Regiocontrolled Synthesis of Poly(3-alkylthiophenes) Mediated by Rieke Zinc: Their Characterization and Solid-State Properties

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Abstract: A systematically regiocontrolled synthesis of poly(3-alkylthiophenes) (P3AT) mediated by Rieke zinc is reported. Rieke zinc undergoes oxidative addition to 2,5-dibromo-3-alkylthiophene or 2-bromo-5-iodo-3-alkylthiophene regioselectively to afford 2-bromo-5-(bromozincio)-3-alkylthiophene (**2**) or 2-bromo-5-(iodozincio)-3-alkylthiophene (**10**). The intermediate **2** or **10** can be polymerized catalytically to a series of regiospecific poly(3-alkylthiophenes) using different catalysts. The regioregularity of the polymer chain is solely controlled by the structure of the catalyst. An almost completely regioregular head-to-tail (HT) P3AT (**4**) is obtained by using Ni(DPPE)Cl₂ ([1,2-bis-(diphenylphosphino)ethane]nickel(II) chloride). Use of Pd(DPPE)Cl₂ leads to a reduction in the regioregularity (70: 30 HT/HH), while using Ni(PPh₃)₄ also leads to a much reduced regioregular P3AT (63:35 HT/HH). A totally regiorandom (50:50 HT/HH) P3AT (**5**) is afforded by using Pd(PPh₃)₄. The poly(3-butylthiophene) **4a** is a 97% HT regioregular polymer. Other poly(3-alkylthiophenes) (alkyl = hexyl (**4b**), octyl (**4c**), decyl (**4d**), dodecyl (**4e**), and tetradecyl (**4f**)) are regioregular P3ATs with the HT linkage larger than 98.5% based on NMR analysis. Electronic absorption, X-ray diffraction, and crossed polarizing micrograph studies show that the cast films of the regioregular P3ATs (**4**) are self-organized, crystalline, flexible, and bronze-colored films with a metallic luster, while that of the regiorandom P3ATs (**5**) are amorphous and orange-colored films. The regioregular P3ATs exhibit a small bandgap (1.7 eV) which is 0.4 eV lower than that of regiorandom P3ATs (2.1 eV). Regioregular HT P3ATs have considerably improved electroconductivity and other physical properties over regiorandom P3ATs.

Introduction

Of the many conjugated polymers, poly(3-alkylthiophenes) (P3ATs) have been found to be an unusual class of polymers with good solubility, processability, environmental stability, electroactivity, and other interesting properties.[1] Practical and potential applications of P3ATs include rechargeable battery electrodes, electrochromic devices, chemical and optical sensors,[2a] light-emitting diodes,[2b-c] molecular-based devices, such as microelectrochemical amplifiers[2d] and field-effect transistors,[2e] and nonlinear optical materials.[2f-h] With such a wide range of potential applications, they have attracted interest, both from synthetic considerations as well as from material science.

Since the discovery of insoluble polythiophene and the

determination of its electroconductivity in 1980,[3] many studies have been completed to improve the synthetic feasibility, chemical, and physical properties of this conjugated polymer. A milestone step in the development of polythiophene occurred in 1985 when the poly(3-alkylthiophene), which was a soluble, processable, and stable polymer, was achieved by introducing an alkyl group into the β-position of the thiophene ring.[4] Three general synthetic methods for polymer synthesis were developed. These included electrochemical polymerization,[5] oxidative polymerization of 3-alkylthiophene by oxidants such as FeCl₃,[6] and polymerization by catalyzed dedihalogenation of 2,5-dihalo-3-alkylthiophene, such as nickel-catalyzed coupling of thiophene Grignard reagents[4] or dihalothiophene monomers.[7] An important challenge remained, that being the development of method which would yield regioregular P3ATs.

Little work has been done for the systematically structure-controlled synthesis of conjugated polymers. One elegant example is the conformation-controlled synthesis of polyacetyl-

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ene. Shirakawa et al.[8] have succeeded in synthesizing the all-cis and all-trans isomers of polyacetylene, and have developed techniques for controlling the ratio of cis to trans isomers in the product. The trans-polyacetylene polymer has quite different physical properties and conductivity than does the cis isomer. Furthermore, the Naarmann's conformation-unique polyacetylene[9] has fewer sp[3] defects and less cross-linking in the polymer chain and leads to a large improvement in conductivity. It is clear, that the higher order and regular polymer chain resulted in higher conductivity, nonlinearity, and other improved physical properties of the material.

For poly(3-alkylthiophene), the 3-alkyl substituent in a thiophene ring can be incorporated into a polymer chain with two different regioregularities: head-to-tail (HT) and head-to-head (HH). Furthermore, this results in four triad regioisomers in the polymer chain: HT−HT, HT−HH, TT−HT, and TT−HH triad. Recent research on poly(3-alkylthiophene) and other

HT–HT   TT–HT

HT–HH   TT–HH
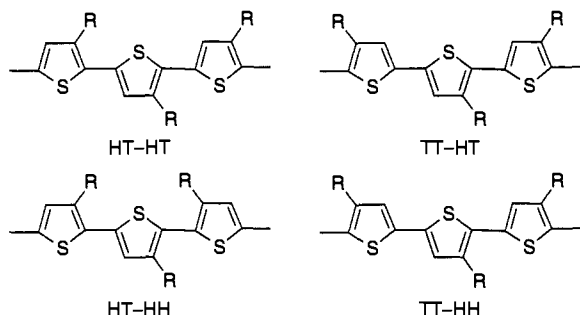
conjugated polymers has concentrated on the regularity and structure of the polymer chain.[10−14] The HT regiospecific polymers have improved electroconductivities, optical nonlinearity, and magnetic properties over regiorandom polymers, in which more sterically hindered HH linkages can cause defects in the conjugated polymer chain and reduce the desired physical properties of the material.[11−13,15,16] Currently, our group and others have developed different methods for the synthesis of regioregular HT poly(3-alkylthiophenes). One approach in-

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Scheme 1. Regiocontrolled Synthesis of Poly(3-alkylthiophene) Mediated by Zn*
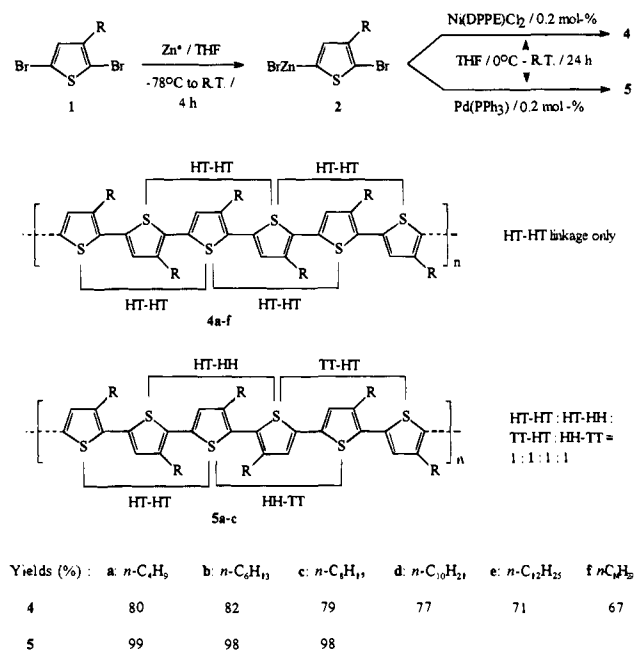
volves the synthesis of HT regioregular P3ATs by a Ni-catalyzed coupling polymerization of a regiospecific thiophene Grignard reagent.[15] Our methodology involves a regiocontrolled synthesis for a series of regiospecific P3ATs, including HT regioregular P3ATs and completely regiorandom HT-HH P3ATs, as well as other regioisopolymers with a variety of degrees of regioregularity on the percentage of the HT linkage in the polymer chain. The reactions involve Ni- or Pd-catalyzed coupling polymerizations of regiospecific thiophene organozinc reagents.[16] These organozinc reagents were formed by reacting Rieke zinc (Zn*) with 2,5-dihalothiophenes (Scheme 1). Herein we report the detailed results of the regiocontrolled syntheses, mechanistic implications of these polymerizations, polymer characterizations, and solid-state properties, including spectroscopic studies, molecular weight determinations, polarizing microscopy, X-ray diffraction, and the crystallinity of the materials.

Results and Discussion

Regiocontrolled Synthesis of Poly(3-alkylthiophenes) Mediated by Rieke Zinc. Rieke zinc (Zn*)[16] underwent direct oxidative addition to 2,5-dibromothiophene chemoselectively to afford 2-(bromozincio)-5-bromothiophene quantitatively.[16c] Significantly, no bis(bromozincio)thiophene was formed:
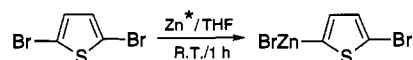

We further examined the reactions of 2,5-dibromo-3-alkylthiophene with Zn* and found that the Zn* also underwent oxidative addition to 2,5-dibromo-3-alkylthiophene regioselectively, especially at low temperature, to afford the regioisomer 2-bromo-5-(bromozincio)-3-alkylthiophene (**2**) predominantly and 5-bromo-2-(bromozincio)-3-alkylthiophene (**3**) as a very minor regioisomer (Table 1).

Zn* undergoes oxidative addition to the C−Br bond primarily at the 5-position of **1**. The selectivity of the oxidative addition is enhanced at lower temperature (Table 1): the lower the reaction temperature, the higher the regioselectivity. At −78

Regiocontrolled Synthesis of Poly(3-alkylthiophenes)

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Table 1. Regioselectivities of the Reactions of Zn* with 2,5-Dibromo-3-alkylthiophenes

R	T/t	2/3 (%)[a]
n-hexyl	R.T./1 h	90:10
n-hexyl	−45 °C to R.T./4 h	93:7
n-hexyl	−78 °C to R.T./4 h	97:3
n-butyl	−78 °C to R.T./4 h	94:6
n-hexyl	−78 °C to R.T./4 h	97:3
n-octyl	−78 °C to R.T./4 h	98:2
n-decyl	−78 °C to R.T./4 h	98:2
n-dodecyl	−78 °C to R.T./4 h	98:2
n-tetradecyl	−78 °C to R.T./4 h	98:2

[a] The regioselectivity was identified by ^{1}H NMR analysis of the crude reaction mixture after quenching with a saturated NH_4Cl solution.

Scheme 2. Regiocontrolled Synthesis of Poly(3-alkylthiophenes) Starting with 3-Alkyl-2-bromo-5-iodothiophenes
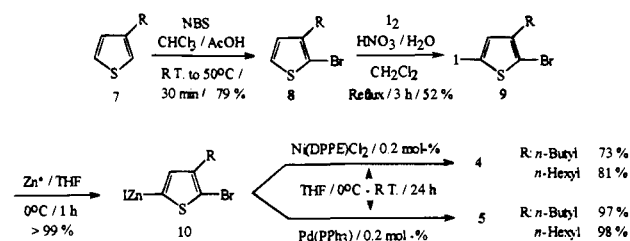
°C, the regioselectivity was as high as 97−98% for most cases. The total yield for two regioisomers **2** and **3** was larger than 99% by gas chromatography analysis in all cases. This novel regioselective reaction of Zn* with dihalothiophenes and other dihaloarylenes[16c] represents a significant new approach for the synthesis of unsymmetrical heterocyclic compounds and arylene derivatives,[16d] particularly since organozinc reagents are stable and are formed under mild conditions with the tolerance of many functional groups.[17] The reaction with Zn* is an indispensable step to fulfill the regiospecific polymerizations. The polymerizations are performed in a simple one-pot reaction. **2** (and the very minor isomer **3**) was treated *in situ* either with Ni-(DPPE)Cl₂ ([1,2-bis(diphenylphosphino)ethane]nickel(II) chloride) to afford a completely regioregular head-to-tail P3AT **4** or with Pd(PPh₃)₄ to afford a totally regiorandom P3AT **5**.[18] The turnover number of the catalysts was quite high since only a very small amount (0.2 mol %) of catalyst was used and high yield of product was achieved in these polymerizations. The use of the small amount catalyst also facilitated the purification of the polymer products.

An alternate and efficient synthesis for **4** and **5** is shown in Scheme 2. 3-Alkyl-2-bromo-5-iodothiophenes (**9**) were synthesized by the regiospecific bromination,[19a] then the iodina-

Table 2. Regioregularity of P3ATs Controlled by Different Catalysts[a]

catalyst structure	initialized species of the catalyst	resulting P3ATs	regioregularity (%) HT/HH
Ni(DPPE)Cl₂		**4**	HT > 98.5
Pd(DPPE)Cl₂		**11**	70:30
Ni(PPh₃)₄		**12**	65:35
Pd(PPh₃)₄		**5**	50:50

[a] The reaction conditions are all the same as shown in Scheme 1 (catalyst amount: 0.2 mol %; 0 °C to RT for 24 h).

tion,[20] followed by the alkylation[21] of 3-bromothiophene. Rieke zinc oxidatively inserted into the C−I bond to afford the regiospecific 3-alkyl-2-bromo-5-(iodozincio)thiophenes **10** exclusively. **10** was treated either by Ni(DPPE)Cl₂ to afford **4** or by Pd(PPh₃)₄ to afford **5**.

Mechanistic Implications of the Polymerizations. The polymerizations described in Schemes 1 and 2 not only resulted in two extremely regiospecific P3ATs **4** and **5**, but moreover, the reactions can be expanded to a more diversified regiocontrolled syntheses for a series of different regiospecific poly(3-alkylthiophenes) by choosing a different catalysts (Table 2).

The mechanism of Ni- and Pd-catalyzed cross-coupling organozinc compounds with organic halides has been extensively investigated[22,18c] Yamamoto and co-workers[23] have examined the mechanism of the Ni- and Pd-catalyzed cross-coupling polymerization of dihaloarylenes. The polymerizations were performed by a series of oxidative addition, transmetallation (or disproportionation[23c]), and reductive elimination steps. Transmetalation (or the disproportionation) for these reactions was the rate-determining step. In our research, it was found that the degree of regioregularity of P3AT was a function of both the metal (Ni vs Pd) and the ligands (DPPE vs PPh₃) of the catalysts in polymerizations. Using Ni(DPPE)Cl₂ led to a completely regioregular HT coupling P3AT. Switching the ligand of the catalyst from DPPE to a more liable ligand PPh₃ (as Ni(PPh₃)₄) led to a reduction in the regioregularity (65:35 HT/HH) of the P3AT, while switching a larger size atom Pd in the catalyst (as Pd(DPPE)Cl₂) also led to a much reduced regioregular P3AT (70:30 HT/HH). A totally regiorandom P3AT (50:50 HT/HH) was obtained when both the metal and the ligand were changed in the catalyst [Pd(PPh₃)₄]. The smaller ionic radius of Ni^{2+} vs Pd^{2+} along with the higher steric demands for DPPE indicated that the degree of stereoregularity was controlled by steric congestion of the transmetalation (or disproportionation) step. The polymerizations were also per-

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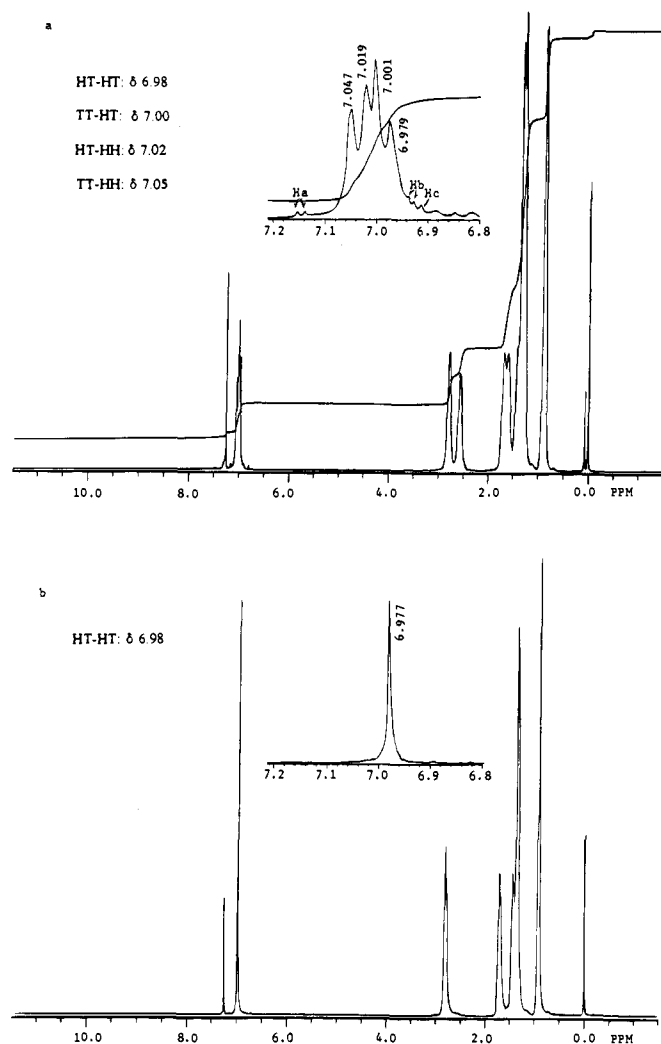
Figure 1. ¹H NMR spectra of (a) regiorandom P3HT **5b** (1:1:1:1 HT−HT/HT−HH/TT−HT/TT−HH) and (b) regioregular P3HT **4b** (HT linkage >98.5%).

formed by a series of transmetalation (or disproportionation), reductive elimination, followed by oxidative addition.

Spectroscopic Studies and Other Characterization

NMR Spectroscopy. All polymers were studied by solution 500-MHz ¹H NMR and 125-MHz ¹³C NMR spectroscopy. The ¹H and ¹³C NMR spectra of P3ATs provide sensitive probes for the substitution pattern in the polymer backbone.[11,24,25] The proton in the 4-position of the thiophene ring bears four different chemical environments in a mixture of the four possile triad regioisomers (Figure 1a). These four chemical shift distinct protons are uniquely distinguishable by NMR spectroscopy. This is clearly demonstrated in the ¹H NMR spectra of **5** (for example, Figure 1a for polymer **5b**, regiorandom P3HT). The observed spectra are consistent with a totally random (1:1:1:1 HT−HT (δ, 6.98)/TT-HT (7.00)/HT-HH (7.02)/TT-HH (7.05) linkages based on NMR integration) mixture of the four triad structures depicted. Previous reports[24,26] showed that the α-methylene protons of the alkyl group could be resolved by two different diads: head-to-tail (HT) and head-to-head (HH). We found even β-methylene protons could be resolved by these

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diads. The expanded ¹H NMR spectrum of polymer **5b** (Figure 2a) also showed the polymer had a regiorandom chain structure with an equal distribution of HT and HH linkages (for α-methylene protons, 1:1 HT (δ, 2.80)/HH (2.58); for β-methylene protons, 1:1 = HT (δ, 1.72)/HH (1.63)). All of the thiophene carbons (16 peaks are theoretically possible) can be resolved in the mixture of the four triad regioisomers. This is clearly demonstrated, again, in the ¹³C NMR spectra of regiorandom P3ATs **5** (see Figure 3a for **5a**). The observed spectra are consistent with a equal distribution of the four triad structures (HT−HT, TT−HT, HT−HH, TT−HH).[16a] (Table 3).

In contrast, only one sharp band for the thiophene proton, which denotes the HT−HT structure, is observed in the ¹H NMR spectra of **4** (see Figure 1b for regioregular P3HT **4b**). The spectra did not indicate the presence of other irregular linkages as observable within the NMR resolution in this region. The expanded ¹H NMR spectrum in the α-methylene proton region was indicative of >98.5% for the HT linkage, and in the β-methylene proton region only the HT linkage was present (Figure 2b). In the ¹³C NMR spectra, only four sharp bands for the thiophene carbon atoms (one band for each carbon), which also denotes the HT−HT structure, are observed (Figure 3b for **4b**, and Table 3). The NMR data analyses and the signal-to-noise ratio characterized that the polymer **4b** was a structurally homogeneous, regioregular poly(3-hexylthiophene) containing at least 98.5% HT linkage in the polymer chain.

By analyses of NMR data, polymers **4**, which are catalyzed by Ni(DPPE)Cl₂, are regioregular HT P3ATs with at least 98.5% of HT linkage when the alkyl group is hexyl **4b**, octyl **4c**, decyl **4d**, dodecyl **4e**, and tetradecyl **4f**, and with 97% of the HT linkage when the alkyl group is butyl **4a**, in the polymer chain. Polymers **5**, formed via Pd(PPh₃)₄ catalysis, are regiorandom P3ATs with a equal distribution of different regioisomers in the polymer chain (1:1:1:1 HT−HT/TT−HT/HT−HH/TT−HH or 1:1 HT/HH). Polymer **11**, catalyzed by Pd(DPPE)Cl₂, is a P3HT with 70% HT and 30% HH linkage in the polymer chain. Polymer **12**, catalyzed by Ni(PPh₃)₄, contains 65% HT and 35% HH. The NMR analyses confirm that our methodology is a regiocontrolled synthesis for a series of regiospecific P3ATs.

The two doublet peaks (7.15, 6.93 ppm) and one singlet peak at 6.91 ppm (Figure 1a) are assigned as the terminal ring protons Ha, Hb, and Hc in polymer chain.[13a] The percentage of these terminal protons in polymer chain is less than 1% based on the NMR integration.
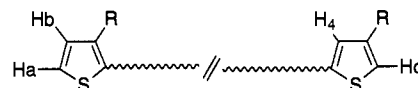
Infrared Spectroscopy. The principal IR absorption bands observed in all P3ATs samples and their assignments are listed in Table 4. All of the P3ATs have very similar infrared spectra with most peaks at essentially the same frequencies but with small differences in intensity or in energy for some peaks.

The butyl hexyl, octyl, decyl, dodecyl, and tetradecyl moieties in the regioregular and regiorandom P3ATs show absorption peaks that are in close correspondence to one another. The ring stretching vibrations in the vicinity of 1520−1450 cm⁻¹, the aromatic C−H stretching vibrations at about 3055 cm⁻¹, and the aromatic C−H out-of-plain vibrations at 820−830 cm⁻¹ are characteristic of 2,5-disubstituted-3-alkylthiophene.[27] An obvious difference was noted for the C−H out-of-plain vibrations. Regioregular HT-P3ATs (**4a−f**) have the absorption peaks at

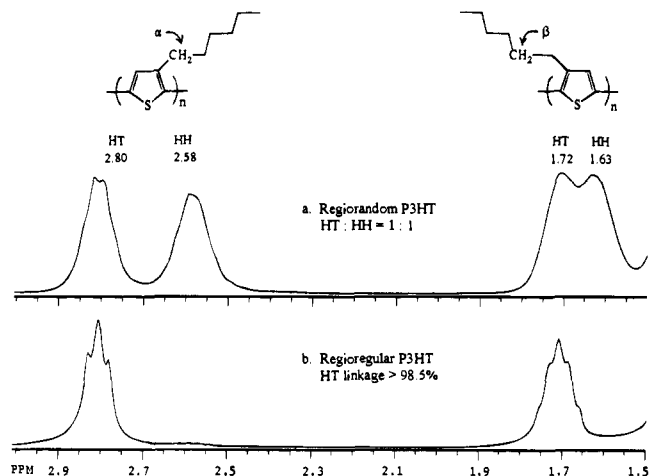(27) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212−215.

Figure 2. Expanded ^{1}H NMR spectra of (a) regiorandom P3HT **5b** (1:1 HT/HH) and (b) regioregular P3HT **4b** (HT linkage >98.5%).
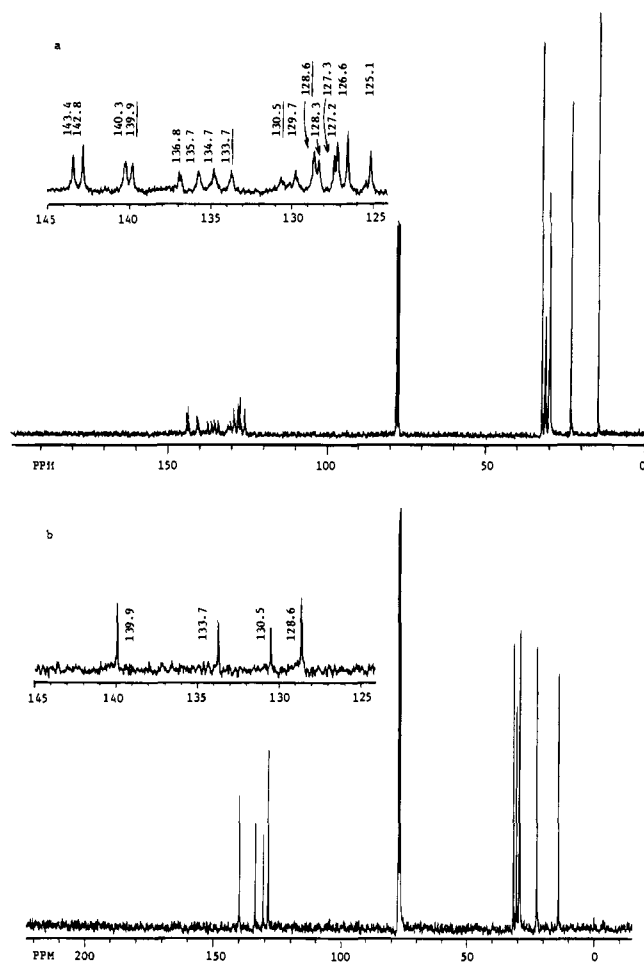

Figure 3. ^{13}C NMR spectra of (a) regiorandom P3HT **5b** (1:1:1:1 HT−HT/HT−HH/TT−HT/TT−HH) and (b) regioregular P3HT **4b** (HT linkage only).

820−822 cm^{-1}, while regiorandom P3ATs (**5a−c, 11, 12**) have peaks at 827−829 cm^{-1} (Table 4).

Another clear difference in IR spectra for regioregular and regiorandom P3ATs is the intensity ratio of the symmetric ring stretch at ∼1460 cm^{-1} to the asymmetric ring stretch at ∼1510 cm^{-1} (I_{sym}/I_{asym}). Previous analysis[28] of the vibrational spectra of polythiophenes and oligomers showed that the ratio I_{sym}/I_{asym}

Table 3. NMR Chemistry Shift (ppm) of ^{1}H and ^{13}C in Different Regiostructures

	HT−HT	TT−HT	HT−HH	TT−HH
C2	130.5	128.3	129.7	127.2
C3	139.9	142.8	140.3	143.4
C4	128.6	126.6	127.3	125.1
C5	133.7	135.7	134.7	136.8
H4	6.98	7.00	7.02	7.05

	head-to-tail	head-to-head
α-methylene-H	2.80	2.58
β-methylene-H	1.72	1.63

was indicative of the conjugation length in the polymer backbone. Longer conjugation length in the polymer backbone results in smaller ratio of I_{sym}/I_{asym}. The ratios of our regioregular P3ATs (**4a−f**) are 6−9, which are only about half of the ratios (15−20) of the regiorandom P3ATs (**5a−c, 11, 12**). The analysis is consistent, qualitatively, with a longer conjugation length of regioregular head-to-tail P3ATs than that of regiorandom P3ATs, and is consistent with the UV−vis results.

Electronic (UV−Vis) and Fluorescence Spectroscopy. The UV−vis and fluorescence data of poly(3-alkylthiophenes) in chloroform are listed in Table 5. Typical UV−vis and fluorescence spectra are shown in Figure 4 (see Figure 4a for regioregular P3HT **4b**, and Figure 4b for regiorandom P3HT **5b**).

The λ_{max} data of UV−vis spectra showed that all the regioregular HT P3ATs (**4a−f**) had lower $\pi−\pi^*$ transition energy than that of regiorandom P3ATs (**5a−c, 11, 12**). The regioregular P3ATs have a maximum absorption wavelength at ∼450 nm ranging from 449 to 456 nm, which are 21−28 nm longer than regiorandom P3ATs with a characteristic λ_{max} of 428 nm. This suggests that in solution the regioregular head-to-tail polymer chain has a more rod-like[29] conformation with longer conjugation length,[14c] while regiorandom polymer chains have a more coil-like[29] conformation with shorter conjugation length. The prepared regioregular HT P3ATs have the absorption maximum significantly longer than do the other P3ATs[1i,27,29] and even than that of other regioregular HT P3ATs.[15b]

The chloroform solutions of regioregular P3ATs give a bright-yellow fluorescence with the maximum emission wavelength of 570 nm, corresponding to the onset of $\pi−\pi^*$ transition of the electronic absorption spectra. The solutions of regiorandom P3ATs give a greenish-yellow fluorescence with the maximum emission wavelength of 550 nm (20 nm blue shift from 570 nm) which is also corresponding to the onset of their absorption spectra.

Molecular Weight Chromatography. The molecular weights and corresponding polydispersity index, which are determined (relative to polystyrene standard) by gel permeation chromatography in THF, are listed in Table 6.

The molecular weight and molecular weight distribution of the polymer products obtained by different workup procedures were determined in order to find out the efficiency of the polymerization and the catalyst. The polymer was precipitated with a solution of 2 N HCl/MeOH (2:1 by volume) after the reaction was completed. The polymer was purified by re-precipitation from chloroform solution upon addition of metha-

(28) Furukawa, Y.; Akimoto, M.; Harad, I. *Synth. Met.* **1987**, *18*, 151−156.

(29) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25*, 1071−1078.

Table 4. Comparison of IR Band Positions (cm^{-1}) and Their Assignments for Poly(3-alkylthiophenes)

P3AT	HT/HH	aromatic C—H str	aliphatic C—H str	ring str	methyl def	aromatic C—H out-of-plain	methyl rock
P3BT, **4a**	97/3	3057	2951, 2925, 2858	1508, 1452	1377	822	742
P3HT, **4b**	HT >98.5%	3055	2954, 2925, 2856	1510, 1454	1377	820	725
P3OT, **4c**	HT >98.5%	3057	2954, 2921, 2850	1510, 1454	1377	820	721
P3DT, **4d**	HT >98.5%	3057	2954, 2926, 2852	1510, 1466	1377	820	721
PDDT, **4e**	HT >98.5%	3057	2954, 2920, 2850	1512, 1468	1377	822	719
PTDT, **4f**	HT >98.5%	3055	2952, 2920, 2850	1510, 1466	1377	822	719
P3BT, **5a**	50/50	3053	2954, 2927, 2867	1514, 1464	1377	829	729
P3HT, **5b**	50/50	3053	2953, 2925, 2854	1514, 1464	1377	827	725
P3OT, **5c**	50/50	3055	2953, 2924, 2852	1516, 1464	1377	829	721
P3HT, **11**	70/30	3057	2954, 2925, 2854	1514, 1464	1377	827	725
P3HT, **12**	65/35	3053	2954, 2925, 2854	1516, 1464	1377	827	725

Table 5. Comparison of Solution UV—Vis and Fluorescence Data of Poly(3-alkylthiophenes)^a

regular	PEBT, **4a**	P3HT, **4b**	P3OT, **4c**	P3DT, **4d**	PDDT, **4e**	PTDT, **4f**
λ_{max} (nm)	449 (569)	456 (570)	451 (570)	447 (570)	453 (570)	450 (570)
random	P3BT, **5a**	P3HT, **5b**	P3OT, **5c**	P3HT, **11**	P3HT, **12**	
λ_{max} (nm)	428 (548)	428 (550)	428 (549)	429 (550)	428 (550)	

^{a} Solvent: CHCl$_3$; fluorescence data in parentheses.
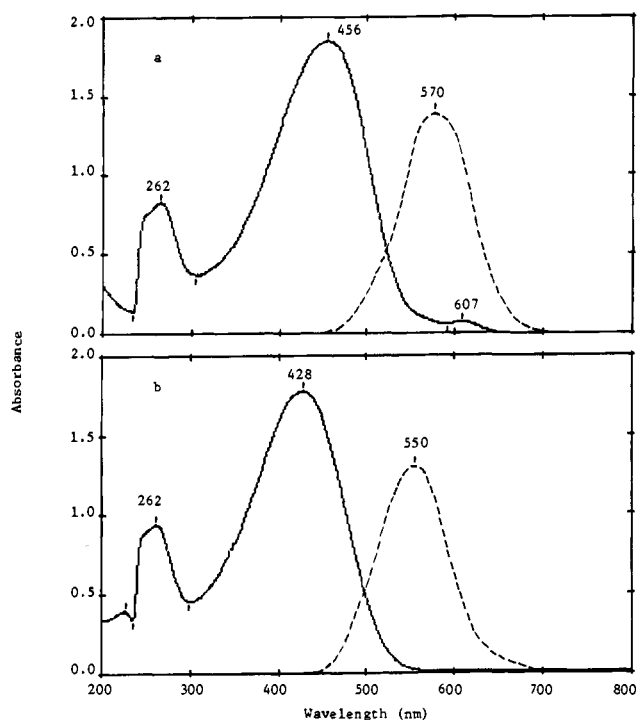
Figure 4. UV—vis and fluorescence spectra of (a) regioregular HT P3HT **4b** and (b) regiorandom P3HT **5b** of CHCl$_3$ solution. (- - -): UV—vis; (- - -): fluorescence.

Table 6. Molecular Weight and Polydispersity of Poly(3-alkylthiophenes) Determined by GPC (Relative to Polystyrene Standard)

polymer	$\bar{M}_w$	$\bar{M}_n$	polydispersity index
random P3HT, **5b**	24 400	5 650	4.32
regular P3HT, **4b** (before extraction)	15 000	4 130	3.63
regular P3HT, **4b** (after extraction)	37 680	25 500	1.48
regular P3OT, **4c**	39 210	34 580	1.13
regular P3DT, **4d**	42 220	30 480	1.39
regular PDDT, **4e**	49 210	34 650	1.42
regular PTDT, **4f**	44 190	30 230	1.46

nol. The yields of polymers are almost quantitative (90—98%) at this point. The resulting polymers were repurified by Soxhlet extractions with methanol for 24 h and then with hexane for 24 h. The yields are about 70—80% after extraction (see Scheme 1 for polymer **4**). The polymer samples without extraction are essentially the same as the polymer samples with extraction since they have the same characterization of NMR, FTIR, and UV— vis. Both samples gave satisfactory elemental analysis data, but the molecular weight and molecular weight distribution were quite different based on GPC analysis. Polymer samples, before extraction, had a much lower molecular weight and a wider molecular weight distribution than that of a sample after extraction. Polymer **4b**, for example, had $\bar{M}_w = 1.50 \times 10^4$ and $\bar{M}_n = 4.13 \times 10^3$ with polydispersity index $= 3.63$ before extraction. The $\bar{M}_n$ corresponded to 25 repeat units per chain (the degrees of the polymerization were estimated versus

polystyrene standards). The molecular weight was sharply increased ($\bar{M}_w = 3.77 \times 10^4$, and $\bar{M}_n = 2.55 \times 10^4$), and the molecular weight distribution was strikingly narrowed (polydispersity index $= 1.48$) with the $\bar{M}_n$ corresponding to 154 repeat units per chain after extraction. The analysis indicated that the monomers were cross-coupled almost quantitatively in the polymerization reaction with 70—80% of the monomers reaching the degree in terms of "polymer". About 20% of the monomers were only coupled to the degree of oligomers, which are soluble in hot hexane with essentially the same regiostructure as the polymer.

Solid-State Properties

X-ray Diffraction. In contrast to other P3ATs where the microcrystallization and orientation of the polymers were induced by electric poling or mechanical stretching, the regioregular HT P3ATs are polycrystalline and self-orienting polymers. The self-assembly properties of conjugated alkylthiophene oligomers were previous reported by Garnier et al.[2e] The self-orienting properties of regioregular P3ATs was first reported by McCullough et al.[15c] The X-ray structural studies of P3ATs were well established by Winokur and co-workers.[30] The studies provided, at the microscopic level, insights on the molecular organization, which necessarily impacts any comprehensive evaluation of electronic properties of poly(3-alkylthiophenes).

The simple cast films of all our regioregular HT P3ATs (**4a**— **f**) solutions (the solvent can be chloroform, methylene chloride,

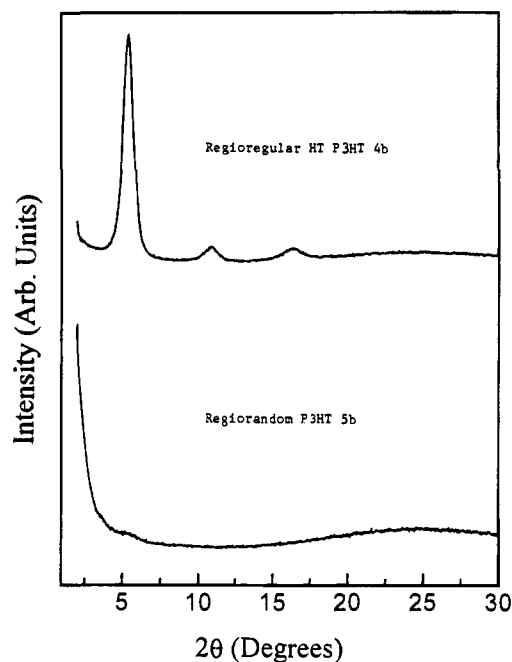(30) Winokur, M. J.; Prosa, T. J.; Moulton, J.; Smith, P.; Heeger, A. J. *Macromolecules* **1992**, *25*, 4364—4372.

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Figure 5. X-ray diffraction pattern of poly(3-hexylthiophenes) films (cast from chloroform solutions by air evaporation).

carbon tetrachloride, toluene, or xylenes) showed a self-crystalline, self-organized lamellar morphology with three-dimensional ordering of the polymer chains, while that of the regiorandom P3ATs (5) was a totally amorphous phase by the X-ray diffraction analysis. For example, the X-ray diffraction pattern of HT P3HT (4b) film, which was cast from chloroform solution by air evaporation, showed the strong first-, second-, and third-order reflections at 2θ angle of 5.4, 10.8, and 16.3°. This corresponded to an interlayer d-spacing of 16.36 Å of the well-organized lamellar structure.[15c,30] The X-ray diffraction pattern of the regiorandom P3HT (5b) film, under the same conditions, showed a totally amorphous phase (Figure 5).

The X-ray diffraction studies of our regioregular HT P3ATs also showed that the interlayer d-spacing was increased with the elongation of the length of alkyl side chain (Figure 6 and 7): the longer the side chain, the larger the interlayer spacing, which clearly indicated the stacks of planar thiophene main chains were uniformly spaced by the alkyl side chain. The calculated structures (see Figure 8 in the case of HT-P3BT) supported the previously reported model,[30] "an alternating inverse comb," in which there was a tilted packing of the side chains with an alternating zigzag conformation to the backbone.

Another diffraction centered at 23.5° for HT-P3BT, P3HT, P3OT, and P3DT corresponded to a spacing of 3.79 Å. This side-chain-length-independent spacing could be attributed to the stacking distance of successive thiophene rings between two polymer chains (Figure 8). HT-P3DDT had the diffraction centered at 22.5° corresponding to a larger spacing of 3.95 Å (Figure 6). This disruption of stacking distance by the longer alkyl side chain was also observed and defined by Winokur.[30] This disruption can be easily seen from Figure 6 through the systematic increase in the relative intensity of the wide-angle area (20−25°) with the elongation of the P3AT alkyl chain length. The broad diffraction at this wide angle area can be attributed to the disordered phase of P3ATs. In general, our regioregular HT P3ATs showed a much weaker intensity in this area than do the other stretch-ordered P3ATs,[30−32] implying that
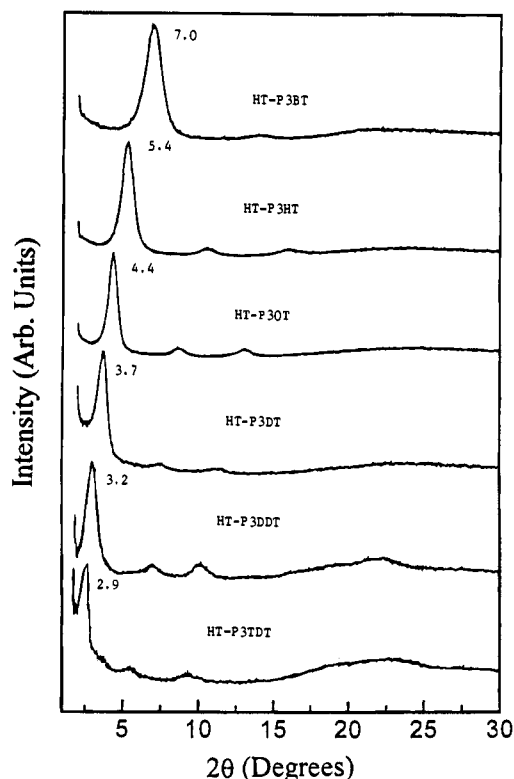

Figure 6. X-ray diffraction pattern of regioregular head-to-tail poly-(3-alkylthiophenes) films (cast from chloroform solutions) (labeled numbers are the degrees of first-order diffraction of P3AT).
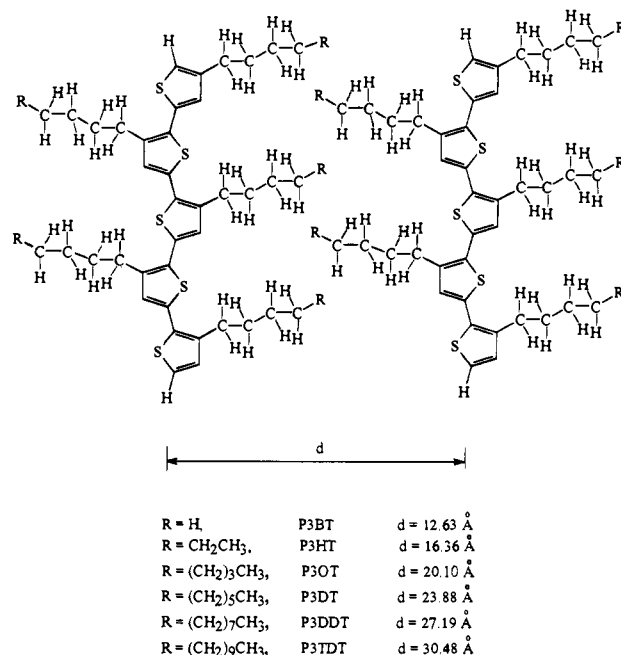

R = H,	P3BT	d = 12.63 Å
R = CH₂CH₃,	P3HT	d = 16.36 Å
R = (CH₂)₃CH₃,	P3OT	d = 20.10 Å
R = (CH₂)₅CH₃,	P3DT	d = 23.88 Å
R = (CH₂)₇CH₃,	P3DDT	d = 27.19 Å
R = (CH₂)₉CH₃,	P3TDT	d = 30.48 Å

Figure 7. Schematic diagram of two-dimension lamellar structure with interlayer spacing of regioregular head-to-tail poly(3-alkylthiophenes).

our self-organized HT P3ATs had a more ordered and crystalline structure.

Polarized Microscopy. If the X-ray diffraction study represents the ordering character of the P3AT polymer chains in a microscopic scale, the polarized microscope investigation gives an outline of assembly properties of P3ATs in a relatively macroscopic scale.

(31) Chen, S.-A.; Ni, J.-M. *Macromolecules* **1992**, *25*, 6081−6089.

(32) Mårdalen, J.; Samuelsen, E. J.; Gautun, O. R.; Carlsen, P. H. *Synth. Met.* **1992**, *48*, 363−380.
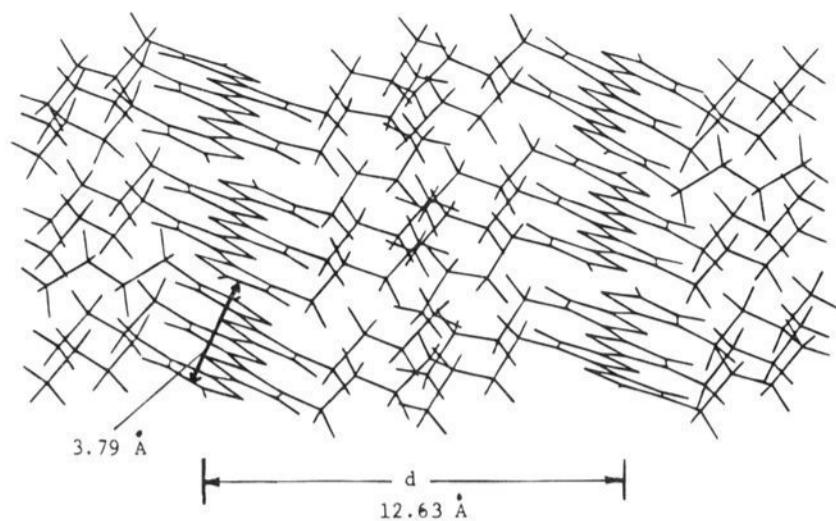
Figure 8. Calculated three-dimensional stacking structure for six HT 3-butylthiophene pentamers using molecular modeling system (Insight II, 2.3.0, Biosym Technologies) based on the X-ray data.
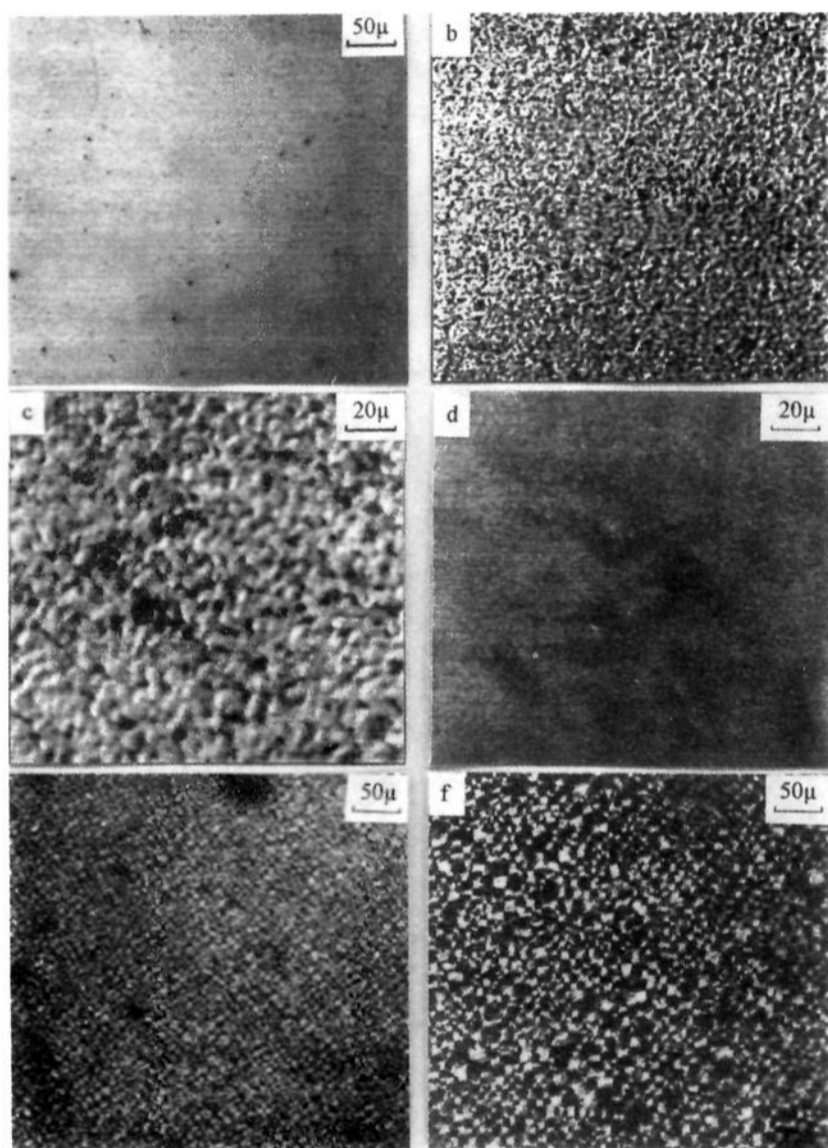

Figure 9. (a) The amorphous morphology of regiorandom P3OT (**5c**) film under cross-polarizers at room temperature (×200). (b) The matted crystalline texture of regioregular HT-P3OT (**4c**) film under cross-polarizing microscope at room temperature (×200). (c) The expanded view of the same sample as in (b) showing the matted fibrils of HT-P3OT (×500). (d) The melted morphology of same sample as in (b) under cross-polarizing microscope at 200 °C (×500). (e) The matted crystalline texture of the sample sample as in (b) (after 200 °C annealing) under cross-polarizing microscope at room temperature (×200). (f) The matted crystalline texture of the same sample as in (b) (after the second annealing of 300 °C) under cross-polarizing microscope at room temperature (×200).

A self-assembled crystalline texture and nicely matted fibrils of regioregular HT P3ATs films, cast from xylenes or chloroform solution by simple air evaporation, were surprisingly observed under a cross-polarizing microscope (Figure 9b−c). The similar structure was observed for the as-grown polyacetylene films.[8a] For polythiophenes, only electrochemically deposited, very thin films (0.5−1 μm) of polythiophene and

poly(3-methylthiophene) on electrode showed the similar structure.[33] For poly(3-alkylthiophenes), especially for chemically synthesized P3ATs to our knowledge, the similarity in structure has not yet been observed. This crystalline textured and matted fibril was obviously caused by the self-organized "alternating inverse comb" structure of polymer chains which was induced by the head-to-tail regiospecificity of poly(3-alkylthiophenes). The regiorandom P3ATs film showed a totally amorphous morphology under the same conditions (Figure 9a).

Upon heating, the crystalline phase was converted to a amorphous phase (Figure 9d) at the melting temperature with a thermochromism from bronze-luster to red-orange in approximately 5 °C range. This short melting range implied the crystalline phase was rather uniform: the longer the alkyl side chain on P3ATs, the lower the melting temperature. The melting temperature range was ∼240−245 °C for HT-P3HT, ∼200−205 °C for HT-P3OT, and ∼175−180 °C for HT-P3DT, respectively. Upon cooling, the crystalline phase and bronze metal-like surface were recovered, and a more smooth matted crystalline texture was formed (Figure 9e). The microcrystalline texture grew in size to form a more thermostable, larger sized crystalline texture after a second annealing (Figure 9f). The regiorandom P3ATs remained in an amorphous phase after annealing.

UV−Vis Electronic Spectroscopy. The solid-state properties, such as electronic transitions, bandgaps, and chromic effects of polymer materials can be obtained from their electronic absorption spectra. The solid-state UV−vis spectra of our regiorandom P3HT films showed the maximum absorption for the $\pi-\pi^*$ transition at ∼438 nm with the isobestic point at 590 nm (Figure 10a and Table 7), while that of regioregular HT P3HT films showed much longer maximum absorption wavelength with two almost equally intense maximum peaks at 560 and 610 nm and a shoulder at 526 nm (Figure 10d and Table 7). The red shifts of these three peaks relative to the regiorandom one were 122, 172, and 88 nm, respectively. The absorption isobestic point for the spectrum of HT P3HT was around 730 nm and corresponds to a 140-nm red shift from that of regiorandom P3HT. The band edge (determined[34] by the isobestic point of $\pi-\pi^*$ transition of the absorption spectra) of the regioregular HT P3HT was 1.7 eV which was 0.4 eV lower than that of the regiorandom P3HT (2.1 eV). It is interesting to compare the bandgap of P3ATs with their theoretical values of 1.71−1.79 eV calculated by the valence effective Hamiltonian technique.[35] Obviously, the regioregular HT P3ATs had a considerably longer conjugation length than that of the regiorandom P3ATs in the condensed state: the higher percentage of head-to-tail linkages in the polymer chains, the longer the maximum absorption wavelength of the spectra. This is clearly demonstrated in the electronic absorption spectra of poly(3-alkylthiophenes) with the differences in the percentages of head-to-tail linkages in the polymer chain (Figure 10a−d). The spectra of HT P3ATs also showed a relatively stronger intensity of maximum absorption at the longer wavelength area (560 and 610 nm), which implied a larger proportion of the longer conjugation length polymer chain, or a longer average conjugation length of the polymer chain in HT P3ATs.

The X-ray, polarized microscopy, UV−vis, fluorescence, FTIR, and NMR spectra data of our polymers gave consistent

(33) (a) Yassar, A.; Roncali, J.; Garnier, F. Macromolecules **1989**, 22, 804−809. (b) Tourillon, G. In Handbook of Conducting Polymers: Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; pp 293−350.

(34) (a) Jenekhe, S. A. Nature **1986**, 322, 345−347. (b) Chung, T. C.; Haufman, J. H.; Heeger, A. J.; Wudl, F. Phys. Rev. B, **1984**, 30, 702−710.

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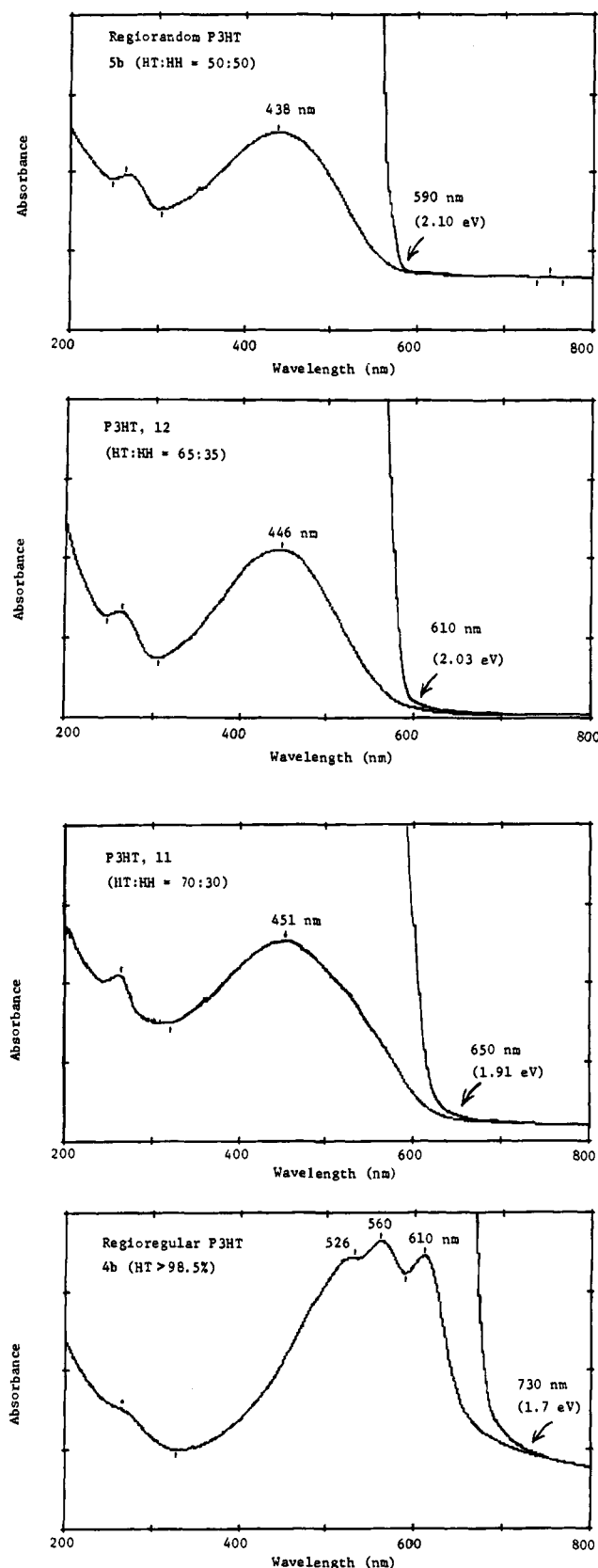*J. Am. Chem. Soc., Vol. 117, No. 1, 1995* 241

Figure 10. Solid-state UV—vis absorption spectra of the films of poly-(3-hexylthiophenes) with different regioregularity.

and corresponding results. The regioregular HT poly(3-alkyl-thiophenes) were characterized as a polymer the head-to-tail regiospecificity, significantly extended conjugation length, self-organized structure of polymer chain, and self-assembly crystalline texture. All of these characteristics produce the regioregular

head-to-tail poly(3-alkylthiophenes) with an electroconductivity several orders of magnitude higher than do the regiorandom P3ATs.[36] The neutral HT P3ATs (pressed pellet) had a conductivity of 10^{-6}—10^{-7} S/cm, while that of the regiorandom P3ATs was 10^{-9}—10^{-10} S/cm. We have previously reported[16b] that the I_2 vapor heavily doped HT P3ATs films had conductivities around 10^3 S/cm, while the regiorandom P3ATs had conductivities less than 10^1 S/cm.

Conclusion

We have demonstrated a systematically regiocontrolled synthesis of poly(3-alkylthiophenes) mediated by Rieke zinc. Starting with the same compounds, a series of P3ATs with different regioregularities were obtained, among which, a completely regioregular head-to-tail and a totally regiorandom poly(3-alkylthiophene) were most significant. The regio-regularity of the polymers was controlled by the structure of different catalysts in the polymerization. The regioregular HT P3ATs were consistently characterized as a class of polymers with regiospecific head-to-tail conformation, significantly ex-tended conjugation length, self-organized structure of polymer chain, low bandgap, and polycrystalline texture. The regio-regular HT P3ATs had considerably higher neutral and doping conductivities than those of regiorandom P3ATs. Further exploration of their nonlinear optical properties will help in understanding of the properties of this important class of polymers.

Experimental Section

Reagents. Lithium (ribbon), Ni(DPPE)Cl$_2$, Pd(DPPE)Cl$_2$, and Ni(PPh$_3$)$_4$ were purchased from Aldrich Chemical Co., ZnCl$_2$ (anhy-drous) from Cerac Inc., and 3-n-dodecylthiophene from TCI America. Pd(PPh$_3$)$_4$ was prepared according to ref 37. Other chemicals were purchased from Aldrich Chemical Co. or Lancaster Synthesis Inc. and used as received unless otherwise specified.

General Aspects. All manipulations were carried out under an atmosphere of argon on a dual manifold/argon—vacuum system. The Linde prepurified grade argon was further purified with a BASF R3-11 catalyst column at 150 °C, a phosphorus pentoxide column, and a granular potassium hydroxide column. Lithium, naphthalene, and ZnCl$_2$ were weighed as needed and charged into reaction flasks in an argon Vacuum Atmosphere Co. drybox. Tetrahydrofuran was distilled from a Na/K alloy under an argon atmosphere immediately before use.

NMR spectra were obtained from a G.E. Omega-500 or G.E. Omega-300. All NMR samples were dissolved in CDCl$_3$. ^{1}H NMR spectra chemical shifts were reported in parts per million (δ) downfield from tetramethylsilane as an internal standard. ^{13}C NMR chemical shifts (δ) were reported in reference to the 77.00-ppm peak for CDCl$_3$. Infrared spectra were taken on an Analect RFX-65 FTIR spectropho-tometer with neat polymer films cast from CHCl$_3$ solutions on NaCl disks and reported as ν in cm^{-1}. UV—vis spectra were taken on a Shimadzu UV-160 UV-visible recording spectrophotometer with both polymer solutions in CHCl$_3$ and neat polymer thin films cast from CHCl$_3$ solutions on a quartz plate and reported in nm or eV. Fluorescence spectra were taken on a Shimadzu spectrofluorophotom-eter RF-540 with polymer solutions of CHCl$_3$ (excitation wavelength 430 nm). Elemental analyses were performed by Desert Analytics (Tucson, AZ). Molecular weights were determined (relative to polystyrene standard) on a Waters gel permeation chromatography (GPC) with a Waters Ultrastyragel KF-804 (Shodex KF-804) column at room temperature using THF as eluant. Analytical GC was performed on a Hewlett-Packard 5890 A gas chromatograph equipped with 12-ft lengths of $^1/_8$-in. stainless steel tubing packed with 5% SP

(36) A manuscript on the systematic study of the conductivity of the regiospecific poly(3-alkylthiophenes) is in preparation by Reghu, M.; Yoon, C. O.; Moses, D.; Heeger, A. J.; Chen, T.-A.; Wu, X., and Rieke, R. D.

(37) Coulson, D. R.; Satek, L. C.; Grim, S. O. *Inorg. Synth.* **1972**, *13*, 121—123.

Table 7. Comparison of Solid-State UV—Vis Data of Regioregular and Regiorandom Poly(3-alkylthiophenes)

regioregular	HT-P3BT 4a	HT-P3HT 4b	HT-P3OT 4c	HT-P3DT 4d	HT-PDDT 4e	HT-PTDT 4f
λ_{max} (nm)	522	526	522	526	524	526
	556	556	556	558	560	560
	605	610	608	606	610	610
regiorandom	P3BT, 5a	P3HT, 5b (HT/HH 50:50)	P3OT, 5c	P3HT, 12 (HT/HH 65:35)		P3HT, 11 (HT/HH 70:30)
λ_{max}	433	438	435	445		451

2100 on a Supelco support, and interfaced with a Perkin-Elmer LCI-100 integrator. GC yields were quantified by determining response factors for pure samples and calculating the yield relative to an internal standard. High-resolution mass spectra were obtained from the Midwest Regional Center of Mass Spectrometry, University of Nebraska—Lincoln.

X-ray diffraction profiles were measured using a Rigaku Model D/Max-B with the DMAXB computer-controller. The X-ray beam was nickel-filtered Cu Kα ($\lambda = 1.5418$ Å) radiation from a sealed 900-W tube with a horizontal line focus operated at 40 kV and 20 mA. Data were obtained from 2 to 30° (2θ) at a scan rate of 1°/min. Polarizing microscopy was performed on a Zeiss Axiotron polarizing microscope with a hot stage. The P3ATs samples for X-ray measurement and polarizing microscopy were the films cast from the chloroform (or toluene, xylenes, and/or carbon tetrachloride) solutions onto 120-μm glass coverslips by air evaporation. Molecular mechanice calculations were performed on a Silicon Graphics Iris 4D computer using Insight II molecular modeling system (Version 2.3.0, Biosym Technologies).

The electroconductivities of neutral (pressed pellets) and doped polymers (films cast from CHCl₃ solutions and doped with iodine vapor) were determined by an SSM 240 resistivity mapping system using both two- and four-probe techniques at 23 °C, and by a Keithley 580 four-wire (two sense, two source) micrometer at 25 °C with up to five-point average. So determine the thicknesses of the films, films were spin cast on polyester film (0.15 mm thick) from CHCl₃ solutions. The films and substrate (polyester) were cut by knife together and embedded in Epon 812 (epoxide resin) and solidified at 60 °C oven for 24 h. Samples were cut with a diamond knife on LKB ultrotome III. Sections about 0.1 μ thick were observed with a Philips 201 transmission electron microscope operated at 60 kV.

Preparation of 2,5-Dibromo-3-alkylthiophenes. All 3-*n*-alkylthiophenes were prepared according to ref 21a,b. All 2,5-dibromo-3-alkylthiophenes were further prepared by the dibromination of 3-alkylthiophenes with Br₂ in chloroform at room temperature according to ref 19b. The yields of the crude products for bromination were near quanitative (95—98%). The products were purified by distillation in ca. 80% yield or by column chromatography with the use of Merck flash silica gel 60 (230—400 mesh) in ca. 85% yield with the purity >98% determined by GC.

2,5-Dibromo-3-butylthiophene (1a): bp 88—89 °C (0.05 mmHg); ¹H NMR (300 MHz) 6.76 (s, 1 H), 2.50 (t, 2 H), 1.52 (pentet, 2 H), 1.37 (sextet, 2 H), 0.92 (t, 3 H); ¹³C NMR (75 MHz) 142.88, 130.91, 110.29, 107.93, 31.69, 29.17, 22.19, 13.85; EIMS *m/z* (relative intensity) 255 (100, C₅H₃SBr₂⁺), 176 (99, C₅H₄SBr⁺). HRMS: calcd for C₈H₁₀SBr₂, 297.8847; found, 297.8847.

2,5-Dibromo-3-hexylthiophene (1b): bp 95—96 °C (0.05 mmHg); ¹H NMR (300 MHz) 6.77 (s, 1 H), 2.50 (t, 2 H), 1.53 (pentet, 2 H), 1.29 (m, 6 H), 0.89 (t, 3 H); ¹³C NMR (75 MHz) 142.98, 130.94, 110.29, 107.91, 31.56, 29.54, 29.48, 28.78, 22.56, 14.07; EIMS *m/z* (relative intensity) 255 (48, C₅H₃SBr₂⁺), 176 (100, C₅H₄SBr⁺): HRMS: Calcd for C₁₀H₁₄SBr₂ 325.9159, found 325.9164.

2,5-Dibromo-3-octylthiophene (1c): bp 102.5—103.5 °C (0.03 mmHg); ¹H NMR (300 MHz) 6.77 (s, 1 H), 2.50 (t, 2 H), 1.53 (pentet, 2 H), 1.27 (m, 10 H), 0.88 (t, 3 H); ¹³C NMR (75 MHz) 142.93, 130.91, 110.27, 107.90, 31.86, 29.57, 29.46, 29.33, 29.21, 29.11, 22.67, 14.12; EIMS *m/z* (relative intensity) 255 (50, C₅H₃SBr₂⁺), 176 (100, C₅H₄-SBr⁺). HRMS: calcd for C₁₂H₁₈SBr₂ 353.9471, found 353.9464.

2,5-Dibromo-3-decylthiophene (1d): bp 147—148 °C (0.4 mmHg); ¹H NMR (300 MHz) 6.77 (s, 1 H), 2.50 (t, 2 H), 1.52 (pentet, 2 H), 1.26 (m, 14 H), 0.88 (t, 3 H); ¹³C NMR (75 MHz) 142.99, 130.95,

110.29, 107.91, 31.90, 29.58, 29.56, 29.53, 29.47, 29.36, 29.32, 29.10, 22.68, 14.11; EIMS *m/z* (relative intensity) 255 (37, C₅H₃SBr₂⁺), 176 (100, C₅H₄SBr⁺). HRMS: calcd for C₁₄H₂₂SBr₂ 381.9776, found 381.9775.

2,5-Dibromo-3-dodecylthiophene (1e). The crude product was purified by column chromatography: ¹H NMR (300 MHz) 6.77 (s, 1 H), 2.50 (t, 2 H), 1.54 (pentet, 2 H), 1.26 (m, 18 H), 0.89 (t, 3 H); ¹³C NMR (75 MHz) 142.97, 130.92, 110.30, 107.93, 31.93, 29.64, 29.55, 29.48, 29.36, 29.10, 22.70, 14.11; EIMS *m/z* (relative intensity) 255 (25, C₅H₃SBr₂⁺), 176 (100, C₅H₄SBr⁺); HRMS: calcd for C₁₆H₂₆SBr₂ 410.0095, found 410.0073.

2,5-Dibromo-3-tetradecylthiophene (1f). The crude product was purified by column chromatography: ¹H NMR (300 MHz) 6.77 (s, 1 H), 2.50 (t, 2 H), 1.53 (pentet, 2 H), 1.26 (m, 22 H), 0.89 (t, 3 H); ¹³C NMR (75 MHz) 142.96, 130.92, 110.31, 107.92, 31.94, 29.58, 29.57, 29.48, 29.38, 29.12, 22.70, 14.11; EIMS *m/z* (relative intensity) 255 (17, C₅H₃SBr₂⁺), 176 (100, C₅H₄SBr⁺); HRMS: calcd for C₁₈H₃₀SBr₂ 438.0407, found 438.0399.

Preparation of 2-Bromo-5-iodo-3-alkylthiophenes. 2-Bromo-5-iodo-3-alkylthiophenes were prepared by the iodination²⁰ of 2-bromo-3-alkylthiophenes with iodine in 52% yield by distillation, while 2-bromo-3-alkylthiophenes were prepared by the regiospecific bromination of 3-ethylthiophenes with NBS according to ref 19a in 79% yield by distillation. The purity of the compounds were >98% as determined by GC.

2-Bromo-3-butylthiophene (8a): bp 58—59 °C (0.6 mmHg); ¹H NMR (300 MHz) 7.16 (d, *J* = 5.6 Hz, 1 H), 6.78 (d, *J* = 5.6 Hz, 1 H), 2.56 (t, 2 H), 1.58 (pentet, 2 H), 1.35 (sextet, 2 H), 0.92 (t, 3 H); ¹³C NMR (75 MHz) 141.88, 128.20, 125.09, 108.78, 31.87, 29.08, 22.29, 13.88; EIMS *m/z* (relative intensity) 176 (100, C₅H₄SBr⁺), 97 (100, C₅H₅S⁺); HRMS: calcd for C₈H₁₁SBr 218.9752, found 218.9764.

2-Bromo-3-hexylthiophene (8b): bp 74.5—75.5 °C (0.5 mmHg); ¹H NMR (300 MHz) 7.17 (d, *J* = 5.6 Hz, 1 H), 6.78 (d, *J* = 5.6 Hz, 1 H), 2.55 (t, 2 H), 1.57 (pentet, 2 H), 1.31 (m, 6 H), 0.88 (t, 3 H); ¹³C NMR (75 MHz) 141.98, 128.23, 125.07, 1110.29, 31.74, 29.45, 29.58, 28.81, 22.56, 14.07. Anal. Calcd for C₁₀H₁₅SBr: C, 48.59; H, 6.12. Found: C, 48.48; H, 6.21.

2-Bromo-5-iodo-3-butylthiophene (9a): bp 108.5—109.5 °C (0.8 mmHg); ¹H NMR (300 MHz) 6.95 (s, 1 H), 2.52 (t, 2 H), 1.52 (pentet, 2 H), 1.35 (sextet, 2 H), 0.92 (t, 3 H); ¹³C NMR (75 MHz) 144.14, 137.92, 111.67, 71.05, 31.75, 28.85, 22.20, 13.85; EIMS *m/z* (relative intensity) 302 (59, C₅H₃SBrI⁺), 223 (100, C₅H₄SI⁺); HRMS: calcd for C₈H₁₀SBrI 344.8719, found 344.8715.

2-Bromo-5-iodo-3-hexylthiophene (9b): bp 120—121 °C (0.6 mmHg); ¹H NMR (300 MHz) 6.95 (s, 1 H), 2.53 (t, 2 H), 1.53 (pentet, 2 H), 1.30 (m, 6 H), 0.89 (t, 3 H); ¹³C NMR (75 MHz) 144.24, 137.95, 111.67, 71.03, 31.62, 29.48, 29.20, 28.78, 22.56, 14.07. Anal. Calcd for C₁₀H₁₄SBrI: C, 32.19; H, 3.78. Found: C, 32.01; H, 3.84.

Typical Preparation of Rieke Zinc (Zn*). Procedure a. Finely cut (ca. 5 × 5 × 0.75 mm) lithium (0.15 g, 22.0 mmol) and a catalytic amount (10 mol %) of naphthalene (0.28 g, 2.20 mmol) were weighed into a 100-mL, two-neck round-bottom flask equipped with an elliptical Teflon stir bar in an argon drybox; the flask was sealed with a septum and a condenser topped with stopcock outlet. Similarly, ZnCl₂ (1.50 g, 11.0 mmol) was weighed into a 50-mL, two-neck round-bottom flask, equipped with a stir bar; the flask was sealed with a septum and stopcock. The flasks were then transferred to the manifold system and the argon inlet fitted. THF (15 mL) was added to the flask with lithium and naphthalene while ZnCl₂ was dissolved in 25 mL of THF. To the flask with lithium and naphthalene, the THF solution of ZnCl₂ was

transferred via cannula dropwise so as addition was complete in ca. 1.5 h under moderate stirring. The reaction mixture was further stirred until the lithium was consumed (ca. 30 min), and the resulting black suspension of active zinc thus prepared was ready for use.

Procedure b. Finely cut Li (0.15 g, 22.0 mmol) and a stoichiometrical amount of naphthalene (2.80 g, 22.0 mmol) were weighed into a 100-mL flask, and ZnCl₂ (1.5 g, 11.0 mmol) was weighed into a 50-mL flask. The Li and naphthalene were dissolved in 20 mL of THF in ca. 2 h. ZnCl₂ was dissolved in 20 mL of THF and the solution was transferred into the flask with lithium naphthalide via cannula over 10 min. The reaction mixture was further stirred for 1 h, and the resulting black suspension of active zinc thus prepared was ready for use.

General Preparation of Regioregular HT Poly(3-alkylthiophenes) from 2,5-Dibromo-3-alkylthiophenes. Preparation of Regioregular HT Poly(3-hexylthiophene) (4b). 2,5-Dibromo-3-hexylthiophene (3.26 g, 10.0 mmol, in 20 mL of THF) was added via a cannula to the newly prepared Zn* (11.0 mmol, in 40 mL of THF) by procedure a at −78 °C. The mixture was stirred for 1 h at this temperature and allowed to warm to 0 °C naturally in ca. 3 h; 0.2 mol % of Ni(DPPE)Cl₂ (11.0 mg, 0.02 mmol, in 20 mL of THF) was added via cannula at 0 °C. The mixture was stirred for 24 h at room temperature. A dark-purple precipitate was formed gradually in this period. The mixture was poured into a solution of MeOH (100 mL) and 2 N HCl (50 mL); the resulting dark precipitate was filtered and washed with MeOH and 2 N HCl solution, and then dried. Reprecipitation of polymer from chloroform solution upon addition of MeOH and drying under vacuum gave 1.62 g of dark polymer of regioregular HT poly(3-hexylthiophene) (98% yield). The product had apparently the same NMR, IR, UV–vis, and fluorescence characterization as the product after extractions (see below). The polymer had average molecular weight $\bar{M}_w = 15\,000$ and $\bar{M}_n = 4130$ with a polydispersity index (PD) of 3.63 determined by GPC. Anal. Calcd for $(C_{10}H_{14}S)_n$: C, 72.22; H, 8.49; S, 19.29. Found: C, 71.91; H, 8.36; S, 18.67.

Repurification of polymer by Soxhlet extractions with MeOH for 24 h and then with hexane for 24 h afforded 1.37 g (82% final yield) of regioregular HT poly(3-hexylthiophene): ¹H NMR (500 MHz) 6.98 (s, 1 H) for HT−HT linkage, 2.80 (t, 2 H) for HT linkage (less than 1.5% intensity for HH linkage in this α-proton region at δ 2.58 was also observed), 1.72 (pentet, 2 H) for HT linkage, 1.44 (m, 2 H), 1.35 (m, 4 H), 0.92 (t, 3 H); ¹³C NMR (125 MHz, only HT−HT pattern was observed) 139.9, 133.7, 130.5, 128.6, 31.7, 30.5, 29.5, 29.2, 22.6, 14.1. The polymer was characterized as a regioregular poly(3-hexylthiophene) with at least 98.5% HT linkage in the polymer chains by NMR analysis. See text for IR, UV−vis, and fluorescence characterization. The polymer after extractions had much higher average molecular weight than did the polymer before extractions. The $\bar{M}_w = 37\,680$ and $\bar{M}_n = 25500$ corresponding to a PD of 1.48. Anal. Calcd for $(C_{10}H_{14}S)_n$: C, 72.22; H, 8.49; S, 19.29. Found: C, 71.90; H, 8.48; S, 18.73.

Other regioregular HT poly(3-alkylthiophenes) were prepared in an analogous manner.

Regioregular HT Poly(3-butylthiophene) (4a). A yield of 1.10 g (80%) of black polymer was obtained. The polymer was a 97% HT regioregular poly(3-butylthiophene) based on NMR analysis: ¹H NMR (300 MHz) 6.99 (s, 1 H), 2.82 (t, 2 H), 1.70 (pentet, 2 H), 1.46 (sextet, 2 H), 0.98 (t, 3 H); ¹³C NMR (75 MHz) 139.9, 133.7, 130.5, 128.6, 32.7, 29.2, 22.7, 14.0. Molecular weights were not available owing to the limited solubility of the polymer in THF. Anal. Calcd for $(C_8H_{10}S)_n$: C, 69.52; H, 7.29; S, 23.19. Found: C, 68.82; H, 7.22; S, 22.54.

Regioregular HT Poly(3-octylthiophene) (4c). A yield of 1.53 g (79%) of dark-purple polymer was obtained. The obtained was a regioregular HT (>98.5%) poly(3-octylthiophene) based on NMR analysis: ¹H NMR (500 MHz) 6.98 (s, 1 H), 2.80 (t, 2 H), 1.71 (pentet, 2 H), 1.45−1.20 (m, 10 H), 0.89 (t, 3 H); ¹³C NMR (125 MHz) 139.9, 133.7, 130.5, 128.6, 31.9, 30.5, 29.6, 29.4, 29.3, 22.7, 14.1; $\bar{M}_w = 39\,210$ and $\bar{M}_n = 34\,580$ with a PD of 1.13. Anal. Calcd for $(C_{12}H_{18}S)_n$: C, 74.16; H, 9.34; S, 16.50. Found: C, 73.73; H, 9.23; S, 16.43.

Regioregular HT Poly(3-decylthiophene) (4d). A yield of 1.71 g (77%) of dark-purple polymer was obtained. The polymer was a

regioregular HT (>98.5%) poly(3-decylthiophene) based on NMR analysis: ¹H NMR (500 MHz) 6.98 (s, 1 H), 2.81 (t, 2 H), 1.71 (pentet, 2 H), 1.40−1.20 (m, 14 H), 0.88 (t, 3 H); ¹³C NMR (125 MHz) 139.9, 133.7, 130.5, 128.6, 31.9, 30.5, 29.7, 29.6, 29.5, 29.4, 29.3, 22.7, 14.1; $\bar{M}_w = 42\,220$ and $\bar{M}_n = 30\,480$ with a PD of 1.39. Anal. Calcd for $(C_{14}H_{22}S)_n$: C, 75.61; H, 9.97; S, 14.42. Found: C, 75.73; H, 10.01; S, 14.64.

Regioregular HT Poly(3-dodecylthiophene) (4e). A yield of 1.77 g (71%) of dark-brown polymer was obtained. The polymer was a regioregular HT (>98.5%) poly(3-dodecylthiophene) based on NMR analysis: ¹H NMR (500 MHz) 6.99 (s, 1 H), 2.81 (t, 2 H), 1.72 (pentet, 2 H), 1.50−1.20 (m, 18 H), 0.88 (t, 3 H); ¹³C NMR (125 MHz) 139.94, 133.79, 130.57, 128.66, 31.95, 30.56, 29.73, 29.68, 29.59, 29.53, 29.48, 29.37, 22.69, 14.07; $\bar{M}_w = 42\,210$ and $\bar{M}_n = 34\,650$ with a PD of 1.42. Anal. Calcd for $(C_{16}H_{26}S)_n$: C, 76.80; H, 10.40; S, 12.80. Found: C, 76.44; H, 10.27; S, 13.11.

Regioregular HT Poly(3-tetradecylthiophene) (4f). A yield of 1.86 g (67%) of dark-brown polymer was obtained. The polymer was a regioregular HT (>98.5%) poly(3-tetradecylthiophene) based on NMR analysis: ¹H NMR (500 MHz) 6.98 (s, 1 H), 2.80 (t, 2 H), 1.71 (pentet, 2 H), 1.50−1.20 (m, 22 H), 0.87 (t, 3 H); ¹³C NMR (125 MHz) 139.92, 133.79, 130.57, 128.64, 31.95, 30.57, 29.74, 29.70, 29.61, 29.53, 29.48, 29.39, 22.69, 14.09; $\bar{M}_w = 44\,190$ and $\bar{M}_n = 30\,230$ with a PD of 1.46. Anal. Calcd for $(C_{18}H_{30}S)_n$: C, 77.70; H, 10.79; S, 11.51. Found: C, 77.51; H, 10.60; S, 11.22.

General Preparation of Regioregular HT Poly(3-alkylthiophenes) from 2-Bromo-5-iodo-3-alkylthiophenes. 2-Bromo-5-iodo-3-butylthiophene (9a: 3.45 g, 10.0 mmol, in 20 mL of THF) or 2-bromo-5-iodo-3-hexylthiophene (9b: 3.73 g, 10.0 mmol, in 20 mL of THF) was added into the flask with newly prepared Zn* (11.0 mmol in 40 mL THF) via cannula at 0 °C and the mixture was stirred for 1 h at this temperature; 0.2 mol % of Ni(DPPE)Cl₂ (11.0 mg, 0.02 mmol, in 20 mL of THF) was added into the flask at 0 °C. The mixture was stirred for 24 h at room temperature and then worked up following the same procedure as above to afford 1.01 g (73% yield) of the regioregular HT poly(3-butylthiophene) (4a) or to afford 1.34 g (81% yield) of the regioregular HT poly(3-hexylthiophene) (4b).

General Preparation of Regiorandom Poly(3-alkylthiophenes) from 2,5-Dibromo-3-alkylthiophenes. Preparation of Regiorandom Poly(3-hexylthiophene) (5b). 2,5-Dibromo-3-hexylthiophene (3.26 g, 10.0 mmol, in 20 mL THF) was added to the flask with newly prepared Zn* (11.0 mmol in 40 mL of THF) via cannula at 0 °C, and the mixture was stirred for 1 h at room temperature. A 0.2 mol % amount of Pd(PPh₃)₄ (23.1 mg, 0.02 mmol, in 20 mL of THF) was added via cannula. The mixture was then stirred for 24 h at room temperature (or reflux for 6 h). The polymer was precipitated with a solution of MeOH (100 mL) and 2 N HCl (50 mL), and purified by reprecipitation from the polymer solution of chloroform upon addition of MeOH. After drying under vacuum, 1.63 g (98% yield) red-brown rubber-like polymer of regiorandom P3HT was obtained: ¹H NMR (500 MHz) 6.98 (1/4 H for HT−HT), 7.00 (1/4 H for TT−HT), 7.02 (1/4 H for HT−HH), and 7.05 (1/4 H for TT−HH linkage), 2.80 (m, 1 H for HT) and 2.58 (m, 1 H for HH linkage), 1.72 (m, 1 H for HT) and 1.63 (m, 1 H for HH linkage), 1.36 (m, 6 H), 0.91 (m, 3 H); ¹³C NMR (125 MHz) 139.9, 133.7, 130.5, and 128.6 for HT−HT, 140.3, 134.7, 129.7, and 127.3 for HT−HH, 142.8, 135.7, 128.3, and 126.6 for TT−HT, 143.4, 136.8, 127.2, and 125.1 for TT−HH linkage, 31.68, 30.71, 30.65, 30.49, 29.55, 29.48, 29.24, 29.12, 22.61, 14.05. The polymer was characterized as a regiorandom P3HT (1:1:1:1 HT−HT/HT−HH/TT−HT/TT−HH or 50:50 HT/HH) by the NMR analysis; $\bar{M}_w = 24400$ and $\bar{M}_n = 5650$ with a PD of 4.32. Anal. Calcd for $(C_{10}H_{14}S)_n$: C, 72.22; H, 8.49; S, 19.29. Found: C, 71.50; H, 8.28; S, 19.77.

Other regiorandom P3ATs were prepared in an analogous manner.

Regiorandom Poly(3-butylthiophene) (5a). A yield of 1.36 g (99%) of red-brown rubber-like regiorandom (50:50 HT/HH) poly(3-butylthiophene) was obtained: ¹H NMR (300 MHz) 7.02 (q, 1 H: 1/4 at 6.98, 1/4 at 7.01, 1/4 at 7.03, and 1/4 at 7.06), 2.80 (m, 1 H for HT), 2.57 (m, 1 H for HH), 1.65 (m, 2 H), 1.47 (m, 2 H), 0.94 (m, 3 H); ¹³C NMR (75 MHz) 143.4, 142.8, 140.2, 139.8; 136.8, 135.7, 134.7, 133.7; 130.5, 129.7, 128.3, 127.2; 128.6, 127.4, 126.6, 125.2; 32.8, 32.6, 29.4, 29.0, 22.8, 22.7, 14.1. Anal. Calcd for $(C_8H_{10}S)_n$: C, 69.51; H, 7.29; S, 23.19. Found: C, 68.94; H, 6.97; S, 22.65.

Regiorandom Poly(3-octylthiophene) (5c). A yield of 1.90 g (98%) of red-brown paste regiorandom (50:50 HT/HH) poly(3-octylthiophene) was obtained: ^{1}H NMR (500 HMz) 7.01 (q, 1 H: 1/4 at 6.98, 1/4 at 7.00, 1/4 at 7.02, and 1/4 at 7.05), 2.80 (m, 1 H for HT), 2.56 (m, 1 H for HH), 1.68 (m, 1 H for HT), 1.60 (m, 1 H for HH), 1.50—1.20 (m, 10 H), 0.88 (t, 3 H); ^{13}C NMR (75 MHz) 143.4, 142.8, 140.2, 139.8; 136.9, 135.8, 134.7, 133.7; 130.5, 129.7, 128.3, 127.2, 128.6, 127.4, 126.5, 125.1, 31.8, 30.6, 30.5, 29.5, 29.4, 29.3, 29.0, 22.7, 14.1. Anal. Calcd for $(C_{12}H_{18}S)_n$: C, 74.16; H, 9.34; S, 16.50. Found: C, 73.70; H, 8.81; S, 16.65.

Preparation of Regiorandom Poly(3-alkylthiophenes) from 2-Bromo-5-iodo-3-alkylthiophenes. Use of 2-bromo-5-iodo-3-alkylthiophenes (**9a**, alkyl = butyl; **9b**, alkyl = hexyl) instead of 2,5-dibromo-3-alkylthiophenes, following the same procedure as that for regiorandom P3AT above, resulted in regiorandom P3AT **5a** in 97% yield and P3AT **5b** in 98% yield.

Preparation of Regiorandom Poly(3-hexylthiophene) (11) Using Pd(DPPE)Cl$_2$. Using catalyst Pd(DPPE)Cl$_2$ instead of Pd(PPh$_3$)$_4$, following the same procedure as that for P3AT **5b**, resulted in the regiorandom poly(3-hexylthiophene) (**11**) with 70:30 of HT/HH linkage in the polymer chains based on the NMR analysis.

Preparation of Regiorandom Poly(3-hexylthiophene) (12) Using Ni(PPh$_3$)$_4$. Use of Ni(PPh$_3$)$_4$ instead of Pd(PPh$_3$)$_4$, following the same procedure as that for polymer **5b**, resulted in the regiorandom poly-(3-hexylthiophene) (**12**) with 65:35 of HT/HH linkage in the polymer chains based on the NMR analysis.

Registry numbers supplied by author: 2,6-Dibromo-3-butylthiophene (**1a**), 116971-10-9; 2,5-dibromo-3-hexylthiophene (**1b**), 116971-11-0; 2,5-dibromo-3-octylthiophene (**1c**), 149703-84-4; 2-bromo-3-hexylthiophene (**8b**), 69249-61-2; poly(3-butylthiophene), 98837-51-5; poly(3-hexylthiophene), 104934-50-1; poly(3-octylthiophene), 104934-51-2; poly(3-decylthiophene), 110851-65-5.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of regioregular HT poly(3-alkylthiophenes) **4a, 4c, 4d, 4e, 4f**, and regiorandom poly(3-alkylthiophenes) **5a, 5c** (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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