*Macromolecules* **1998,** *31,* 5051−5058

# Effect of Molecular Weight on Spectroscopic and Spectroelectrochemical Properties of Regioregular Poly(3-hexylthiophene)

**Miroslaw Trznadel***

*Department of Materials Science and Ceramics, Academy of Mining and Metallurgy,*
*30 059 Krakow, Mickiewicza 30, Poland*

**Adam Pron and Malgorzata Zagorska**

*Faculty of Chemistry, Warsaw University of Technology, 00 664 Warsaw, Noakowskiego 3, Poland*

**Ryszard Chrzaszcz and Jan Pielichowski**

*Department of Chemistry, Technical University of Cracow, 31 155 Krakow, Warszawska 24, Poland*

*Received May 6, 1997; Revised Manuscript Received January 20, 1998*

ABSTRACT: Using experimentally established sequence of extractions, we were able to fractionate regioregular poly(3-hexylthiophene) (R-P3HT) into four fractions differing significantly in their molecular weight ($M_n$) and exhibiting low polydispersity coefficients. $^1$H NMR analysis of low molecular fractions enabled us to propose the dominant chain termination mechanisms and identify the sources of regioregularity defects. In particular, it turned out that the presence of small amounts of undesired isomer of 2-bromo-3-hexylthiophene, namely, 2-bromo-4-hexylthiophene, strongly influences the molecular weight and to a much lesser extent the regioregularity of the polymer obtained via Grignard type polycondensation. In the reaction with the growing chain, 2-bromo-4-hexylthiophene either causes its termination, lowering in this manner the molecular weight of the resulting polymer, or introduces regioregularity defects of TT−HH (TT = tail to tail; HH = head to head) type. The average conjugation length in R-P3HT increases with the increase of $M_n$ as manifested by a bathochromic shift of the $\lambda_{max}$ and the appearance of the vibrational structure in the UV−vis−near-IR spectra of the fractions of higher molecular weight. This conclusion is supported by FTIR data. The onset of the oxidative doping of R-P3HT shifts to lower potentials with the increase of the molecular weight as evidenced by cyclic voltammetry and UV−vis−near-IR spectroelectrochemistry.

## Introduction

Poly(3-alkylthiophenes) (here abbreviated as P3ATs) belong to the most extensively studied conductive polymers in the past decade due to their solubility, which is rare in polyconjugated systems, and their interesting electrochemical and physical properties. However, P3ATs remained, for several years, poorly defined systems because they usually showed a rather low degree of regioregularity of their macromolecular chains. It turned out that the preparation of a regioregular polymer with the degree of regioregularity approaching 100% is a difficult task. Since the substrates used for the preparation of P3ATs, i.e., 3-alkylthiophenes (3ATs), are neither centrosymmetric nor possess a symmetry axis, two isomeric diads can be formed upon coupling of 3-alkylthiophene rings: head to tail (HT) and head to head (HH). This in turn gives rise to the coexistence of four structurally nonequivalent triads: HT−HT, HT−HH, TT−HT, and TT−HH, which can be detected spectroscopically in the NMR spectra of nonregioregular poly(3-alkylthiophenes).[1−3]

Several methods of P3ATs preparation have been elaborated, leading to polymers with different regioregularity degrees. The most frequently used are chemical or electrochemical oxidative polymerizations of 3ATs.[4−7] Although both methods lead to polymers of a rather high molecular weight, the regioregularity of the obtained P3ATs, expressed as the percentage of HT−HT triads, is rather low (usually between 50 and 60%). It increases with the increase of the alkyl substituent length.

Even higher molecular weights can be obtained if trialkylsilyl derivatives of 3-alkylthiophenes are used as substrates in the electrochemical polymerization.[8] However, the defects of regioregularity are still observed in the NMR spectra of the polymers obtained by this method.

P3ATs were initially prepared[9] by Grignard coupling of 2,5-dihalo derivatives of 3-alkylthiophenes in the presence of Ni(dppp)Br$_2$ catalyst. The degree of regioregularity depends strongly on the halogen atom and the catalyst used. Although PATs obtained by this method can be more regioregular than those obtained by oxidative polymerization,[10] they always exhibit significantly lower molecular weight, as expected for the Grignard type polycondensation.

Recently two modifications of Grignard type polycondensation led to P3ATs of high regioregularity. The first synthesis of regioregular P3AT was by McCullough and Lowe.[11] They used 2-bromo-3-alkylthiophenes which after lithiation at the 5 position and the transformation into the Grignard reagent condensed regiospecifically to P3ATs.[12−14]

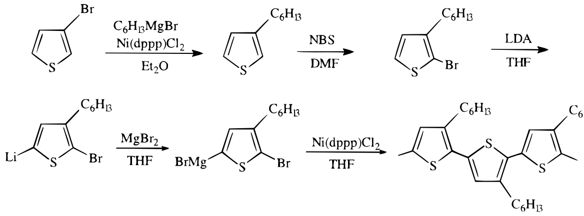
Alternatively Rieke et al.[15−17] obtained regioregular PATs via polycondensation of 2,5-dibromo-3-alkilothiophene in the presence of active zinc.

---

* Author to whom corespondence should be addressed. Present address: CEA, Departement de Recherche Fondamentale sur la Matiere Condense, Laboratoire de Physique des Metaux Synthetiques, 17 Rue des Martyrs, 38 054 Grenoble, France. E-mail: trznadel@drfmc.ceng.cea.fr.

S0024-9297(97)00627-X CCC: $15.00

**Scheme 1. Synthesis of Regioregular Poly(3-hexylthiophene)**



Regioregular P3ATs can be considered as much better defined materials as compared to previously prepared PATs, but taking into account a rather low molecular weight of the polymers prepared by the Grignard type coupling, their spectroscopic and spectroelectrochemical properties may depend on the $M_n$ and the polydispersity coefficient. For this reason we have undertaken a task of fractionation of regioregular poly(3-hexylthiophene) into relatively sharp fractions. In the next step we have studied spectroscopic, electrochemical, and spectroelectrochemical properties of P3HT as a function of the average molecular weight.

## Experimental Section

Regioregular poly(3-hexylthiophene) (P3HT) was prepared using a modification of the method of McCullough et al.[14] (Scheme 1).

3-Hexylthiophene was obtained from 3-bromothiophene (97%, Aldrich) by Grignard coupling in the presence of Ni(dppp)$Cl_2$ (Aldrich).[18] Then it was brominated in the 2 position using *N*-bromosuccinimide (NBS) in (Merck) in dimethylformamide (DMF) as the brominating agent. In this step we have slightly modified the original procedure of McCullough since the bromination with NBS gives better yields[19] than the bromination with $Br_2$ in acetic acid.[20] In the next step 2-bromo-3-hexylthiophene was lithiated in the 5 position using lithium diisopropylamide (LDA). The lithiation with this reagent carried out at low temperatures is very selective.[21,22] Lithium was then substituted with the MgBr group and the resulting Grignard reagent condensed regiospecifically to P3HT. The detailed description of the polymerization can be found in ref 14.

The fractionation of P3HT can be briefly described as follows. P3HT obtained via polycondensation of the Grignard reagent was first precipitated with methanol, filtered, and washed with a mixture of water and methanol. This crude polymer was then dried until constant mass was reached. The crude polymer was first extracted with acetone in a Soxhlet apparatus until the filtrate was colorless. The remaining insoluble part was then extracted consecutively with hexane, dichloromethane, tetrahydrofuran (THF), and trichloromethane in the same manner as in the case of acetone.

The separated fractions of neutral P3HT were then subjected to the following characterization tests: GPC, $^1H$ and $^{13}C$ NMR, FTIR, UV−vis−near-IR. Additionally oxidative doping studies of each fraction were carried out using cyclic voltammetry and UV−vis−near-IR spectroelectrochemistry.

**Gel Permeation Chromatography.** The determinations of the molecular weight and the polydispersity coefficient for each fraction were carried out using a KNAUER GP chromatograph equipped with a PL-GEL column and a refractometric detection system. The column was calibrated by sharp fractions of polystyrene available commercially from Waters. The temperature of the measurement was 297.2 K and the eluent rate 1 mL/min. Carefully dried THF containing BHT antioxidant was used as the eluent.

**Spectroscopic Techniques.** NMR spectra were recorded on a Bruker 500 MHz spectrometer. The samples of each fraction were dissolved in $CDCl_3$, and tetramethylsilane (TMS) was used as the internal standard.

FTIR spectra were recorded on a Digilab FT-60 IR spectrometer in a transmission geometry using the KBr pellet technique.

UV−vis−near-IR spectra of P3HT fractions were measured in the spectral range of 200−1100 nm both in THF solutions and in the solid state (Lambda 2 spectrometer of Perkin Elmer).

**Cyclic Voltammetry and Spectroelectrochemistry.** For cyclic voltammetry studies thin uniform polymer films were deposited on a platinum electrode by casting from THF solution. The deposition of uniform film required very slow evaporation of the solvent. The evaporation was therefore carried out in the small desiccator whose overpressure due to THF vapors was periodically released. Finally the electrode was pumped in vacuo in order to remove all traces of the solvent.

The experimental setup for cyclic voltammetry consisted of an airtight electrochemical cell equipped with a platinum working electrode covered with a layer of the polymer, a platinum counter electrode, and an Ag/AgCl reference electrode. The electrolyte consisted of 0.1 M $Bu_4NBF_4$/acetonitrile solution. The voltammograms were recorded on a EG&G potentiostat/galvanostat 273 (Princeton Applied Research). To exclude the so-called memory effect,[23,24] which is manifested by the dependence of the position of the oxidative doping peaks on the history of the sample, before the registration of the cyclic voltammogram the sample was cycled three times in the potential range of 0−1.2 V with the scan rate of 20 mV/s.

For UV−vis−near-IR spectroelectrochemistry, the same electrochemical cell was used but the polymer was deposited on an ITO working electrode. This limited the spectral range to 340 nm due to high absorption of the ITO electrode at shorter wavelengths.

## Results and Discussion

The literature data concerning the fractionation of poly(3-alkylthiophenes) are scarce,[25−27] and to our knowledge no such studies have been reported for regioregular poly(3-alkylthiophenes). Nonregioregular poly(3-alkylthiophenes) were fractionated by selective precipitation from THF or chloroform solutions. The obtained fractions showed, however, a rather large polydispersity coefficient (3.0−5.0). Wei and Tian[4] exploited a different route in the preparation of poly(3-alkylthiophenes) with different molecular weights. They observed that the addition of small amounts of 2,2′-bithiophene into the electrolytic solution used for the polymerization of 3-alkylthiophenes leads to an increase of the average molecular weight of the resulting polymers. However this method cannot be used for the preparation of the samples significantly differing in their molecular weight.

The sequence of extracting media used in this research at first seems rather surprising, but it turned out to be extremely efficient in the fractionation of regioregular P3HT. In Figure 1 the chromatograms of all fractions are shown, whereas in Table 1 macromolecular parameters, derived from the gel permeation chromatographic measurements, are collected.

Four fractions with increasing $M_n$ were obtained, the most abundant being the dichloromethane fraction and THF fraction which jointly constituted 82 wt % of the soluble polymer. After the extraction with THF a small amount (1.6 wt %) of R-P3HT still dissolves in chloroform. However taking into account the significantly larger $P_i$ of this fraction and a small amount of the material available, we have limited ourselves to the systematic studies of the first four fractions. The results of the fractionation are surprisingly good. The polydispersity coefficients in each case are below 1.5, and the value of $M_n$ approximately doubles for each consecutive fraction.

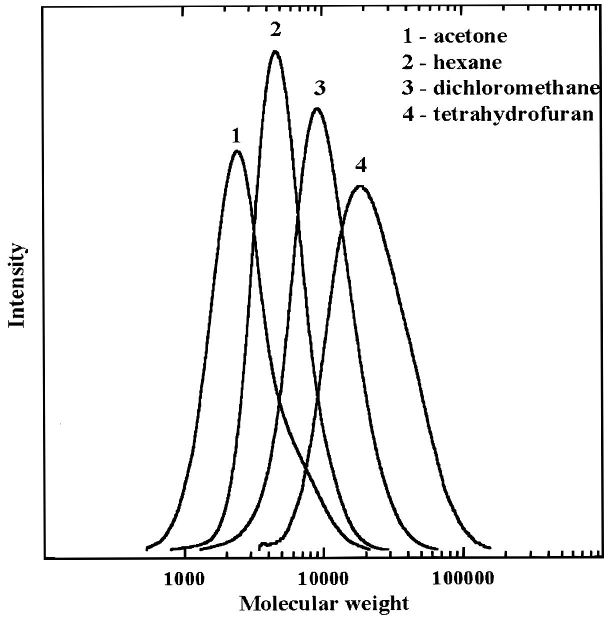


**Figure 1.** Elution curves of regioregular poly(3-hexylthiophene) fractions obtained by selective extraction.

**Table 1. Macromolecular Parameters of R-P3HT Fractions Obtained by Selective Extraction ($M_n$, Number Average Molecular Weight; $M_w$, Weight Average Molecular Weight; $P_i$, Polydispersity Coefficient; $D_n$, Degree of Polymerization)**

| fraction | wt % | $M_n$ | $M_w$ | $P_i$ | $D_n$ |
|---|---|---|---|---|---|
| PHT/acetone | 6.5 | 2 280 | 3 150 | 1.38 | 14 |
| PHT/hexane | 9.7 | 4 380 | 5 340 | 1.22 | 26 |
| PHT/$CH_2Cl_2$ | 33.1 | 8 370 | 11 100 | 1.33 | 50 |
| PHT/THF | 49.2 | 17 700 | 25 700 | 1.45 | 106 |
| PHT/$CHCl_3$ | 1.6 | 10 800 | 21 300 | 1.97 | 65 |

Some information concerning the source of polydispersity in R-P3HT and the chain termination mechanisms can be extracted from NMR spectra of the separated fractions. In the aromatic part of the $^1H$ NMR spectra (Figure 2), in addition to the principal signal at 6.98 ppm which is ascribed to HT−HT triads, two types of satellite peaks are expected: (1) signals corresponding to regioregularity defects, i.e., singlets ascribed to HT−HH, TT−HT, and TT−HH (Figure 3) which appear at 7.00, 7.02, and 7.05 ppm; (2) signals corresponding to the protons in the terminal thiophene rings (end groups); these lines are located mainly in the higher field part of the spectrum with respect to the principal line, and their intensity quickly decreases with the increase of the average molecular weight).

Similarly a triplet attributed to α-methylene groups of the alkyl substituent is accompanied by a significant number of satellite signals whose intensity decreases with the increase of the molecular weight (Figure 2). These two observations seem to indicate that several chain termination mechanisms may exist.

The two obvious termination mechanisms involving the reaction of the Grignard reagent with the growing chain should first be postulated. They are depicted in Scheme 2a1,a2.

According to Scheme 2a1, the termination involves the reaction of the monomer with the polymer chain containing bromine at the 5 position of the terminal ring. In the resulting end group only one aromatic proton can be distinguished, H(3). Plausible attribution of the NMR lines is presented in Table 2.

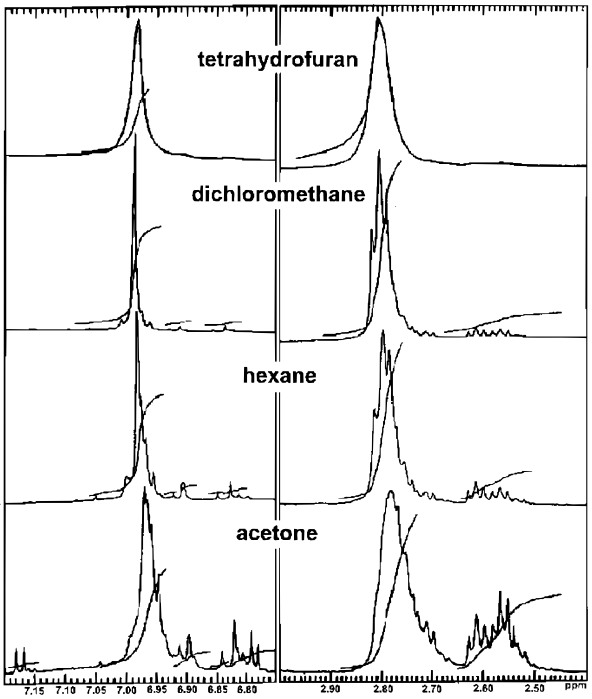


**Figure 2.** $^1H$ NMR spectra of regioregular poly(3-hexylthiophene) fractions differing in their average molecular weight.

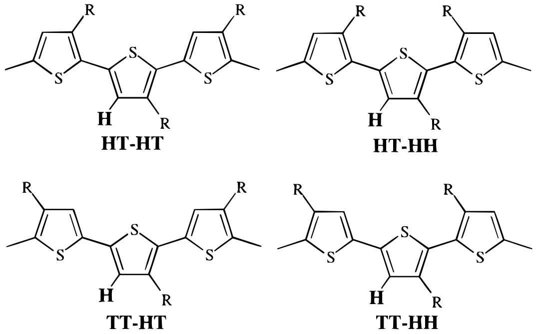


**Figure 3.** Possible structurally nonequivalent triads and their NMR parameters. Apart from HT−HT triads, all other triads constitute regioregularity defects.

In the second termination mechanism involving the monomer (Scheme 2a2) the terminal ring of the chain contains the MgBr group in the 5 position. In such case the highly reactive bromomagnesium subsituent is exchanged for a hydrogen atom in the hydrolysis occurring during the steps of polymer purification and fractionating (Scheme 3). The condensation with unreacted monomer (i.e., the monomer which did not form the Grignard reagent) 2-bromo-3-hexylthiophene leads to identical chain ends (Scheme 3). In the termination according to Scheme 2a2, two doublets with high coupling constants are expected, corresponding to protons connected to the adjacent carbon atoms in the terminal thiophene ring. The attribution of these signals can also be found in Table 2.

However, in the NMR spectra of low molecular weight fractions, there exist additional satellite lines whose presence cannot be rationalized by the termination mechanism of Scheme 2a1,a2 type. We have studied this problem in greater detail. The majority NMR signals in the aromatic part of the spectrum are singlets. However, one more doublet can be distinguished at 6.90 ppm ($J$ = 1.2 Hz). The existence of a doublet with a relatively weak coupling constant seems to indicate that

**Scheme 2. Possible Types of Chain Termination in the Propagation of Poly(3-hexylthiophene) Synthesis via Grignard Coupling: (a) Termination Involving the Reaction with 2-Bromo-3-hexylthiophene; (b) Termination Involving the Reaction with 2-Bromo-4-hexylthiophene**

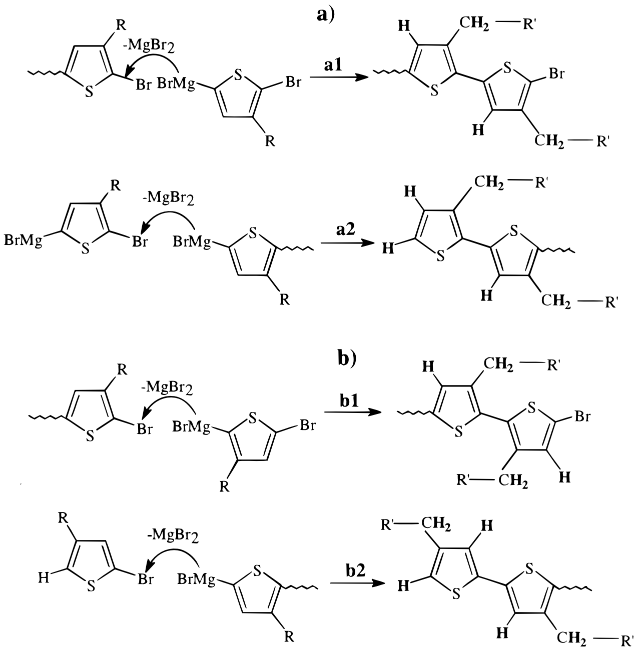
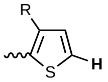
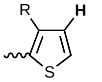
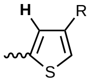
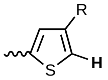
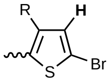
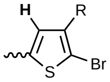
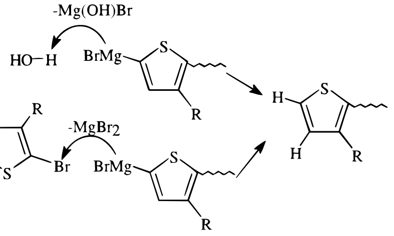


**Table 2. $^1$H NMR of Aromatic and α-Methylene Protons in Triads and End Groups of Poly(3-hexylthiophene)[a]**

| | $\delta$ (ppm) [m, $J$(Hz)] | triplet | ref |
|---|---|---|---|
| | Triads | | |
| ***HT−HT*** | ***6.98 s*** | | ***1, 3, 14, 16*** |
| TT−HT | 7.00, s | | 3 |
| HT−HH | 7.02, s | | 3 |
| TT−HH | 7.05, s | | 1, 3, 28, 29 |
| | Diads | | |
| ***H−T*** | | ***2.79*** | ***1, 14, 16*** |
| H−H | | 2.56 | 1, 28, 29 |
| | Terminal Protons | | |
|  | 7.16 [d, 5.3] | | 16, 30, 31 |
|  | 6.93 [d, 5.3] | | 16, 30, 31 |
|  | ***7.00 [d, 1.2]*** | ***2.7−2.8*** | ***28, 30, 31*** |
|  | ***6.90 [d, 1.2]*** | ***2.7−2.8*** | ***16, 28, 30, 31*** |
|  | 6.84 s | 2.5−2.7 | 3 |
|  | ***6.82 s*** | ***2.5−2.7*** | ***3*** |

[a] Dominating signals are shown in italics.

**Scheme 3. Termination Involving the Hydrolysis of MgBr Group or Its Condensation with 2-bromo-3-hexylthiophene**



in the chain terminating thiophene ring two protons at the 3 and 5 positions are present. According to the literature the coupling constant for such protons depends on the type of substituents in the adjacent positions (2 and 4) and usually is in the range 1−3 Hz (Table 2).

Neither the termination with 2-bromo-3-hexylthiophene nor with the Grignard reagent originating from it produce the chain end with two protons in the 3 and 5 positions of the terminal thiophene ring. This observation leads to the conclusion that the termination of the propagating chain must involve other, than above-mentioned, molecules present in the reaction mixture.

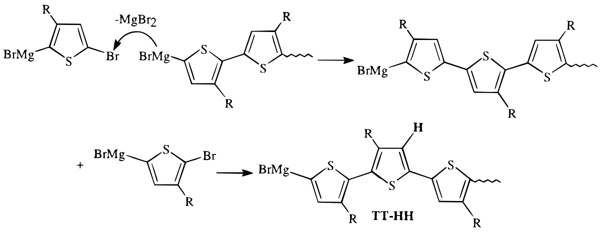
Detailed gas chromatographic studies showed that the main contaminant of 2-bromo-3-hexylthiophene is 2-bromo-4-hexylthiophene. Due to similar polarity and similar boiling point, total removal of this monomer is extremely difficult. We have always observed from 0.5 to 2.3% of 2-bromo-4-hexylthiophene in carefully purified 2-bromo-3-hexylthiophene. The presence of small amounts of 2-bromo-4-hexylthiophene in the reaction mixture may generate two additional types of chain ends, which are schematically depicted in Scheme 2b.

In Scheme 2b1 the termination occurs by the reaction with 5-bromo-2-bromomagnesium-3-hexylthiophene, i.e., the Grignard reagent obtained from 2-bromo-4-hexylthiophene. As has already been mentioned, the preparation of this reagent involves lithiation and the exchange of Li with the bromomagnesium group. The lithiation of 2-bromo-4-hexylthiophene is much more difficult than the lithiation of 2-bromo-3-hexylthiophene for both energetic and steric reasons. First, the 5 position of the latter is less deactivated with respect to the nucleophilic attack and deprotonation.[32] Second, since bulky LDA is used for the metalation, the steric phenomena should be less important in the case of 2-bromo-3-hexylthiophene. For the above reasons, it is expected that only a small fraction of 2-bromo-4-hexylthiophene should form the Grignard reagent and the termination via the Scheme 2b1 mechanism will not be dominant. This is indeed the case since the NMR lines corresponding to this type of termination are rather weak (Table 2).

It should be mentioned here that the chain end created according to the Scheme 2b1 mechanism is still reactive and the polymer may continue to grow. The reaction of this chain end with the Grignard reagent obtained from 2-bromo-3-hexylthiophene, i.e., 2-bromo-5-bromomagnesium-3-hexylthiophene, leads to the regioregularity defect of the TT−HH type, as shown in Scheme 4. This is however a rare phenomenon since the NMR line at 7.05 ppm, corresponding to this defect, is very weak even for the lowest molecular weight fractions (acetone, hexane) and essentially nonexistent for the highest fraction (THF). No signals are observed within the 7.01 and 7.04 ppm range; it can be concluded therefore that the TT−HH defect is isolated.

Much more frequent as judged from the NMR spectra is the termination via the condensation of unreacted

**Scheme 4. Formation of the TT−HH Defect Associated with the Presence of 2-Bromo-4-hexylthiophene in the Reaction Medium**



2-bromo-4-hexylthiophene with the bromomagnesium group of the growing chain (Scheme 2b2) which results in the presence of two aromatic protons in the terminal ring (Table 2).

$^1$H NMR signals corresponding to α-methylene groups are presented in Figure 2. In this chemical shift range the spectra of all fractions are dominated by a triplet at 2.80 ppm corresponding to α-methylene groups in a HT couple diad. In Table 2 the assignment of the α-methylene groups connected to the terminal thiophene rings is proposed. Due to small differences in the chemical shifts and multiplicity problems the exact assignment is more difficult than in the case of the aromatic part of the spectrum. However, similar tendencies can clearly be observed. Two triplets at 2.61 and 2.76 ppm can be ascribed to the Scheme 2b2 termination mechanism, whereas two triplets at 2.57 and 2.72 ppm, to the Scheme 2a1 mechanism.

To summarize briefly the NMR part of the paper, the studies of four fractions differing in their molecular weight enabled us to identify possible chain termination mechanisms and the role of 2-bromo-4-hexylthiophene in this termination. This principal contaminant of 2-bromo-3-hexylthiophene, i.e., the monomer used for the polymerization, may act as a source of the chain nonregioregularity defects of the HH−TT type, but the number of defects caused by its presence is very low and, for higher molecular weight fraction, negligible. The principal role of 2-bromo-4-hexylthiophene is to promote the chain termination via the reaction with the bromomagnesium group of the growing chain. For this reason the chain ends originating from this isomer are present, in their major part, in the low molecular weight fractions, and its influence on higher fractions is negligible.

Both HH−TT couplings and chain ends constitute regioregularity defects. The increase of the regioregularity with the increase of the average molecular weight should therefore be manifested in UV−vis spectra of all four fractions studied. In Figure 4 the solution spectra of all fractions are collected. The solid-state spectra recorded for thin films obtained after evaporation of the solvent are presented in Figure 5.

Both in the solution spectra and in the solid-state ones a bathochromic shift of $\lambda_{\max}$ can be observed which increases with the increase of the average molecular weight of the fraction. This effect is however much more pronounced in the case of the solid films. In other words the solvatochromic effect usually observed for poly(3-alkylthiophene) is amplified from 25 nm for the acetone fraction to 113 nm for the THF one.

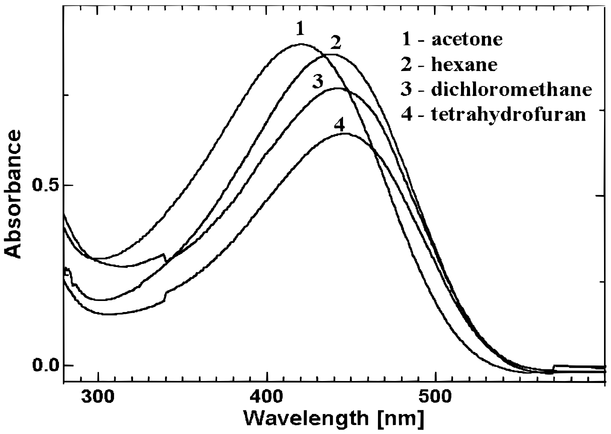


**Figure 4.** THF solution UV−vis spectra recorded for the fractions of regioregular poly(3-hexylthiophene) differing in their average molecular weight. The observed red shift for fractions of higher molecular weight is indicative of higher conjugation length.

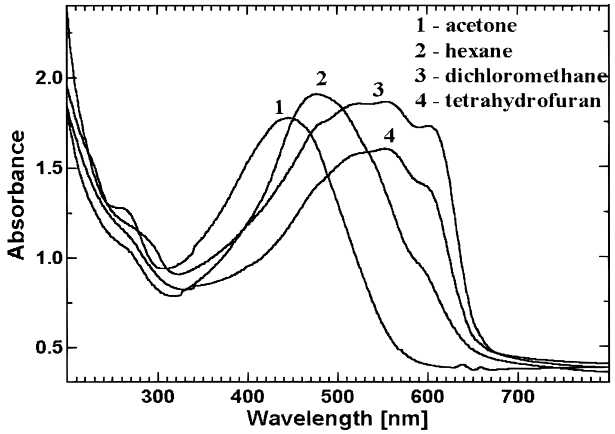


**Figure 5.** Solid-state UV−vis spectra recorded for the fractions of regioregular poly(3-hexylthiophene). Note that the batochromic shift observed for higher molecular weight fractions is much more pronounced than in the case of solution spectra.

**Table 3. Absorption Maxima in Electronic Spectra of Fractionated P3HT Recorded for THF Solutions and in the Solid State[a]**

| | | solid state | | | |
|---|---|---|---|---|---|
| fraction | THF soln | 0−0 | 0−1 | 0−2 | 0−3 |
| PHT/acetone | 420.6 | 445.7 | | | |
| PHT/hexane | 438.0 | *602.0* | *545.6* | 476.6 | |
| PHT/$CH_2Cl_2$ | 441.2 | *608.1* | *559.9* | *512.0* | *472.1* |
| PHT/THF | 446.9 | *615.3* | *559.9* | *512.5* | *472.1* |

[a] Given in italics are the maxima of $-d^2A/d\lambda^2$.

The behavior of the acetone fraction closely resembles that of poly(alkylthiophene) with a low value of the average conjugation length. In such cases either no solvatochromic shift is observed or its value is very low.[16,28,29] The hexane fraction gives in turn, UV−vis spectra similar to those recorded for nonregioregular poly(3-alkylthiophene) obtained by oxidative polymerization whose polymerization degree ($D_n$) is roughly 8 times higher.[6] This means that, despite large differences in the molecular weight, the average conjugation length is comparable in both cases. However in the solid-state spectra of the hexane fraction there are indications of a vibrational structure which is nonexistent in P3HT prepared by the oxidative route.

This fine structure is even more pronounced for the dichloromethane and THF fractions. The exact positions of the individual peaks originating from the vibrational structure were obtained through the second derivative analysis. They are listed in Table 3.

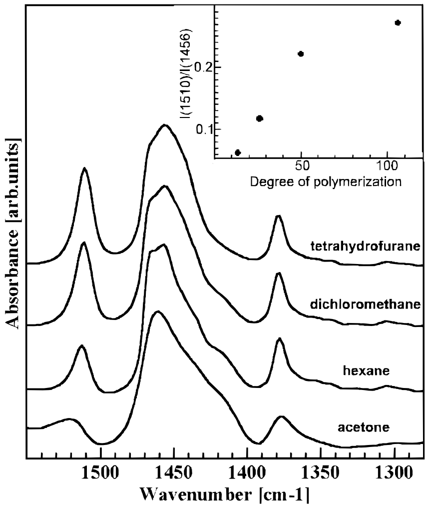


**Figure 6.** FTIR spectra of four fractions of regioregular poly(3-hexylthiophene). Increasing $I_{1510}/I_{1456}$ ratio is indicative of higher conjugation length.

Vibrational structure in the solid-state optical spectra of polymers is a typical manifestation of the electron–lattice coupling. The energy of the 0–0 transition, i.e., the transition from the ground state to the relaxed excited state in conjugated polymers, is inversely proportional to the conjugation length. The bathochromic shift of this transition observed for consecutive hexane, dichloromethane, and THF fractions is therefore consistent with an increase of the average conjugation length with increasing molecular weight. For the fractions of the highest molecular weight the spacing between the first and the second shoulders correspond to vibrational transition involving C=C stretching observed in Raman spectra of regioregular poly(3-alkylthiophenes).[33]

FTIR spectra of fractionated R-P3HT corroborate the conclusions derived from the electronic spectra. According to Furukawa et al.,[34] relative intensity of the IR mode at 1510 $cm^{-1}$ (asymmetric C=C stretching) increases with the increase of the average conjugation length. In Figure 6 FTIR spectra from the wavenumber range of 1300–1600 $cm^{-1}$ are presented for all fractions studied. If the ratio $I_{1510}/I_{1456}$ is plotted against the degree of polymerization ($D_n$), the increase of the average conjugation length with increasing $M_n$ is evident (Figure 6).

Voltammetric behavior of R-P3HT also depends strongly on its molecular weight. Cyclic voltammograms recorded for all fractions of this polymer are collected in Figure 7. The voltammograms of all fractions but the acetone one exhibit some common features. They can be described as consisting of three strongly overlapping oxidative doping peaks and their three reductive counterparts associated with dedoping of the polymer. Relative intensities of these peaks vary with the average molecular weight. The intensities of the oxidative peaks at 0.58–0.60 and 0.97–1.00 V vs Ag/AgCl increase with the increase of $M_n$, whereas the "middle" peak at 0.74 V decreases with increasing molecular weight.

In the simplest interpretation, the first and the third oxidation peaks correspond to the doping of defect-free chain segments with relatively long conjugation. Such segments are isoenergetic, and they are doped in a very narrow potential range (first oxidation peak in the cyclic voltammograms). The doping of regioregular poly(3-alkylthiophenes) is however a two step process, as evidenced by electrochemical and spectroelectrochemical studies.[35] For this reason a second oxidative doping peak is observed at higher potential. This sequence of peaks reflects the following sequence of redox processes occurring upon the doping of R-P3HT.

$$\text{neutral polymer} \rightarrow \text{polaron} \rightarrow \text{bipolaron}$$

Of course the doping of long segments with unperturbed conjugation will occur at lower potentials. For segments in which the average conjugation length is low, a significant distribution of the oxidation potentials is expected. For this reason in classical nonregioregular P3HT obtained by oxidative polymerization of 3HT one broad peak is observed with no indication of a two step oxidation. The cyclic voltammogram of the hexane fraction of R-P3HT to a first approximation can be treated as a superposition of the voltammogram of the high molecular weight THF fraction of R-P3HT and the voltammogram of nonregioregular P3HT. Since, with the increasing molecular weight of R-P3HT, the average conjugation length increases, the contribution from the doping of poorly conjugated segments will decrease for each consecutive fraction, as observed experimentally. The coexistence of segments with short conjugation with those with significantly higher conjugation length, which gives rise to complicated cyclic voltammograms in the case of the hexane fraction, is also manifested in the optical spectra of this fraction by a relatively high intensity of the low-energy component of the spectrum. Thus the UV–vis results are very consistent with cyclic voltammetry.

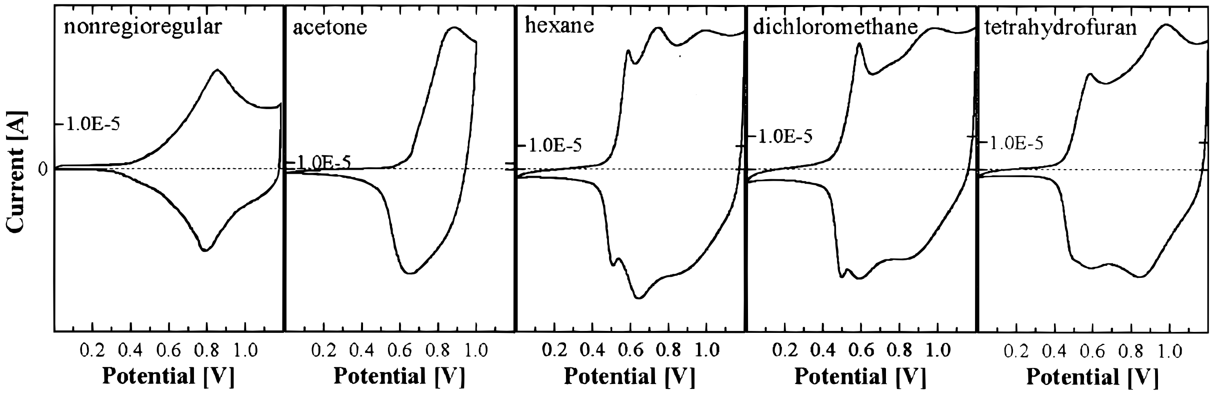


**Figure 7.** Cyclic voltammograms (20 mV/s) of four fractions of regioregular poly(3-hexylthiophene) differing in their molecular weight. For comparison cyclic voltammogram of nonregioregular P3HT obtained by the oxidation of 3-hexylthiophene with $FeCl_3$.

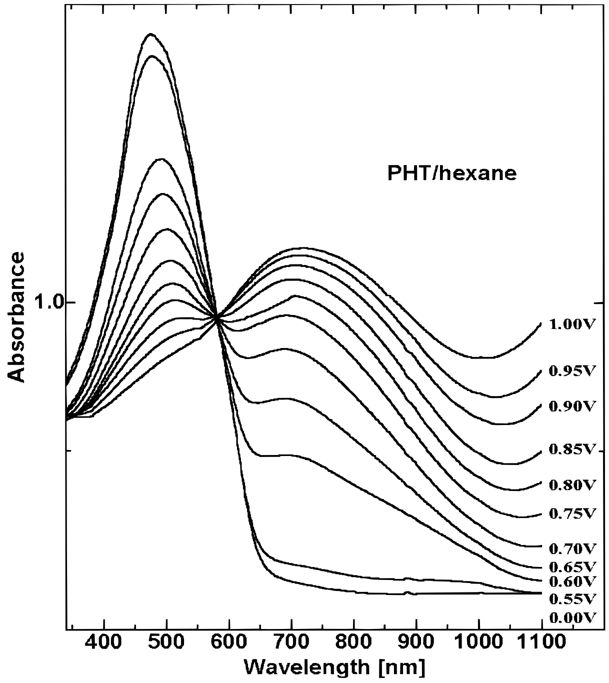


**Figure 8.** UV−vis−near-IR spectroelectrochemical data for hexane fraction of regioregular poly(3-hexylthiophene): $M_n$ = 4380.

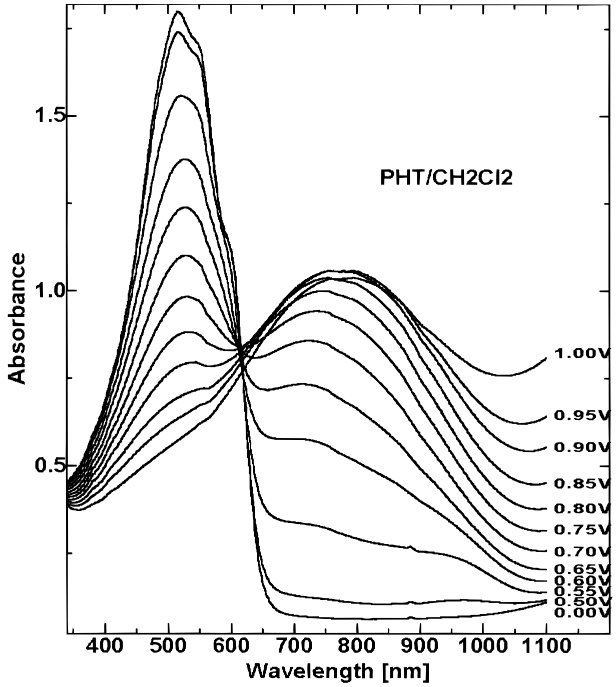


**Figure 9.** UV−vis−near-IR spectroelectrochemical data for dichloromethane fraction of regioregular poly(3-hexylthiophene): $M_n$ = 8730.

The increasing average conjugation length for each consecutive fraction is also manifested in UV−vis spectroelectrochemical data. In Figures 8−10 optical spectra of three principal fractions of R-P3HT, recorded for increasing electrode potential, are collected. The potential of the onset of the oxidative doping as probed by UV−vis depends on the molecular weight. Thus the hexane fractions which shows the lowest molecular weight and the lowest conjugation length of all fraction studied spectroelectrochemically starts to oxidize at 0.55 V vs Ag/AgCl, whereas for the dichloromethane and THF fractions this potential is 0.50 and 0.45 V, respectively. This result is not unexpected since better conjugated segments oxidize more easily.

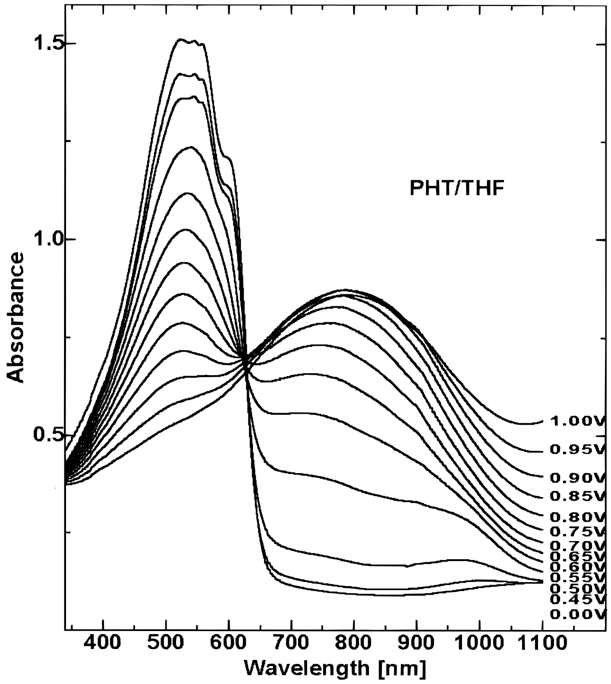


**Figure 10.** UV−vis−near-IR spectroelectrochemical data for THF fraction of regioregular poly(3-hexylthiophene): $M_n$ = 17 700.

With increasing electrode potential the vibrational structure of the $\pi-\pi^*$ transition becomes less and less pronounced, which means that highly conjugated segments are oxidized first and the remaining unoxidized (undoped) parts exhibit lower conjugation length. In addition to the bleaching of the $\pi-\pi^*$ transition, the doping causes the appearance of two (bipolaronic) or three (polaronic) bands in the less energetic part of the spectrum. The formation of the first bipolaronic band at higher electrode potentials is clearly manifested in the presented spectra. It should be stressed, however, that in the case of the THF fraction at initial doping stages a polaronic band appears with the maximum at ca. 950−1000 nm (1.25−1.30 eV). This means that for the fraction of the highest $M_n$ and the highest average conjugation length the separation of the two oxidation processes, characteristic of regioregular poly(3-alkylthiophenes), is the most clear.

## Conclusions

To summarize, using selective extraction we were able to obtain four fractions of regioregular poly(3-hexylthiophene) exhibiting increasing $M_n$ and study their spectroscopic and spectroelectrochemical properties as a function of the average molecular weight. In particular $^1$H NMR investigations of low molecular weight fractions of R-P3HT enabled us to propose the most probable chain termination mechanism and the source of the regioregularity defects in the Grignard type polycondensation widely utilized for the preparation of regioregular poly(3-alkylthiophenes). It turned out that the presence of small amounts of the undesired isomer of 2-bromo-3-hexylthiophene, namely, 2-bromo-4-hexylthiophene in the reaction mixture, may cause either the termination of the chain lowering in this manner, the average molecular weight of the resulting polymer, or create a regioregularity defect of the TT−HH type. The former is however much more frequent. UV−vis−near-IR and IR spectroscopic properties strongly depend on the molecular weight showing increasing conjugation length with increasing $M_n$. Similarly the onset of the electrochemical doping can be correlated with the average molecular weight being shifted to lower potentials with increasing $M_n$.

**Acknowledgment.** This research was financially supported by Grant No. 3-P405-05707 of the Committee for Scientific Research in Poland (KBN).

## References and Notes

(1) Sato, M.; Morii, H. *Macromolecules* **1991**, *24*, 1196.
(2) Sato, M.; Morii, H. *Polym. Commun.* **1991**, *32*, 436.
(3) Barbarella, G.; Bongini, A.; Zambianchi, M. *Macromolecules* **1994**, *27*, 3039.
(4) Wei, Y.; Tian, J. *Polymer* **1992**, *33*, 4872.
(5) Kaeriyama, K.; Sato, M.; Tanaka, S. *Synth. Met.* **1987**, *18*, 233.
(6) Roncali, J. *Chem. Rev.* **1992**, *92*, 1.
(7) Sugimoto, R.; Takeda, S.; Gu, M. B.; Yoshino, K. *Chem. Express* **1986**, *1*, 635.
(8) Bouachrine, M.; Lere-Porte, J. P.; Moreau, J. J. E.; Wong Chi Man, M. *J. Mater. Chem.* **1995**, *5*, 797.
(9) Jen, K. Y.; Miller, G. G.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1346.
(10) Stein, P. C.; Botta, C.; Bolognesi, A.; Catellani, M. *Synth. Met.* **1995**, *69*, 305.
(11) McCullough, R. D.; Lowe, R. D. *J. Chem. Soc., Chem. Commun.* **1992**, 70.
(12) McCullough, R. D.; Tristram-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910.
(13) McCullough, R. D.; Williams, S. P. *J. Am. Chem. Soc.* **1993**, *115*, 11608.
(14) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904.
(15) Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087.
(16) Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233.
(17) Chen, T.-A.; O'Brien, R. A.; Rieke, R. D. *Macromolecules* **1993**, *26*, 3462.
(18) Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *38*, 3347.
(19) Mitchell, R. H.; Lai, Y. H.; Williams, R. V. *J. Org. Chem.* **1979**, *44*, 4733.
(20) Consiglio, G.; Gronowitz, S.; Hornfeldt, A. B.; Maltesson, B.; Noto, R.; Spinelli, D. *Chem. Scr.* **1977**, *11*, 175.
(21) MacEarchern, A.; Soucy, C.; Leitch, L. C.; Arnason, T.; Morand, P. *Tetrahedron* **1988**, *44*, 2403.
(22) Soucy-Breau, C.; MacEachern, A.; Leitch, L. C.; Arnason, T.; Morand, P. *J. Heterocycl. Chem.* **1991**, *28*, 411.
(23) Odin, C.; Nechtschein, M. *Synth. Met.* **1991**, *41−43*, 2943.
(24) Lapkowski, M.; Zagorska, M.; Kulszewicz-Bajer, I.; Pron, A. *Synth. Met.* **1993**, *55−57*, 1570.
(25) Hourquebie, P.; Olmedo, L. *Synth. Met.* **1994**, *65*, 19.
(26) Ishikawa, H.; Xu, X.; Kobayashi, M.; Satoh, M. *J. Appl. Phys.* **1992**, *25*, 897.
(27) Ishikawa, H.; Amano, K.; Kobayashi, A.; Satoh, M.; Hasegawa, E. *Synth. Met.* **1994**, *64*, 49.
(28) Zagorska, M.; Krische, B. *Polymer* **1990**, *31*, 1379.
(29) Souto Maior, R. M.; Hinkelmann, K.; Eckert, H.; Wudl, F. *Macromolecules* **1990**, *23*, 1268.
(30) Mao, H.; Holdcroft, S. *Macromolecules* **1992**, *25*, 554.
(31) Bidan, G.; De Nicola, A.; Enée, V.; Guillerez, S. *Chem. Mater.*, in press.
(32) Joule J. A.; Smith G. F. *Chemia zwiazkow heterocyklicznych*; PWN: Warsaw, 1984.
(33) Louarn, G.; Trznadel, M.; Buisson, J. P.; Laska, J.; Pron, A.; Lapkowski, M.; Lefrant, S. *J. Phys. Chem.* **1996**, *100*, 12532.
(34) Furukawa, Y.; Agimoto, M.; Harada, I. *Synth. Met.* **1987**, *151*, 18.
(35) Trznadel, M.; Zagorska, M.; Lapkowski, M.; Louarn, G.; Lefrant, S.; Pron, A. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1387.

MA970627A