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A Study of Small Band Gap Polymers: Head-to-Tail Regioregular Poly[3-(alkylthio)thiophenes] Prepared by Regioselective Synthesis Using Active Zinc

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ABSTRACT: A series of regioregular head-to-tail poly[3-(alkylthio)thiophenes] have been synthesized. The synthetic approach includes the *in-situ* preparation of 2-bromo-3-(alkylthio)-5-(bromozincio)thiophenes via regiospecific oxidative addition of Rieke zinc (Zn*) to 2,5-dibromo-3-(alkylthio)thiophenes, and the regiospecific polycondensation of 2-bromo-3-(alkylthio)-5-(bromozincio)thiophenes catalyzed by Ni(DPPE)-Cl_2. These poly[3-(alkylthio)thiophenes] are highly regioregular polymers with head-to-tail linkages as high as 90% as determined by proton NMR integration. The structures, solution properties, and solid-state properties of the polymers were also investigated by the analyses of FTIR, UV−vis spectroscopy, and the X-ray diffraction data. The regioregular polymers are soluble in carbon disulfide, however, only slightly soluble in other common organic solvents, such as THF, chloroform, and xylenes. A golden film can be casted from a solution of carbon disulfide. A self-organized lamellar structure of the films was revealed by X-ray diffraction analysis. The p-doped poly[3-(alkylthio)thiophene] films upon exposure to iodine vapor are highly electroconductive with a conductivity range of 10^2 S/cm.

Introduction

Poly(3-alkylthiophenes) display properties superior to polythiophene, namely, higher conductivity, solubility in organic solvents, and the capability of melting at a higher temperature.[1] Since poly(3-alkylthiophenes) were introduced as an unique electroactive polymer, they have attracted interest in material science for practical as well as potential applications. These applications include rechargeable battery electrodes, electrochromic devices,[2a,b] chemical and optical sensors,[2c] light-emitting diodes,[2d,e] molecular-based devices,[2f,g] and nonlinear optical active materials.[2h−j] Furthermore, the introduction of long-chain functional groups into the 3-position of the thiophene units in polythiophene not only influence solubility and meltability but also control and modify other physical, electronic, and electroptical properties of polythiophene. A variety of polymers with functionalized substituents on the 3-position of the thiophene units have been synthesized. The ethereal or thioethereal side chains allowed the fine-tuning of electrical and optical properties to polythiophenes:[3a,7c] the crown ether side chain resulted in ionochromic activity in the polythiophene,[3b,c] the chiral side chain yielded an optically active polythiophene,[3d] and an alkanesulfonic acid side chain produced a water soluble polymer which was a self-doping conducting polymer.[3e,f] On the other hand, the 3-substituents also broke the C_2 symmetry of the thiophene structure. These unsymmetrical thiophene rings can be incorporated into a polymer chain with two different regioregularities, head-to-tail (HT) and head-to-head (HH), which may cause four regioisomeric triads in the polymer chain: HT−HT, HT−HH, TT−HT, and TT−HH triad. The regioregularity strongly affects the polymer's properties[4] due to the steric hindrance of the 3-substituents on the HH linked thiophene units. In the regiorandom polymers, the steric hindrance of the substituents results in an out-of-plane conformation for the units along the polymer chain. In contrast, the planar backbone in the HT regioregular polymers increased the conductivity, nonlinearity, and the other physical properties of the material. Accordingly, considerable effort has been directed toward the synthesis of regioregular polymers.[4]

Recently, two effective methods for synthesizing totally HT regioregular poly(3-alkylthiophenes) have been explored. These chemical routes include Ni-catalyzed polycondensation of 2-bromo-5-(bromozincio)-3-alkylthiophenes generated from oxidative addition of Rieke zinc[5] (Zn*, a highly activated zinc powder) to 2,5-dibromo-3-alkylthiophenes[6] and Ni-catalyzed polycondensation of regiospecific thiophene Grignard reagents created from metathesis of the corresponding organolithium reagents with $MgCl_2$.[7] The slow oxidative polymerization of 3-(4-octylphenyl)thiophene using $FeCl_3$ as oxidant is also a regioselective synthesis.[8] These regiocontrolled synthetic methods produced a series of poly(3-alkylthiophenes) with exceptionally improved properties as compared to others prepared by other methods. The regioregular polymers synthesized through our method using Rieke zinc have a totally HT regiospecific unit linkage, a significantly extended conjugation length, a low band gap, a self-organized structure of the polymer chain, and a polycrystalline texture.[9] Besides the control of regioregularities of polythiophenes, modifying the structure of the side chain can also be used to adjust the electronic properties of the polymers. One of the simple modifications would be the substitution of thiophene units at the 3-position with a functional group. The introduction of an electron pushing group, such as an alkoxy or alkylthio group, into the β-position of thiophene unit was presumed to be able to decrease the band gap of the polymer by raising the energy of the highest occupied molecular orbital.[10] Hence a series of poly[3-alkoxythiophenes][10] and poly[3-(alkylthio)thiophenes][11] have been synthesized, and a decrease in the band gap has been reported.[12] Accordingly, it can be expected that a HT regioregular poly(3-substituted thiophene) with a strong electron-donating group in the 3-position of the thiophene units will have a lower band gap and subsequently a higher conductivity than the HT regioregular poly(3-alkylthiophenes). The I_2-doped HT regioregular poly(3-alkylthiophenes) have conductivities on the order of 10^2

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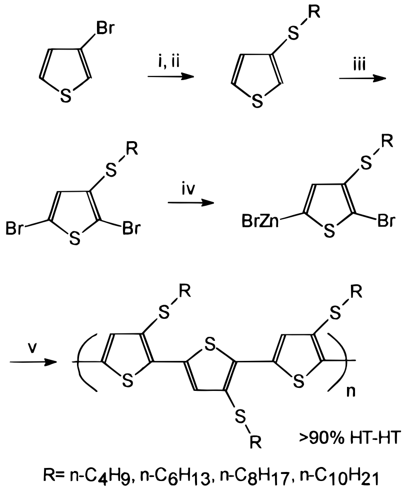
to 10^3 S cm^{-1}.[7,9] In order to obtain a series of polythiophene derivatives with further increased conductivities, therefore, we expanded this regiocontrolled synthetic method for regioregular poly(3-alkylthiophenes) with Rieke zinc to synthesize totally HT regioregular poly[3-(alkylthio)thiophenes].[13] The detailed experimental procedure including the synthesis and characterization of the monomers and polymers, as well as a discussion of the results, will be covered in this report.

Results and Discussion

Regioselective Synthesis of Poly[3-(alkylthio)thiophenes] Using Rieke Zinc. The Pd- or Ni-catalyzed coupling reaction of organometallic reagents with organic halides[14] has become a general method for the synthesis of polymers. Yamamoto with his coworkers first applied this method to prepare polyarylenes including poly(*p*-phenylene), polythiophene, and poly(3-methylthiophene).[15] Since then, many polyarylenes have been synthesized by the same or a similar technique using dihaloarylene as the polymers' precursors.[16] However, the poly(3-alkylthiophenes) prepared by these reactions were found to have head-to-head and head-to-tail linkages in the polymer units along the main chains. This random coupling at the 2- and 5-positions of the 3-alkylthiophene units was probably the result of polycondensation of different regioisomeric organometallic reagents that were generated from the regiorandom oxidative addition of metal to 2,5-dibromothiophenes.[17] This fact suggested that using regiospecific halothienyl organometallic reagents as monomers could result in higher HT regioregular polymers. Recently, this was verified by our group and others. The Ni(dppe)Cl_2-catalyzed polymerization of 2-bromo-5-(bromozincio)-3-alkylthiophenes or 2-bromo-5-bromomagnesio-3-alkylthiophenes led to a series of nearly 100% HT regioregular poly(3-alkylthiophenes).[6,9]

Recently, the regiocontrolled synthetic route using Rieke zinc was also an efficient synthesis for HT regioregular poly[3-(alkylthio)thiophenes]. A general synthetic route for HT regioregular poly[3-(alkylthio)thiophenes] using Rieke zinc has been reported.[13] This synthetic procedure includes synthesis of 3-(alkylthio)thiophenes (ATTs) by the reaction of room temperature stable 3-lithiothiophene[18] with alkyl disulfides. 2,5-Dibromo-3-(alkylthio)thiophenes (DBATTs) were prepared via bromination of the ATTs in $CHCl_3$. Oxidative addition of Rieke zinc to DBATTs afforded 2-bromo-5-(bromozincio)-(3-alkylthio)thiophenes. The catalytic polymerization of these organozinc reagents and quenching of the polymerization with HCl/MeOH solution followed by Soxhlet extraction with MeOH and hexanes each for 24 h yielded the regioregular poly[3-(alkylthio)thiophenes]. In this multistep approach, the regiospecific preparation of the organozinc reagents using Zn* was a key step (Scheme 1).

Scheme 1. Regioselective Synthesis of HT Regioregular P3ATTs[a]



[a] (i) BuLi, THF/hexanes; (ii) RSSR, THF/hexanes; (iii) Br_2, $CHCl_3$; (iv) Zn*, THF; (v) Ni(DPPE)Cl_2.

The oxidative addition of Zn* to 2,5-dibromo-3-(alkylthio)thiophenes was complete in 2 h and led exclusively to a monoaddition product,[19] 2-bromo-5-(bromozincio)-3-(alkylthio)-thiophene. The regioselectivities of the oxidative addition were surprisingly greater than 99% based on the GC analysis of the acidically quenched reactions. This is a unique advantage of Rieke zinc, providing a convenient route for the synthesis of regiospecific organometallic reagents. Although the formation of the regiospecific organometallic reagents plays a key role, the choice of catalyst for polymerization is also important. It was determined that the regioregularity of the polythiophenes was controlled by the structure of catalysts. Catalysts such as Ni(DPPE)Cl_2, Pd(DPPE)Cl_2, Ni$(PPh_3)_4$, and Pd$(PPh_3)_4$ could be used in the polymerization, but it was found that the poly(3-alkylthiophenes) synthesized by the use of Ni(DPPE)Cl_2 as catalyst gave the highest HT regioregularity (>98.5%).[9] On the basis of this result, we selected Ni(DPPE)Cl_2 as the catalyst to polymerize the 2-bromo-5-(bromozincio)-3-(alkylthio)thiophene to HT regioregular poly[3-(alkylthio)thiophenes] (P3ATTs) (Scheme 1). The HT regioregularity of the poly[3-(octylthio)thiophene] from this process was higher than 90%.

Characterization of the Polymers via Spectroscopy. Liquid NMR Study. Because of the poor solubility of regioregular P3ATTs in general organic solvents like chloroform, methylene chloride, and xylene, the liquid NMR studies of the polymer could be only performed in a carbon disulfide solution using $CDCl_3$ as an external standard. The poly[3-(octylthio)thiophene] (P3OTT) in CS_2 was characterized by solution 360 MHz ^{1}H NMR. In general, ^{1}H NMR data provided important information about the regioregularity of poly(3-substituted thiophenes). The β-protons of thiophene units in different regiochemical circumstances, HT−HT, HT−HH, TT−HT, and TT−HH, had different chemical shifts and showed four singlet peaks in the aromatic area. The ratio of the integration of these peaks was used to determine the regioregularity of the polythiophenes. Since the β-proton of the thiophene units in an HT regioregular poly(3-substituted thiophene) is located in a unique HT−HT arranged regioenvironment, only one singlet aromatic proton peak will be observed in the ^{1}H NMR spectrum. As shown in Figure 1, a sharp and strong singlet aromatic H peak at δ 7.54 was assigned as β-H and indicated at least 90% HT−HT linkage of the thiophene units based upon the integration. The other hydrogen peak assignments are also present in Figure 1.

Infrared Spectroscopy. The FTIR spectra also provided structural information on the polymers. The solid state FTIR spectrum of poly[3-(hexylthio)thiophene] (P3HTT) is shown in Figure 2. Since all the polythiophene derivatives have similar structures, the FTIR spectra of these polymers are almost identical. A strong peak at 628−630 cm^{-1} can be attributed to the C−S stretching vibration from the alkylthio groups connected

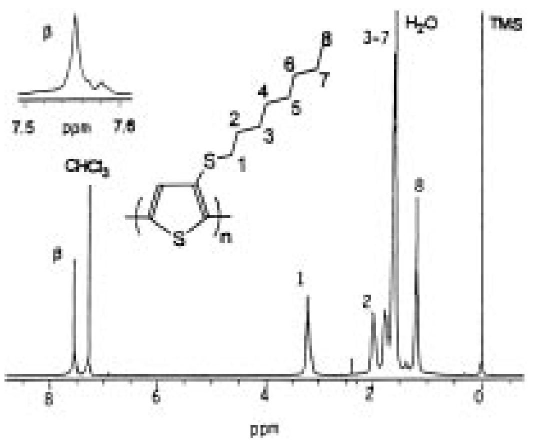


Figure 1. ^{1}H NMR spectrum of regioregular poly[3-(octylthio)-thiophene] in CS_2 solution ($CDCl_3$ as the external standard).

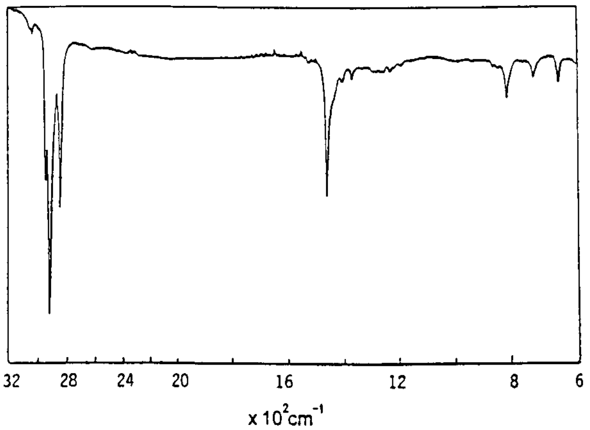


Figure 2. FTIR spectrum of poly[3-(hexylthio)thiophene] cast on NaCl.

into the 3-position of the thiophene.[20] The FTIR spectra also displayed C−H stretching and an out-of-plane vibration of thiophene ring at ∼3056 and ∼819 cm^{-1}, respectively. The aliphatic C−H stretching frequencies were present at ∼2954, ∼2923, and ∼2852 cm^{-1}, and a sharp peak at ∼1411 cm^{-1} was assigned as the ring stretching vibration. The spectrum assignments are summarized in Table 1.

Determination of Polymer Molecular Weight. The molecular weight of the polymers P3HTT, P3OTT, and poly[3-(decylthio)thiophene] (P3DTT) were experimentally determined by gel permeation chromatography (GPC). Because of the low solubility of poly[3-(butylthio)thiophene] (P3BTT), its molecular weight is unmeasurable. The molecular weights of the rest of the polymers were estimated using GPC with THF as the eluent along with polystyrene standards. The poly[3-(alkylthio)thiophenes] were only partially soluble in THF. Accordingly, the higher molecular weight fractions were not dissolved. As a result, these GPC data can be taken only as a rough estimate of the polymer's molecular weight. The approximate molecular weights are found in Table 2. The polymer's molecular weight was also estimated from elemental analysis (C, H, S, Br) assuming the terminal thiophene unit of each polymer contains one bromine atom. This approach suggested, for example, that P3OTT has an average polymer length of 29 thiophene units with an average molecular weight of $M = 6600$.

Solubility in Organic Solvents. The black−brown poly[3-(alkylthio)thiophene] solids, HT regioregular P3HTT, P3OTT, and P3DTT, were slightly soluble in $CHCl_3$, THF, and xylene at room temperature. Increasing the temperature did improve the solubility, and the polymers were eventually dissolved at higher temperatures. For instance, at ambient temperature, $CHCl_3$ partially dissolved P3OTT to form a purple slurry. When the temperature was increased, the mixture gradually turned to a clear, transparent red solution under reflux. Upon cooling, the polymer precipitated from solution. A variety of other solvents was tried, but none demonstrated an improved solubility expect for one. Carbon disulfide was found to dissolve all four polymers. However, the solubility of the polymers in carbon disulfide was dependent on the length of side chains. The longer the side chain, the higher the solubility of the polymers. P3DTT had the best solubility and P3BTT had the worst solubility. The slow evaporation of the dark red carbon disulfide solutions produced golden, shiny thin films on glass, except for P3BTT.

Table 1. Comparison of IR Band Position (cm^{-1}) and Their Assignment for Poly[3-(alkylthio)thiophenes]

	P3HTT	P3OTT	P3DTT
aromatic C−H str	3054	3056	3054
aliphatic C−H str	2954	2954	2954
	2923	2923	2921
	2854	2852	2852
ring str	1465	1465	1465
aromatic C−H out-of-plane	819	819	819
C−S str	628	628	628

Table 2. Molecular Weights and Polydisperisties of Poly[3-(alkylthio)thiophenes] Determined by GPC and Calculation

P3ATT	M_w	M_n	M_w/M_n	M_{calcd}
P3BTT				2354
P3HTT	6990	6090	1.15	7000
P3OTT	4890	4420	1.11	6000
P3DTT	4170	4030	1.03	6000

Solution UV−vis Spectroscopy. Since the relation between electronic structure and the backbone conformation is a general and interesting feature of conjugated polymers, the UV−vis data of the P3ATT solutions provided conformational information on the polymer chain. As the literature indicated, the poly(3-substituted thiophenes) in solution have two conformations: rod-like and coil-like. The more rod-like conformation resulted from the longer conjugation length along the main chain responding to a λ_{max} with a larger wavelength in the UV spectrum.[21] The UV experiments in our study were carried out by using very dilute polymer solutions in chloroform. As the UV experiments were carried out in a dilute chloroform solution, solubility was not a problem and the UV spectra were determined for the complete polymer mix obtained in the synthesis. The solution UV−vis spectra in Figure 3 showed that the regioregular HT P3ATTs had a maximum absorption wavelength (λ_{max}) at ∼500 nm ranging from 497 to 510 nm. Compared to the solution UV−vis data of regioregular HT poly(3-alkylthiophenes) (P3ATs), the P3ATTs have a longer λ_{max}, and the difference between the UV−vis λ_{max} of the sister series of polythiophenes in $CHCl_3$ is about 45 nm (Figure 4). Accordingly, the poly[3-(alkylthio)thiophenes] have a lower $\pi-\pi^*$ transition energy than regioregular poly(3-alkylthiophenes) in $CHCl_3$ solution. A similar phenomenon was observed in the 3-ethereal-substituted polythiophenes, and was explained as the contribution of the electron-donating nature of the heteroatom on the 3-position.[10b] Part of the red-shift may also be coupled to conformational

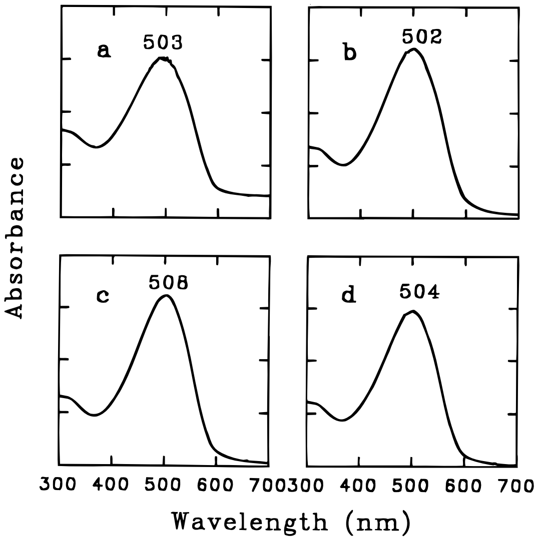


Figure 3. Solution UV–vis spectra of poly[3-(alkylthio)-thiophenes] in $CHCl_3$: (a) P3BTT, (b) P3HTT, (c) P3OTT, and (d) P3DTT.

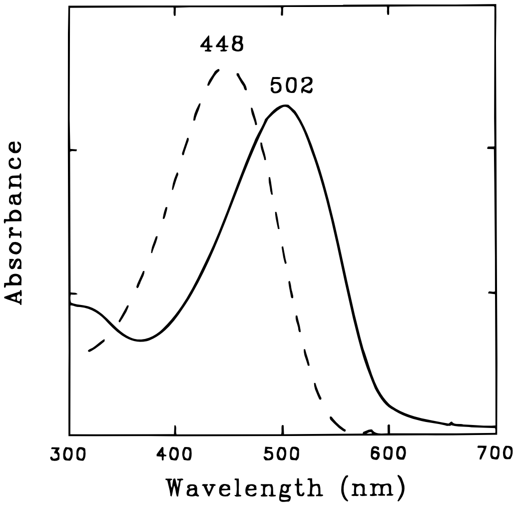


Figure 4. The comparison of the solution UV–vis spectra of poly(3-octylthiophene) and poly[3-(octylthio)thiophene] in $CHCl_3$: P3OTT, —; P3OT, - - -.

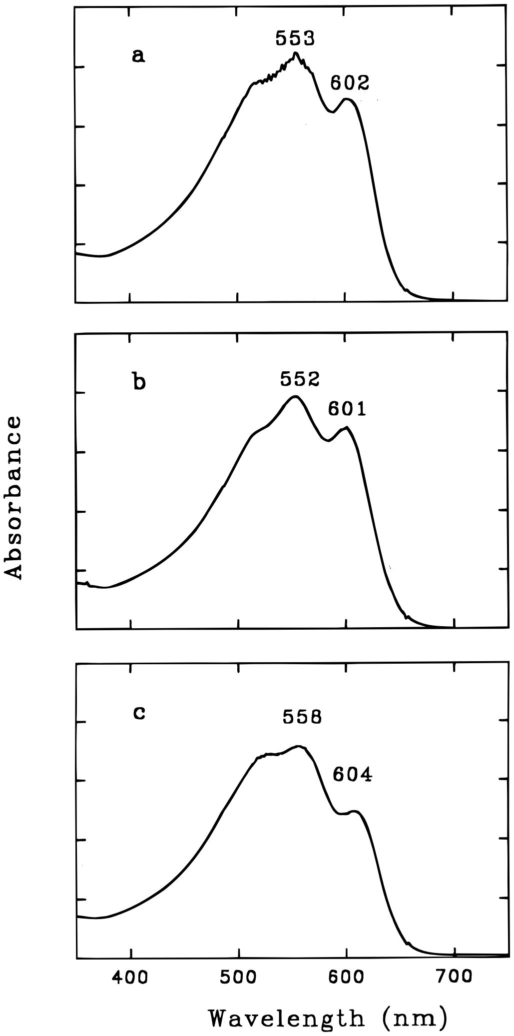


Figure 5. Solid-state UV–vis spectra of regioregular poly[3-(alkylthio)thiophenes]: (a) P3HTT, (b) P3OTT, and (c) P3DTT.

factors which are expected to be different for a alkylthio side chain versus an alkyl side chain. However, no definitive conclusions can be stated in this regard.

Solid-State UV–vis Spectroscopy. Insight into the extent of the polymer conjugation and structure, as well as the solid-state electronic effects of the polymeric materials can be inferred from the solid-state UV–vis spectra. A low $\pi-\pi^*$ transition energy was observed in the spectra of P3HTT, P3OTT, and P3DTT thin cast film on glass (Figure 5) The $\pi-\pi^*$ transition is exhibited by the absorption with maximum wavelength (λ_{max}) at ~605 nm, along with a peak at ~550 nm and a shoulder at ~520 nm. The onset of the $\pi-\pi^*$ transition is located at ~700 nm. A comparative research displays that these data are very similar to the HT regioregular P3ATs UV spectra. This indicates that the HT regioregular poly[3-(alkylthio)thiophenes] and poly(3-alkylthiophenes) have approximately the same energy in the $\pi-\pi^*$ transition in solid state. The fact that regioregular P3ATTs has a higher λ_{max} value than regioregular P3ATs in dilute solution UV spectra but has the same λ_{max} in solid-state UV suggests that the thioethereal junction between the alkyl group and the thiophene units in polythiophenes weakens the solvated side chain's mechanical influence on the backbone conformation in solution. This also implies that the electron-donor property of alkylthio side chains do not affect the electronic structure of the material as significantly as the regioregularity does.

X-ray Diffraction Study. The X-ray structural studies of the oriented poly(3-alkylthiophenes) have been well-established by Winokur and his co-workers.[22] This research shows that the oriented polymer solution-cast films have well-organized lamellar structures, and the long planar polymer main chains are uniformly spaced by the alkyl side chains. The self-orienting properties of regioregular P3ATs, synthesized by regiocontrolled polymerization, have been clearly elucidated through X-ray diffraction studies.[9,23] Similarly, the regioregular HT poly[3-(alkylthio)thiophenes] are another series of polycrystalline and self-orienting polymers. The X-ray diffraction pattern of the cast film of the P3ATTs presented strong first-, second-, and third-order 2θ reflections (Figure 6). These film X-ray data show a unique feature of these polymers, a *d*-spacing of well-organized lamellar structure. The X-ray indicates that the different P3ATTs have their own unique 2θ values, which can be interpreted into the distance of the *d*-space between two adjacent parallel polymer main chains. The 2θ degree values as well as the *d*-spacing distance are found in Table 3. It can be seen that the longer side chain of the polymers causes a

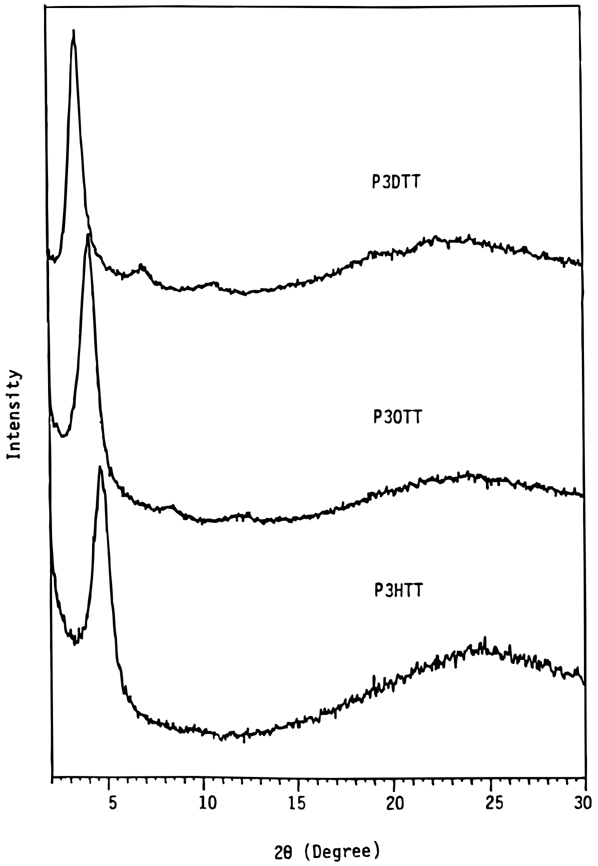


Figure 6. X-ray pattern of the cast films of regioregular poly-[3-(alkylthio)thiophene].

Table 3. 2*θ* Reflections of the X-ray Diffraction Pattern of Poly[3-(alkylthio)thiophenes] and *d*-Spacing

	2*θ* (deg)			*d*-spacing distance (Å)
	1st	2nd	3rd	
P3BTT	–	–	–	
P3HTT	4.8	–	–	18.39
P3OTT	4.1	8.2	12.2	21.54
P3DTT	3.5	7.0	10.6	25.20

longer *d*-spacing distance. A comparative analysis of the X-ray data of the P3OT and P3OTT indicates that the P3OTT has a longer *d*-spacing, 21.54 Å, 1.44 Å longer than that of P3OT (Scheme 2). The longer *d*-spacing of P3OTT is the result of the longer side chains due to an additional sulfur atom in the octyl group of the thiophene unit.

The Electroconductivity of P3ATTS. The narrow band gap suggests that the P3ATTs might yield highly conducting polymers on doping. A shiny, golden cast film of the P3ATTs, exposed to I_2 vapor, turned to a black–blue film. The I_2-doped polymers exhibited a conductivity of approximately 10^2 S cm^{-1} (determined by the four-probe method). This conductivity is 5 orders of magnitude higher than that of the regiorandom poly-[3-(ethylthio)thiophene][11a] and 4 orders of magnitude higher than that of the regiorandom poly[3-(methylthio)-thiophene][11b,c] generated by other methods. The polymer's solid-state, solution UV–vis data and the I_2-doped conductivities are present in the Table 4.

Conclusion

A series of highly regioregular poly[3-(alkylthio)-thiophenes] have been synthesized. A key step in the synthesis is the highly regioselective oxidative addition of Rieke zinc to the 5-position of the 2,5-dibromo-3-(alkylthio)thiophene. The resulting organozinc reagent was conveniently polymerized in a highly regioregular manner with $Ni(DPPE)Cl_2$. The films of the polymers are polycrystalline and yield highly conducting film upon doping with I_2. The conductivities are similar to that of the highly regioregular poly(3-alkylthiophenes).

Scheme 2. Comparison of *d*-Spacings between HT Regioregular Poly[3-(octylthio)thiophene] and Poly(3-octylthiophene)

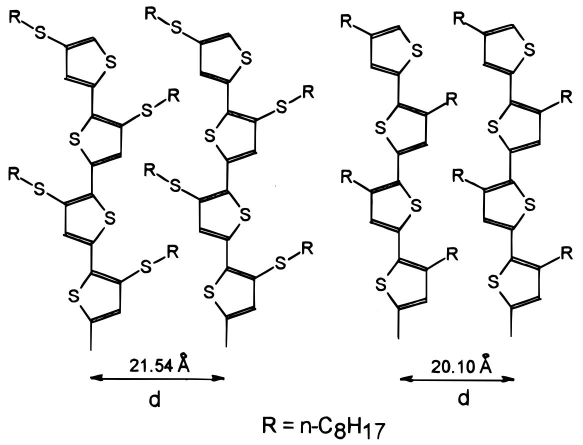


Table 4. UV–Vis Data of Poly[3-(alkylthio)thiophenes] and the Electroconductivities of the I_2-Doped Polymers

	λ_{max} (nm)		I_2-doped conductivity (S/cm)
	solution	solid	
P3BTT	497	–	–
P3HTT	503	526, 553, 610	200–500
P3OTT	510	525, 552, 600	400–700
P3DTT	505	525, 563, 616	200–600

Experimental Section

Reagents. Lithium (ribbon), $Ni(DPPE)Cl_2$, *n*-BuLi (2.5 M in hexanes) were purchased from Aldrich Chemical Co., $ZnCl_2$ (anhydrous) was from Cerac Inc., and alkyl disulfides were prepared according to the literature procedure.[24] 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 pentocide 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 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 instrument. All the monomer NMR samples were dissolved in $CDCl_3$. ^1H NMR spectra chemical shifts were reported in parts per million (δ) in reference to the 7.26 ppm peak for $CDCl_3$ or downfield from TMS ($\delta = 0$) as an internal standard. ^{13}C NMR chemical shifts (δ) were reported in reference to the 77.00 ppm peak for $CDCl_3$. The poly[3-(octylthio)thiophene] NMR sample was dissolved in CS_2. The chemical shifts were reported in ppm in reference to the 7.26 ppm peak for $CDCl_3$ as the external standard. Infrared spectra were taken on an Analect RFX-65 FTIR spectrophotometer with neat polymer films cast from CS_2 solutions on NaCl disks and reported in ν as cm^{-1}. UV–vis spectra were taken on a Hewlett-Packard 8452A diode array spectrophotometer with both polymer solutions in $CHCl_3$ and neat polymer thin films cast from CS_2 solutions on a glass plate and reported in nanometer. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Molecular weights were determined (relative to polystyrene standard) on a Waters gel permeation chromatograph (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 2100 on a Supelco support and interfaced with a Perkin-Elmer LCI-100 integrator. 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. The P3ATs samples for X-ray measurement were the films cast from CS_2 solution onto 120 μm glass coverslip by slow evaporation.

The electroconductivities of doped polymers (films cast from CS_2 solution 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. The thicknesses of the films, cast on glass from CS_2 solutions, were determined by a Dektak 3030 Profilometer.

The Typical Procedure for the Preparation of 3-(Alkylthio)thiophenes. Preparation of 3-(Butylthio)thiophene. To a solution of 3-bromothiophene (0.02 mol) was added n-butyllithium (0.021 mol, 2.5 M in hexane) in hexane (30 mL) at −40 °C under argon. THF (3 mL) was added by syringe. A white 3-lithiothiophene suspension formed immediately upon the addition of THF. After 3-bromothiophene was completely consumed (ca. 15 min), fresh hexane (10 mL) was added and the mixture was then warmed to room temperature. At this temperature, the 3-lithiothiophene suspension was cannulated into an *n*-butyl disulfide (0.02 mol) solution in hexane (20 mL). The reaction was worked up with saturated NH_4Cl aqueous solution (20 mL) in 0.5 h, and the organic layer was extracted with ethyl ether (20 mL). The crude product was obtained by the evaporation of the solvents and purified via chromatography on flash silica gel with hexanes in 54% yield. 3-(Butylthio)thiophene was characterized with ^{1}H, ^{13}C NMR, and mass spectrum. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.31 (dd, 1H), 7.11 (dd, 1H), 7.02 (dd, 1H), 2.85 (t, 2H), 1.59 (m, 2H), 1.45 (m, 2H), 0.92 (t, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 132.3, 129.6, 125.9, 122.8, 34.9, 31.4, 21.8, 13.6. EIMS *m/z* (relative intensity): 172 (38, $C_8H_{12}S_2^+$), 116 (100, $C_4H_4S_2^+$). HRMS: calcd for $C_8H_{12}S_2$ 172.0380, found 172.0382.

3-(Hexylthio)thiophene. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.30 (dd, 1H), 7.11 (dd, 1H), 7.01 (dd, 1H), 2.84 (t, 2H), 1.62 (m, 2H), 1,41 (m, 2H), 1.31 (m, 4H), 0.89 (t, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 132.3, 129.6, 125.9, 35.3, 31.3, 29.3, 28.4, 22.5, 14.0. Anal. Calcd: C, 59.95; H, 7.99; S, 32.00. Observed: C, 59.86; H, 8.30; S, 32.37. EIMS *m/z* (relative intensity): 200 (38, $C_{10}H_{16}S_2^+$), 116 (100, $C_4H_4S_2^+$). HRMS: Calcd for $C_{10}H_{16}S_2$ 200.0693, found 200.0698.

3-(Octylthio)thiophene. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.31 (q, 1H), 7.13 (dd, 1H), 7.02 (dd, 1H), 2.84 (t, 2H), 1.64 (m, 2H), 1.38 (m, 2H), 1.29 (m, 8H), 0.88 (t, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 132.4, 129.6, 125.9, 122.8, 35.3, 31.8, 29.4, 29.1, 28.7, 22.7, 14.0. Anal. Calcd: C, 63.10; H, 8.83; S, 28.07. Observed: C, 63.33; H, 9.09; S, 28.10. EIMS *m/z* (relative intensity): 228 (27, $C_{12}H_{20}S_2^+$), 116 (100, $C_4H_4S_2^+$). HRMS: Calcd for $C_{12}H_{20}S_2$ 228.1006, found 228.1002.

3-(Decylthio)thiophene. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.31 (q, 1H), 7.11 (dd, 1H), 7.02 (dd, 1H), 2.84 (t, 2H), 1.60 (m, 2H), 1.38 (m, 2H), 1.28 (m, 10H), 0.88 (t, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 132.4, 129.6, 125.9, 122.8, 35.3, 31.9, 29.5, 29.5, 29.4, 29.3, 29.1, 28.7, 22.6, 14.1. Anal. Calcd: C, 65.6; H, 9.36; S, 24.97. Observed: C, 65.81; H, 9.63; S, 24.65. EIMS *m/z* (relative intensity): 256 (36, $C_{14}H_{24}S_2^+$), 116 (100, $C_4H_4S_2^+$). HRMS: Calcd for $C_{14}H_{24}S_2$ 256.1319, found 256.1327.

Preparation of 2,5-Dibromo-3-(Alkylthio)thiophenes. All 2,5-dibromo-3-(alkylthio)thiophenes were prepared by the dibromination of 3-(alkylthio)thiophenes with Br_2 in chloroform at room temperature. To 3-(octylthio)thiophene solution in $CHCl_3$ (30 mL) was added dropwise 3.5 g of Br_2 in $CHCl_3$ (20 mL) through a dropping funnel. The colorless 3OTT solution gradually turned into dark yellow−green during the addition of the Br_2 solution. And HBr as the byproduct was released and trapped by a NaOH aqueous solution. The bromination reaction was quenched with a saturated $NaHCO_3$ solution in 4 h, and the organic layer was extracted with ethyl ether (30 mL). The organics were concentrated and chromatographed on silica gel with hexanes. The pure 2,5-Dibromo-3-(octylthio)thiophene was obtained in 80% yield. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.90 (s, 1H), 2.56 (t, 2H), 1.52 (m, 2H), 1.40 (m, 2H), 1.25 (m, 8H), 0.90 (t, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 134.1, 132.3, 112.8, 110.9, 35.3, 31.8, 29.5, 29.0, 28.5, 22.6, 14.1. Anal. Calcd: C, 37.32; H, 4.70; S, 16.60; Br, 41.38. Observed: C, 37.57; H, 4.75; S, 16.24; Br, 40.99. EIMS *m/z* (relative intensity): 384 (32, $C_{12}H_{18}S_2Br_2^+$), 276 (55, $C_4H_2S_2Br_2^+$). HRMS: Calcd for $C_{12}H_{18}S_2Br_2$ 383.9216, found 383.9222.

2,5-Dibromo-3-(butylthio)thiophene. ^{1}H NMR ($CDCl_3$, 360 MHz): δ 6.89 (s, 1H), 2.82 (t, 2H), 1.54 (m, 2H), 1.24 (m, 2H), 0.90 (t, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 147.9, 132.3, 112.8, 109.9, 34.9, 31.5, 21.6, 13.6. Anal. Calcd: C, 29.1; H, 3.1; S, 19.4; Br, 48.4. Observed: C 29.36; H, 2.98; S, 19.79; Br, 48.6.

2,5-Dibromo-3-(hexylthio)thiophene. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.90 (s, 1H), 2.82 (t, 2H), 1.58 (m, 2H), 1.37 (m, 2H), 1.26 (m, 6H), 0.88 (t, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 134.0, 132.3, 112.8, 110.8, 35.3, 31.3, 29.5, 28.2, 22.5, 14.0. Anal. Calcd: C, 33.54; H, 3.94; S, 17.90; Br, 44.62. Observed: C 33.40; H, 3.84; S, 17.89; Br, 44.30. EIMS *m/z* (relative intensity): 356 (23, $C_{10}H_{14}S_2Br_2^+$) 276 (41, $C_4H_2S_2Br_2^+$). HRMS: Calcd for $C_{10}H_{14}S_2Br_2$ 355.8903, found 355.8901.

2,5-Dibromo-3-(decylthio)thiophene. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.88 (s, 1H), 2.58 (t, 2H), 1.52 (m, 2H), 1.36 (m, 2H), 1.24 (m, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 134.1, 132.4, 112.8, 110.9, 35.3, 31.9, 29.5, 29.4, 29.3, 29.1, 28.5, 22.6, 14.0. Anal. Calcd: C, 40.59; H, 5.35; S, 15.54; Br, 38.58. Observed: C, 40.71; H, 5.44; S, 15.08; Br, 38.34. EIMS *m/z* (relative intensity): 412 (26, $C_{14}H_{22}S_2Br_2^+$), 276 (47, $C_4H_2S_2Br_2^+$). HRMS: Calcd for $C_{14}H_{22}S_2Br_2$ 411.9530, found 411.9518

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, and the flask was sealed with a septum and a condenser topped with stopcock outlet. Similarly, $ZnCl_2$ (1.50 g, 11.0 mmol) was weighed into a 50-mL, two-neck round-bottom flask, equipped with a stir bar, and 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 $ZnCl_2$ was dissolved in 25 mL of THF. To the flask with lithium and naphthalene, the THF solution of $ZnCl_2$ was transferred via cannula dropwise so as addition was complete in ca. 1.5 h with 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 $ZnCl_2$ (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. $ZnCl_2$ was dissolved in 20 mL of THF and the solution was transferred into the flask with lithium naphthalide via cannula in 10 min. The reaction mixture was stirred for an additional hour, and a black slurry of active zinc was thus prepared.

General Preparation of Regioregular HT Poly[3-(alkylthio)thiophenes] from 2,5-Dibromo-3-(alkylthio)thiophenes. Preparation of Regioregular HT Poly[3-(hexylthio)thiophene] (P3HTT). 2,5-Dibromo-3-(hexylthio)thiophene (1.79 g, 5.0 mmol, in 20 mL of THF) was added via cannula to the newly prepared Zn* (5.5 mmol, in 40 mL of THF) by following procedure a at 0 °C. The mixture was stirred for 1 h at this temperature and allowed to warm to 25

°C naturally in ca. 3 h. A 1.0 mol % portion of Ni(DPPE)Cl_2 (26.4 mg, 0.05 mmol, in 20 mL THF) was added via cannula at 0 °C. The mixture was stirred for 10 h at room temperature. A dark red−purple precipitate was formed gradually during this period. Then the temperature was increased to 30−40 °C and kept there for an additional 10 h. The mixture was poured into a solution of MeOH (100 mL) and 2 N HCl (50 mL), and the resulting dark precipitate was filtered and washed with MeOH and 2 N HCl solution, and then dried in a Büchner funnel. The oligomeric residue was subjected to Soxhlet extraction with MeOH and then hexanes each for 24 h. The final product is a black−brown solid weighed 0.6 g with a yield of 63%.

Poly[3-(butylthio)thiophene] (P3BTT). Anal. Calcd for $-(C_8H_{10}S_2)-_n$: C, 56.43; H, 5.88; S, 37.69. Observed: C, 54.54; H, 5.60; S, 36.86; Br, 3.13.

Poly[3-(hexylthio)thiophene] (P3HTT). Anal. Calcd for $-(C_{10}H_{14}S_2)-_n$: C, 60.57; H, 7.07; S, 32.36. Observed: C, 59.28; H, 6.74; S, 30.93; Br, 2.4.

Poly[3-(octylthio)thiophene] (P3OTT). Anal. Calcd for $-(C_{12}H_{18}S_2)-_n$: C, 63.68; H, 7.96; S, 28.36. Observed: C, 63.61; H, 7.72; S, 27.78; Br, 1.2.

Poly[3-(decylthio)thiophene] (P3DTT). Anal. Calcd for $-(C_{14}H_{22}S_2)-_n$: C, 66.11; H, 8.66; S, 25.23. Observed: C, 65.00; H, 8.12; S, 25.16; Br, 1.48.

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(12) The decrease in the band gap of poly[3-(alkoxy)thiophenes] and poly[3-(alkylthio)thiophenes] was generally reported according to a red-shift of $\lambda_{\max}$ in UV spectra (see refs 11 and 12). However, the conductivities were lower than those of poly(3-alkylthiophenes). This conflict between the reality and the presumption had three rationalizations: (a) $\alpha-\beta'$ coupling decreased the conjugation length in the doped state, (b) lower solubility led to a lower molecular weight polymer with a shorter conjugation, and (c) the heteroatom of the substituents localized the electron charge. But these explanations are still questionable. The clear elucidation is the subject of further research.

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