(7) (a) Sitz, H.-D.; Speikamp, H.-D.; Bandermann, F. *Makromol. Chem.* **1988**, *189*, 429. (b) Speikamp, H.-D.; Bandermann, F. *Ibid.* **1988**, *189*, 437.
(8) Hertler, W. R. *Macromolecules* **1987**, *20*, 2976.
(9) Jaacks, V.; Eisenach, C. D.; Kern, W. *Makromol. Chem.* **1972**, *161*, 139.
(10) Dixon, D. A.; Hertler, W. R.; Chase, D. B.; Farnham, W. B.; Davidson, F. *Inorg. Chem.* **1988**, *27*, 4012.

Registry No. (MMA)(styrene)(divinylbenzene (graft copolymer), 121876-32-2; (AN)(styrene)(divinylbenzene) (graft copolymer), 107939-65-1.

Synthesis and Characterization of Two Regiochemically Defined Poly(dialkylbithiophenes): A Comparative Study†

R. M. Souto Maior, K. Hinkelmann, H. Eckert, and F. Wudl*

Institute for Polymers and Organic Solids, Departments of Physics and Chemistry, University of California, Santa Barbara, California 93106. *Received April 25, 1989; Revised Manuscript Received July 18, 1989*

ABSTRACT: The polymerization of 3,3′-dimethyl-2,2′-bithiophene and 3,3′-dihexyl-2,2′-bithiophene affords the stereoregular head-to-head versions of poly(3-methyl- and poly(3-hexylthiophene), respectively. The properties of the stereoregular polymers are compared to those of the conventional polymers obtained from polymerization of 3-methylthiophene and 3-hexylthiophene. Regiospecificity was determined via 500-MHz NMR (both ^1H and ^{13}C) in solution for the hexyl-substituted case and 300-MHz ^{13}C CPMAS for all polymers. The regiospecific polymers have their maximum absorption at considerably shorter wavelengths than their nonregiospecific counterparts; thus, poly(3,3′-dimethyl-2,2′-bithiophene) absorbs at a 91 nm shorter wavelength (417 vs 508 nm) and poly(3,3′-dihexyl-2,2′-bithiophene) absorbs at a 110 nm shorter wavelength (398 vs 508 nm). This change in band positions is not due to a difference in molecular weight since the two types of polymer are essentially of equal $\bar{M}_w$, with the stereoregular hexyl derivative having a slightly higher $\bar{M}_w$. We conclude that the intrachain sulfur–alkyl steric repulsion must be dominant, forcing the backbone out of coplanarity and π-conjugation. Interestingly, this pronounced steric effect on the electronic spectroscopy is not reflected in the conductivity. Finally, the stereoregular polymers are the most magnetic defect-free conjugated chains prepared to date, as determined via ESR spectroscopy.

Introduction

The isolation of amorphous solids from the reaction of thiophene with various catalysts dates back to 1883 with Victor Meyer's[1] "sulfuric acid wash" process for the purification of coal tar benzene in which thiophene was present as a contaminant. Since then, many reports on the polymerization of thiophene have appeared in the literature, but the products obtained were not well characterized and a structure was not determined.[2] Well characterized poly(thiophene) with a regular poly(2,5-thienylene) structure was obtained in 1979 by chemical polymerization[3] and later by electrochemical polymerization.[4] Since then, poly(thiophene) has been extensively studied and because of the ease with which the thiophene monomer can be 3-substituted, a large family of poly(thiophene) derivatives with remarkable properties has emerged.

Derivatives have been synthesized with the objective of obtaining a lower energy band gap and possibly intrinsically conducting polymers.[5] Polymerization of benzo[c]thiophene (isothianaphthene)[6] has produced the polymer, poly(isothianaphthene),[7] with the smallest band gap among the organic conducting polymers. Another polymer with an equally small band gap was more recently obtained from dithienothiophene.[7d] The decrease in the band gap when going from poly(thiophene) (2 eV) to poly(isothianaphthene) (1 eV) is explained[5] by an increase in the quinoid contribution to the electronic structure, caused by the fusion of the benzene to the thiophene ring. The same argument applies to poly(thieno[c]thiophene), which should also have a band gap of lower energy than poly(thiophene). Attempts to polymerize dihydrothieno[c]thiophene have been unsuccessful.[8]

Due to their rigid π-conjugated backbone and strong interchain interactions, all unsubstituted organic conducting polymers are insoluble and infusible. This constituted a major obstacle in their study and in the development of practical applications. An important step in the study of these materials occurred in 1983 with the preparation of solutions of organic conducting polymers in their doped form.[11] This was accomplished through a procedure in which the undoped polymer, suspended in AsF_3 solvent, was exposed to AsF_5 and doping occurred with concomitant dissolution. Films of the doped polymer could be cast by evaporation of the solvent. The process evolved to an in situ polymerization and doping, through dissolution of the monomer in liquid AsF_3/AsF_5. Solvation of the doped polymers in this system is attributed in large part to interactions between the inorganic dopant ions and the solvent. Two major drawbacks to this development are (1) the polymers cannot be redissolved after they have been cast into films and (2) the high toxicity of the AsF_3/AsF_5 system.

A major advance in the field of organic conducting polymers was the synthesis[12] of polymers that were soluble in common organic solvents in both their doped and

† Abstracted from Rosa Maria Souto Maior's Ph.D. Dissertation, Department of Chemistry, University of California, Santa Barbara, CA 93106.

0024-9297/90/2223-1268$02.50/0

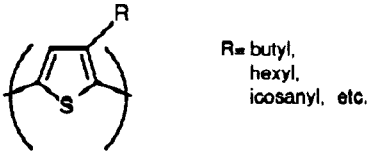


Figure 1. Organic solvent soluble poly(alkylthiophenes).

undoped forms. These polymers were the poly(alkylthiophenes) obtained by the substitution of long alkyl chains ($n \geq 4$) in the β-position of the thiophene rings. The first well-characterized poly(alkylthiophenes) were poly(3-methylthiophene) and poly(3,4-dimethylthiophene),[3] these were followed by longer alkyl chain substitution[12] (Figure 1) as well as preparation of copolymers of long-chain alkylthiophenes with 3-benzylthiophene,[16] 3-methylthiophene,[12a,b,16] and thiophene.[16]

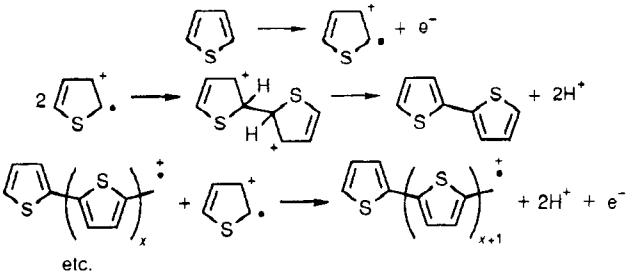
It was known that incorporation of side groups on conjugated polymer chains increased their processability[13] but it was also expected that substitution of long chains in the polymer backbone would seriously affect its conductivity by affecting the planarity of the backbone and interfering with the electron transport between polymer chains. And, indeed, the conductivities of the long-chain substituted poly(thiophenes) were lower than those of the parent polymer, but the loss in conductivity was not dramatic and it was well compensated by the acquired solubility. Long-chain 3-substituted thiophenes containing ether and amide linkages[14] in the alkyl side chain (Figure 1) were later polymerized, giving rise to soluble polymers that in some cases were claimed to have conductivities that surpassed that of the parent poly(thiophene). The synthesis of 3-substituted poly(thiophenes) having chiral groups as part of the substituent and capable of recognizing chiral anions used as doping agents has also been reported.[10]

The development of organic solvent soluble poly(thiophenes) was followed by that of water soluble poly(thiophenes).[15] These derivatives have an alkylsulfonic acid or alkali-metal cation alkylsulfonate substituted in the 3-position of the thiophene ring. With the synthesis of these polyelectrolytes a new concept was born, that of "self-doped" conducting polymers. In these polymers the counterion in the oxidized conducting form of the polymer is covalently bound to its backbone.

The poly(3-alkylthiophenes) are obtained by the chemical or electrochemical polymerization of 3-alkylthiophenes. Electrochemically the polymer is prepared[17] by electrolysis of a solution of the monomer and an electrolyte salt in an organic solvent. One-compartment cells are normally used, and the most commonly used solvents are nitrobenzene and propylene carbonate. Electrolyte salts such as tetrabutylammonium perchlorate and tetrabutylammonium hexafluorophosphate have been used. The polymerization is carried out in a moisture- and air-free environment, and the electrolytic solution is degassed prior to polymerization. Early work[18] has shown that polymerization on nondegassed systems results in polymers of lower conductivities.

The polymerization consists of the oxidative coupling of the 3-alkylthiophenes with deposition of the polymer as a film on the anode. The polymer is obtained in the oxidized form with the counterion of the charged polymer coming from the supporting electrolyte. Since the polymer is obtained in the oxidized, conducting form, the polymerization continues even after the electrode has been totally coated with the film. The polymer can be undoped electrochemically by reversal of the polarity of the cell after synthesis or chemically by "compensation" with reducing agents such as ammonia or hydrazine.

Scheme I
Possible Mechanism for the Electropolymerization of Thiophene and Derivatives



The electropolymerization of poly(thiophenes) and other aromatic rings to form conducting polymers is a stoichiometric process in which 2–2.5 Faraday/mol of monomer is consumed. The mechanism for the electropolymerization of pyrrole was studied by Genies et al.[19] and can be extended to the other heterocycles. The general mechanism for the electrochemical process is depicted in Scheme I.

The electrochemical process is very convenient and gives rise to pure and relatively high molecular weight poly(thiophenes), but it has the major drawback of being a low yield [as low as 3% for poly(3-hexylthiophene)] reaction.

In nonelectrochemical methods, the poly(alkylthiophenes) were first obtained by the nickel-catalyzed Grignard coupling of 2,5-diiodothiophenes.[12a,b] This method produced polymers with lower molecular weights[27] than the electrochemically obtained polymers.[12c] More recently, poly(alkylthiophenes) have been obtained by the coupling of the alkylthiophenes through metal halides such as $FeCl_3$, $MoCl_5$, $RuCl_3$, and $AlCl_3$.[20,21] Polymerizations of unsubstituted thiophene with Lewis acids have been performed before. In one case[2a] neat thiophene was treated with ferric chloride in a molar ratio of 3.5:1 and a light brown uncharacterized solid was obtained. In a more recent work by Kovacic,[2e] polymerization of thiophene in carbon disulfide as solvent using $AlCl_3$ in a 4:1 ratio yielded a polymer whose structure had thiophene and dihydrothiophene rings linked through the 2,5- and 2,4-positions.

Poly(thiophene) with properties very similar to those of the electrochemically obtained polymer, having a well-defined poly(2,5-thienylene) structure, was reported in 1984 by Yoshino et al.[22]. In their work a ferric chloride solution in anhydrous chloroform or dioxane was poured onto a flat substrate and the liquid layer was exposed to gaseous thiophene; the polymer was obtained as a film on the surface of the nonconducting substrate.

The more recent syntheses of poly(alkylthiophenes) mediated by metal halides[20,21] involve dilute solutions and a ratio of metal halide to monomer of 3 or 4:1. The polymers obtained have a well-defined poly(3-alkyl-2,5-thienylene) structure. The yields are on the order of 60% and molecular weights are at least twice as high as those of the electrochemically obtained polymers. Films cast from solution have been stretch-oriented up to five times their original length, with an increase in conductivity of 1 order of magnitude. Besides being soluble, these polymers are also fusible and can be processed into fibers[23] that show conductivities higher than those of the unstretched films (cast from solution or pressed from the molten state), possibly because of alignment of the chains during fiber formation. Their melting temperatures depend on the alkyl chain length and vary from around

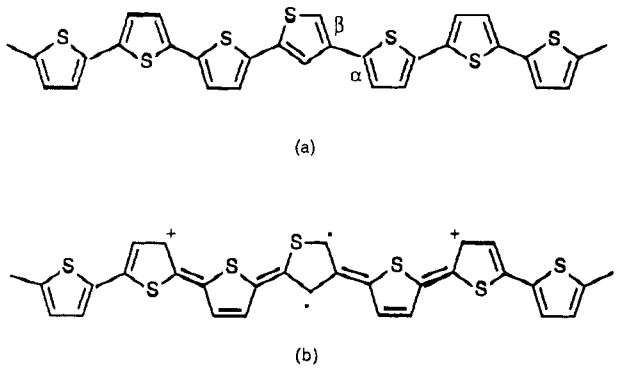


Figure 2. Schematic representation of poly(thiophene) containing α,β-mislinkages: (a) nonoxidized polymer; (b) oxidized polymer.

275 °C for poly(3-butylthiophene) to less than 100 °C for poly(3-docosylthiophene).

The long-chain poly(alkylthiophenes) show thermochromism and solvatochromism. Solutions of poly(alkylthiophenes) show marked color change with change in the quality of the solvent. Thus, addition of methanol (a nonsolvent) to a chloroform (a good solvent) solution of poly(3-hexylthiophene) causes a color change from yellow to magenta. This solvatochromic effect is attributed to a change in the conformation of the polymer backbone.[24-27] These chromism properties appear to be a general phenomenon associated with conjugated backbone polymers and have been extensively studied in substituted poly(diacetylenes).[28a]

Thermochromism is observed both in the solid state[24,25] and in solution.[26,27] In the solid state it has been attributed to the effect of the substituents acting as solvent molecules and "driving the thermochromic effect in solid films in a manner similar to the solution case".[24] X-ray studies[25] indicate that a bulk structural order–disorder transition occurs concurrently with the thermochromic transition. According to these studies the disordering process can be caused by a conformational transition in the side chains that disrupts the structure of the ordered phase of the polymer and the planarity of the backbone.

Introduction of substituents into the backbone of conducting polymers gave rise to potential steric effects, which were absent in the parent systems. One of the factors that could affect the properties of a conducting polymer is the stereoregularity of its backbone. The stereoregularity in the poly(thiophenes) is determined by the regiochemistry of bonding and the regiochemistry of substitution. Bonding in the five-membered heterocyclic rings can occur through the α- or β-position. In the thiophene ring the reactivity of the α-position is much higher[28] than that of the β-position so that coupling of the thiophene units to form the polymer is expected to happen essentially through the α,α'-positions. In this case a stereoregular polymer is obtained with a fully conjugated backbone that can be easily oxidized and is capable of supporting bipolarons, which are the main form of charge storage in poly(thiophenes).[29] Mislinkages through the β-position (Figure 2), on the other hand, cause defects in the backbone that can destroy the straight-chain geometry, shorten the conjugation length,[31] raise the oxidation potential,[31] and interfere with the formation of bipolarons in the oxidized polymer.[32]

The presence of substituents at the β-position of the starting monomers should increase the stereoregularity of the polymer by decreasing the chance of α,β- or β,β-coupling. The higher conductivity of poly(3-methylthiophene) with respect to that of poly(thiophene) has been attributed to a more stereoregular structure.[33] Infrared spectroscopy[34] indicates that bonding in poly(3-methylthiophene) is in fact more regular than in poly(thiophene).

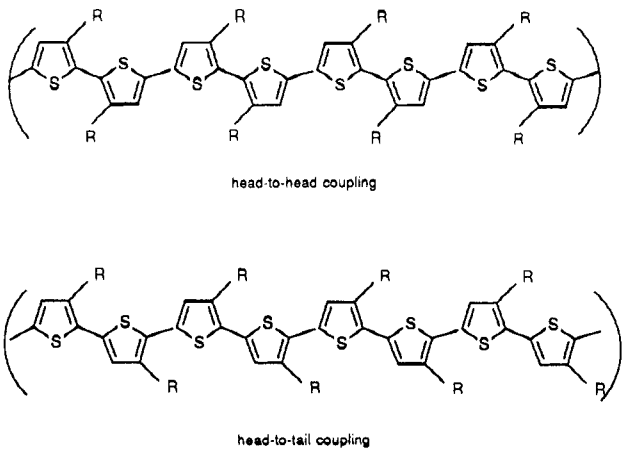


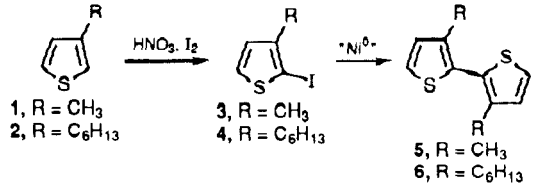
Figure 3. Structures of poly(thiophenes) with different regiochemistry of substitution arising from different modes of coupling of substituted thiophene monomers.

Another strategy used to obtain a polymer with fewer α,β- or β,β-mislinkages is to use dimers or longer oligomers as starting material.[42a] Here one decreases the number of mislinkages through the β-position in the final polymer by having performed α,α-linkages in the dimers or trimers. On the other hand, theoretical calculations[35] on pyrrole show that as the number of units increases the difference in reactivity between the α- and β-positions of the radical cation, generated in the first step of the polymerization, decreases.

The regiochemistry of substitution in the polymer depends on the mode of coupling of monomers (Figure 3), i.e., head-to-head or head-to-tail coupling. Even though head-to-tail is the preferred mode of coupling, head-to-head coupling also occurs. In the polymer obtained from 3-substituted monomers, through either chemical or electrochemical methods, head-to-head coupling occurs to an extent of about 10%, as determined by ^{1}H NMR spectroscopy.[37] In order to minimize head-to-head interaction, a thiophene dimer with substituents on the 3,4′-position was used by Elsenbaumer et al.[37] as starting material for the polymerization; conductivity was indeed improved. Although a completely stereoregular polymer with only head-to-tail interactions cannot be obtained by this method, a polymer where only head-to-head interactions occur can be obtained by polymerization of 3,3′-substituted thiophene dimers. Our results indicate that in this case, steric hindrance seems to be maximized, and the maximum degree to which it will affect the properties of the polymer can be assessed. During the course of our studies, the synthesis of polymers from the 3,3′-substituted dimers (as well as 4,4′-substituted dimers) was disclosed by Krische et al.[38] in a study to determine the importance of β-coupling in bithiophene polymerization.

We began the work on the synthesis of 3-alkyl-substituted poly(thiophenes) from the 3,3′-substituted dimers with the aim of obtaining higher molecular weight polymers. Because in the 3,3′-substituted dimer the polymerization sites are not subject to steric hindrance, it was expected that a longer chain, higher molecular weight polymer would be obtained. In addition, there is experimental evidence that better quality polymers are obtained from bithiophenes.[39] In the case of electrochemical syn-

Scheme II



thesis there is also the advantage, due to the lower oxidation potential of dimers when compared to the monomers, that the polymerization can be carried out at lower applied voltages, thus minimizing side reactions and possible overoxidation of the polymer.[39b] In this work we describe the synthesis and characterization of 3,3′-dimethyl- and 3,3′-dihexylbithiophene and their regiospecific polymerization to methyl- and hexyl-substituted polythiophene. As a consequence of the regiochemistry of substitution in the starting dimers, we obtained regioselectively substituted polymers. The study of these polymers, along with that of the ones with different substitution pattern obtained so far, allows a better understanding of the extent to which steric interaction, due to substituents, affects the properties of these materials.

Results and Discussion

The poly(3,3′-dialkyl-2,2′-bithiophenes) were obtained from the electrochemical and/or chemical coupling of the respective 3,3′-dialkyl-2,2′-bithiophene dimers. The dimers were obtained by the homocoupling of the respective 3-alkyl-2-iodothiophenes,[40] according to the method of Iyoda et al.[41] (Scheme II).

The repeat unit in these polymers is the same as that in the polymer obtained from the 3-substituted monomers, but in this case we have regiospecificity with respect to the substitution pattern in the backbone.

A. Poly(3,3′-dimethyl-2,2′-bithiophene). Poly(3,3′-dimethyl-2,2′-bithiophene) was synthesized both chemically and electrochemically, preparative details are described in the Experimental Section. Both methods produce soluble lower molecular weight polymer in addition to an insoluble product. Attempts to undope an electrochemically synthesized, thicker film, by reversal of the cell's polarity, caused some dissolution of the polymer. A very thin film, on the other hand, did not dissolve and turned yellow immediately upon electrochemical undoping. The chemically synthesized product also had a small fraction of soluble lower oligomers.

In contrast to the product of polymerization of monomeric 3-methylthiophene, the electrochemical polymerization of the dimer does not result in coherent self-supporting films. A very thin film adhered strongly to the electrode but thicker films, which are actually powdery deposits, come off the electrode very easily. Results from the literature[42] as well as work performed in our laboratory showed that electrochemical polymerization of unsubstituted thiophene dimers and trimers also afforded powdery polymers instead of films.

A.1. UV–Vis–Near-IR Spectroscopy. Poly(3,3′-dimethyl-2,2′-bithiophene) is yellow and absorbs in the visible region with a maximum at 417 nm. This absorption, due to a $\pi-\pi^*$ transition, is sharp and has its onset at around 600 nm. Poly(3-methylthiophene) has a maximum absorption at 508 nm with an onset at about 650 nm.[43] Thus, as the energy of the $\pi-\pi^*$ absorption indicates, poly(3,3′-dimethyl-2,2′-bithiophene) exhibits a lower degree of conjugation than poly(3-methylthiophene). An acetone-soluble fraction, which is a mixture of lower oligomers (mostly hexamers), as evidenced by ^{1}H NMR and thin layer chromatography, is also a yellow solid that absorbs at 386 nm in the solid state; in chloroform solution it absorbs at 374 nm. A sulfolane-soluble fraction has maximum absorption at 386 nm in sulfolane solution.

The polymer shows electrochromism; upon oxidation it becomes dark blue and the 417-nm $\pi-\pi^*$ absorption virtually disappears, giving rise to two new absorptions at 637 and 1170 nm. These absorptions correspond to transitions to the two localized bipolaron[43] energy levels that appear in the interband gap upon oxidation. The intensity of the bipolaron transitions depends on the degree of oxidation or doping level. Upon the conditions of electrochemical growth, a thin film is fully oxidized and the $\pi-\pi^*$ transition is absent, being replaced by two sharp bipolaron transitions at 637 and 1170 nm.

The spectrum of the powdery, as-grown polymer, taken on a KBr pressed pellet, always shows a strong absorption corresponding to the $\pi-\pi^*$ transitions in addition to those corresponding to the midgap (bipolaron) transitions. It is possible that the polymer produced later in the polymerization cannot be fully doped or just that it is partially reduced by water present in the KBr or by the bromide ion itself. The increase in the intensity of the bipolaron absorption with concomitant depletion of the $\pi-\pi^*$ transition absorption can be monitored as the polymer is electrochemically doped. In situ optoelectrochemical spectroscopy is a powerful technique for the study of conducting polymers, and coupled with electron voltage spectroscopy it can give information on the mechanism of doping and the nature of the charge-storage species in the polymer chains.[43-45]

In poly(3-methylthiophene), it has been determined by in situ experiments, that charge is stored in the form of bipolarons except for the lowest doping levels.[43,46,47] The changes in the visible–near-infrared spectrum accompanying doping of poly(3,3′-dimethyl-2,2′-bithiophene) follow the same trends as in poly(3-methylthiophene). For the latter a smooth broad-band IR absorption characteristic of free carriers in metals is not observed even at the highest doping levels. This metallic regime is achieved in unsubstituted poly(thiophene) at an applied voltage of 4.3 V vs Li.[45] On the other hand, in poly(3,3′-dimethyl-2,2′-bithiophene), an increase of the applied voltage to 4.1 V (vs Li) causes the appearance of a third peak around 340 nm, which does not vanish when the applied voltage is stepped down to 3.7 V. The spectrum of the polymer at 2.6 V vs Li before and after the doping cycle shows that the $\pi-\pi^*$ absorption at the end of the doping–undoping cycle is slightly blue-shifted, which might be due to some degradation of the polymer caused by overoxidation.

A.2. Infrared Spectroscopy. Infrared spectroscopy is a useful technique in the characterization of poly(thiophenes). It gives important information on the regularity of the polymer chain with respect to the bonding sites. The absorption bands between 850 and 670 cm^{-1} are characteristic of the substitution pattern; these bands are due to the ring C–H out-of-plane bending vibrations.[48] Chemically synthesized poly(thiophene), which due to the synthetic route should have a well-defined 2,5-substitution pattern, shows a sharp absorption band at 780 cm^{-1}.[49,30] In contrast, poly(thiophene) in which the thiophene units are coupled through the 2,4-positions shows two strong bands at 730 and 820 cm^{-1}.[30] In poly(3-methylthiophene) the ring C–H out-of-plane bending vibration appears around 810 cm^{-1}.[30,50,51]

The infrared spectrum of electrochemically synthesized poly(3,3′-dimethyl-2,2′-bithiophene) shows a strong absorption at 823 cm^{-1}, characteristic of the C_β–H out-of-plane bending. The band at 705 cm^{-1}, which is very strong in the absorption spectrum of the starting material, becomes very weak in the spectrum of the polymer and has been attributed to the out-of-plane bending of C_α–H from the terminal thiophene rings.[50] The C_β–H aromatic stretching mode[52] appears at 3057 cm^{-1}, while the band at 3100 cm^{-1}, due to the C_α–H stretch, which is strong and well defined in the spectrum of the starting material, is absent in the spectrum of the polymer. Chemically synthesized poly(3,3′-dimethyl-2,2′-bithiophene) has an infrared spectrum that is essentially the same as that of the electrochemically obtained polymer.

A.3. NMR Spectroscopy. Due to the low solubility of poly(methylthiophenes), the ^{13}C NMR spectroscopic characterization necessitates the use of solid-state cross-polarization magic angle spinning (CPMAS), a technique that has proven invaluable in the structural characterization of many amorphous conducting polymers, including poly(thiophenes).[53-56] Our studies were carried out at 75 MHz, using a General Electric GN-300 spectrometer equipped with Henry Radio amplifiers and a Chemagnetics CPMAS probe. A ^{13}C 90-kHz pulse of 7 μs, a cross-polarization contact time of 1 ms, and a decoupling field of 50 kHz were used. Recycle delays of 2–5 s were found sufficient to obtain spectra undistorted from relaxation effects. Typical spinning speeds were 3–4 kHz. Spectral assignments were confirmed in the usual manner on the basis of reference compounds and by delayed decoupling and variable contact time experiments.

The ^{13}C CPMAS spectrum of poly(3-methylthiophene) obtained in our study shows the methyl resonance at 16 ppm and a very broad, unresolved resonance centered at 133 ppm due to the aromatic carbons of the thiophene ring, in good agreement with previously reported literature data. As shown by variable contact time experiments, the hydrogen-bearing C atoms contribute to the upfield portion of this resonance, at 128.7 ppm.[57] A well-resolved ^{13}C NMR spectrum of poly(3-methylthiophene) with absorptions in the aromatic region at 133.9, 132.4, 129.7, and 127.2 ppm has already appeared.[58] The absorption at 129.7 ppm was assigned to C_2, the one at 132.4 ppm to C_3, the one at 127.2 ppm to C_4, (hydrogen-bearing carbon), and the absorption at 133.9 ppm to C_5. In contrast, the spectrum of poly(3,3′-dimethyl-2,2′-bithiophene) shows two clearly resolved peaks in the aromatic region at 128.5 and 135 ppm. Again, variable contact time and dipolar dephasing experiments confirm that the H-bearing C atoms contribute to the 128.5 ppm resonance. This assignment is also consistent with the literature results on unsubstituted poly(thiophene).[56,57] While the ^{13}C NMR data reveal clear structural differences between both polymers, the resolution is insufficient to assess the degree of regiospecificity obtained in the polymerization of poly(3-methylthiophene).

A.4. Electron Spin Resonance Spectroscopy. Poly(3,3′-dimethyl-2,2′-bithiophene) grown electrochemically at 16 °C from a solution of the starting material (0.1 M) and $LiClO_4$ (0.5 M) in CH_3CN using the conditions described in the Experimental Section has relatively few spin carrying defects upon chemical undoping with hydrazine. Electron spin resonance spectroscopy shows an asymmetric line at a g value of 2.0017 ± 0.0003. The line is a combination of two components, a narrow line ($\Delta H \cong 3$ G) corresponding to a doped region and a broad line ($\Delta H \cong 10$ G) corresponding to an undoped region with a few localized defects. The room temperature magnetic spin susceptibility has a value $\chi = 1.9 \times 10^{-7}$ emu/mol, corresponding to 1 spin per 6500 rings. The number of spins decreases when the sample is further purified by extraction with acetone, and a spin magnetic susceptibility of $\chi = 6.3 \times 10^{-8}$ emu/mol, equivalent to 1 spin per 20 000 rings, is measured, indicating that it is a very pure material in terms of localized spin defects.

A.5. Conductivity. Poly(3-methylthiophene) exhibits the highest conductivities among the poly(thiophenes). Values as high as 2000 S/cm have been reported for very thin films.[59] Conductivities measured on the polymer obtained chemically in the form of powders have values around 5 S/cm.[60] The conductivities measured vary, not only with the morphology (film or powder) of the sample and the oxidizing species but also with the technique employed for the measurement, the four-probe measurement yielding higher and more accurate values.[61] On the other hand, poly(3,3′-dimethyl-2,2′-bithiophene), electrochemically grown under the same conditions employed for poly(3-methylthiophene),[43] gives a conductivity value around 2.5 S/cm, measured in air on a pressed pellet, by the two-probe technique. When doped with $NOPF_6$ in an acetonitrile solution poly(3,3′-dimethyl-2,2′-bithiophene) has a conductivity, measured by the two-probe technique, of 2×10^{-3} S/cm. The sample was grown at 16 °C with acetonitrile as solvent and $LiClO_4$ as the electrolyte salt and was undoped chemically by hydrazine. After $NOPF_6$ doping, the sample was stored under nitrogen for 12 days before the measurement was made. A visible–near-infrared spectrum taken on a pressed KBr pellet shows that the polymer is not fully doped, and this might be the cause for the low value obtained for the conductivity. On the other hand, as discussed before, partial undoping might occur by action of water on the polymer or reduction by bromide ions. A four-probe conductivity measurement was made on a sample grown electrochemically according to the conditions described in the Experimental Section. The polymer was deposited on an electrode consisting of four stripes of gold (0.5 mm apart) deposited on a glass slide. A layer of approximately 8-μm thickness grew evenly across the gaps between the gold stripes. The electrode was removed, washed by dipping quickly in distilled acetonitrile, and stored in nitrogen for approximately 30 h before the measurement was made. The conductivity measured in air was 5.9×10^{-2} S/cm.

B. Poly(3,3′-dihexyl-2,2′-bithiophene). Poly(3,3′-dihexyl-2,2′-bithiophene) was synthesized by chemical oxidative coupling of the bis(thiophene)s as described in the Experimental Section. For comparison, poly(3-hexylthiophene) obtained from 3-hexylthiophene was also synthesized under the same conditions. Poly(3-hexylthiophene) obtained chemically and electrochemically has been extensively studied, while poly(3,3′-dihexyl-2,2′-bithiophene) had not been synthesized before. Poly(3-hexylthiophene) and poly(3,3′-dihexyl-2,2′-bithiophene) are soluble in many organic solvents, including chloroform, tetrahydrofuran, 2-methyltetrahydrofuran, and, to a lesser extent, methylene chloride. Under the same conditions for dissolution (the polymer and solvent were shaken at low frequency), more than twice as much poly(3,3′-dihexyl-2,2′-bithiophene) (2 mg/mL) than poly(3-hexylthiophene) (0.8 mg/mL) dissolved in chloroform. Films of poly(3,3′-dihexyl-2,2′-bithiophene) can be easily cast from solution. The cast films were yellow and transparent while poly(3-hexylthiophene) films were black-

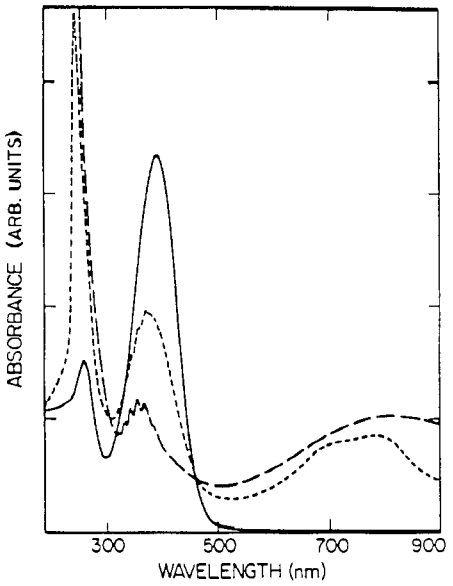


Figure 4. Electronic spectra of poly(3,3-dihexyl-2,2-bithiophene) in $CHCl_3$ solution at different doping levels. The amount of added dopant ($NOPF_6$): solid line, undoped polymer; dotted line, intermediate doping level; dashed line, fully doped.

ish red on reflection and bright red on transmission.

B.1. UV–Vis–Near-IR Spectroscopy. Poly(3,3′-dihexyl-2,2′-bithiophene) shows two absorptions in the UV–vis region. The strongest absorption, with an onset around 500 nm, has its maximum intensity at 389 nm and is a result of the π–π^* absorption transition. A less intense band at 262 nm is attributed to π–π^* transitions that do not depend on conjugation length.[26,62] The absorption spectrum in solution is virtually identical with that in the solid state. Poly(3-hexylthiophene), on the other hand shows maximum absorption at 508 nm in the solid state, while absorbing with maximum intensity at 439 nm in chloroform solution. This blue shift has been attributed to conformational changes, which decrease the degree of conjugation in the backbone[26,27] of the polymer chains in solution, as compared to the condensed state. The blue shift in absorption on going from poly(3-hexylthiophene) to poly(3,3′-dihexyl-2,2′-bithiophene) might arise from the fact that in poly(3,3′-dihexyl-2,2′-bithiophene), steric effects might be such that they prevent the attainment of a more ordered conformation with longer conjugation lengths even in the solid state. It was not obvious, though, why the 3,3′-substituted polymer should be much more sterically hindered than the polymer substituted mostly in a 3,4′-fashion, as is poly(3-hexylthiophene).

In view of these results, as well as results from the literature,[37] it seems that the regiochemistry of substitution influences critically the attainment of a more ordered, planar conformation of the backbone of a polythiophene chain. It is worth noting that the starting dimers 3,3′-dihexyl-2,2′-bithiophene and 3,3′-dimethyl-2,2′-bithiophene are viscous liquids and do not crystallize even at liquid nitrogen temperature, forming a glass instead. The 3,4′-substituted dimethylbithiophene isomer, on the other hand, is a solid[63] at room temperature.

Solid and solution phases of poly(3,3′-dihexyl-2,2′-bithiophene) show strong electrochromism; a relatively thick film or a chloroform solution of the polymer, when exposed to an $NOPF_6$ solution, turns deep blue. As is shown in Figure 4, addition of a solution of $NOPF_6$ in acetonitrile to a solution of the polymer in chloroform causes the usual changes in absorption in the UV–visible region; the band at 389 nm loses intensity and a new broad band around 800 nm appears and the solution changes from yellow to blue (an excess of $NOPF_6$ has to be added, see below). The interband gap absorption does not disappear completely and is shifted to higher energy. Upon standing the solution slowly goes back to a greenish yellow color. After 1 day, the absorption around 800 nm has lost its intensity considerably and the band at higher energy shows an increase in intensity. After 3 days a fine solid precipitate is observed, the absorption at 800 nm has disappeared, and the π–π^* absorption is shifted to 370 nm. As far as oxidations with other oxidizing agents are concerned, when a thin solid film cast on a quartz cuvette from chloroform solution is exposed to I_2 vapor, it shows two new absorption bands in the visible–near-infrared region as shown in Figure 5. As can be seen, the π–π^* absorption band is still present and strong but upon exposure to hydrazine vapor the polymer changes to its original yellow color; however, the absorption maximum in the electronic spectrum is slightly blue-shifted to 378 nm. This blue shift was also observed in the case of poly(3,3′-dimethyl-2,2′-bithiophene) upon electrochemical doping and undoping. Poly(3-hexylthiophene) in chloroform solution behaves in a similar way. A lower energy absorption appears as the polymer is oxidized and the interband gap transition loses intensity and is shifted to higher energies, but less $NOPF_6$ is needed to accomplish the same changes in the absorption spectra and after the solution stands for 18 h the absorption at around 820 nm is still intense. The interband gap is blue-shifted to 371 nm. After 4 days there is still a weak absorption band at 806 nm and an intense absorption band at 387 nm. No precipitation is observed. In poly(3-hexylthiophene) the doping efficiency in solution is dependent on concentration,[64] being higher in more concentrated solutions. This might be the cause for the need of a larger excess of dopant in the oxidation of poly(3,3′-dihexyl-2,2′-bithiophene), because, for the latter, a more concentrated solution could not be used under the conditions due to the high absorptivity of this polymer. The solution of poly(3,3′-dihexyl-2,2′-bithiophene) was initially $\sim 3 \times 10^{-4}$ M while that of poly(3-hexylthiophene) was $\sim 5 \times 10^{-3}$ M.

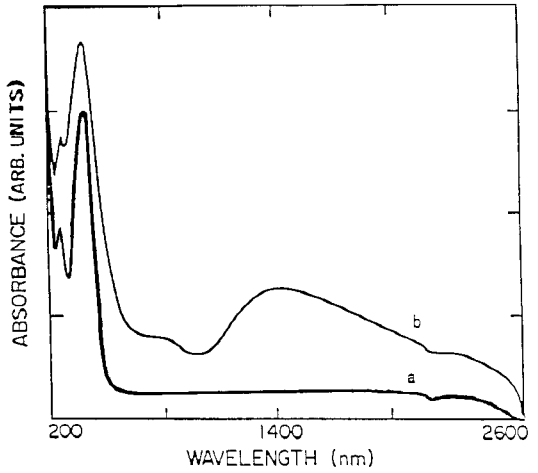


Figure 5. Electronic spectra of solid poly(3,3-dihexyl-2,2-bithiophene). Curve a, undoped polymer; curve b, intermediate doping with iodine vapor.

B.2. Infrared Spectroscopy. The infrared spectrum of poly(3,3′-dihexyl-2,2′-bithiophene) shows the absorptions characteristic of 2,5-coupled substituted poly(thiophenes). One single broad peak is observed at 3061 cm^{-1} (C_β–H stretch).[52] The absorption due to the C_α–H

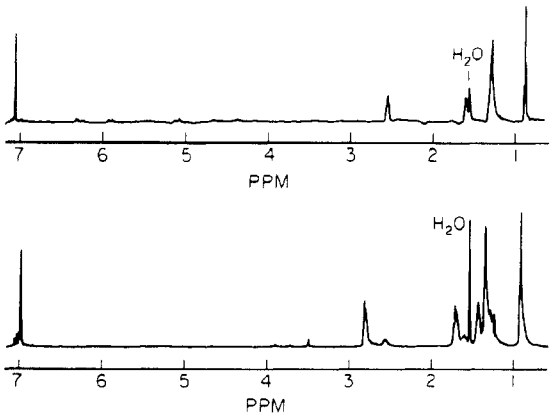


Figure 6. (a, Top) 500-MHz ^1H NMR spectrum of poly(3,3-dihexyl-2,2-bithiophene) in $CDCl_3$ and (b, bottom) ^1H NMR spectrum of poly(3-hexylthiophene) under identical conditions.

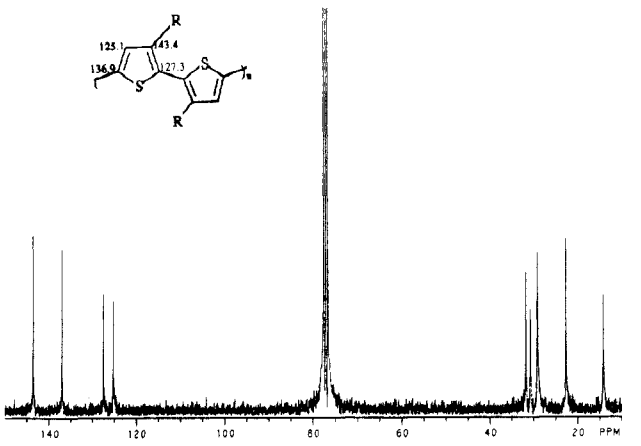


Figure 7. 125-MHz ^{13}C NMR spectrum of poly(3,3-dihexyl-2,2-bithiophene) in $CDCl_3$ solution. The inset shows the peak assignments.

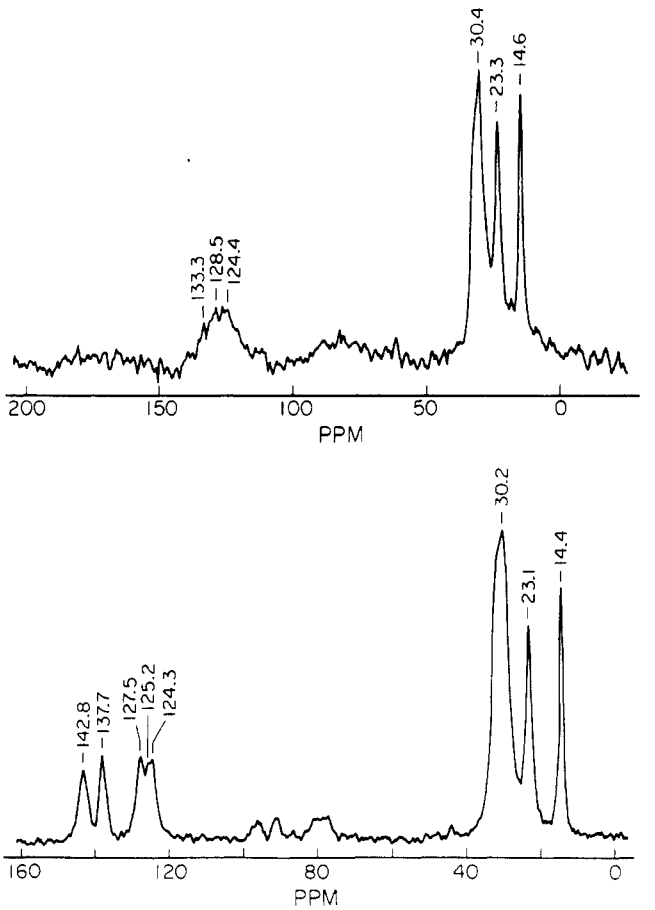


Figure 8. (a, Bottom) 75-MHz ^{13}C CPMAS NMR spectrum of poly(3,3-dihexyl-2,2-bithiophene). (b, Top) Same spectroscopy for poly(3-hexylthiophene) under identical conditions.

stretching mode, present in the spectrum of 3,3′-dihexyl-2,2′-bithiophene at 3105 cm^{-1}, is absent. In the region of the thiophene ring stretching modes, two absorptions are seen at 1535 and 1447 cm^{-1}. In the spectrum of poly(3-hexylthiophene) three absorptions are present in this region at 1462, 1512, and 1581 cm^{-1}. The absorption at 1647 cm^{-1}, which is very weak in the spectrum of poly(3-hexylthiophene), is stronger in that of poly(3,3′-dihexyl-2,2′-bithiophene) and is assigned to an overtone of the thiophene ring C–H out-of-plane bend.[65] When strong, this absorption has been attributed to the presence of carbonyl groups.[66] We do not believe this is the case in poly(3,3′-dihexyl-2,2′-bithiophene) in view of our ^{13}C NMR data, which do not show any absorption in the carbonyl region, and in view of the elemental analysis results. A weak absorption at 1261 cm^{-1} together with stronger ones at 1180 and 1083 cm^{-1} are Raman-active modes that become infrared active due to disorder in the polymer.[25] The 1261-cm^{-1} mode corresponds to C–C stretching of the carbons that connect the thiophene rings. The 1180-cm^{-1} mode is due to twisting and rocking of the methylene groups and the 1083-cm^{-1} mode is from C–H in-plane bending of the thiophene rings.[25] The absorption at 833 cm^{-1} is due to the thiophene ring C–H out-of-plane bend, which in poly(3-hexylthiophene) comes at 825 cm^{-1}. The band at 736 cm^{-1} is assignable to the methylene group bending modes.[25]

B.3. NMR Spectroscopy. Owing to the higher solubility of poly(hexylthiophenes), parallel spectroscopic studies in the solution and the solid state are possible. Figures 6–9 show the solution state ^1H NMR spectra and the ^{13}C NMR spectra, obtained both in solution and in the solid state, on poly(3-hexylthiophene) and poly(3,3′-dihexyl-2,2′-bithiophene), respectively. Since information concerning the regioselectivity of polymerization can be drawn mainly from the aromatic portions of the ^1H and ^{13}C NMR spectra, we will limit our discussion to this spectral region. Figure 6 shows the 500-MHz ^1H NMR spectra of the two polymeric materials. Poly(3-hexylthiophene) shows a dominant signal at 6.98 ppm and, in addition, three weaker, well-defined signals at 7.05, 7.03, and 7.00 ppm, all due to aromatic hydrogen in the rings. It is revealing to compare this spectrum with that of poly(3,3′-dihexyl-2,2′-bithiophene), which shows exclusively the 7.05 ppm resonance. Considering triades of monomeric units, illustrated below, we can distinguish four different cases that would create slightly different environments for the protons in the central rings; (a) two head-to-tail linkages, (b) two head-to-head (tail-to-tail) linkages, and (c) one head-to-tail and one head-to-head (tail-to-tail) linkage. Due to the structural asymmetry two inequivalent cases exist for the latter possibility. On the basis of the experiment with poly(3,3′-dihexyl-2,2′-bithiophene) the 7.05 ppm resonance is assigned to the H atoms in rings that are involved in two head-to-head linkages. The 6.98 ppm resonance arises from rings involved in two head-to-tail linkages, and the resonances at 7.03 and 7.00 ppm account for the cases of mixed connectivities.

Our conclusions are entirely reinforced by the corresponding solution- and solid-state ^{13}C NMR spectra of these materials. The aromatic region of the solution-state NMR spectrum of poly(3-hexylthiophene) shows four

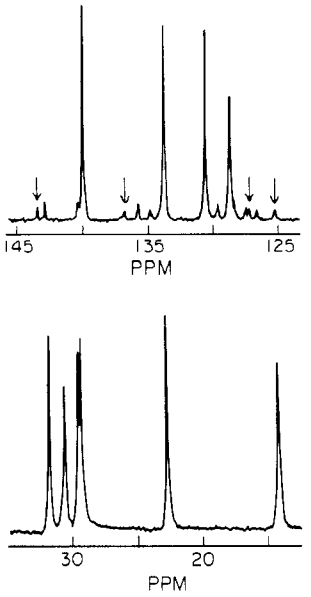
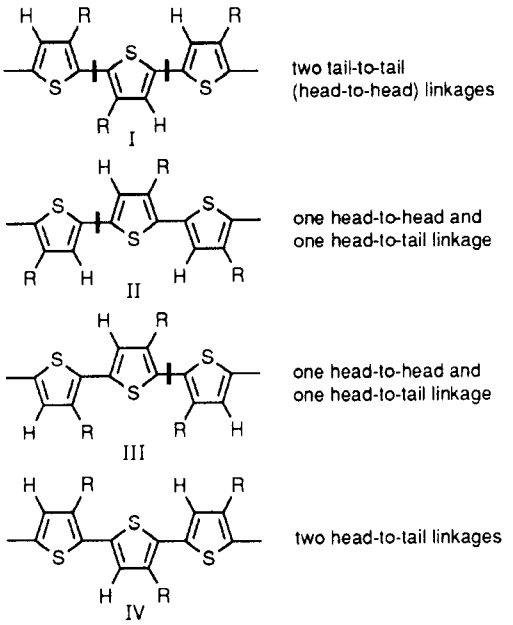


Figure 9. Detailed ^{13}C NMR spectrum of poly(3-hexylthiophene) in $CDCl_3$ solution. The arrows in the aromatic region of the spectrum correspond to absorptions observed for the ring carbon atoms in poly(3,3-dihexyl-2,2-bithiophene) under identical conditions.

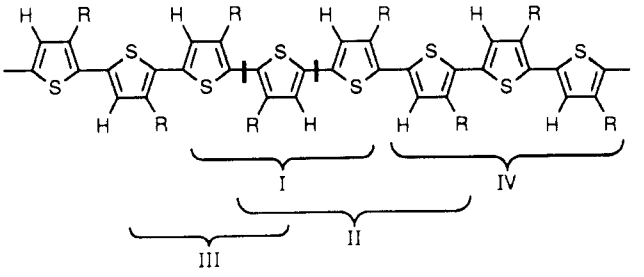
intense absorptions at 128.6, 130.5, 133.7, and 139.9 ppm along with weak but well-defined absorptions at 125.2, 126.6, 127.2, 127.4, 128.3, 129.6, 134.9, 135.7, 136.8, 140.3, 142.9, and 143.4 ppm. In the context of the information obtained from the ^1H NMR spectrum, we assign the four intense peaks to the carbon atoms of rings entirely involved in head-to-tail linkages. In excellent correspondence with the ^1H NMR results, four of the 12 weaker aromatic resonances detected in the spectrum of poly(3-hexylthiophene) comprise the entire aromatic portion of the ^{13}C NMR spectrum of poly(3,3′-dihexyl-2,2′-bithiophene). These resonances, with chemical shifts of 143.4, 136.9, 127.3, and 125.1 ppm, are thus assigned to C atoms within rings involved in two head-to-head (tail-to-tail) linkages. The approximately 1:1:1:1 area ratio of the peak pattern in this latter material is consistent with regiospecific 2,2′-polymerization and the complete absence of 2,3′-polymerization and cross-links. The signals in the aromatic region are assigned, as shown in the inset in Figure 7, on the basis of literature assignments for terthiophene, 3′-methoxy-2,2′:5,2″-terthiophene,[67] 3-methylthiophene, and 3-methoxythiophene[68] and on the basis of the solid-state CPMAS ^{13}C NMR of poly(3,3′-dihexyl-2,2′-bithiophene) seen in Figure 8a. In the solid state, four absorptions in the aromatic region appear almost in the same position as in the solution spectrum, at 142.8, 137.7, 127.5, and 124.7 ppm. In a variable contact time experiment the signal at 124.7 ppm grows at a faster rate than the other signals in the aromatic region, and it is absent in a dipolar dephased experiment.[69]

The remaining resonances seen in the aromatic region of poly(3-hexylthiophene) belong to thiophene units involved in one head-to-head and one head-to-tail linkage. Although providing much less resolution, the solid-state ^{13}C CPMAS NMR spectra show close correspondence with the respective solution-state NMR results. This confirms further that the chemical shift differences between the two polymers do not arise simply from different solution-state conformations but from real differences in the regiochemistry of poly-(3-hexylthiophene) versus poly-(3,3′-dihexyl-2,2′-bithiophene). Additional experiments were undertaken to show that the soluble and the insoluble fractions of poly(3,3′-dihexyl-2,2′-bithiophene) are identical in their respective connectivities.

The approximately equal intensity of the minority peaks in poly(3-hexylthiophene), both in the ^1H and the ^{13}C NMR experiments, indicates that the number of rings involved in two head-to-head linkages equals the number of rings involved in either of the two cases with one head-to-head and one head-to-tail linkage. This is exactly what one would expect if the polymerization defects introduced into perfectly head-to-tail polymerized poly(hexylthiophene) are paired, as indicated below:



Pairing of the above chain defects can give the following result:



From the relative integration of the most downfield ^1H NMR signal with respect to the intensity of absorption for all aromatic hydrogen atoms (approximately 1:10), we conclude that ca. 20% of all linkages are either head-to-head or tail-to-tail. The ^1H NMR spectrum of the electrochemically synthesized poly(3-hexylthiophene), obtained as described in the literature,[70] shows that essentially the same ratio exists in this sample as in the chemically synthesized polymer.

B.4. Electron Spin Resonance Spectroscopy. Poly(3,3′-dihexyl-2,2′-bithiophene) presents possibly the lowest number of spins found so far in the undoped polythiophenes. The number of spins calibrated against a ruby standard is 2.99×10^{18} spin/mol, that is, 1 spin per approximately 200 000 rings. This corresponds to a room temperature magnetic susceptibility of $\chi = 6.21 \times 10^{-9}$ emu/mol. The ESR spectrum shows a broad line ($\Delta H_{pp} \sim 7$ G) at $g = 2.0056 \pm 0.0003$ of very low intensity. The broad signal is attributed to the presence of localized spins arising from defects in the backbone. Poly(3-hexylthiophene), on the other hand, has a number of spins (2.4

$\times 10^{21}$ spin/mol) that corresponds to approximately 1 spin per 250 rings and is 3 orders of magnitude higher than that of poly(3,3′-dihexyl-2,2′-bithiophene). The magnetic susceptibility measured at 300 K is $\chi = 5 \times 10^{-6}$ emu/mol. A plot of magnetic susceptibility as a function of the inverse of temperature indicates Curie law behavior with a very minor Pauli component. The ESR spectrum shows a narrow ($\Delta H_{pp} = 2.5$ G) and symmetrical line at $g = 2.0027 \pm 0.0003$. The larger number of spins in poly(3-hexylthiophene) can thus be attributed to residual doping of the sample.

B.5. Conductivity. The conductivity of poly(3,3′-dihexyl-2,2′-bithiophene) was measured by a two-probe technique. A cast film, 20 μm thick, was doped by dipping in an $NOPF_6$ solution (4 mg/mL) for 1 h. The film was then carefully laid across the gap between two gold stripes deposited on glass, where metallic contacts for the measurement had been attached. The film adhered completely to the glass as well as to the gold layer. After the film had dried, the conductivity was measured, giving a value of 3.7 S/cm. The whole operation, doping and measurement, was done in a dry bag under a nitrogen atmosphere. After 17 h at ambient atmosphere, the conductivity dropped by 1 order of magnitude. The conductivity of chemically polymerized poly(3-hexylthiophene) doped with $NOPF_6$ and measured under the same conditions as poly(3,3′-dihexyl-2,2′-bithiophene) has a value of approximately 15 S/cm.

B.6. Molecular Weight. The weight-average molecular weight ($\bar{M}_w$) and number-average molecular weight ($\bar{M}_n$) of poly(3,3′-dihexyl-2,2′-bithiophene) and poly(3-hexylthiophene) were determined by gel permeation chromatography.[71,72] Since in this technique the molecular weights are determined as a function of molecular size (hydrodynamic radius), the values, obtained from a standard polystyrene calibration curve, should be taken as only very approximate. Poly(3-hexylthiophene) has $\bar{M}_w = 1.4 \times 10^5$ and $\bar{M}_n = 3.2 \times 10^4$, corresponding to a polydispersity index of 4.4, and poly(3,3′-dihexyl-2,2′-dithiophene) has $\bar{M}_w = 1.2 \times 10^5$ and $\bar{M}_n = 3.7 \times 10^4$, which implies a polydispersity index of 5.3. These weight-average molecular weights correspond to an average of 837 rings per chain in poly(3-hexylthiophene) and 1190 rings per chain in poly(3,3′-dihexyl-2,2′-bithiophene). The degree of polymerization in both cases is higher, by 3–4 times, than that in the electrochemically polymerized poly(3-hexylthiophene).[70]

The value measured for poly(3,3′-dihexyl-2,2′-bithiophene) could be biased toward a lower molecular weight fraction because part of the sample failed to dissolve in THF even after 5 days at room temperature. The insolubility of this fraction could also be due to cross-linking. The molecular weight value described above should thus be redetermined. In spite of this, it is clear that poly(3,3′-dihexyl-2,2′-bithiophene) presents a higher degree of polymerization than poly(3-hexylthiophene), as was expected.

Conclusions

We have demonstrated that by regioselectively coupling two 3-substituted thiophene rings to produce a new "monomer" for the formation of polythiophenes through electrochemical or chemical coupling, a regioselectively substituted poly(thiophene) can be produced. Poly(3-hexylthiophene) and poly(3-methylthiophene) were the two regioselectively substituted poly(thiophenes) that were prepared and studied. Of these, the hexyl-substituted polymer rendered the largest amount of information due to its solubility in most polymer solvents. Crucial to the determination of regioselectivity were the proton and carbon nuclear magnetic resonance spectrometry studies both in the solid state (CPMAS) and in solution. From the analysis of the spectra of poly(3,3′-dihexyl-2,2′-bithiophene) and poly(3-hexylthiophene) one can deduce that the percentage of head-to-head coupling in the polymerization of 3-hexylthiophene is at least 20%. We also showed that the ^1H NMR spectrum of electrochemically synthesized poly(3-hexylthiophene) shows the ratio of head-to-head to head-to-tail coupling to be virtually the same as in the chemically synthesized polymer. Poly(3-hexylthiophene) in the solid state does not show the well-resolved spectrum of poly(3,3′-dihexyl-2,2′-bithiophene). The signals from the aromatic carbons appear as a broad absorption containing four signals. This lack of resolution might be due to residual doping of the polymer. As in its proton NMR spectrum in solution, we attribute the large number of absorptions in the aromatic region of the carbon NMR spectrum of poly(3-hexylthiophene) to the existence of different environments for the otherwise equivalent carbons in the ring due to the presence of head-to-head as well as head-to-tail coupled monomers.

The regiospecific head-to-head polymers have their maximum absorption at considerably shorter wavelengths than their counterparts polymerized in a nonregiospecific manner; thus, poly(3,3′-dimethyl-2,2′-bithiophene) absorbs at a 91 nm shorter wavelength (417 vs 508 nm) and poly(3,3′-dihexyl-2,2′-bithiophene) absorbs at a 110 nm shorter wavelength (398 vs 508 nm). We conclude that the intrachain sulfur–alkyl steric repulsion must be dominant, forcing the backbone out of coplanarity and π-conjugation. Interestingly, this pronounced steric effect on the electronic spectroscopy is not reflected in the conductivity.[73]

Finally, the stereoregular polymers are the most magnetic defect-free conjugated chains prepared to date, as determined via ESR spectroscopy.

Experimental Section

All operations were carried out under inert atmosphere conditions using either argon or pure nitrogen atmospheres using solvents dried and distilled according to established procedures.[74] "Standard workup" means: The aqueous phase was extracted with ether (2×) and the combined organic phases were washed with dilute hydrochloric acid (1×) and water (2×). The solution was dried with magnesium sulfate and the ether and most of the tetrahydrofuran were distilled or removed by rotary evaporation. All samples subjected to ^1H NMR, ^{13}C NMR, high-resolution mass spectroscopy (HRMS), and elemental analysis were doubly thick-layer chromatographed and showed no spurious resonances in nuclear magnetic resonance spectroscopy. All NMR experiments are reported in parts per million as δ relative to internal TMS and were recorded in $CDCl_3$, unless stated otherwise; spectra were recorded on a Varian EM360L instrument and General Electric GN-300 and GN-500 instruments. Electron spin resonance measurements were performed on an IBM Bruker 200D electron spin resonance spectrometer interfaced with an Apple IIe computer for data acquisition and analysis. Infrared spectra (KBr pellet for solids and neat film on NaCl disks for liquids and polymers) were recorded by using a Perkin-Elmer Model 1330 spectrophotometer and an IBM/98 FTIR instrument and are reported in wavenumbers (ν, cm^{-1}). UV–vis spectra were obtained with Perkin-Elmer Model Lambda 5 and Perkin-Elmer Model Lambda 9 instruments and are reported as λ (log ε). Molecular weights were measured by Dr. L. Fetters at Exxon Research and Engineering, Anandale, NJ, on a Waters 150C SEC instrument using a seven-column ultra-Styragel set.

3,3′-Dimethyl-2,2′-bithiophene (V). To a mixture of $NiCl_2(PPh_3)_2$ (3.925 g, 0.006 mol), activated Zn (7.848 g, 0.120 mol), and Et_4NI (15.42, 0.06 mol) previously dried by heating it to

80–90 °C overnight under dynamic vacuum, was added 40 mL of distilled THF. The mixture, initially green, turned almost instantly to red and was stirred for 1 h at room temperature. A solution of 2-iodo-3-methylthiophene[40,41] (13.44 g, 0.060 mol) in THF (15 mL) was added slowly and the reaction mixture warmed up slightly and turned black. After the addition, the reaction mixture, protected from light, was left to react for 3.5 h at room temperature. The reaction mixture was cooled down with an ice bath, quenched by addition of 30 mL of 10% aqueous HCl, followed by extraction of the aqueous layer with hexanes (3 × 20 mL). The organic extracts were combined and washed with saturated aqueous $NaHCO_3$ (2 × 20 mL) and followed by water (2 × 30 mL). The crude extract was dried over K_2CO_3, the solvent was rotary evaporated, and the mixture was column chromatographed (silica gel, eluted with hexanes) and then distilled. The product, a colorless liquid, was obtained in 31% yield (3.6 g). Anal. Calcd for $C_{10}H_{10}S_2$: C, 61.81; H, 5.19; S, 33.00. Found: C, 61.91; H, 5.23; S, 32.93. ^1H NMR: 7.27 (d, J = 4.2 Hz, 2 H), 6.89 (d, J = 4.2 Hz, 2 H), 2.17 (s, 6 H). IR: 3100 m, 3060 m, 2910 s, 2850 m, 1450 s, 1380 m, 1245 m, 1090 m, 1040 w, 1010 m, 920 m, 830 s, 710 s, 610 m.

Poly(3,3′-dimethyl-2,2′-bithiophene). Electrochemical Polymerization. The polymerization was carried out under strict moisture- and oxygen-free conditions in a one-compartment cell[75] identical with the one published in ref 70; the anode consisted of indium tin oxide coated glass and the cathode of aluminum foil. The electrodes were washed with hexanes followed by methylene chloride and acetone and dried in the oven (120 °C) overnight. The bottom part of the electrochemical cell was also left in the oven overnight after an acetone rinse. The cell was assembled hot and immediately put under vacuum and the top part was then flame-dried. After the cell cooled, it was filled with argon and put under vacuum again. The whole cell was then flame-dried and, after it cooled, refilled with argon. The polymerization was carried out under an argon atmosphere. Thus, 3,3-dimethyl-2,2′-bithiophene (0.55 g, 2.8 mmol) and dry lithium tetrafluoroborate (1.31 g, 14 mmol) were weighed in a glovebag under a nitrogen atmosphere directly to a dry two-necked round-bottomed flask. The flask was connected to an argon line and the acetonitrile solvent (28 mL) added. The solution was cooled by a dry ice/acetone bath (−78 °C) and left under vacuum for 1–2 h for degassing. The cooling bath was then removed, the flask was filled with argon, and the solution was warmed up slowly. After reaching room temperature, it was transferred by syringe to the electrochemical cell. The solution in the electrochemical cell was cooled by a dry ice/ethylene glycol bath (−18 to −14 °C) for 1 h and then connected to a direct current power supply to commence electrolysis. Polymerization was carried out under constant current and under the polymerization conditions the potential across the cell remained nearly constant. For thin-film formation, for UV–vis spectroscopic measurements, the polymerization was allowed to proceed for 10–30 min and a current density of 0.01 mA/cm^2 ($V \sim 3$ V) was applied. The films were washed by briefly dipping them in distilled CH_3CN and then dried under vacuum. To obtain the polymer in larger amounts for elemental analysis, ESR, and IR spectroscopy, the polymerization was carried out for 2–4 h at an applied current density of 0.5 mA/cm^2 ($V \sim 4$ V). Anal. Calcd for C_5H_4S: C, 62.46; H, 4.19; S, 33.35. Found: C, 60.62; H, 4.27; S, 31.61; residue, 2.6.

Poly(3,3′-dimethyl-2,2′-bithiophene). Chemical Polymerization. Dry $FeCl_3$ (1.674 g, 0.010 mol) was suspended in 50 mL of dry, distilled $CHCl_3$ and stirred for 15 min. To the partially dissolved solid, was added dropwise 3,3′-dimethyl-2,2′-bithiophene (0.5 g, 0.0026 mol) dissolved in 20 mL of dry, distilled $CHCl_3$. The reaction mixture was warmed in an oil bath to 45 °C and was stirred for 23 h. Methanol (150 mL) was then added with stirring. Stirring was stopped and after the black solid had settled, the liquid was decanted and the solid filtered though a glass frit. The black solid was Soxhlet-extracted with methanol, followed by acetone. It was then extracted with methanol to which some drops of aqueous NH_4OH were added. It was further extracted with hexanes to dissolve any grease that might be present. Poly(3,3′-dimethyl-2,2′-bithiophene) was obtained in 74% yield (0.37 g). Anal. Calcd for C_5H_4S: C, 62.46; H, 4.19; S, 33.35. Found: C, 61.34; H, 4.22; S, 32.31; residue, 2.3.

3-Hexyl-2-iodothiophene (4). To 3-hexylthiophene[75] (28.07 g, 0.167 mol) and iodine (21.27 g, 0.084 mol) dissolved in 100 mL of ethyl ether, was added dropwise 6.5 mL of concentrated aqueous HNO_3 diluted with 6.5 mL of water. When the addition was complete, the reaction mixture was warmed to reflux and at this point a brown gas (NO_2) evolved. After 3 h under reflux, the temperature was turned down and the reaction mixture, while being heated by an oil bath at 40 °C, was stirred overnight. The next morning the presence of starting material could be detected by both TLC and ^1H NMR. The temperature was increased and the reaction mixture was refluxed for 6 h. Concentrated HNO_3 (1 mL) was added and a brown gas evolved but after 3 h there was no apparent increase in the amount of product formed. Concentrated HNO_3 (1.5 mL) diluted in water (1.5 mL) was added with no evolution of the brown gas. Iodine (2.538 g, 0.01 mol) was then added and the reaction was refluxed overnight. The following day the remaining starting material was consumed. A new peak in the ^1H NMR appeared at 6.86 ppm that could be attributed to the presence of the diiodinated product. The reaction was worked up by washing the mixture with distilled water (2 × 60 mL), followed by 10% aqueous NaOH (3 × 30 mL), and more distilled water (2 × 30 mL). The organic solution was dried over K_2CO_3 and, after filtration and rotary evaporation, it was column chromatographed (silica gel, eluted with hexanes). A light-colored fraction (pinkish yellow) containing the product was washed with 10% (w/v) aqueous $Na_2S_2O_3$ to remove iodine. This fraction contained 26.37 g (54% yield) of 2-iodo-3-hexylthiophene. ^1H NMR (60 MHz): δ 7.35 (d, J = 6 Hz, 1 H), 6.71 (d, J = 6 Hz, 1 H), 2.57 (t, J = 6 Hz, 2 H), 1.3 (m, 8 H), 0.8 (m, 3 H).

3,3′-Dihexyl-2,2′-bithiophene (VI). Tetrahydrofuran (70 mL) was added to a mixture of $NiBr_2(PPh_3)_2$ (6.325 g, 0.0085 mol), activated Zn (12 g, 0.183 mol), and Et_4NI (22.478 g, 0.087 mol), previously dried by heating under vacuum at ~95 °C for approximately 10 h. The partially dissolved mixture turned quickly from green to brown-red. After this mixture had been allowed to stir for 1 h at room temperature, a solution of 3-hexyl-2-iodothiophene (25.23 g, 0.086 mol) in 30 mL of THF was added dropwise. A water bath was used during the addition to cool down the slightly exothermic reaction. The mixture was stirred at room temperature for 5 h, was cooled to 0 °C, and was quenched by slow addition of 200 mL of 10% aqueous HCl. The mixture was then extracted with hexanes (2 × 75 mL); the combined hexanes layers were washed with aqueous saturated $NaHCO_3$ (2 × 75 mL) followed by distilled water (2 × 100 mL) and dried over K_2CO_3. The mixture was column chromatographed; the fractions containing mainly product were combined, yielding a yolk-yellow oil after removal of solvents. This oil was distilled (100 °C, 1 × 10^{-3} Torr) through a Vigreaux column yielding an off-white viscous liquid (2.9 g, 0.015 mol, 35% yield). Anal. Calcd for $C_{20}H_{30}S_2$: C, 71.86; H, 8.98; S, 19.16. Found: C, 71.91; H, 8.97; S, 19.02. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.295 (d, J = 5.1 Hz, 2 H), 7.024 (d, J = 5.2 Hz, 2 H), 2.485 (t, J = 7.8 Hz, 2 H), 1.52 (m, 2 H), 1.24 (m, 6 H), 0.846 (m, 3 H). IR: 3100 vw, 3060 vw, 2980 s, 2940 s, 2850 s, 1470 m, 1420 w, 1375 w, 1240 vw, 1090 w, 880 w, 840 m, 730 m, 700 w, 655 w.

Poly(3-hexylthiophene). Chemical Polymerization. A suspension of dry $FeCl_3$ (3.87 g, 0.024 mol) in 100 mL of dry, distilled $CHCl_3$ was stirred for approximately 15 min. A dark green solution with some residual $FeCl_3$ was obtained. To this solution, 3-hexylthiophene (1 g, 0.006 mol), dissolved in 40 mL of dry, distilled $CHCl_3$, was added dropwise over a period of 15 min. The mixture turned black immediately. The reaction mixture, warmed by an oil bath to 35 °C, was stirred for 17 h; after this period of time, a very faint spot corresponding to starting material could still be seen on a TLC plate. The reaction was worked up at this point by addition of 200 mL of MeOH; the solvent was decanted and more MeOH (200 mL) was added. The mixture was filtered and the red solid extracted in a Soxhlet apparatus; first with methanol and then with acetone. The extracted polymer (0.69 g, 69%) was then dried under vacuum and further purified by dissolution in approximately 200 mL of 2-methyltetrahydrofuran and precipitation from this solution by slow addition of 500 mL of methanol. The precipitate

was filtered, washed with methanol, and dried under vacuum to yield 0.47 g (47%) of purified poly(3-hexylthiophene). Anal. Calcd for $C_{10}H_{14}S$: C, 72.29; H, 8.43; S, 19.28. Found: C, 68.95; H, 8.39; S, 17.88; Cl, 0.84; Fe, 0.082. NMR and IR spectroscopy are reported in the Results and Discussion section.

Poly(3,3′-dihexyl-2,2′-bithiophene). Chemical Polymerization. Dry $FeCl_3$ (1.9 g, 0.012 mol) was dissolved in 100 mL of dry, distilled $CHCl_3$ to give an orange-brown slightly turbid solution. To this solution, 3,3′-dihexyl-2,2′-bithiophene (1 g, 0.003 mol) dissolved in 10 mL of dry, distilled $CHCl_3$ was added dropwise. The solution turned black immediately and the reaction mixture, warmed by an oil bath to 40 °C, was stirred for approximately 44 h. The solvent was then removed by distillation until a volume of approximately 15 mL of solution remained. Methanol (200 mL) was added and most of the blue-black solid that separated in the previous operation turned yellowish. The methanol solution was decanted and the polymer came out in one piece and was washed once more with methanol. It was then transferred to a Soxhlet extractor and extracted with methanol followed by acetone until the extracts were colorless. To this semipurified polymer (0.66 g, 65.5%) was added 150 mL of $CHCl_3$, and the mixture was heated to reflux. The refluxed mixture was cooled and the solid was separated. The supernatant orange solution was cooled by an ice–water bath and acetone (350 mL) was added dropwise with occasional stirring. A yellow solid formed, which was filtered and washed with acetone. Poly(3,3′-dihexyl-2,2′-bithiophene) was obtained in 40% yield (0.40 g). Anal. Calcd for $C_{10}H_{14}S$: C, 72.29; H, 8.43; S, 19.28. Found: C, 71.99; H, 8.48, S, 19.05. Spectroscopic properties were described in the Results and Discussion section.

Acknowledgment. We thank the National Science Foundation and the Office of Naval Research for support.

References and Notes

(1) Meyer, V. *Chem. Ber.* **1883**, *16*, 1465.
(2) (a) Bruce, J.; Challenger, F.; Gibson, H. B.; Allenby, W. E. *J. Inst. Petrol.* **1948**, *34*, 226–235. (b) Meisel, S. L.; Johnson, G. C.; Hartough, H. D. *J. Am. Chem. Soc.* **1950**, *72*, 1910–1912. (c) Armour, M.; Davies, A. G.; Upadhyay, J.; Wassermann, W. *J. Polym. Sci. A-1* **1967**, *5*, 1527–1538. (d) Curtis, R. F.; Jones, D. M.; Thomas, W. A. *J. Chem. Soc.* **1971**, 234–238. (e) Kovacic, P.; McFarland, K. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1963–1976.
(3) Yamamoto, T.; Sanechika, K.; Yamamoto, A. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *180*, 13–16.
(4) (a) Afanasev, V. L.; Nazarova, I. B.; Khidekel, M. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, 1687. (b) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1982**, *135*, 173–178. (c) Bargon, J.; Mohmand, S.; Waltman, R. J. *IBM J. Res. Dev.* **1983**, *27*, 330–341. (d) Hotta, S.; Hosaka, T.; Shimotsuma, W. *Synth. Met.* **1983**, *6*, 69.
(5) (a) Brédas, J.-L.; Themans, B.; André, J. M.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1985**, *11*, 343. (b) Brédas, J.-L.; Heeger, A. J.; Wudl, F. *J. Chem. Phys.* **1986**, *85*, 4673–4678.
(6) Cava, M. P.; Pollack, N. M.; Mamer, O. A.; Mitchell, M. J. *J. Org. Chem.* **1971**, *36*, 3932.
(7) (a) Wudl, F.; Kobayashi, M.; Heeger, A. J. *J. Org. Chem.* **1984**, *49*, 3382. (b) Kobayashi, M.; Colaneri, N.; Boysel, M.; Wudl, F.; Heeger, A. J. *J. Chem. Phys.* **1985**, *82*, 5717. (c) Jen, K.; Elsenbaumer, R. L. *Synth. Met.* **1986**, *16*, 379–380. (d) Bolognesi, A.; Castellani, M.; Destri, S.; Zamboni, R.; Taliani, C. *J. Chem. Soc., Chem. Commun.* **1988**, 246.
(8) Roncali, J.; Garnier, F.; Garreau, R.; Lemaire, M. *J. Chem. Soc., Chem. Commun.* **1987**, 1500–1502.
(9) Jen, K.; Maxfield, M.; Shackelette, L.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1987**, 309–311.
(10) Lemaire, M.; Delabouglise, D.; Garreau, R.; Guy, A.; Roncali, J. *J. Chem. Soc., Chem. Commun.* **1988**, *10*, 658–661.
(11) Frommer, J. E. *Acc. Chem. Res.* **1986**, *19*, 2–9.
(12) (a) Jen, K.; Oboodi, R.; Elsenbaumer, R. L. *Polym. Mater. Sci. Eng.*, **1985**, *53*, 79–83. (b) Elsenbaumer, R. L.; Jen, K. Y.; Oboodi, R. *Synth. Met.* **1986**, *15*, 169. (c) Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* **1986**, 873.
(13) Deits, W.; Cukon, P.; Rubner, M.; Jopson, H. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 696–704.
(14) Bryce, M. R.; Chissel, A.; Kathirganathan, P.; Parker, D.; Smith, N. *J. Chem. Soc., Chem. Commun.* **1987**, 467–468.
(15) (a) Ikenoue, Y.; Chiang, J.; Patil, A. O.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1988**, *110*, 2983–2985. (b) Patil, A. O.; Ikenoue, Y.; Wudl, F.; Heeger, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 1858. (c) Sundaresan, N. S.; Basak, S.; Pomerantz, M.; Reynolds, J. R. *J. Chem. Soc., Chem. Commun.* **1987**, 621.
(16) Hotta, S. *Synth. Met.* **1987**, *22*, 103.
(17) Sato, M.; Tanaka, S.; Kaeriyama, K. *Makromol. Chem.* **1987**, *188*, 1763–1771.
(18) Tourillon, G.; Garnier, F. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *135*, 173.
(19) Genies, E. M.; Bidan, G.; Diaz, A. F. *J. Electroanal. Chem.* **1983**, *149*, 101.
(20) Yoshino, K.; Nakajima, S.; Sugimoto, R. *Jpn. J. Appl. Phys.* **1987**, *26*, L1038–L1039.
(21) Hotta, S.; Soga, M.; Sonoda, N. *Synth. Met.*, **1988**, *26*, 267–279.
(22) Yoshino, K.; Hayashi, S.; Sugimoto, R. *Jpn. J. Appl. Phys.* **1984**, *23*, L899–L900.
(23) Yoshino, K.; Nakajima, S.; Fuji, M.; Sugimoto, R. *Polym. Commun.* **1987**, *28*, 309–310.
(24) Salanek, W. R.; Inganäs, O.; Thémans, B.; Nisson, J. O.; Sjögren, B.; Österholm, J.-E.; Brédas, J.-L.; Svensson, S. *J. Chem. Phys.*, in press (we thank Dr. J.-L. Brédas for a preprint of this article).
(25) Winokur, M. J.; Spiegel, D.; Kim, Y.; Hotta, S.; Heeger, A. J. *Proceedings of the International Conference in Synthetic Metals*; Santa Fe, NM, June, 1988; *Synth. Met.* **1989**, *28*, C419–426.
(26) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1071–1078.
(27) Inganäs, O.; Salaneck, W. R.; Österholm, J.-E.; Laakso, J. *Synth. Met.* **1988**, *22*, 395–406.
(28) (a) Chance, R.; Bloor, D. *Polydiacetylenes*; M. Nijhoff: Dordrecht, 1985. (b) Kellogg, R. M. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: Oxford, 1984; Vol. 4 (3), p 713. (c) Marino, G. In *Adv. Heterocycl. Chem.* **1971**, *13*, 235.
(29) Colaneri, N.; Nowak, M.; Spiegel, D.; Hotta, S.; Heeger, A. J. *Phys. Rev. B* **1987**, *36*, 7964.
(30) Yamamoto, T.; Sanechika, K.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1497–1502.
(31) Laguren-Davidson, L.; Pham, C. V.; Mark, H. B.; Ondrus, D. J. *J. Electrochem. Soc.* **1988**, *135*, 1406. Heinze, J.; Mortensen, J.; Hinkelmann, K. *Synth. Met.* **1987**, *21*, 209–214.
(32) Tanaka, K.; Shichiri, T.; Yamabe, T. *Synth. Met.* **1986**, *14*, 271–277.
(33) Tourillon, G.; Garnier, F. *J. Phys. Chem.* **1983**, *87*, 2289.
(34) Neugebauer, H.; Neckel, A.; Brinderkoropic, N. *Electronic Properties of Polymers and Related Compounds*; Springer-Verlag: Berlin, 1985; p 227.
(35) Waltman, R. J.; Bargon, J. *Tetrahedron* **1984**, *40* (20), 3963–3970.
(36) Brédas, J. L.; Street, G. B.; Thémans, B.; André, J. M. *J. Chem. Phys.* **1985**, *83*, (3), 1323–1329.
(37) Elsenbaumer, R. L.; Jen, K.; Miller, G. G.; Eckhardt, H.; Shacklette, L. W.; Jow, R. Presented at the International Winter School on Conducting Polymers, March 15, 1987, Kirchberg, Austria (we thank Dr. Elsenbaumer for sending us a copy of this work).
(38) Krische, B.; Hellberg, J.; Lilja, C. *J. Chem. Soc., Chem. Commun.* **1987**, *19*, 1476.
(39) (a) Chung, T. C.; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phys. Rev. B* **1984**, *30*, (2), 702–709. (b) Krische, B.; Zagorska, M. *Proceedings of the International Conference on Science and Technology of Synthetic Metals*; Santa Fe, NM, June 26–July 2, 1988; *Synth. Met.* **1989**, *28*, c263–268.
(40) Barker, J. M.; Huddleston, P. R.; Wood, M. L. *Synth. Commun.* **1975**, *5*, 59–64.
(41) Iyoda, M.; Sato, K.; Oda, M. *Tetrahedron Lett.* **1985**, *26*, 3829.
(42) (a) Roncali, J.; Garnier, F.; Lemaire, M.; Garreau, R. *Synth. Met.* **1986**, *15*, 323. (b) Krische, B.; Hellberg, J.; Lilja, C. *J. Chem. Soc., Chem. Commun.* **1987**, *19*, 1476.
(43) Colaneri, N.; Nowak, M.; Spiegel, D.; Hotta, S.; Heeger, A. J. *Phys. Rev. B* **1987**, *36*, 7964.
(44) Heeger, A. J. *Mol. Cryst. Liq. Cryst.* **1985**, *125*, 289–302.
(45) Chung, T.-C.; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phys. Rev. B* **1984**, *30*, 702–710.
(46) Harbeke, G.; Meier, E.; Kobel, W.; Egli, M.; Kiess, H.; Tosatti, E. *Solid State Commun.* **1985**, *55*, 419–422.
(47) A recent work demonstrates that polarons are the dominant charge storage state in poly(3-methylthiophene) doped with BF_4^-, see: Schärli, M.; Kiess, H.; Harbeke, G.; Berlinger, W.; Blazey, K. W.; Müller, K. A. *Synth. Met.* **1988**, *22*, 317–336.
(48) Horak, M.; Hyams, I. J.; Lippincott, E. R. *Spectrosc. Acta* **1966**, *22*, 1355–1363.

(49) Kobayashi, M.; Chen, J.; Chung, T.-C.; Moraes, F.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1984**, *9*, 77–86.
(50) Hotta, S.; Hosaka, T.; Soga, M.; Shimotsuma, W. *Synth. Met.* **1984**, *9*, 381–387.
(51) Hotta, S.; Hosaka, T.; Soga, M.; Shimotsuma, W. *Synth. Met.* **1984/85**, *10*, 95–99.
(52) Neugebauer, N.; Neckel, A.; Brinderkoropic, N. In *Electronic Properties of Polymers and Related Compounds*; Springer-Verlag: Berlin, 1985; p 227.
(53) Brown, C. E.; Khoury, I.; Bezoari, M. D.; Kovacic, P. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1697–1707.
(54) Clarke, T. C.; Scott, J. C.; Street, G. B. *IBM J. Res. Dev.* **1983**, *27*, 313–320.
(55) Devreux, F.; Bidan, G.; Syed, A. A.; Tsitavis, C. *J. Phys.* **1985**, *46*, 1595–1601.
(56) Hotta, S.; Hosaka, T.; Shimotsuma, W. *J. Chem. Phys.* **1984**, *80*, 954–956.
(57) Osterholm, J.-E.; Sunila, P.; Hjertberg, T. *Synth. Met.* **1987**, *18*, 169–176.
(58) Hotta, S.; Hosaka, T.; Soga, M.; Shimotsuma, W.; Taketani, M.; Kohiati, S. *J. Chem. Soc. Jpn., Chem. Ind. Chem.* **1986**, *3*, 365–372.
(59) Roncali, J.; Yassar, A.; Garnier, F. *J. Chem. Soc., Chem. Commun.* **1988**, *9*, 581–582.
(60) Elsenbaumer, R. L.; Jen, K. Y.; Oboodi, R. *Synth. Met.* **1986**, *15*, 169.
(61) Basescu, N. Ph.D. Thesis, University of California, Santa Barbara, 1988; p 108.
(62) Curtis, R. F.; Phillips, G. T. *Tetrahedron* **1967**, *23*, 4419–4424.
(63) Krische, B., private communication.
(64) Nowak, M. J.; Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J. *Macromolecules* **1987**, *20*, 965–968.
(65) Bradley, D. D. C.; Friend, R. H.; Lindenberger, H.; Roth, S. *Polymer* **1986**, *27*, 1709.
(66) Tourrillon, G.; Garnier, F. *J. Electroanal. Chem.* **1982**, *135*, 173–178.
(67) Bohlmann, F.; Zdero, C. *Chem. Ber.* **1976**, *109*, 901–905.
(68) Takahashi, K.; Sone, C.; Fujieda, K. *J. Phys. Chem.* **1970**, *74*, 2765.
(69) Yesinowski, J. P.; Eckert, H.; Sandman, D. J.; Velasquez, C. S. In *Crystallographically Ordered Polymers*; Sandman, C. J., Ed.; ACS Symposium Series 337; American Chemical Society: Washington, DC, 1987; p 233.
(70) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212.
(71) Cazes, J. *J. Chem. Ed.* **1966**, *43*, A567–A582; *J. Chem. Ed.* **1966**, *43*, A625–A642.
(72) Sperling, L. H. *Introduction to Physical Polymer Science*; Wiley: New York, 1986; p 85.
(73) A referee asked for speculation regarding interpretation of this unusual result. The balance between intermolecular and intramolecular interactions that are responsible for the observation of high conductivities in doped conjugated polymers is still a matter of much controversy. No clean experimental results exist that establish a minimum conjugation length associated with high conductivity. In the poly(3,3′-dihexyl-2,2′-bithiophene) case, the conjugation length may, in fact be large but the intramolecular π overlap is diminished by a decrease in coplanarity of the polythiophene backbone and electronic transport may not be as sensitive to p_z–p_z π overlap as intuitively expected. Alternatively, in the poly(3,3′-dihexyl-2,2′-bithiophene) case intermolecular interactions may be enhanced relative to the predominantly head-to-tail poly(3-hexylthiophene) but intramolecular delocalization is inhibited, resulting in essentially no change in transport properties between these two regioisomeric polymers.
(74) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Oxford, 1987.
(75) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; John Wiley & Sons: New York, 1972.
(76) Hotta, S. *Synth. Met.* **1987**, *22*, 103.

Registry No. **2**, 1693-86-3; **2** (homopolymer), 104934-50-1; **3**, 16494-40-9; **4**, 124561-55-3; **5**, 67984-20-7; **5** (homopolymer), 99836-43-8; **6**, 124535-72-4; **6** (homopolymer), 124535-74-6; iodine, 7553-56-2.

Junction Point Motion from ^{31}P NMR Line Shapes and Relaxation Times in Poly(propylene glycol)/Urethane Networks

L. Charles Dickinson,* J. C. W. Chien, and W. J. MacKnight

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003. *Received May 8, 1989; Revised Manuscript Received August 2, 1989*

ABSTRACT: ^{31}P NMR line shapes and spin–lattice relaxation times in the lab (T_1^P) and rotating ($T_{1\rho}^P$) frames have been measured over a wide range of temperatures for a series of network polymers with molecular weight between cross-links (M_c) ranging from 400 to 3000. The networks are formed from α,ω-dihydroxypoly(propylene glycol) and tris(4-isocyanatophenyl)thiophosphate. The line shapes are interpreted in terms of a diffusional motion model; the fit is reasonably good for short correlation times. The discrepancy between calculated and observed minimum relaxation times indicates the inadequacy of an isotropic motional model especially for lower M_c samples. Some computation of factors to correct for the nonisotropic motional case are included. Comparison with previous ^{13}C relaxation data shows that the ^{31}P motional frequency lags the segmental motion by a factor of 3 and 5 for the M_c 1000 and M_c 3000 cases, respectively. Correlation times obtained from the line-shape fitting and from the relaxation times do not agree; the former is about 3 times longer. This discrepancy may be attributed to the inadequacy of the relaxation model of isotropic averaging of the chemical shift anisotropy or to the over-simple motional model of the line-shape fitting, or both.

Introduction

The improvements in spectroscopic techniques and their use in combination are making possible the understanding of macroscopic phenomena of polymeric materials on a detailed molecular level. For instance, the dynamic mechanical modulus temperature dependence in polycarbonates has been analyzed in terms of a distribution of correlation times determined from nuclear magnetic resonance[1] with motion including libration and 180° aromatic ring flips.[2]

For poly(dimethylsiloxane) network systems neutron

0024-9297/90/2223-1279$02.50/0