Nuclear Magnetic Resonance Studies on Electrochemically Prepared Poly(3-dodecylthiophene)

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ABSTRACT: Soluble and electrically conductive poly(3-dodecylthiophene) (PDDT) films were prepared by means of electrochemical polymerization of 3-dodecylthiophene. We observed the ^{1}H and ^{13}C NMR spectra of PDDT in chloroform-*d*. The resonances of the 4-protons on the successive 2,5-linked thiophene rings are resolved into four peaks, which arise from different triad sequences due to the alignment of monomers. With the aid of ^{1}H–^{1}H NOESY and ^{1}H NOE difference spectroscopy for PDDT, the configurational structures were determined. A pair of doublet peaks at $\delta = 6.93$ and 7.16 are assigned to the 4- and 5-protons on the terminal 2-substituted 3-dodecylthiophene rings, and peaks attributable to the other terminal units were not detected. The fractions of the sequences and the end-group analysis reveal the mechanism for the propagation of the electrochemical polymerization of 3-dodecylthiophene. The diad and triad fractions are accounted for in terms of Bernoulli statistics. The 3-dodecylthiophene monomer is proved to be attacked predominantly at the 2-position of the thiophene ring with a probability of 82% in spite of the terminal configuration. The relative intensity of the peaks ascribable to the terminal unit and the results on the mechanism of the propagation suggest that the degree of polymerization of PDDT is 140.

Introduction

The electrical and optical properties of π-conjugated polymers have received much attention from the viewpoint of both fundamental interest and potential application.[1,2] Recently, several researchers have electrochemically and chemically prepared conducting poly[3-(long alkyl)-thiophenes] which have not only considerable conductivity ranging from 10 to 95 S/cm but also good solubility in common organic solvents.[3-5] The favorable processability of the polymers has enabled the application of π-conjugated polymers to new fields, for example, the preparation of Langmuir–Blodgett films,[6,7] solvatochromism,[8,9] and thermochromism.[10]

The electrical and optical properties of the π-conjugated polymers depend on their electronic structures, which are influenced by the chemical structures of the polymers. Therefore, the elucidation of the structure is an important part of polymer research. IR spectra of poly[3-(long alkyl)-thiophenes] show that the polymers have a regular structure, which can be denoted as poly(3-alkyl-2,5-thiophenediyl).[11-13] Further, results of one-dimensional ^{1}H NMR studies on the poly(3-alkylthiophenes) have been reported.[13-15] The two chemical shifts for the α(1)-methylene protons of poly(3-alkylthiophenes) were explained by the presence of head-to-head and head-to-tail configurations.

In this paper, the configurational aspects of electrochemically prepared poly(3-dodecylthiophene) (PDDT) are investigated on the basis of NMR spectra including two-dimensional spectra, which are useful in making sequence assignments in synthetic polymers.[16] We estimated the propagation mechanism of the electrochemical polymerization of 3-dodecylthiophene by using data on fractions of the sequences and end-group analysis determined by NMR spectroscopy.

Experimental Section

Materials. 3-Dodecylthiophene was prepared by coupling of alkylmagnesium bromide with 3-bromothiophene in the presence of a nickel catalyst.[17] ^{1}H NMR (270 MHz, $CDCl_3$) (chemical shift (ppm) from tetramethylsilane): 0.88 (t; $J = 6.8$ Hz, 3 H), 1.26–1.30 (m; 18 H), 1.60 (m; 2 H), 2.61 (t; $J = 7.7$ Hz, 2 H), 6.86 (dd; $J = 1.2$, 2.7 Hz, 1 H), 6.89 (dd; $J = 1.2$, 4.9 Hz, 1 H), 7.16 (dd; $J = 2.7$, 4.9 Hz, 1 H).

PDDT films were prepared by electrochemical polymerization of 3-dodecylthiophene in nitrobenzene. The polymerization was carried out galvanostatically by means of a one-compartment cell equipped with two electrodes as reported previously.[13] An indium/tin oxide conducting glass (ITO) (2 × 2 cm^2) and a platinum plate (2 × 2 cm^2) were used as an anode and a cathode, respectively. These electrodes were dipped in 20 mL of nitrobenzene solution containing 2 mmol of 3-dodecylthiophene and 0.25 mmol of tetraethylammonium hexafluorophosphate. The doped, oxidized, PDDT films were synthesized at 5 °C at a current density of 2 mA/cm^2 for 8 min. The doped films on ITO were neutralized (reduced) by reversing the polarity of the electrodes. The neutralization was performed at a current density of 0.25 mA/cm^2 until the voltage between the two electrodes increased to 4 V. The obtained films were soaked with hot ethanol for 24 h in order to obtain highly neutral films and dried in vacuo at 120 °C.

IR and NMR Spectroscopy. IR spectra were recorded on a Perkin-Elmer 1720 IR spectrometer. NMR experiments were performed at 270 MHz for ^{1}H and 67.5 MHz for ^{13}C on a JEOL GSX270 spectrometer in the pulse Fourier transform mode. The sample solutions prepared on refluxing with $CDCl_3$ for 8 h contained about 3 wt % PDDT. ^{1}H NMR spectra were obtained at 20-55 °C with 6.0-s pulse repetition, 2700-Hz spectral width, 16K data points, and 80 accumulations. Chemical shifts (δ) are given in ppm relative to the internal tetramethylsilane. Peak areas were determined from unenhanced spectra by spectrometer integration and/or by computational curve fitting. The 67.5-MHz ^{13}C NMR spectra were recorded at 27 °C with 5.0-s pulse repetition, 16000-Hz spectral width, 32K data points, and 18 400 accumulations by means of bilevel broad-band decoupling. The ^{1}H–^{13}C heteronuclear correlated spectra (^{1}H–^{13}C HETCOR) were observed at 27 °C with 256 data points for the ^{1}H axis and 2048 data points for the ^{13}C axis, using the standard pulse sequence of the JEOL PLX software. The ^{1}H–^{1}H double-quantum-filtered correlation spectra (DQF-COSY) and the ^{1}H–^{1}H nuclear Overhauser effect spectra (NOESY) were recorded at 27 °C with 512 × 4096 data points, using the standard pulse sequence with a delay time of 200 ms and a mixing time of 400 ms, respectively. ^{1}H nuclear Overhauser effect difference spectra (NOEDS) were obtained at 27 °C, using a gated irradiation-pulse sequence with a pulse delay of 4.00 s and an acquisition time of 3.03 s.

Results and Discussion

IR Spectroscopy. The spectra of 3-dodecylthiophene in a thin-layer cell and a PDDT film cast from a chloroform

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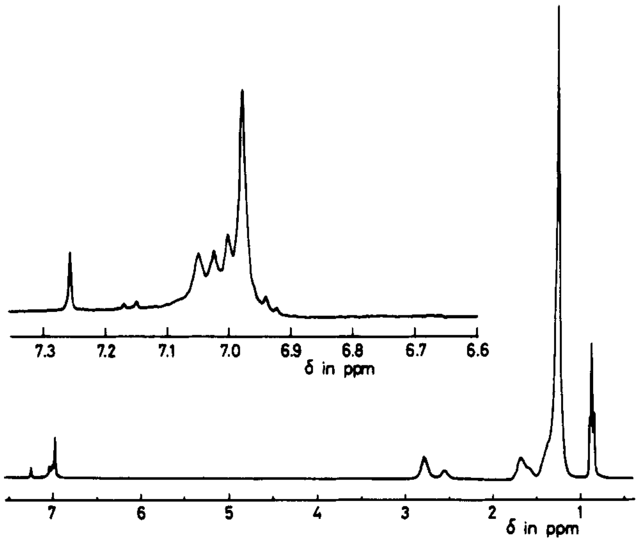


Figure 1. 270-MHz ^{1}H NMR spectrum of PDDT at 27 °C in chloroform-d. The inset shows an expanded ^{1}H NMR spectrum in the range of aromatic resonances.

solution were essentially identical with that reported in previous papers.[12,13]

3-Dodecylthiophene has a band at 3050 cm^{-1} assignable to the stretching vibration of the β(4)-C–H bond on the thiophene ring and a more intense band at 3110 cm^{-1} assignable to the α(2 and 5)-C–H bonds. The polymer film has only one band at 3060 cm^{-1} attributable to the β(4)-C–H bond in the region of the aromatic C–H stretching vibration and no band attributable to the α(2 or 5)-C–H bond. These observations indicate that 2,4- and 4,5-linked 3-dodecylthiophene units in the PDDT film are negligible. The spectrum of the PDDT film shows a band at 830 cm^{-1}, assigned to the C–H deformation vibration of a 2,3,5-trisubstituted thiophene ring, and a band at 730 cm^{-1}, assigned to the rocking vibration of a methylene group. In the spectrum of the PDDT film, there is a weak band at 700 cm^{-1}, which may be assigned to the terminal 2-monosubstituted thiophene ring.[18,19] These results demonstrate that the PDDT film has a highly defined structure, which would be denoted as poly(3-alkyl-2,5-thiophenediyl).

NMR Spectroscopy. Figure 1 shows the 270-MHz ^{1}H NMR spectrum of PDDT at 27 °C. The peak at $\delta = 7.26$ is due to $CHCl_3$ as an impurity in the $CDCl_3$ as solvent. The spectrum shows a triplet peak at $\delta = 0.87$ assigned to the methyl proton, a peak at $\delta = 1.26$ accompanied by a shoulder at ca. $\delta = 1.4$ assigned to the γ to λ (3–11) methylene protons relative to the thiophene ring, a peak at $\delta = 1.69$ and a shoulder at ca. $\delta = 1.6$ assigned to the β(2)-methylene protons, and peaks at $\delta = 2.56$ and 2.79 assigned to the α(1)-methylene protons. The ^{1}H–^{1}H DQF-COSY spectrum (Figure 2) shows that the peaks at $\delta = 2.56$ and 2.79 are correlated with the peak at $\delta = 1.69$ and the shoulder at ca. $\delta = 1.6$, respectively. In addition, decoupling of the peak and shoulder of the β(2)-methylene protons causes the peaks at $\delta = 2.56$ and 2.79 to sharpen without a shift. These observations corroborate the above assignment. The intensity ratio and chemical shift of the peaks at $\delta = 2.56$ and 2.79 did not change over the temperature range 20–55 °C, indicating that the splitting of the α(1)-methylene and β(2)-methylene resonances would be explained by the difference in configuration of PDDT, not by the difference in the conformation of PDDT.[14] On the basis of the shielding effect of the thiophene ring[13] and comparison with the spectrum of poly(3,4-dihexylthiophene),[15] the peaks at $\delta = 2.56$ and $\delta = 2.79$ were previously estimated to be due to head-to-head (HH) and head-to-tail (HT) configurations, respectively. Our observations are consistent with the previous results and show that the β(2)-methylene resonance splits owing to the difference in the configurations. Furthermore, the intensity ratio of the splitting peaks assignable to the α(1)-methylene protons suggests that PDDT chiefly consists of a HT configuration but contains the proper amount of HH configurations.

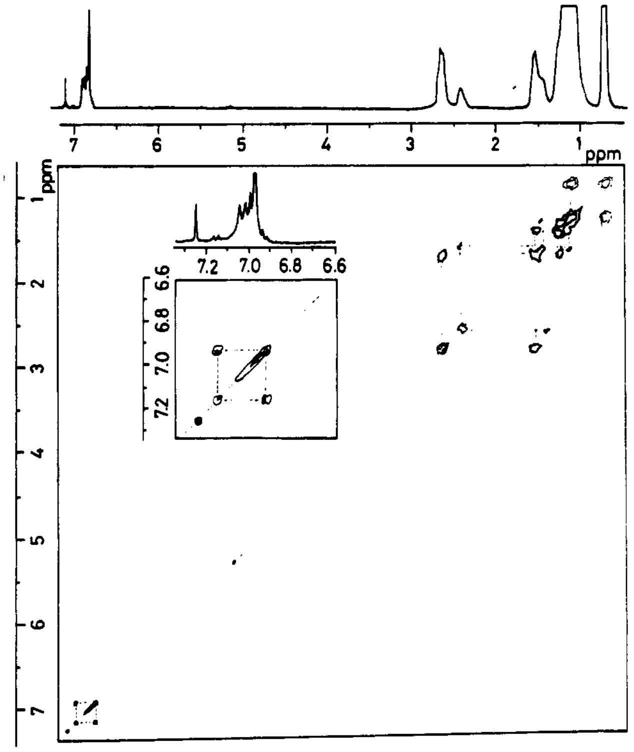


Figure 2. ^{1}H–^{1}H DQF-COSY spectrum of PDDT at 27 °C in chloroform-d. The inset shows an expansion of the aromatic region.

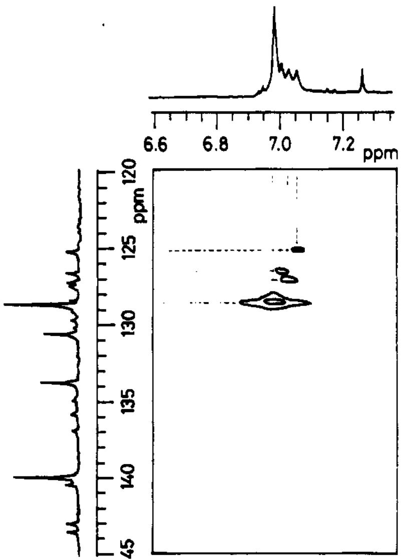
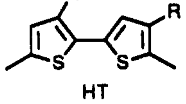
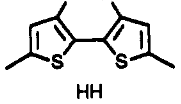


Figure 3. Expanded ^{1}H–^{13}C HETCOR spectrum of PDDT at 27 °C in chloroform-d.

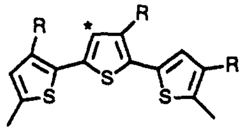


HT

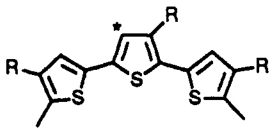


HH

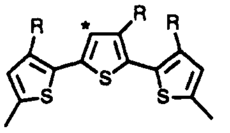
In the region of chemical shifts of aromatic protons, the spectrum in the inset of Figure 1 shows four moderate peaks at $\delta = 6.98, 7.00, 7.02$, and 7.05. The intensity ratios and the chemical shifts of the four peaks did not change over the temperature range 20–50 °C. These peaks show no homonuclear correlation in the ^{1}H–^{1}H DQF-COSY spectrum (the inset of Figure 2). Moreover, the expanded ^{1}H–^{13}C HETCOR spectrum (Figure 3) shows that there are one-to-one correlations between the chemical shifts of these ^{1}H peaks and four ^{13}C peaks of the polymers. The ^{1}H peaks at $\delta = 6.98, 7.00, 7.02$, and 7.05 are correlated with the ^{13}C peaks at $\delta = 128.6, 126.5, 127.1$, and 125.1, respectively. These results indicate that the four proton peaks are assigned to the isolated 4-proton on the successive thiophene ring and arise from different configurations. The four possible configurational triads in PDDT are represented as follows (the asterisk denotes the position under observation):



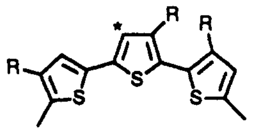
HT–HT



TT–HT



HT–HH



TT–HH

Since the main configuration of PDDT is the HT one noted above, the most intense peak at $\delta = 6.98$ among the four proton peaks would be attributed to the HT–HT configuration. This assignment leads to the conclusion that the HT– and the –HT configurations have peaks due to the 4-proton on the central ring at higher field than the TT– and the –HH configurations, respectively. Therefore, the peaks at the lowest field ($\delta = 7.05$) would be attributable to the TT–HH configuration and the other peaks at $\delta = 7.00$ and 7.02 would be attributed to the HT–HH and the TT–HT configurations.

Interestingly, the splitting peaks that would be attributable to the four configurational triads were also observed for all aromatic carbon resonances in the ^{13}C NMR spectrum as shown in the inset in Figure 3. The chemical shifts are δ = (139.8, 140.3, 142.8, 143.3), (133.7, 134.8, 135.7, 136.7), (130.5, 130.0*, 129.5*, 129.0*, 128.3*, 127.4*), and (128.6, 127.1, 126.5, 125.1), where undefined peaks are denoted with asterisks. The first value in each set is the chemical shift of the most intense peak, which would be assigned the HT–HT configuration. It is difficult to make configurational assignments of the other peaks because of their similar intensities. The most intense peak is located at the lowest field in the first and the second sets, and at the highest field in the third and the forth sets. The peaks in the second and third sets are relatively less intense, suggesting that these peaks are assigned to the 2- and 5-carbons on the rigid main chain. Thus the peaks in the first and forth sets would be assigned to the 3- and 4-carbons, respectively. The peaks due to the HT–HT configuration have fine structures such as shoulders or adjunct peaks, perhaps due to pentad sequences.

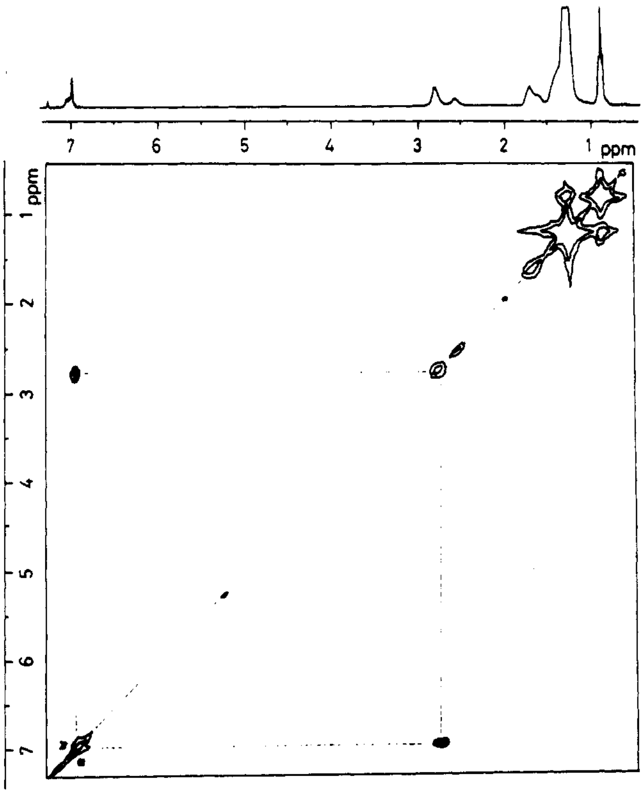


Figure 4. ^{1}H–^{1}H NOE spectrum of PDDT at 27 °C in chloroform-*d*.

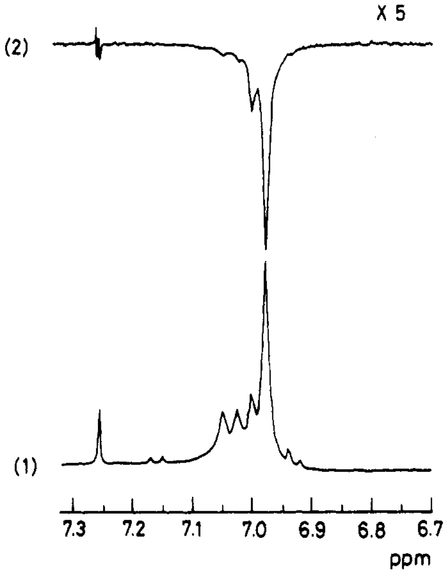


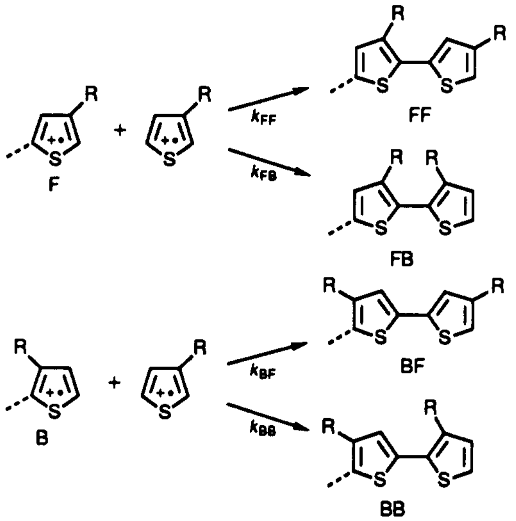
Figure 5. Control spectrum and NOE difference spectrum of PDDT at 27 °C in chloroform-*d*: (1) off-resonance control spectrum without NOE; (2) difference spectrum obtained by preirradiation of the peak at $\delta = 2.79$. The difference spectrum is expanded vertically by a factor of 5 relative to the control spectrum.

In order to assign the four aromatic proton resonances with higher reliability, the ^{1}H–^{1}H NOE and ^{1}H NOE difference spectra were observed (Figures 4 and 5, respectively). It is well-known that signal enhancement by NOE is inversely proportional to the sixth power of the ^{1}H–^{1}H internuclear distance. The shorter the ^{1}H–^{1}H internuclear distance, the more significant the NOE enhancement appears up to the value of the maximum NOE, which is a 50% enhancement.[20] Comparing the HT– and the TT– configurations, the average distance between the 4-proton on the central ring and the $\alpha(1)$-methylene protons on the neighboring ring to the left is clearly shorter in the case of the HT– configuration than of the TT– configuration. The 4-proton resonances of the HT–HT and the HT–HH configurations are expected to show a stronger NOE enhancement for the $\alpha(1)$-methylene proton resonance than the 4-proton resonances of the TT–HT and the TT–HH configurations. The former 4-proton

Table I
Diad and Triad Fractions in the ^{1}H NMR Spectrum of PDDT

	chem shift, ppm		frac found		frac calcd	
config	α-CH_2	arom H	α-CH_2	arom H	α-CH_2	arom H
HH	2.56		0.279		0.296	
HT	2.79		0.721		0.704	
HT–HT		6.98		0.541		0.557
HT–HH		7.00		0.167		0.151
TT–HT		7.02		0.131		0.147
TT–HH		7.05		0.161		0.145

Scheme I[a]



[a] F and B denote the forward and the opposite orientations of monomer units defined for propagating terminal radicals, respectively.

Table II
Relationship between the Sequences and the Configuration (Diad and Triad) and the Expression of Their Fractions

confign[a]	sequence[b]	frac
HT	XFF, BBX	$F_FP_{FF}P_{FF} + F_BP_{BF}P_{FF} + F_BP_{BB} = (\alpha\beta - \beta + 1) + C(\alpha - 1)(\alpha - \beta + 1)$
HH	XFB, FBX	$F_FP_{FF}P_{FB} + F_BP_{BF}P_{FB} + F_FP_{FB} = (1 - \alpha)\beta + C(\alpha - 1)(-\alpha + \beta - 1)$
HT–HT	FFF, BBB	$F_FP_{FF}P_{FF} + F_BP_{BB}P_{BB} = (1 - \beta)^2 + C(\alpha + \beta - 1)(\alpha - \beta + 1)$
HT–HH	FFB, FBB	$F_FP_{FF}P_{FB} + F_FP_{FB}P_{BB} = C(\alpha - \beta + 1)(1 - \alpha)$
TT–HT	BFF, BBF	$F_BP_{BF}P_{FF} + F_BP_{BB}P_{BF} = (\alpha - \beta + 1)\beta + C(-\alpha + \beta - 1)\beta$
TT–HH	BFB, FBF	$F_BP_{BF}P_{FB} + F_FP_{FB}P_{BF} = (1 - \alpha)\beta$

[a] These are related to the assignment for NMR peaks. [b] F and B denote the orientation of monomer units defined for propagating terminal radicals as mentioned in the text and Scheme I. X represents both F and B, here.

resonances would have a pronounced NOE for only the α(1)-methylene proton resonance due to the HT configuration in considering the bond rotation. In Figure 4, a pair of cross peaks between the α(1)-methylene proton resonance ($\delta = 2.79$) due to the HT configuration and the aromatic proton resonances reflect the NOE and the other cross peaks represent the coupling.

The ^{1}H-NOEDS (Figure 5) provided precise information on the configurations of PDDT. The ^{1}H-NOEDS was obtained by subtraction as the peak of $CHCl_3$ is canceled. When the α(1)-methylene proton resonance due to the HT configuration ($\delta = 2.79$) was presaturated, well-defined and negative NOEs were observed for the peaks at $\delta = 6.98$ and 7.00. These results confirm the peak at $\delta = 6.98$ to be assigned to the HT–HT configuration and suggest that the peaks at $\delta = 7.00$ and 7.02 are assigned to the HT–HH and TT–HT configurations, respectively.

Further, the spectrum in the inset of Figure 1 shows two weak doublet peaks at $\delta = 6.93$ and 7.16. These peaks show a strong correlation in the ^{1}H–^{1}H DQF-COSY spectrum (Figure 2). The coupling constant ($J = 5.0$ Hz) and the chemical shifts were consistent with the ^{1}H NMR data of 3,3′-dimethyl-2,2′-bithiophene.[21] Therefore these doublet peaks are assigned to the 4- and 5-protons on the terminal 2-substituted 3-alkylthiophene rings. Peaks due to the other terminal units were not detected.

Propagation of the Polymerization. The relative intensities for each α(1)-methylene and aromatic proton resonance derived from the diad and the triad fractions are listed in Table I. The observed fractions of diad and triad may be interpreted in terms of the statistics of the polymerization involving the propagation steps in Scheme I. It has been suggested that the electrochemical polymerizations of polypyrroles and polythiophenes take place by the condensation of the radical cation of the monomer with the radical cation of the propagating terminal.[22] In Scheme I, k_{XY} is the rate constant of step XY. We define and use here the fraction F_X of X as the radical cation of propagating terminal with the relation that $F_F + F_B = 1$ and the additional probability P_{XY} of step XY with the relations that $P_{FF} + P_{FB} = 1$ and $P_{BF} + P_{BB} = 1$. Then we introduce the independent parameters C, α, and β as follows:

$$F_F = C$$

$$P_{FF} = k_{FF}/(k_{FF} + k_{FB}) = \alpha$$

$$P_{BF} = k_{BF}/(k_{BF} + k_{BB}) = \beta$$

All fractions of the diad and triad such as the HT and/or HT–HT configurations, are expressed with two fractions, F_X's, and four additional probabilities, P_{XY}'s, as listed in Table II. Here we should draw attention to the fact that the term diad, i.e., the HT or the HH configuration in this paper, relates to the complex triad sequences as listed in Table II. We combined the theoretical expressions with the observed fractions of diad and triad, using the least-squares analysis method. Taking into consideration that the main terminal units are 2-substituted 3-alkylthiophene rings expressed here with monomeric sequence B (i.e., the fraction of B is larger than that of F), the values of α, β, and C were determined to be 0.190, 0.179, and 0.184, respectively. For comparison, the diad and triad distributions calculated with the values of α, β, and C are also given in Table I. The calculated fractions of diad and triad are in good agreement with the observed ones with the standard deviation of 0.018. This fitting confirms the assignments of NMR peaks in turn. P_{FF}, P_{BF}, and F_F have almost the same value, indicating the probabilities of forming terminal F and B sequences are independent of the configuration of the chain already formed. These results mean that the generation of the chain is a Bernoulli-trial process. The polymerization of 3-dodecylthiophene is considered to proceed with the predominant formation of B (82%).

The relative intensity of the peaks due to the terminal unit and the value of F_F lead to the result that the average degree of polymerization of PDDT is 140. This value is sufficiently large to adopt the statistical estimation for the propagation process and is in fair agreement with the values (90 and 150) determined previously by vapor phase osmometry[23] and gel permeation chromatography.[5]

References and Notes

(1) Brédas, J. L.; Street, G. B. *Acc. Chem. Res.* **1985**, *18*, 309.

(2) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1988**, *88*, 183.
(3) Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* **1986**, 873.
(4) Jen, K. Y.; Miller, G. G.; Elsenbaumer, R. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1346.
(5) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212.
(6) Watanabe, I.; Hong, K.; Rubner, M. F.; Loh, I. H. *Synth. Met.* **1989**, *30*, C473.
(7) Sato, M.; Okada, S.; Matsuda, H.; Nakanishi, H.; Kato, M. *Thin Solid Films* **1989**, *179*, 429.
(8) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1071.
(9) Yoshino, K.; Love, P.; Onoda, M.; Sugimoto, R. *Jpn. J. Appl. Phys., Part 2* **1988**, *27*, L2388.
(10) Yoshino, K.; Nakajima, S.; Sugimoto, R. *Jpn. J. Appl. Phys., Part 2* **1988**, *27*, L454.
(11) Sato, M.; Tanaka, S.; Kaeriyama, K. *Makromol. Chem.* **1987**, *188*, 1763.
(12) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J. *Synth. Met.* **1987**, *22*, 79.
(13) Sato, M.; Shimizu, T.; Yamauchi, A. *Makromol. Chem.* **1990**, *191*, 313.
(14) Love, P.; Sugimoto, R.; Yoshino, K. *Jpn. J. Appl. Phys., Part 2* **1988**, *27*, L1562.
(15) Leclerc, M.; Diaz, F. M.; Wegner, G. *Makromol. Chem.* **1989**, *190*, 3105.
(16) Mirau, P. A.; Bovey, F. A. *Macromolecules* **1986**, *19*, 210.
(17) Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *38*, 3347.
(18) Akiyama, M. J. *Mol. Spectrosc.* **1972**, *43*, 226.
(19) Hotta, S.; Hosaka, T.; Soga, M.; Shimotsuma, W. *Synth. Met.* **1984/1985**, *10*, 95.
(20) Noggle, J. H.; Schirmer, R. E. *The Nuclear Overhauser Effect: Chemical Applications*; Academic Press: New York, London, 1971.
(21) Krishe, B.; Helberg, J.; Lija, C. *J. Chem. Soc., Chem. Commun.* **1987**, 1476.
(22) Diaz, A. F.; Bargon, J.; Tourillon, G. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1, pp 81, 293.
(23) Sato, M.; Tanaka, S.; Kaeriyama, K. *Synth. Met.* **1987**, *18*, 229.

Registry No. PDDT (homopolymer), 104934-53-4; DDT, 104934-52-3.