Synthesis and Structure–Property Relationships of Regioirregular Poly(3-hexylthiophenes)

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ABSTRACT: The regioselectivity of coupling reactions has been investigated in order to determine the origin of regioregularity in poly(3-alkylthiophenes) prepared by the Grignard method. Reaction of equimolar quantities of 2,5-diiodo-3-hexylthiophene and Mg results in the formation of Grignards primarily at the 5-position, while di-Grignard accounts for ~60% of reacted magnesium. Condensation of di-Grignards with 2-iodo-3-hexylthiophene, the most sterically crowded coupling reaction, shows only modest regioselectivity in favor of head-to-tail configurational isomers. Polymerization of reaction mixtures containing large fractions of di-Grignards resulted in polymers with low degrees of regioregularity. The optical and electronic properties of poly(3-hexylthiophene) are correlated to the degree of regioregularity. Polymers with the largest percentage of head-to-tail linkages, prepared by oxidative coupling, exhibit a higher degree of long-range order, higher electronic conductivities, and longer wavelengths of maximum absorbance.

Introduction

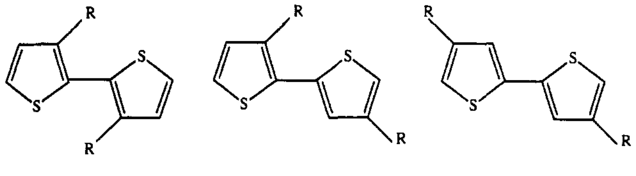
There is active interest in π-conjugated polymers from both fundamental and technological viewpoints: fundamental because charge-carrying polaronic and bipolaronic states can be generated in individual polymer chains and the response of the polymer to the formation of these states is nonlinear; technological because bipolarons can be generated optically, electronically, or chemically, lending them to a wide variety of technologies and potential applications in electrooptical and microelectronic device manufacturing.[1-4]

Coplanarity of π-orbital coupling along the main chain is a requirement of π-conjugation and one-dimensional charge transport. Furthermore, the relatively short contour length of the individual polymer chains requires that interchain migration of charge play a role in the transport of charge through the bulk polymer. A strong correlation exists between structural integrity, crystallinity, and material performance of polymers in general.[5] Similarly, a high degree of structural order is preferred for efficient transport of charge. The configurational stereochemistry of π-conjugated polymers requires close scrutiny in order to improve molecular order and thus tune electrooptical properties.

Polythiophene is a π-conjugated polymer which continues to attract considerable attention.[1] In this heterocyclic polymer the double bonds between adjacent thienyl rings can adopt trans or cis configurations by virtue of adjacent rings being syn or anti. Ab initio Hartree–Fock calculations indicate that the anti conformation is stable by only 1.3 kcal mol^{-1}.[6] Gas-phase measurement on 2,2′-bithiophene establish the angle of twist around the central bond as 34° whereas polarized light spectroscopy of the dimer in cyclohexane favors the anti conformer.[7,8] X-ray diffraction analysis reveals a planar, anti conformation in the solid state.[9] A syn conformation between adjacent rings of polythiophene imparts curvature to the chain, promoting helical structures, whereas the anti configuration leads to straight-chain molecules. X-ray diffraction data of thin films and powdered samples of polythiophene have been interpreted as revealing planar straight chains with an orthorhombic unit cell,[10,11] although evidence suggesting helical structures has also been reported.[12,13]

Polythiophene is an intractable solid irrespective of the synthetic route, limiting analysis to solid state techniques. From a technological viewpoint, lack of processability is one reason why these materials are presently of little commercial value. Derivatization of the 3-position of the thienyl ring with long alkyl chains or a methoxy, alkylmercapto, or ether functionality prior to polymerization yields polymers which are soluble in common organic solvents.[14-21] Adjacent rings maintain coplanarity, exhibit extensive π-conjugation, and hence possess the electronic and optical attributes of unsubstituted polythiophenes.

Coupling of 3-substituted thiophenes via the 2- and 5-positions leads to polymers with various degrees of regioregularity due to the formation of head-to-head (H–H), head-to-tail (H–T), and tail-to-tail (T–T) configurational isomers. Regioregularity refers to the structural regularity of H–H, H–T, and T–T isomers in the chain. The relative predominance of one coupling reaction over the other to form a particular isomer is said to be regioselective, whereas it is termed regiospecific if only a single isomer is present.[22]



Polymerization of 3-alkylthiophenes by electrochemical methods or oxidative coupling with ferric chloride yields polymers with 50–80% head-to-tail coupling.[23-28] Polymers containing a high degree of regioregularity in the form of H–H and T–T linkages have been obtained by oxidative coupling of 3,3′-dialkyl-2,2′-bithiophene[29] and 4,4′-dialkyl-2,2′-bithiophene.[30] Synthesis of poly(3-alkylthiophenes) by coupling Grignard reagents of 2,5-diiodothiophenes has received considerable attention because linear polymers can be prepared which are absent of β-linkages.[20,21,27,28,31-34] Polymers prepared in this way have molecular weights that are dependent on the composition of the polymerization mixture[34] and typically consist of 2,5-dihalogeno-3-alkylthiophene and mono- and di-Grignard reagents thereof.

Evidence indicates that the electrical and optical properties of these materials are largely controlled by

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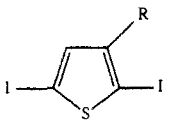
symmetry and stereochemical factors.[27,28,35,36] McCullough et al. have shown that poly(3-dodecylthiophene) containing a high percentage of H–T dyads (91%) exhibits electrical conductivities 60-fold higher than $FeCl_3$- or electrochemically-prepared polymers.[27] Ruiz et al. have reported that substituted poly(1,4-bis(2-thienyl)phenylene)s exhibit higher degrees of crystallinity and higher conductivities when substitution on the phenyl is symmetric.[35] 3-Substitution of polythiophenes with a larger functionality, such as cyclohexane, imposes steric constraints on interannular interactions and leads to polymers which exhibit shorter wavelengths of maximum absorption and lower electronic conductivities.[36]

In this paper we illustrate how the composition of the polymerization solution determines regioregularity of polythiophenes prepared by Grignard polycondensation of dihalogenated thiophenes. Investigation of regioselective coupling reactions between small-molecule analogues has been used to illustrate the origin of regioirregularity. The versatility of the synthetic technique has been used to prepare a series of polymers with varying degrees of regioregularity. Comparisons of the optical, electronic, and physical properties of this series provides a valuable insight into structure–property relationships of poly(3-alkylthiophenes) and illustrates how regiochemistry can be controlled to afford materials with tunable electronic and optical properties.

Experimental Section

Preparation of 2,5-Diiodo-3-hexylthiophene (I). 3-Hexylthiophene was synthesized by coupling the Grignard reagent of 1-bromohexane (Aldrich) with 3-bromothiophene using [1,3-bis(diphenylphosphino)propane]nickel(II) chloride ($Ni(dppp)_2Cl_2$) as catalyst.[37] The product was purified by fractional distillation under reduced pressure. 3-Hexylthiophene (7.8 g, 46 mmol) and 12.2 g (48 mmol) of I_2 (BDH Chemicals Ltd.) were added to a mixture comprising 18 mL of chloroform, 3 mL of concentrated HNO_3, and 3 mL of H_2O.[38] The mixture was refluxed for 16 h. The product I, was purified through a silica gel column using hexane. After workup, the yield was 71% (purity, >99%). ^1H NMR (400 MHz, $CDCl_3$), δ: 6.89 (1 H, s), 2.50 (2 H, t, J = 7.2 Hz), 1.53 (2 H, m), 1.4–0.8 (9 H, m).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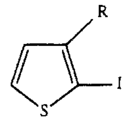
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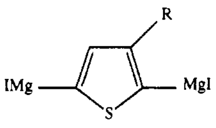
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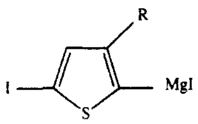
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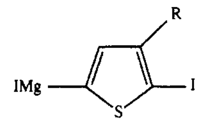

(V)

R = Hexyl

Preparation of 2-Iodo-3-hexylthiophene (II). 3-Hexylthiophene (5.00 g, 27 mmol) was stirred with HgO (5.39 g, 25 mmol) and I_2 (7.80 g, 31 mmol) in 15 mL of benzene for 2 h at 0 °C.[39] The product, 2-iodo-3-hexylthiophene, was filtered out and purified through a silica gel column using hexane for a yield of 90%. ^1H NMR (400 MHz, $CDCl_3$), δ: 7.39 (1 H, d, J = 5.4 Hz), 6.8 (1 H, d, J = 5.4 Hz), 2.63 (2 H, t, J = 7.1 Hz), 1.8–0.7 (11 H, m).

Reaction of 2-Iodo-3-hexylthiophene (II) with the Di-Grignard of 2,5-Diodo-3-hexylthiophene (I). Magnesium metal (0.58 g, 24 mmol) was reacted with 4.22 g (10 mmol) of 2,5-diiodo-3-hexylthiophene (I) in dry ether. The composition of the Grignard mixture was determined periodically by quenching aliquots of the mixture with water and analyzing the resulting products by GC. The response of the detector was calibrated using pure compounds in order to obtain quantitative information. After 8 h only di-Grignard species III was detected (>96%). 2-Iodo-3-hexylthiophene (II) (1.50 g, 5.0 mmol) and $Ni(dppp)_2Cl_2$ catalyst were added to the reaction mixture. After 3 h, the reaction was quenched with $MeOH/H_2O$. The product was a clear oil after purification through a silica gel column using hexane.

Synthesis of Polymers P1/P2. Magnesium metal (0.58 g, 24 mmol) was reacted with 4.2 g (10 mmol) of 2,5-diiodo-3-hexylthiophene (I) in dry ether to obtain the di-Grignard species as described above. An additional quantity of 2,5-diiodo-3-hexylthiophene (up to 4.2 g) was added and polymerization initiated with adding $Ni(dppp)_2Cl_2$. After 24 h the reaction was quenched with $MeOH/H_2O$. The reaction mixture was poured into 5% HCl in methanol to precipitate the polymer. The polymer was purified by repeated precipitations (50% yield).

Synthesis of Polymers P3/P4. Magnesium metal (0.29 g, 12 mmol) was reacted with 4.2 g (10 mmol) of I in ether and the polymerization initiated by $Ni(dppp)_2Cl_2$. The polymer was precipitated and purified as described above. Yields were 60–70%.

Synthesis of Polymers P5/P6. 3-Hexylthiophene (0.1 M) in chloroform was mixed with a 0.4 M chloroform solution of anhydrous ferric chloride[40] and the mixture stirred for 2 h prior to precipitation into acidified methanol. The solid product was filtered out and washed with NH_4OH, water, and methanol. The crude polymer was dissolved in hot dichloromethane, and insoluble products were removed by filtration. Low molecular weight products were removed by cooling the filtrate and adding methanol.

Instrumentation. UV/vis absorption spectra were recorded on a Perkin-Elmer Lamda 3A UV/vis spectrophotometer at 25 °C. ^1H NMR were recorded with a 400-MHz Bruker AMX400 in $CDCl_3$. Gas chromatography was performed on a Hewlett-Packard 5890A gas chromatograph. GC–MS analyses were performed on a Hewlett-Packard HP5985 GC–MS system using a 30-m DB1 column ramped at 20 °C/min (80 → 240 °C). Molecular weight distribution curves of polymers were determined by gel permeation chromatography (GPC) using 10^6, 10^4, and 10^3-Å μ-Styragel columns at 25 °C. Polymers were eluted with tetrahydrofuran and detected using a UV/vis spectrophotometer (Spectra-Physics, Model SP8000) and a refractive index detector (Waters, Model R400). Data were acquired, stored, and analyzed using an IBM personal computer and custom-written software. Polystyrene standards (Polymer Labs. Inc.) of molecular weights ranging 233 000–750 were used for calibrating GPC columns for hydrodynamic volume versus elution volume. The polystyrene calibration curve was converted to a poly(3-hexylthiophene) (P3HT)-based calibration using the following Mark–Houwink constants: $K_{P3HT} = 2.28 \times 10^{-3}$ cm³/g, $a_{P3HT} = 0.96$, $K_{PS} = 1.29 \times 10^{-2}$ cm³/g, and $a_{PS} = 0.713$.[41,42]

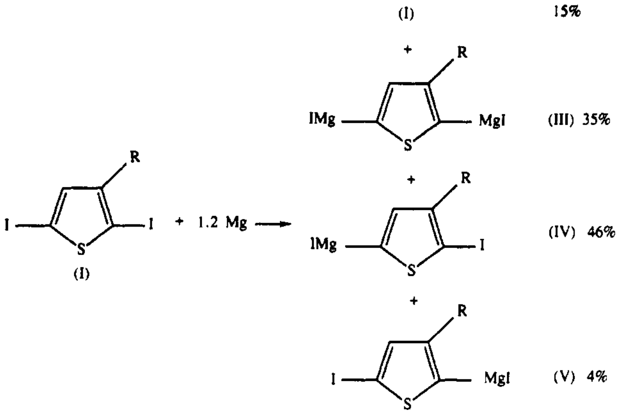
Thin films of polymer (~1.0 μm) were cast onto glass slides from dilute solutions of the polymer in toluene. Neutral polymers were oxidized into their electronically conductive form by submersion of the polymer/substrate into an anhydrous saturated solution of nitrosonium tetrafluoroborate in acetonitrile. Electronic conductivities were measured by the four-point probe technique.

X-ray experiments were performed with a Siemens D-5000 diffractometer with a Cu Kα source and graphite monochromator. The samples had a thickness of 0.5–1.0 μm and a geometry of 2 × 2 cm².

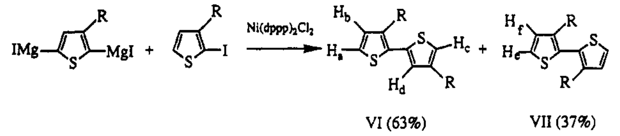
Results and Discussion

Formation of Grignard Reagents. Catalyzed condensation of either mono-Grignard reagents IV or V should provide linear polymers free from HH and TT defects. The reaction of equimolar quantities of 2,5-diiodo-3-hexylthiophene (I) and magnesium metal was investigated to determine the feasibility of forming species IV and V. The preference for Grignard formation at the 2-position, 5-position, or both was determined by GC analysis of the products following replacement of Grignard substituents

Scheme I



Scheme II



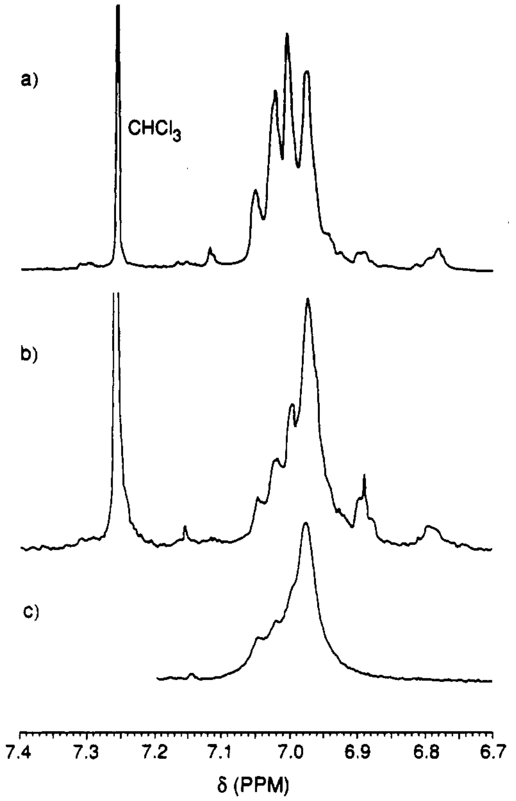


Figure 1. 400-MHz ^{1}H NMR spectra of poly(3-hexylthiophene): (a) P1, (b) P3, and (c) P6 in $CDCl_3$.

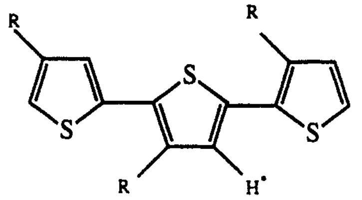
with hydrogen. Four components were observed, unreacted 2,5-diiodo-3-hexylthiophene (I) (14.7 ± 5.8 mol %), 2-iodo-3-hexylthiophene (46.3 ± 7.1 mol %), 5-iodo-3-hexylthiophene (3.8 ± 1.4 mol %), and 3-hexylthiophene (35.2 ± 4.3 mol %), indicating the presence of I, IV, V, and III, respectively (see Scheme I). The 12:1 molar ratio of IV to V indicates a preference for Grignard formation at the 5-position over the 2-position. This observation is in keeping with the observation that aryl halides with bulky ortho substituents are less susceptible to Grignard formation compared to those aryl halides in which steric hindrance is absent.[43]

Initial Grignard formation occurs primarily at the 5-position of 2,5-diiodo-3-hexylthiophene (I), yet the di-Grignard III accounts for ~58 mol % of the consumed magnesium. High yields of di-Grignard are observed because electropositive magnesium in the mono-Grignard IV enhances electron transfer and reactivity at the 2-position. It is not possible therefore to prepare the mono-Grignard reagent in the absence of the di-Grignard by this simple one-pot procedure.

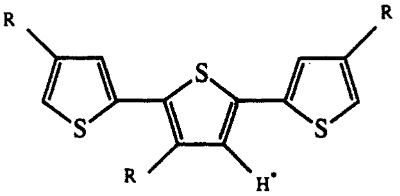
Regioselectivity of the Coupling Reaction between Di-Grignard Reagents and Iodothiophenes. It was pertinent to investigate regioselectivity of coupling reactions between di-Grignard species III and iodothiophenes since the former accounts for 58 mol % of the consumed magnesium. The regioselectivity of coupling between III and 2-iodo-3-hexylthiophene (II) was deemed to reveal the most information since coupling at the 2-position of III would constitute HH coupling, whereas coupling at the 5-position would reveal a preference for HT linkages (see Scheme II). When equimolar quantities of III were coupled to 2-iodo-3-hexylthiophene, several products were identified. Workup of the major component gave two products. GC–mass spectrometry indicated the two products possessed identical molecular weights of 334. The two products could not be readily separated, but comparisons of ^{1}H NMR spectra of the mixture with those of previously reported bithiophenes and terthiophenes[28,29,44–46] revealed the products to be 3,4′-dihexyl-2,2′-bithiophene (VI) and 3,3′-dihexyl-2,2′-bithiophene (VII). Independent preparation and characterization of the latter by dimerization of 2-iodo-3-hexylthiophene using the Grignard route confirmed the presence of VII in the mixture. The informative regions of the spectra (β-protons, α-CH_2 protons) were assigned as follows: (VI) (400 MHz, $CDCl_3$) δ 7.152 (H_a, d, $J = 5.2$ Hz), 6.974 (2 H [$H_c + H_d$] unresolved singlets), 6.923 (H_b, d, $J = 5.2$ Hz), 2.78 (2 H, t, $J = 7.4$ Hz), 2.56 (2 H, t, $J = 7.4$ Hz); (VII) δ 7.297 (2 H_e, d, $J = 5.4$ Hz), 6.970 (2 H_f, d, $J = 5.4$ Hz), 2.50 (4 H, d, $J = 7.4$ Hz). The molar ratio, VI:VII, was calculated as 1.7:1 using comparative integrals of the β-protons and as 1.6:1 using α-CH_2 protons, indicating a slight preference for formation of head-to-tail (HT) couplings. During polymerization the solution contains 2,5-diiodo-3-hexylthiophene and therefore additional coupling reactions involving III are possible. Primarily, these involve coupling at the 5-position of 2,5-diiodo-3-hexylthiophene. Since the 5-position is less sterically crowded than the 2-position, little, if any, regioselectivity is anticipated. Overall this leads to the conclusion that coupling between di-Grignard species and diiodothiophenes exhibits poor regioselectivity.

Regioregularity of Poly(3-hexylthiophene). Polymers prepared using a high percentage of I and III should exhibit a lesser degree of regioregularity if the mechanism of polymerization is consistent with the regioselectivity of the coupling reactions of small molecules described above. Figure 1 shows ^{1}H NMR spectra of three polymers prepared for this study. Analysis of the spectral region 6.9–7.1 ppm corresponding to β-protons reveals configurational and hence regiochemical information on the polymer. Resonances at 6.98, 7.00, 7.02, and 7.05 ppm are assigned to HT–HT, TT–HT, HT–HH, and TT–HH configurations, respectively. The assignments are based on the observation that coupling through HT configurations facilitates coplanarity of adjacent thienyls. β-Protons of triads associated with this configuration resonate at higher fields due to enhanced delocalization of the electron density associated with the hexyl group of adjacent rings. TT configurations maintain coplanarity, but the inductive effect of the alkyl group is diminished due to the greater distance between the alkyl and the β-proton. Steric crowding associated with HH configurations forces adjacent thienyls out of coplanarity, thus decreasing conjugation and diminishing the inductive effect of alkyl groups on adjacent rings. On the basis of these arguments β-protons of triads having HH configurations experience less shielding than those of HT or TT configurations and appear downfield.

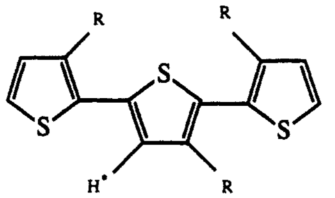
The relative percentage of triad configurations for these and other polymer samples are shown in Table I as a function of the initial composition of the polymerization solution. Additional configurational information can be abstracted from the intensity ratio of the two peaks centered at 2.8 and 2.6 ppm, which correlate to α-CH_2 groups of configurational HT and HH dyads.



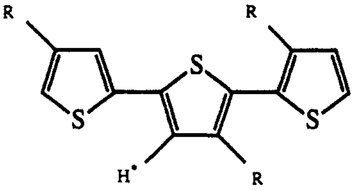
HT-HT



HT-TT



HT-HH



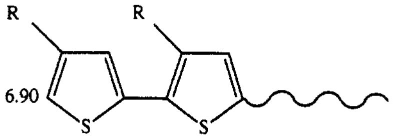
TT-HH

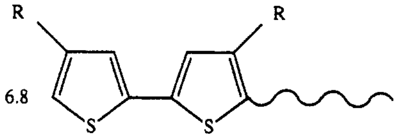
Table I illustrates the dependency of regioregularity on the composition of the polymerization solution. A higher proportion of mono-Grignard species, IV, favors regioselectivity, but it should be noted that IV cannot be prepared without formation of the configurational isomer V by this route.

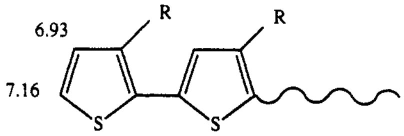
Coupling of the di-Grignard III with iodinated 3-hexylthiophene in which the iodine is located at the 2-position has been shown to be marginally regioselective in favor of HT linkages due to steric crowding of the hexyl side chains. Steric crowding is not present at the 5-position of 3-alkylthiophene monomers and coupling reactions involving these positions are not expected to be regioselective. Consequently, polymerization mixtures containing large fractions of III yield polymers with lower degrees of regioregularity. Polymers **P5/P6**, synthesized by oxidative coupling using ferric chloride, contain larger percentages of HT linkages which is consistent with previous reports.[25,26]

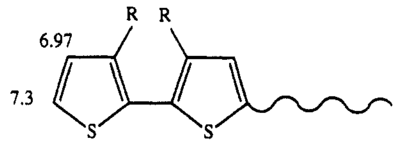
Physical Properties: Molecular Weights. It should be possible to determine the molecular weight of the poly(3-alkylthiophene)s by ^1H NMR spectroscopy if the terminal protons can be accurately quantified relative to the number of β- or α-CH_2 protons. Unfortunately, this cannot be achieved when the molecular weight of the polymer is relatively large. Two previous reports have attempted to assign terminal protons of poly(3-alkylthiophene)s by NMR.[28,34] Using ^1H NMR data on bithiophenes obtained from this and other studies, it is now clear that the chemical shift of terminal protons is correlated to the configuration of the terminal dyad. Approximate chemical shifts for poly(3-hexylthiophene) in $CDCl_3$ are shown below.

The assignments are supported by NMR data obtained from Grignard-synthesized poly(alkylthiophene)s in which the terminal Grignard functionality has been quenched with D_2O. In these experiments polymers were synthesized using polymerization solutions containing a relatively high concentration of III so as to prepare polymers with terminal Grignard species.[34] Following polymerization the reaction mixture was divided into two parts: half was quenched with H_2O and half quenched with D_2O to provide polymers possessing terminal atoms (at the α'- or ω-position) of hydrogen and deuterium, respectively. ^1H NMR spectra of the two polymers are shown in Figure 2. The terminal protons of the H_2O-quenched polymer can be seen at 7.3 (doublet), 7.16 (doublet), 6.9 (singlet), and 6.8 ppm (singlet). These resonances are absent in the D_2O-quenched polymer.









Integration of the appropriate NMR signals leads to accurate molecular weights when the molecular weights are relatively low. In the case of the polymer shown in Figure 2, M_n was determined to be 1600. This compares well to the value of 1500 determined by GPC. Polymers with much larger degrees of polymerization are difficult to assess because signals due to terminal protons disappear into background noise. Polymers prepared by the Grignard route present an additional complication because not all α'- or ω-terminal groups are protons. When the reaction mixture comprises a significant fraction of the mono-Grignard, IV or V, diiodothiophene (I), the final polymer will possess a complement of terminal iodine atoms. Furthermore, β-protons on iodine-terminated

Table I
Composition of Polymerization Solution and Relative Configurations of Poly(3-hexylthiophene)

	composition (%)[a]				configuration of triads (%)[b]				configuration of dyads (%)[b]	
polymer	I	IV	V	III	HT-HT	HT-TT	HT-HH	TT-HH	HT	HH
P1	17	6	0	77	35	23	22	20	52	48
P2	34	2	0	64	34	28	26	12	52	48
P3	22	48	4	26	55	17	15	13	60	40
P4	35	45	4	16	58	19	15	8	63	37
P5[c]	*d*				*e*				69	31
P6[c]	*d*				*e*				80	20

[a] Composition of polymerization mixture determined by GC. [b] Determined by ^{1}H NMR. [c] Prepared by oxidative coupling of 3-hexylthiophene. [d] Not applicable. [e] Indeterminable.

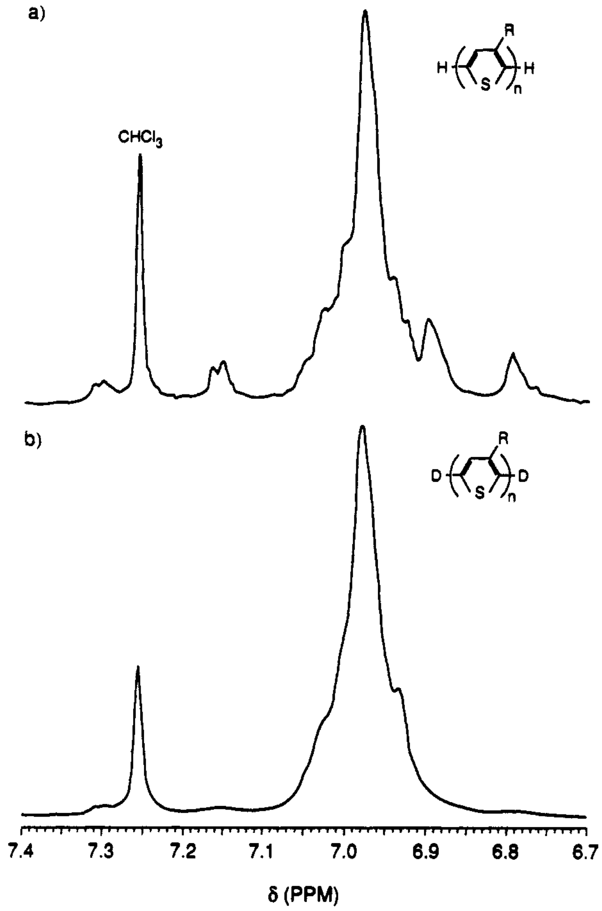


Figure 2. 400-MHz ^{1}H NMR spectra of poly(3-hexylthiophene) prepared by coupling I, IV and V, with an excess of di-Grignard III (see text): terminal Grignards quenched (a) with H_2O and (b) with D_2O ($CDCl_3$).

thienyls interfere with assignments of terminal-H resonances.

Due to the difficulties described above ^{1}H NMR was deemed unsatisfactory for determining molecular weights in this study. Molecular weights of polymers were determined by GPC and are shown in Table II. The average degree of polymerization for polymers prepared by the Grignard route was 15–34. In a previous report polymerization mixtures containing a large proportion of di-Grignard species were shown to have even lower degrees of polymerization. In these studies degrees of polymerization were increased to higher levels by the addition of stoichiometric amounts of diiodo-3-hexylthiophene (see Experimental Section).

Optical Properties. Polymers P1 → P6 exhibited broad UV/vis absorption spectra with maximum wavelengths of absorption, λ_{max}, indicative of extensive π-electron delocalization (Figure 3, Table II). Polymer P6 showed the highest degree of conjugation. Symmetry in poly(3-alkylthiophene)s is not the dominant structural feature in determining the extent of conjugation since highly regioregular poly(3,3′-dihexyl-2,2′-bithiophene) exhibits a maximum absorption at 389 nm.[29] This polymer, however, contains regularly spaced HH (50%) and TT (50%) isomers. Disruption of the π-system results when the polymer contains a significant fraction of HH dyads. The molecular origin of this can be considered by comparing steric interactions of HH and HT dyads. In solution, various interannular conformations can exist but the syn conformation for HH dyads can be ruled out because of strong steric interactions between alkyl chains on adjacent rings. HT dyads on the other hand can adopt

Table II
Physical, Optical, and Electronic Properties of Poly(3-hexylthiophene)

	mol wt[a]		UV/vis spectroscopy λ_{max} (nm)			
polymer	M_n[c]	MWD[d]	solution[e]	film	$\Delta\lambda_{max}$[f]	σ (S cm^{-1})[b]
P1	4200	1.73	413	424	11	0.0089
P2	5700	2.1	419	430	11	0.0074
P3	2600	1.6	420	444	24	0.13
P4	5600	2.1	425	462	37	0.14
P5[g]	12900	3.6	434	488	52	0.55
P6[g]	40600	1.7	440	505	65	6.0

[a] Determined by gel permeation chromatography. [b] Determined using four-point probe on films oxidized with nitrosonium tetrafluoroborate. [c] Number-average molecular weight. [d] Molecular weight distribution. [e] In chloroform. [f] $(\lambda_{max})_{film} - (\lambda_{max})_{solution}$. [g] Prepared by oxidative coupling of 3-hexylthiophene.

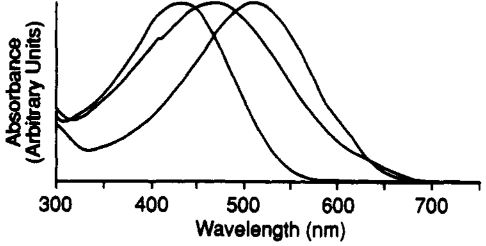


Figure 3. UV/vis optical absorption spectra of poly(3-hexylthiophene): (a) P1, (b) P3, and (c) P6 in $CHCl_3$.

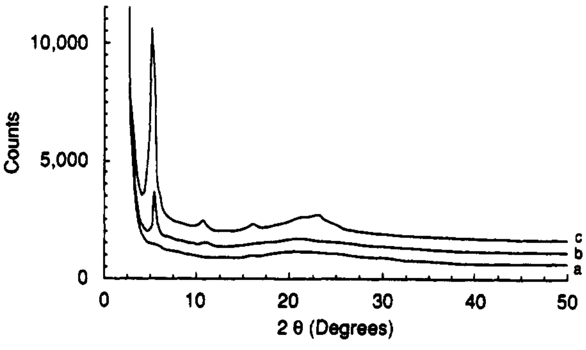


Figure 4. X-ray diffraction profiles of poly(3-hexylthiophene): (a) P1; (b) P3; (c) P6.

the syn conformation. In the anti conformation, the alkyl chains interact with the lone pair of the sulfur which occupies an sp^2 orbital and is perpendicular to the p_z orbitals of the aromatic ring. In the HH dyad there are two alkyl–sulfur interactions compared to the single interaction in the HT dyad, meaning that HH dyads are less likely to be coplanar.

Table II also shows the difference in λ_{max} between samples in solution and the solid state ($\Delta\lambda_{max}$). An increase in λ_{max} for solid samples is evidence for increased coplanarity and longer conjugation lengths. It is useful to call upon the studies of another related polymer poly(3,3″-dihexyl-2,2′:5′,2″-terthiophene).[28] In this regioregular polymer the configuration is repeated every three thienyl units, but the chain is free from sterically crowded HH dyads. The polymer exhibits a large 75-nm shift in absorption maximum (455 → 530 nm) in going from solution to the solid state.[28] Poly(3,3′-dihexyl-2,2′-bithiophene) on the other hand, containing 50% HH dyads yields no shift in λ_{max} for solution and solid-state samples.[29] The change in λ_{max} to longer wavelengths upon going from solvent to solid can be attributed to an increase in π-conjugation length. Loss of rotational freedom of interannular rings and a more planar configuration of conjugated segments might be considered due to favorably intermolecular forces which promote π-stacking of aromatic systems. However, recent studies of the crystal structure of 4,4′,3″,4‴-tetramethyl-2,2′:5′,2″:5″,2‴-quaterthiophene indicate that intermolecular forces are typical van der Waals contacts[47] and suggest that coplanarity is enhanced by loss of solvation energy.

Poly(3-alkylthiophene)s tend to crystallize in the anti arrangement, and therefore arguments can be made that the shorter wavelength for λ_{max} for films containing larger percentages of HH dyads is due to two alkyl chain–sulfur interactions per HH dyad. $\Delta\lambda_{max}$ values reported in Table II indicate that the energy difference between the coplanar and noncoplanar state is considerably less for polymers with HH dyads compared to those predominantly containing HT dyads.

X-ray Diffraction. Physically, polymers P1/P2 were of the consistency of a viscous gum; polymers P3/P4, possessed a tacky rubbery texture, while P5/P6 provided flexible films. X-ray diffraction analysis was performed on three samples of poly(3-hexylthiophene) to determine whether these attributes were due to the presence or absence of long-range order. Polymer P6, which possessed the highest configurational regularity, exhibited strong diffraction peaks at 5.370, 10.749, 16.191, 20.400, and 23.230°. The first three peaks are first-, second-, and third-order reflections attributed to in-plane packing of coplanar polymer chains with an interlayer spacing of 16.4 Å (Figure 4).[48,49] The peak at 23.23° is interpreted as being due to diffraction from a short-range chain stacking having a spacing of 3.8 Å. The interlayer spacing is larger than that observed for poly(3-butylthiophene) but smaller than that of poly(3-octylthiophene) because of the intermediate length and subsequent steric interactions of the hexyl side chain.

X-ray diffraction analysis indicated substantially less long- or short-range order in polymer P3, and polymer P1 was virtually amorphous. This can be directly correlated with the percentage of HH dyads in the polymer and is consistent with the observed morphologies. Solid-state optical spectroscopic studies indicate that head-to-head linkages impose limitations on the coplanarity of the ring, probably through alkyl chain–sulfur interactions. Lack of coplanarity evidently has deleterious effects on the efficiency of chain packing and accounts for large variations in molecular order within different samples of poly(3-hexylthiophene). Regioirregular polymers possessing 50% HT and 50% HH dyads and possessing number-average molecular weights of approximately 10 000 were also prepared. These polymers were considerably tougher than their lower molecular weight counterparts, yet X-ray diffraction revealed them to be just as amorphous. This was in contrast to polymers of similar molecular weight prepared by the oxidative coupling method and possessing ~80% HT dyads which showed considerable microcrystallinity. The results confirm that the dominant feature in determining crystallinity in this study was not necessarily regioregularity of the polymer but the presence or absence of HH dyads.

Electronic Conductivities. Polymers P1→P6 turned blue/black upon oxidation with nitrosonium tetrafluoroborate. UV/vis–near-IR spectroscopy confirmed the presence of bipolaronic charge carriers. The electronic conductivity of thin films increased many orders of magnitude from initial values of 10^{-6} to 10^{-8} S cm^{-1} upon oxidation. The least conductive of this series were polymers P1/P2 with values of 0.0074 and 0.0089 S cm^{-1}, respectively, whereas P5/P6 exhibited conductivities of 0.55 and 6 S cm^{-1}. Again a strong correlation exists between the physical property under scrutiny and regioregularity of the polymer. The results are interpreted as being direct evidence that long-range molecular order facilitates electronic conductivity in conjugated polymers and that long-range order is prevented by irregular configurations, especially HH isomers, even for oxidized materials. However, the oxidized polymer favors the quinoid structure which leads to an increase in the double bond character of the interannular bond. In turn a higher degree of coplanarity is anticipated. The extent to which unfavorable alkyl–sulfur interactions can be overcome by the change in resonance structure determines the electronic properties. From these it can be inferred that polymers containing large percentages of HH dyads have difficulty in achieving coplanarity even in the oxidized state. Further studies of the degree of crystallinity in oxidized polymers will provide useful information concerning the variations in electrical conductivities for this series of polymers.

Conclusions

The origin of regioregularity in Grignard-prepared poly(3-alkylthiophene)s is primarily due to the nature and abundance of a variety of Grignard species and the poor regioselectiveness of their coupling reactions. Pure isomers of mono-Grignard reagents of diiodinated alkylthiophenes cannot be achieved by simple reaction with magnesium and leads to a variety of coupling modes. Polymers prepared by oxidative coupling with a higher degree of regioregularity, primarily in the form of head-to-tail linkages. UV/vis absorption studies of polymers in solution indicate that steric crowding in head-to-head linkages limits the degree to which individual chains become coplanar. In the solid state these materials possess a higher degree of coplanarity and hence conjugation. However, varying degrees in crystallinity and morphology of the neutral polymer and large variations in electronic conductivities of the oxidized form are observed for polymers containing different percentages of HH dyads.

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