHT. There may be shortening of conjugation length for polymers 2 and 3 due to the introduction of bulky side chains as indicated by their blue shifts in UV–vis spectra compared to those of polymer 1 and regioregular PHT. Second, the chemical natures of side chains in polymers 2 and 3 are different from those of polymer 1 and regioregular PHT. It is unknown whether the oxazoline and carboxylic side chains may trap positive charge carriers (holes) in p-channel TFTs. In addition to the above factors, the structural effects should play an important role as discussed below.

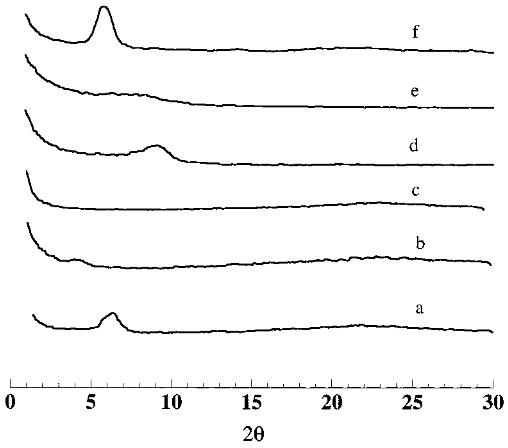

Figure 5. X-ray diffraction patterns of regioregular polythiophene derivatives: (a) polymer 1, cast from chloroform solution at room temperature; (b) polymer 2, cast from chloroform solution at room temperature; (c) polymer 3, cast from DMF under vacuum (25 Torr) at 80 °C; (d) polymer 3, cast from DMSO solution using very slow evaporation by covering the substrate and solution with a Petri dish at 50 °C; (e) polymer 3, cast from DMF solution using very slow evaporation by covering the substrate and solution with a Petri dish at 50 °C; and (f) regioregular poly(3-hexylthiophene), cast from chloroform solution at room temperature.

Structural Studies. X-ray diffraction and electron-diffraction measurements have been performed with powders (X-ray only) of polymers 1–3 and their thin films prepared under the same conditions as their FETs. Since the signal of these experiments depend on polymer orientation to the substrate, results from both kinds of measurements (X-ray and electron diffraction) will give complementary examinations for both parallel and perpendicular orientations. The X-ray diffraction patterns for as-precipitated powders are similar to those for thin films. Figure 5 shows the X-ray diffraction patterns of all polymer films cast from certain solvents. It is known that solvent and film preparation conditions can significantly affect morphology and device performance. We have used several different solvents to prepare films and transistors under various temperature and annealing conditions as shown in Table 1. Indeed, the transistor performance of these films varied significantly depending on solvent and film-forming conditions. The X-ray diffraction patterns were also dependent on the above factors. But none of polymers 1–3 exhibits high crystallinity. Polymer 1 shows a relatively broad diffraction peak at $2\theta \approx 6.3$ ($d = 13.8$ Å) corresponding to the distance between two polythiophene backbones separated by interdigitated side chains (Figure 5a). For comparison, regioregular PHT has a much sharper peak at a spacing of about 16.2 Å (Figure 5f).[15] On the other hand, polymer 2 is characterized

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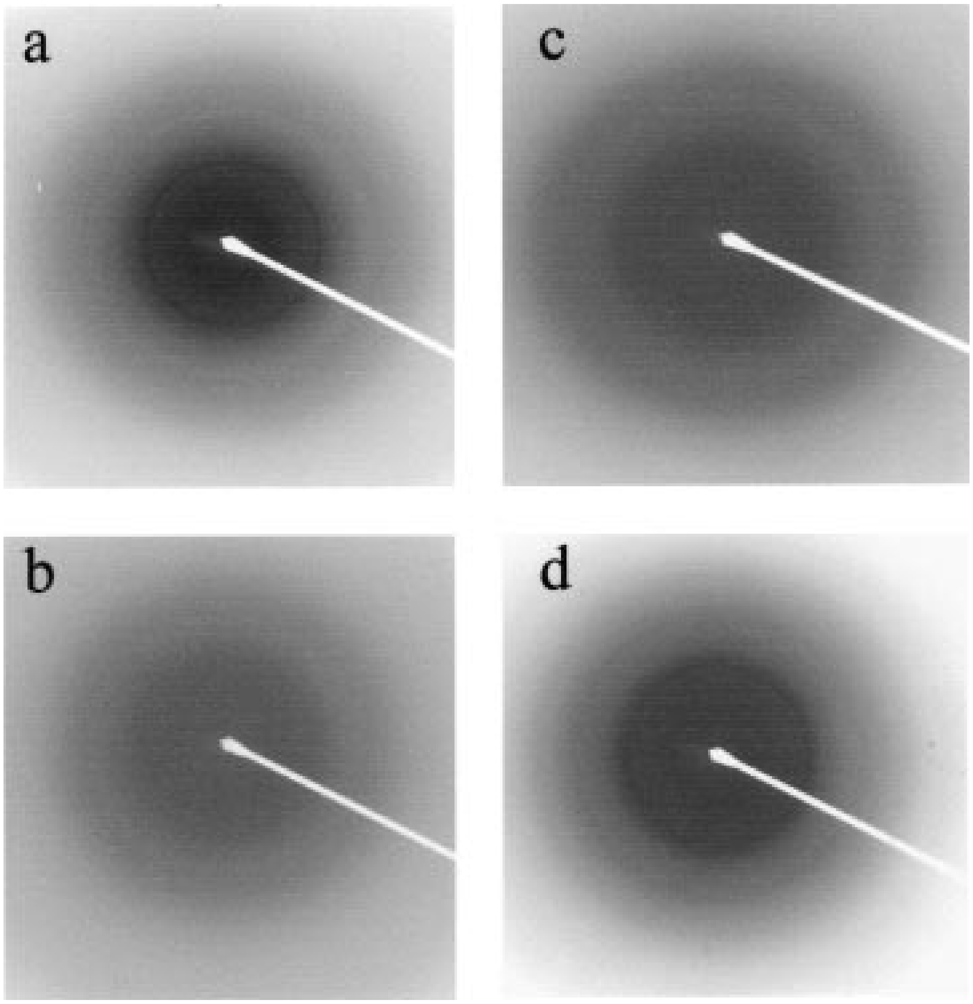

Figure 6. Electron diffraction patterns of regioregular polythiophene derivatives: (a) polymer 1, cast from chloroform solution at room temperature; (b) polymer 2, cast from chloroform solution at room temperature; (c) polymer 3, cast from DMF under vacuum (25 Torr) at 80 °C; (d) and regioregular poly(3-hexylthiophene), cast from chloroform solution at room temperature.

by a very broad and diffuse diffraction shoulder (indicating very limited ordering and crystallinity) at a spacing of about 20 Å. The bulky side chains in polymer 2 may make it more difficult for good chain packing. The ordering might be improved by surveying a broader range of solvents under different conditions. Under most conditions (Table 1, entries 6−8), films cast from polymer 3 did not show any diffraction peak by either X-ray (Figure 5c) or electron diffraction measurements (Figure 6c), indicating that those films are essentially amorphous. However, low crystallinity was found with polymer 3 film cast from DMSO solution under very slow evaporation rate in an almost closed environment by covering the solution and substrate with a Petri dish (Table 1 entry 9) at elevated temperature (50 °C). Its X-ray diffraction pattern (Figure 5d) shows a weak peak at 11.5 Å, which corresponds well to the separation of the backbone macromolecules by the side chains. However, film cast under the same condition from DMF only showed a very broad shoulder in X-ray diffraction pattern (Figure 5e), indicating much lower crystallinity. In addition, poor film-forming properties was found with polymer 3. It tends to form nonuniform grainy films, which may also be attributed to the low field-effect mobility (Table 1, entry 9).[28] The self-assembly properties of the water soluble ammonium salts of polymer 3 have previously been observed in solution characterized by the red shift of the maximum absorption peak when a certain ammonium salt is used.[17] The solid-state X-ray diffraction measurement reflects the preferred long-range ordering in the thin film. Our results here indicate that it is difficult to achieve a long-range preferred ordering with polymer 3 under common crystallization conditions to yield a similar orientation as commonly observed with PHT. It has been shown previously that the polythiophene backbones of PHT are parallel to the substrate and separated by the interdigitation of their side chains. We now see that a similar orientation and separation of polymer 3 chains is obtained only in a very limited fashion and under special slow growth conditions from only DMSO solvent.

The electron diffraction patterns of all polymers, cast from similar conditions as for Figure 5, are shown in Figure 6. Both polymer 1 and regioregular PHT showed sharp diffraction rings corresponding to the $\pi-\pi$ stacking distances (Figure 6a and d). However, this spacing for polymer 1 is about 4.3 Å, which is much larger than that of PHT (3.8 Å). This larger spacing may be caused

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by the methyl branches on the side chains separating the polymer backbones further apart. The substantially reduced π-overlap in polymer 1 may be an important factor for the significant lowering of its field-effect mobility in comparison to PHT, despite its substantial crystallinity. The electron diffraction patterns of polymers 2 and 3 show only diffuse scattering, indicating essentially no crystallinity, which is probably at the root of their very low mobilities.

Conclusions

Regioregular poly(3-alkylthiophene) derivatives have been synthesized and their semiconducting properties as field-effect transistors have been investigated. Regioregular poly(3-(2-(*s*)-methylbutyl)thiophene) (polymer 1) has a relatively high field-effect mobility among soluble polymer semiconductors on the order of 10^{-3} $cm^2/(V\ s)$. This value is, however, lower than that of regioregular poly(3-hexylthiophene), most likely because of the longer $\pi-\pi$ stacking distance resulting from introduction of branches on the side chains. In addition, regioregular polythiophenes with bulky side chains or H-bonding carboxylic acid side chains are difficult to form highly crystalline films and therefore yield very low field-effect mobilities. The above results indicate that the nature of the side chains has a critical impact on the self-assembly, crystallization, and semiconducting properties of regioregular poly(3-alkylthiophene) derivatives. High crystallinity and high transistor performance are more readily obtained with regioregular polythiophenes that contain non sterically hindered linear side chains. The results presented here should provide guidelines for further molecular design and structural modifications of regioregular polythiophenes for transistor and other electronic applications.

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