Regioregular Poly(3-alkylthiophenes): Synthesis, Characterization, and Application in Conductive Fabrics

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ABSTRACT: Poly(3-dodecylthiophene) (P3DDT) and poly(3-decylthiophene) (P3DT) with high contents of head-to-tail linkages (86 and 85%, respectively) were synthesized in high yields by a facile oxidative polymerization with ferric chloride in chloroform at room temperature. We believe that the low concentration and ultraslow addition of monomers to ferric chloride contributed to the high regioregularity. Differential scanning calorimetry thermograms indicated that the formed polymers consisted of crystalline, quasiordered, and disordered phases, which is a common feature of highly regioregular polymers. We prepared conductive fabrics with specific resistance of 30 and 100 Ω/sq by impregnating polyamide fabrics in a chloroform solution of P3DDT and P3DT, respectively. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2131–2135, 2004

Key words: synthesis; conducting polymers; coatings

INTRODUCTION

Since the amazing discovery of highly conducting polyacetylene marking the birth of a new field and resulting in the award of the Nobel Prize for chemistry in 2000,[1] very diverse applications for organic conductive polymers have emerged because of their remarkable electronic and photonic properties.[2] Poly(3-alkylthiophenes) (P3ATs) represent an important class of conducting polymers because of their solubility, processability, and environmental stability; they also possess excellent electrical conductivity, electroluminescent properties, and nonlinear optical activity among the polythiophenes.[3]

Because 3-alkylthiophene is not a symmetrical molecule, there are three relative orientations available when two thiophene rings are coupled between the 2 and 5 positions. The first of these is head-to-tail (HT), coupling, the second is head-to-head (HH) coupling, and the third is tail-to-tail (TT) coupling, as shown in Figure 1. In the latter two linkages, a stearically driven twist of thiophene rings causes a breakdown of the planarity of the main chain, which results in a loss of conjugation and, hence, poor electrical and optical properties. However, a regioregular HT-coupled P3AT can easily access a low-energy planar conformation, which leads to a highly conjugated polymer with superior properties over a random one. Syntheses of several regioregular HT-coupled P3ATs have been reported. The nickel-catalyzed polycondensation of a 3-alkyl-5-bromothienyl Grignard reagent[4] and the related crosscoupling reaction of the corresponding zinc reagent[5] through selective metalation at the 5 position of 3-alkylthiophene derivatives were first reported to give 98–99% HT-coupled P3AT. Both groups have shown that improved regioregularity results in the enhanced physical properties of the polymers, including electroconductivity[6] and electroluminescent properties.[7] These types of polymerization are rather sophisticated and require high purity in the monomers. Therefore, oxidative coupling polymerization with ferric chloride is easy and suitable for large-scale preparation. It was, however, believed that the oxidative coupling polymerization gives only regiorandom polymers,[8] where the standard procedure was to suspend ferric chloride in chloroform and then add the thiophene monomer quickly.[9] Previous reports showed that there is a relationship between the rate of the oxidative polymerization with ferric chloride and the regioregularity of the formed polymer, as a high reaction rate would result in unselective coupling.[10,11] Anderson et al.[10] reported an excellent regioselective synthesis of HT-coupled poly[3-(4-alkylphenyl)thiophene] through the oxidative coupling polymerization of 3-(4-octylphenyl)thiophene by the slow addition of ferric chloride. However, it is quite difficult to perform a controlled addition of a suspension of solid ferric chloride in chloroform. Ueda et al.[11] showed that a high HT coupling content of 88% could be achieved by regioselective oxidative coupling polymerization with ferric chloride when the reaction temperature was −45°C and the initial monomer concentration was 20
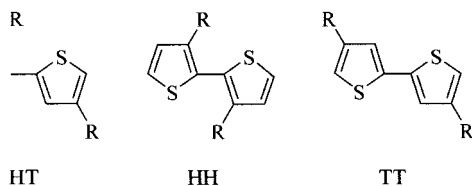
Figure 1 Diad linkages of P3AT.

mmol/L. In this article, we report that regioregular P3ATs with 85–86% HT coupling and with high yields were obtained by oxidative polymerization with ferric chloride at room temperature through low monomer concentration and the ultraslow addition of the monomer to ferric chloride. We believe that the ultraslow addition of the dilute monomer solution allowed for a slow oxidative coupling, and thus, a more selective polymerization occurred, and a more regioregular polymer was formed.

EXPERIMENTAL

Measurement

Ultraviolet–visible (UV–vis) spectra were recorded in chloroform on a PerkinElmer Lambda 18 spectrophotometer at 23°C. ^{1}H-NMR spectra were measured in CDCl$_3$ on a Varian VXR-Unity 500 spectrometer at room temperature. Differential scanning calorimetry (DSC) measurements were performed on a PerkinElmer DSC-7. The instrument was calibrated with an indium standard, and the temperature range chosen was 25–200°C. The sample, typically 5–8 mg, was pressed in a sealed aluminum pan, and the measurements were carried out with a heating rate of 10°C/min under a dry nitrogen environment with a flow rate of 20 psi. Conductivity measurements were carried out on a Keithley 2010 multimeter with the four-probe method with pressure contacts.

Materials

Unless otherwise stated, all of the chemicals used were commercially available and were used as received without further purification. 3-Doceylthiophene and 3-decylthiophene were purchased from Aldrich. Chloroform and acetonitrile (analytical grade) were purchased from Scan-Lab and were dried over magnesium sulfate before use.

Polymerization of 3-dodecylthiophene with FeCl$_3$

A typical procedure was as follows. In a 250-mL, two-necked, round-bottom flask, anhydrous FeCl$_3$ (1.93 g, 11.8 mmol) was suspended in chloroform (50 mL). The flask was then filled with nitrogen, and a solution of 3-dodecylthiophene (0.83 mL, 2.97 mmol) in chloroform (50 mL) was added dropwise over 4 h through an additional funnel to the suspension. The resulting black mixture was stirred for 16 h under a flow of nitrogen. The reaction mixture was poured into methanol (500 mL) containing 10% HCl. The precipitate was collected by filtration and washed by stirring twice with methanol/HCl (10% HCl) and five times with methanol for 2 h each until the washing solution remained colorless. The dark purple solid was collected by filtration and dried under reduced pressure [yield = 0.64 g (86%); number-average molecular weight (M_n) = 39,393, weight-average molecular weight (M_w) = 108,204 (gel permeation chromatography based on polystyrene calibration)].

Polymerization of 3-decylthiophene with FeCl$_3$

The polymerization was performed as described for 3-dodecylthiopene, with 2.89 g (17.8 mmol) of FeCl$_3$, 1.1 mL (4.45 mmol) of 3-decylthiophene, and 100 mL of chloroform [yield = 0.88 g (89%); M_n = 27,340, M_w = 75,491 (gel permeation chromatography based on polystyrene calibration)].

Coating of polyamide fabrics

Polyamide knitted fabrics (2 × 2 cm) were coated by solvent casting from chloroform solutions of poly(3-dodecylthiophene) (P3DDT) and poly(3-decylthiophene) (P3DT) and were consequently slowly dried in air for 24 h.

Doping with FeCl$_3$

We doped the polymer-coated fabrics by treating the coatings with $1M$ FeCl$_3 \cdot 6H_2O$ in acetonitrile for 24 h. The doped fabrics were washed with acetonitrile and dried *in vacuo*.

RESULTS AND DISCSUSSION

^{1}H-NMR spectroscopy

Previous articles have shown that the α-methylene protons of the alkyl group next to the thiophene ring can be resolved by two different dyads: HT and HH. The regioregularity of the polymers is defined as the ratio of HT to HH dyads and is evaluated by the ratio of the intensities of the two peaks associated with HT and HH dyads. In the ^{1}H-NMR spectra of P3DDT [Fig. 2(a)] and P3DT [Fig. 2(b)], two signals at δ = 2.56 and 2.81 ppm for both polymers were observed and were assigned to the HH and HT dyads, respectively. The integration of those two signals resulted in 86% HT dyad content for P3DDT and 85% HT dyad content for P3DT. The chemical shifts of the β-proton of the thiophene ring in four different triad linkages, that are,
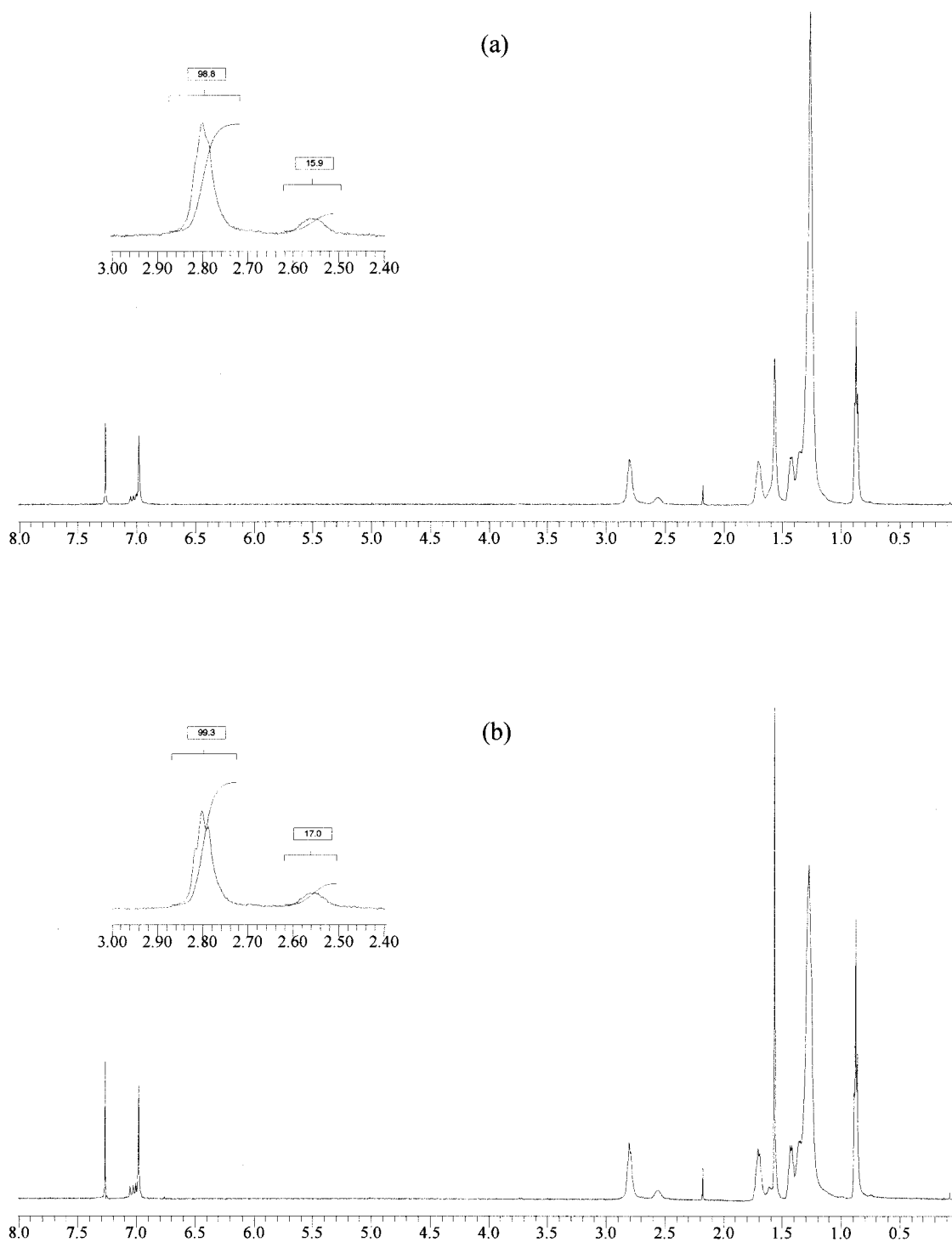
Figure 2 ^{1}H-NMR spectra of (a) P3DDT with an expansion of the α-methylene protons region and (b) P3DT with an expansion of the α-methylene protons region.

HT–HT, TT–HT, HT–HH, and TT–HH, coincided with those reported earlier in the literature for P3ATs.[10]

Electronic UV–vis spectroscopy

In conjugated polymers, the absorption maximum (λ_{max}) in the visible spectrum corresponds to a π–π*

electronic transition and depends on the effective conjugation length. λ_{max} in a solution of P3AT is related to the proportion of HT linkages in the polymer backbone.[12] As shown in Figure 3, λ_{max} was 444 nm for P3DDT and 441 nm for P3DT. Previously reported λ_{max} values for regioregular (≥98% HT) P3DDT and P3DT prepared by Rieke[5] were 453 and 447 nm, re-

spectively, whereas regiorandom P3ATs (70–80% HT) had λ_{max} values at 426–428 nm.[5] This suggests that in solution, a regioregular HT polymer chain has a more rod-like conformation and a longer conjugation length, whereas regiorandom polymer chains have a more coil-like conformation with a shorter conjugation length.[13] The difference in λ_{max} values between differently prepared P3ATs has been attributed to the difference in the degree of regioregularity, in other words, the proportion of HT linkages. In comparison to the reported λ_{max} values for (≥98%) regioregular polymers, the λ_{max} values of the prepared polymers formed strong evidence for the existence of a high content of HT linkages. This was in agreement with the ^{1}H-NMR observations, which suggested 85–86% regioregularity.

DSC

The DSC thermograms of the heating scan are shown in Figure 4. Two first-order transitions were observed at 70 and 138°C for P3DDT. The first transition was due to the melting of ordered side chains, whereas the second transition was attributed to the melting of main chain crystallites indicating its semicrystalline nature. For P3DT, a small peak associated with the melting of side chains at 69°C was observed. However, a broad peak associated with the melting of the main-chain crystallites at 147°C indicated that P3DT was crystalline.

The existence of separate melting transitions of ordered side chains and main chains is often observed for regioregular combolike polymers possessing alkyl side chains with 10 or more carbon atoms.[14–16] Regiorandom polymers, however, tend to have a first-order transition because of the disruption of ordered side chains with no or a small first-order transition depending on the content of HT linkages because of the melting of main chains, as shown by Holdcroft et al., who observed the absence of a melting transition associated with the crystallinity of main chains for a regiorandom P3DT (70% HT), indicating that the poly-
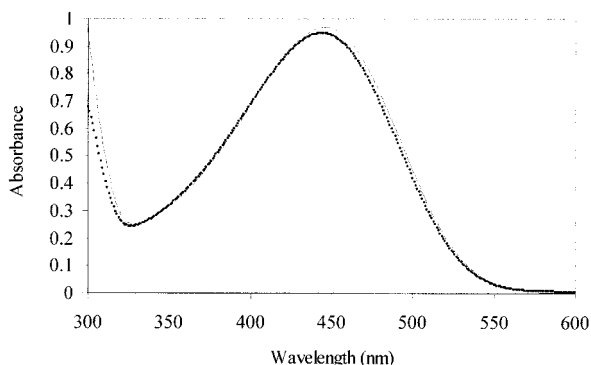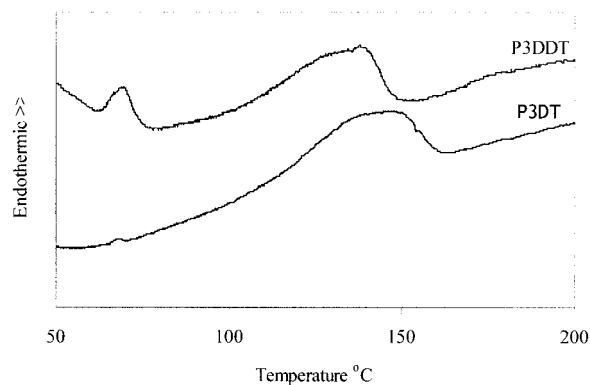
Figure 4 DSC thermograms of P3DDT and P3DT in the heating scan.

mer was not crystalline.[17] However, on studying a regioregular P3DT with a HT content of 98% or greater, they observed a melting first-order transition of main chains crystallites at 147°C, which coincided with our observations, as discussed earlier.

The observed high regioregularity of P3DDT and P3DT was possibly due to the fact that the rate of oxidative coupling was dependant on the reactant concentration. We believe that the low concentration and ultraslow addition of the monomer ensured a low monomer concentration at all times during the reaction, and hence, a slow reaction occurred and a more regioregular polymer was formed.

Conductivity measurements

Polyamide fabrics coated with films of P3DDT and P3DT (1–3 μm) from a chloroform solution showed specific resistances of 30 and 100 Ω/sq, respectively. We believe that the threefold increase in the conductivity of P3DDT over P3DT might be attributable to the fact that P3DDT possessed the best planarity and longest conjugation length among other P3ATs. A better coplanar structure with longer conjugation length facilitates the charge-transfer interactions during the doping process, resulting in a rapid increase in conductivity.[18] Andersson et al.[9] observed a mean conductivity of 4 S/cm for the free-standing films of a regioregular (~94% HT) poly[3-(4-octylphenyl)thiophene] doped with FeCl₃ and, when the films were doped with solid iodine, the same conductivity was observed as when they were doped with FeCl₃. McCullough et al. reported that the conductivity of regioregular P3AT films cast from the same sample differed markedly as a result of the variation of morphology from film to film, where typical conductivities of 100–200 S/cm could be achieved for stretch-oriented films of P3ATs.[19,20] Rieke et al. also showed that films of high-HT P3AT heavily doped with I₂ vapor had conductivities around 1000 S/cm.[7]

Figure 3 UV–vis spectra of (—) P3DDT and (· · ·) P3DT.

CONCLUSIONS

We have shown that it is possible to synthesize P3ATs with high regioregularity by simple oxidative polymerization at room temperature. The HT dyad content was determined by ^{1}H-NMR to be 85–86%. The red-shift of λ_{max} and the semicrystallinity of P3DDT and P3DT, as shown by their DSC thermograms, formed good evidence for the existence of a high HT dyad content. The conductivity of polyamide fabrics coated with P3DDT revealed strong potential for this type of polymer in conductive fabrics applications. As far as we know, the application of P3ATs in conductive fabrics has not been seen before in the literature; therefore, no well-established comparison for conductivity values can be drawn at this stage. The controversy in the literature over conductivity values is attributed to the fact that the thin-film conductivity of P3ATs not only depends on the regioregularity but also on film thickness, processing conditions, and the nature and concentration of dopant. Therefore, further investigations are needed to explore the effects of those factors on the conductivity of P3ATs coated on various types of fabrics.

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