Poly(2,5-ethynylenethiophenediylethynylenes), Related Heteroaromatic Analogues, and Poly(thieno[3,2-*b*]thiophenes). Synthesis and Thermal and Electrical Properties

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ABSTRACT: The novel class of polymers poly(2,5-ethynylenethiophenediylethynylenes) (**1a–f**) and related materials **2** and **3** undergo a cross-linking reaction at moderate temperatures. The thermal reactivity of the polymers containing a diethynyl moiety provided substantial insight into the solid-state cross-linking reaction of polymeric conjugated diacetylenes. The intrinsic conductivities of the poly(2,5-ethynylenethiophenediylethynylenes) were in the insulating region. Upon doping with strong oxidants such as arsenic pentafluoride or the strong reducing agent sodium naphthalide, the conductivity increased into the semiconducting regime. Unreacted and cross-linked materials exhibit similar electrical conductivities. Investigations of the electrical conductivities of novel polymers, poly(5,5′-ethynylene-2,2′-bithiophenediylethynylene) (**2**) and poly[2,5-ethynylene(thieno[3,2-*b*]thiophenediyl)ethynylene] (**3**), were carried out to afford materials which upon doping were also semiconductive. Very little interaction between the aforementioned polymers **1a–f**, **2**, and **3** and the dopants was observed. This result is proposed to be due to a high oxidation potential of the polymers. New syntheses of poly(2,5-thieno[3,2-*b*]thiopheneylene) (**4a**,**5a**) and poly[2,5-(3-methylthieno[3,2-*b*]thiopheneylene)] (**4b**,**5b**) by $FeCl_3$ oxidation and by electrochemical polymerization of the respective monomers afforded conductive materials upon doping.

Introduction

Electrically conductive organic polymers have received considerable attention in recent years.[1] Linear polyenes and heterocyclic polymers often exhibit electrical conductivity and consist of a conjugated polymer backbone that allows extensive electron delocalization. The pristine materials typically are insulating or semiconducting. Doping by partial oxidation or reduction results in charge defects within the polymer. Conductivities in the metallic range have been realized.[2] Long conjugation lengths, $n_L \geq 5$, are thought to be necessary for high conductivities to be achieved.[3] However, conjugation length alone is not sufficient to ensure conductivity, as some interchain hopping or tunneling of the charge carriers must also occur.

Polyacetylene has been the most studied conducting polymer,[4-6] and a high degree of crystallinity of the polymer contributes to its exceptional conductivity. However, its lack of processability and its thermal and environmental instability make this material less attractive than conventional metals. Notable conductivities were also found in other sp^2-hybridized systems such as poly(*p*-phenylene)[7] and polypyrrole.[8] The number of reports on the conductivities of other polymeric systems continues to increase. Materials which offer good thermal, environmental, and processibility characteristics, in combination with high electrical conductivity are in demand. Recent literature directed at understanding the structure–property relationships and the nature of the charge carriers in conducting polymers has proceeded.[1,3,9]

Conducting polymers containing heterocyclic units in the backbone have been described, including polypyrroles,[10] polythiophenes,[11] polycarbazoles,[12] polyquinolines,[13] and polyphthalocyanines.[14] Polyheterocycles offer increased environmental and thermal stability in both the conductive and neutral states when compared with polyacetylene. They are readily synthesized by electrochemical methods due to favorable oxidation potentials, and several chemical methods of synthesis are available.[10] Relative to this work, polythiophenes and polydiacetylenes are of the greatest interest as conducting polymers. Polythiophene and its alkylated derivatives are some of the most thermally and environmentally stable conductive polymers in both neutral and conductive (oxidized) states. Unlike many other conductive polymers, the oxidation potential of polythiophene lies between that of O_2 and H_2O. Hence, the chemical reactivity of polythiophenes toward atmospheric constituents is very low, as compared to polyacetylene, for example, which rapidly decomposes in air.

Polydiacetylenes have been investigated mostly for their nonlinear optical properties rather than their electrical conductivity.[15] Theoretically, polydiacetylene should exhibit conductivities similar to that of polyacetylene. Both have long conjugation lengths and ionization potentials, and band gaps are similar for polyacetylene and polydiacetylene (5.2 vs 4.7 eV and 2.1 vs 1.8 eV, respectively).[16] However, upon doping conductivities of only 10^{-5}–10^{-3} S/cm were realized for polydiacetylene.[17] Typical polydiacetylenes are prepared from crystalline monomers which yield macrosingular crystals. These structures may limit the availability of doping sites and, thus, the number of charge carriers.[3]

Herein, we report the synthesis and characterization of polymers which combine the functionalities of thiophene and diacetylene. Polymers **1a–f**, **2**, and **3** were prepared using the Glaser coupling reaction from diethynyl monomers, which was pioneered by Hay[18] in the oxidative polymerization of diethynylbenzenes. Earlier we reported preliminary results on the synthesis of polymers **1a–d** and our interest in the thermal and electrical properties of these polymers.[19,20] Others have published similar approaches in the polymerization of diethynyl aromatic and heteroaromatic materials.[21-23] In addition to the diethynylene polymers described above, poly(2,5-thieno[3,2-*b*]thiopheneylene) and poly[2,5-(3-methylthieno[3,2-*b*]thiopheneylene)] were prepared either by oxidation of the

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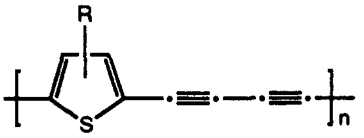
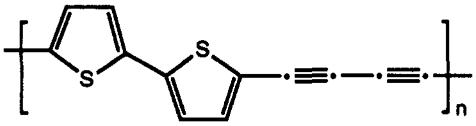
monomers with $FeCl_3$ or by electrochemical polymerization. Insoluble powders **4a** and **4b** were obtained from polymerization with $FeCl_3$. Free-standing films of **5a** and **5b** were obtained from electrochemical polymerization. The electrical conductivities of polymers **4a** and **4b** and **5a** and **5b** were measured. Upon thermolysis of poly(diethynylenethiopheneylene)s, cross-linked materials were generated by the reaction of the diethynyl moiety. The cross-linking reaction proceeds without the evolution of volatiles or the formation of voids. Also, conjugation is maintained along the polymer backbone which provides novel and intriguing polymer networks.



1 a) R = H
b) Me
c) n-C_4H_9
d) n-C_6H_{13}
e) n-C_8H_{17}
f) Ph



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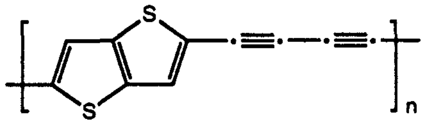

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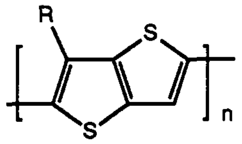


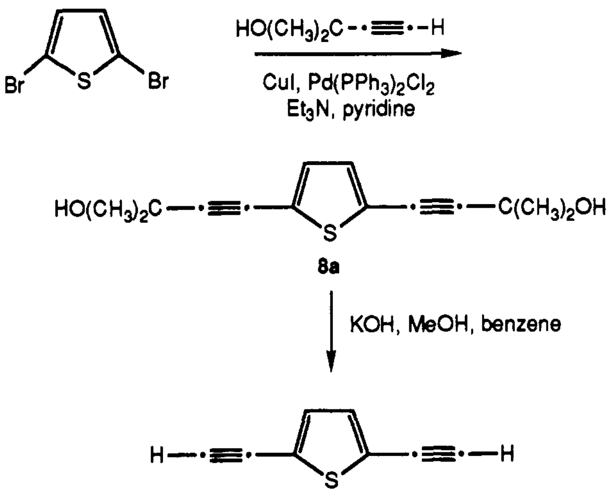
4 (chemical)
5 (electrochemical)
a) R = H
b) Me

Results and Discussion

A new class of reactive, conductive polymers was synthesized by the oxidative polymerization of diethynylthiophene monomers. The synthesis of the diethynylthiophene monomers is outlined in Scheme I. Alkylation and bromination gave the desired dibromothiophenes. These were subjected to a palladium-catalyzed cross-coupling reaction described by the reaction of a (trialkylsilyl)acetylene with the aforementioned dihalothiophene. After hydrolysis, the diethynylthiophene monomers were polymerized by catalytic oxidative cuprous coupling. The unsubstituted diethynylthiophene polymer (**1a**, R = H) was anticipated to be insoluble; therefore, a number of alkylated derivatives, **1b–e**, were prepared.

The synthesis of 2,5-diethynylthiophene (**7a**) was initially attempted via the palladium-catalyzed cross-coupling of 2,5-diiodothiophene with (tributylstannyl)acetylene. Several solvent systems with a variety of catalysts were attempted.[24] The purification steps required in these reactions were too severe to allow isolation of the product in good yield. (Trimethylstannyl)acetylene[25] as a coupling partner allowed a less strenuous purification sequence but gave low yields of desired product. Analysis of the primary byproduct from the above reaction, a yellow solid, by ^1H NMR showed a high ratio of thienyl to acetylenic protons. This indicated that the product **7a** was reactive with 2,5-diiodothiophene under the coupling conditions, to form oligomeric species of alternating thiophene–acetylene units. In related investigations, good yields of alkynyl products were obtained in the palladium-catalyzed coupling reaction of acetylenic tin reagents with electrophiles in the absence of a terminal acetylene.[26]

Although a series of protection–deprotection reactions of the acetylenic tin reagent would give good yields of coupled product, we pursued two other synthetic methods to synthesize the diethynyl aromatics. The first method involved coupling an acetylenic alcohol with 2,5-dibromothiophene in the presence of bis(triphenylphosphine)palladium dichloride, copper(I) iodide, and excess triphenylphosphine.[27] This reaction afforded a 52% yield of the protected derivative, **8a** (eq 1). Deprotection of **8a** was achieved with potassium hydroxide in benzene and methanol at reflux to afford **7a**. Variation in yields was obtained due to the volatility of the diacetylene **7a**.



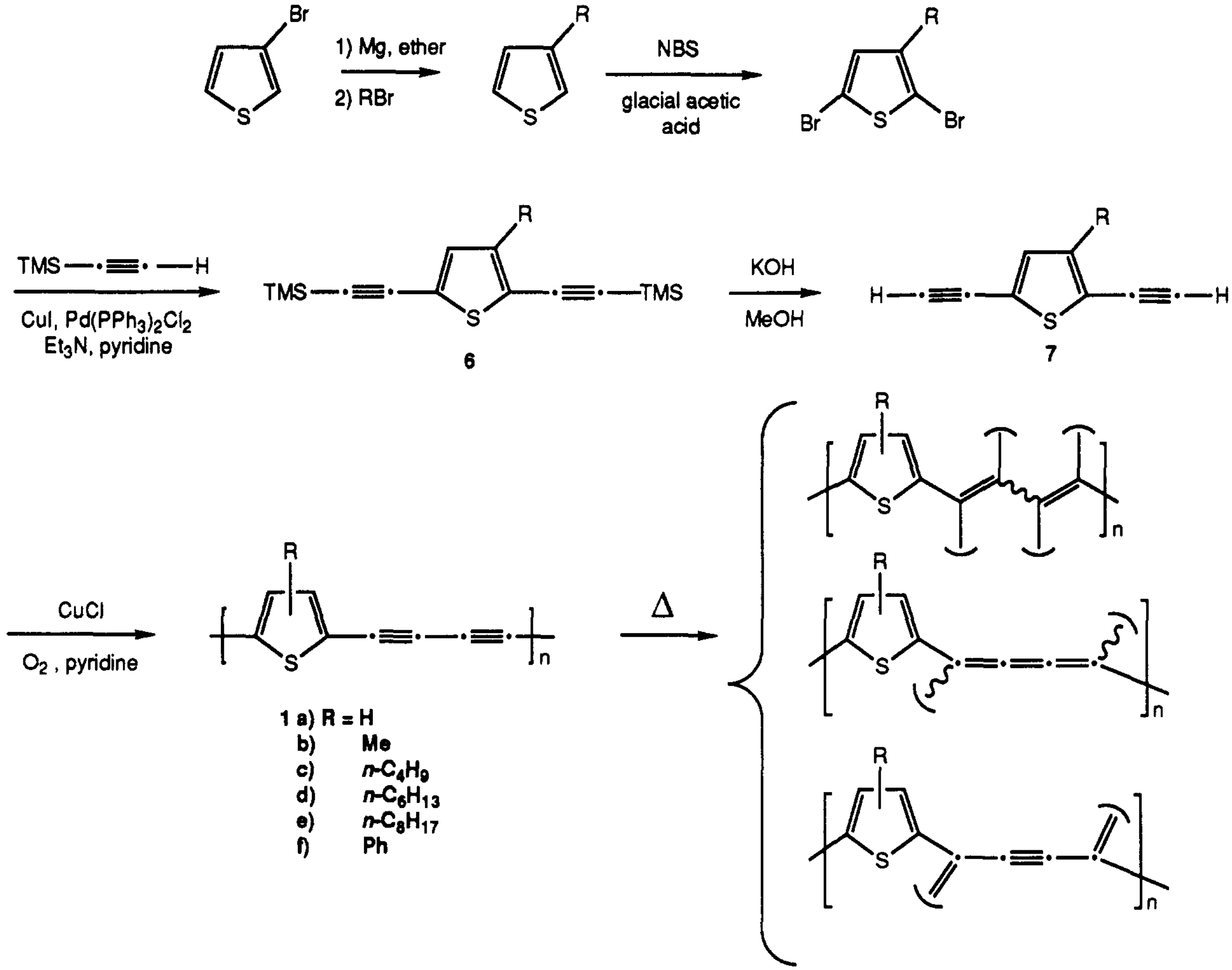
(1)

7a

A coupling reaction which yielded **7a** (68%) with a more easily deprotected product used (trimethylsilyl)acetylene with 2,5-dibromothiophene in the presence of $Pd(PPh_3)_2Cl_2$ and copper(I) iodide[28] (see Scheme I). Deprotection of **6a** was accomplished at ambient temperature with aqueous potassium hydroxide in methanol.[29] However, due to the extreme volatility of the product, careful isolation and purification were needed to obtain respectable yields.

The synthesis of 2,5-diethynyl-3-methylthiophene (**7b**) was carried out by bromination of 3-methylthiophene,[30] followed by ethynylation with (trimethylsilyl)acetylene, and deprotection (Scheme I). A 45% overall yield was obtained in this three-step synthesis. The syntheses of the remaining monomers, **7c–f**, are also described in Scheme I. The more highly alkylated derivatives, **7c–e**, were prepared to study the effect of substitution upon the solubility of the corresponding polymers. The 3-phenyl derivative, **7f**, was included in order to investigate the thermal stability and possible mode of decomposition of the polymers. All monomers were obtained in good overall

Scheme I



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yields from a sequence of alkylation,[31] bromination, ethynylation,[29] and deprotection. In the presence of long alkyl side chains (**6c–e**), it was necessary to use a mild brominating agent such as *N*-bromosuccinimide.[32]

The diethynyl monomers **7a–f** are thermally unstable compounds and must be handled with care. These materials were purified by flash chromatography on silica with pentane as eluent to facilitate solvent removal in the absence of heating. The purified monomers were used immediately in the polymerization reaction or, if necessary, were stored as dilute solutions in pentane at 0 °C. Decomposition of the pentane solutions was apparent by an orange color after storage of more than a few days.

The oxidative polymerization of monomers **7a–f** was accomplished by treatment of a solution of the monomer in pyridine with copper(I) chloride and oxygen.[18] Polymers **1a–f** were obtained in yields varying from 70 to 96%. Polymers **1a** and **1b** were dark-brown and red powders, respectively, which were slightly soluble in hot nitrobenzene or hot chlorobenzene. Shiny, dark pellets could be pressed from both materials at 15 000 psi for 2–3 min. These materials were anticipated to be fairly insoluble due to the rigid, rod-like structure of the polymer. The angle between substituents at C2 and C5 is thought to be approximately 175° by analogy to other 2,5-disubstituted thiophenes.[33]

All substituted polymers could be expected to possess a random orientation of head-to-head and head-to-tail groups. Better solubility was realized with longer alkyl side chains as thienyl substituents. Polymers **1c–e** were dark purple solids which were mostly soluble (75–90%) in solvents such as tetrachloroethane (TCE) or chloroform (except **1c** which was much less soluble in chloroform than in TCE). The polymerization conditions were varied in attempts to prevent the formation of an insoluble fraction of the polymer, which was obtained in small amounts in all instances. All polymerizations were carried out in the absence of light to avoid any photolytic cross-linking during the reaction; however, no differences in the isolated polymers were observed whether or not light was excluded. No further characterization of the insoluble fractions of the polymers was done.

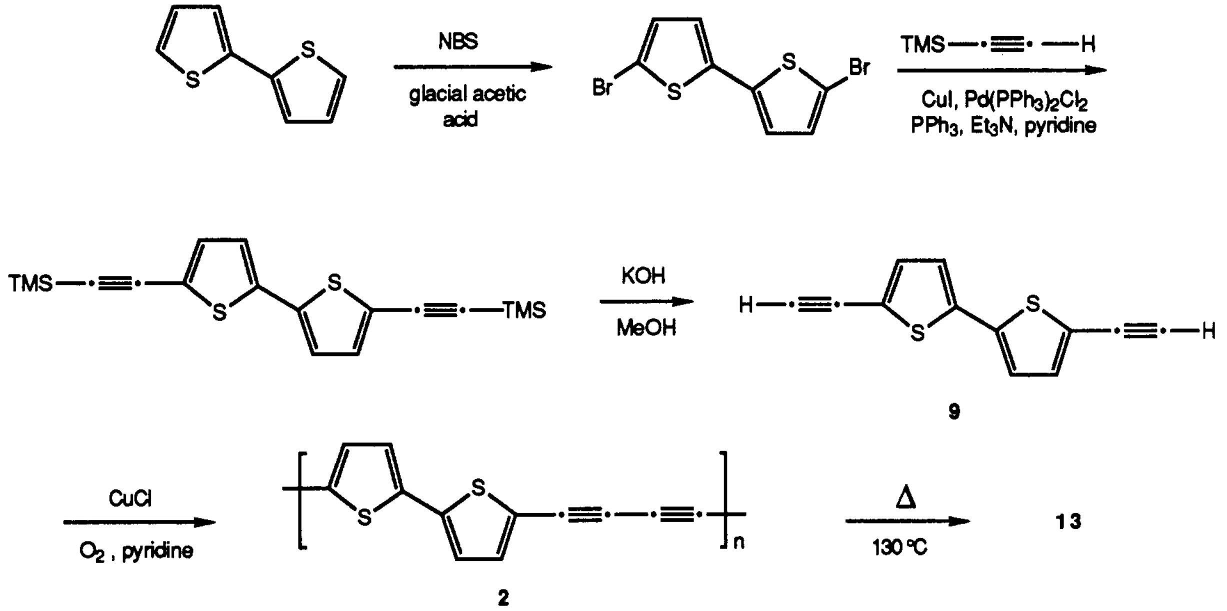
Table I
Molecular Weight Data for 1c–e

		GPC			
polymer	R	M_w	M_n	D	$[\eta]_D$[a]
1c[b]	n-C_4H_9	22 000	4500	4.96	
1d[b]	n-C_6H_{13}	23 100	6200	3.72	2.95
1d[c]		37 600	6600	5.69	6.30
1e[b]	n-C_8H_{17}	21 900	7400	2.69	

[a] In dL/g, $CDCl_3$, 25 °C. [b] Polymerization was carried out in pyridine. [c] Polymerization was carried out in a mixed solvent system of DMF/pyridine.

A notable increase in the solubility was realized from **1c** (R = n-C_4H_9) to **1d** (R = n-C_6H_{13}). This trend was not continued with **1e** (R = n-C_8H_{17}) where approximately the same solubility as **1d** was observed. All discussion of solubilities relates to concentrations obtainable without precipitation of the polymer. Concentrated solutions of

Scheme II



polymers **1c** and **1d** were found to be anisotropic under a polarizing microscope. Polymer **1f** was isolated as a bright-red powder which exhibited only slight solubility in tetrachloroethane and chlorobenzene (15% dissolved in these solvents). Shiny, dark pellets of **1f** were pressed at 15 000 psi for 2 min at ambient temperature.

No molecular weight data were obtained on polymers **1a**, **1b**, and **1f** due to their insolubilities. Molecular weight data were obtained on the soluble polymers (Table I). As would be expected, ^{1}H NMR data on the polymer solutions gave broadened peaks at the appropriate chemical shift [e.g., for **1c**, ^{1}H NMR ($PhNO_2$-d_5 at 120 °C, 200 MHz) δ 7.20 (s, 1 H), 2.77 (m, 2 H), 1.66 (m, 2 H), 1.32 (m, 2 H), 0.98 (t, 3 H)].

Polymer **1d** exhibited $[\eta]$ = 2.15–6.3 dL/g ($CHCl_3$), depending upon the polymerization conditions; thus, several modifications of the polymerization procedure were investigated. Under the original conditions (CuCl, O_2, pyridine) **1d** showed $[\eta]$ = 2.95 ($CHCl_3$, 25 °C), M_w = 23 100, M_n = 6200, and D = 3.72. Polymerization was subsequently performed using air rather than oxygen to regenerate the copper(I) chloride. This modification led to a material which was slightly more soluble than the previous batches. The rate of polymerization was decreased with the use of air, as evidenced by an increase in the length of time from 4 to 8 h required for the consumption of the monomer. This polymer was approximately 80% soluble in tetrachloroethane and 70% soluble in chloroform. The soluble polymer has an intrinsic viscosity of 3.7 in tetrachloroethane solution.

A recent paper reported that higher molecular weight diethynylenephenylene polymers were obtained through use of DMF as the solvent in the polymerization due to the enhanced solubility of the polymer in this solvent.[34] Use of this modification of the polymerization procedure with DMF as a cosolvent produced **1d**, which was approximately 80% soluble in both chloroform and tetrachloroethane. The soluble portion of **1d** exhibited a significantly higher intrinsic viscosity, $[\eta]$ = 6.7 dL/g (TCE), $[\eta]$ = 6.3 dL/g ($CHCl_3$), than had been observed previously. The molecular weight of the soluble polymer (as determined by GPC vs polystyrene standards) was M_w = 37 600, M_n = 6600, and D = 5.69 (Table I).

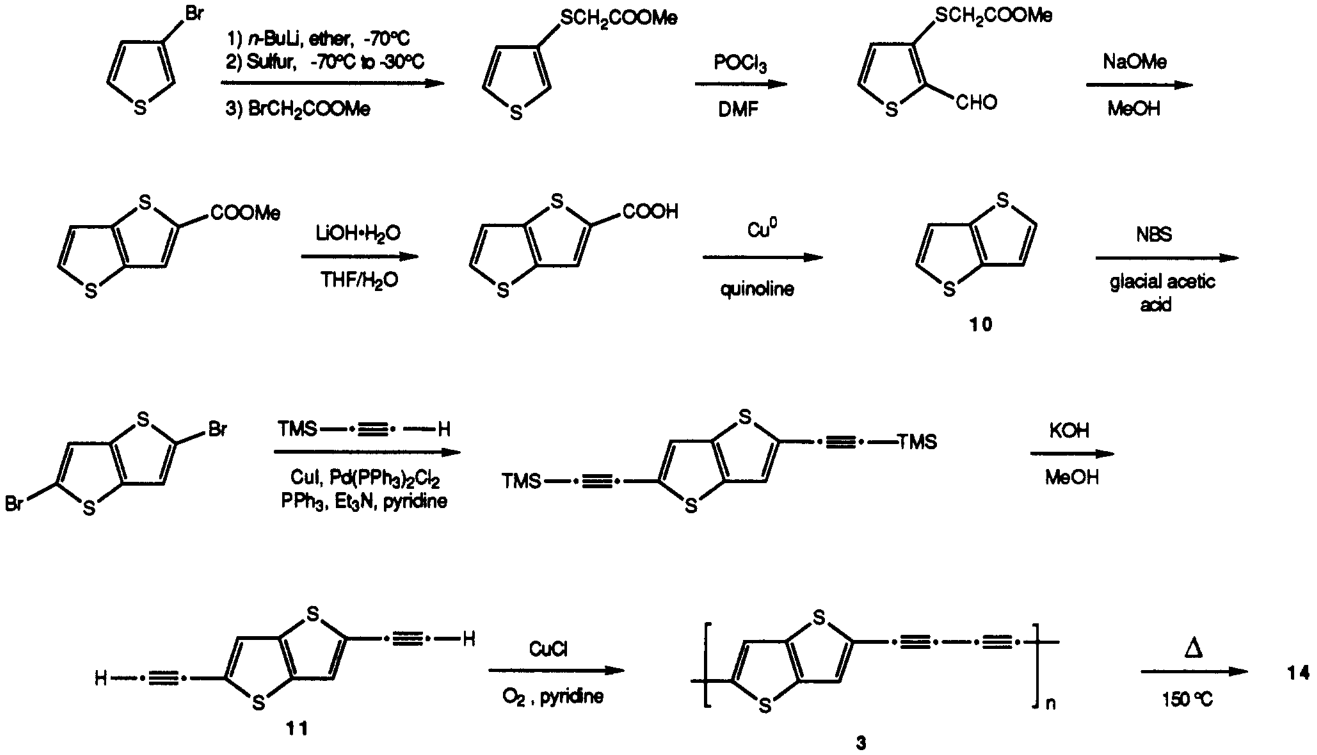
Analysis of polymer **1e** by GPC as a solution in chloroform (vs polystyrene standards) gave M_w = 21 900, M_n = 7400, and D = 2.96. Reported data may not truly reflect the molecular weight distributions of polymers **1c–e** since only the soluble fractions of the materials were analyzed. Efforts to enhance the solubility of the polymers employed the use of an end-capping reagent in the polymerization. Phenylacetylene was the end-cap chosen due to the relative instability and volatility of 2-ethynylthiophene. However, differences in the reactivities of the phenylacetylene and the diethynylthiophene monomer resulted in an inadequate incorporation of the end-cap.

Structure–property relationships of the diethynyl polymers were explored by investigating the effects of variations within the heterocyclic segment of the recurring unit on physical and electrical properties of the polymers. Diethynylene polymers containing heterocyclic segments of lower oxidation potentials were investigated through the synthesis of polymers containing bithiophene and thieno[3,2-*b*]thiophene, **2** and **3**, respectively. The oxidation potentials of thiophene and bithiophene are 2.0 and 1.5 V, respectively,[35] and theoretically this trend may be extrapolated to polymer **2**. Similarly, the fused ring system thieno[3,2-*b*]thiophene was calculated to exhibit a lower ionization potential (5.95 vs 7.02 eV) and higher polarizability than thiophene,[36] and, for this reason, polymer **3** was prepared. Preparation of alkylated derivatives was not attempted but should be possible via the palladium-catalyzed cross-coupling reaction of alkylstannanes with appropriately brominated derivatives of bithiophene.

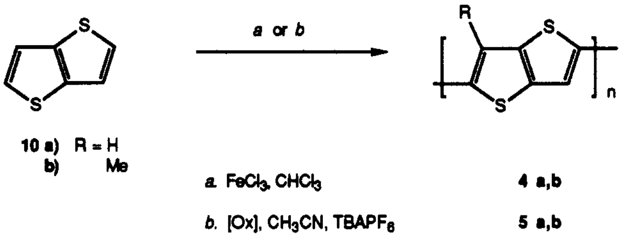
The synthesis of poly(5,5′-ethynylene-2,2′-bithiophenediylethynylene) (**2**) is shown in Scheme II. Monomer **9** was a white crystalline solid which slowly decomposed upon standing at room temperature. No melting point was observed for this material due to its decomposition at approximately 100 °C in a sealed tube. Polymer **2** was obtained as an insoluble orange powder from oxidative polymerization in the mixed solvents DMF/pyridine. This material was insoluble in all solvents and could be pressed into shiny, dark pellets. Polymer **2** was not as stable as polymers **1a–f**, and it darkened after several days upon standing at ambient temperature in air.

Poly[2,5-ethynylene(thieno[3,2-*b*]thiophenediyl)ethynylene] (**3**) was prepared as described in Scheme III. The

Scheme III

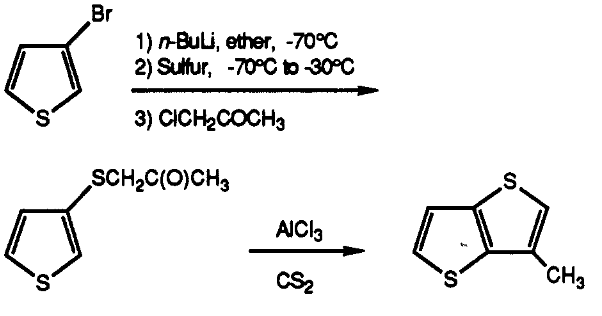


Scheme IV



sequence of reactions to synthesize thieno[3,2-*b*]thiophene was adapted from literature procedures.[37] Most notably, the Vilsmeier–Haack reaction to afford (2-formyl-3-thienylthio)acetate did not give good yields on larger quantities. Yields decreased from 70% to 40–50% when the reaction was performed on more than 10 g of starting material. Sodium methoxide was used to effect the aldol condensation affording methyl thieno[3,2-*b*]thiophenecarboxylate which was subsequently hydrolyzed to the acid with LiOH·H$_2$O in tetrahydrofuran. Decarboxylation of the acid in the presence of copper bronze (Creslite) yielded **10**. Preparation of the dibromide[38] was followed by the coupling reaction with (trimethylsilyl)acetylene. Deprotection to the monomer **11** was achieved in excellent yield after flash chromatography to afford a white solid which exhibited similar behavior to previous monomers. Oxidative polymerization of **11** in the mixed solvent system (DMF/pyridine) afforded the polymer as an orange powder. This material also darkened upon standing at ambient temperature under air for 4–5 days. The polymer was totally insoluble in all solvents but was able to be pressed into shiny, dark pellets at 15 000 psi for 2 min for conductivity measurements. Pressures greater than 20 000 psi caused sulfur extrusion from the polymer, evidenced by the odor of hydrogen sulfide. No molecular weight data were obtained on polymers **2** and **3** due to their insolubilities. Elemental analyses reflect the thermal stability of the materials.

The synthesis of two related polymers, poly(2,5-thieno[3,2-*b*]thiopheneylene) and poly[2,5-(3-methylthieno[3,2-*b*]thiopheneylene)], was effected by two polymerization methods to afford polymers **4a** and **4b** and **5a** and **5b** (Scheme IV). The reaction of 3-bromothiophene with *n*-butyllithium in ether generated the 3-thienyl lithiate which was allowed to react with sulfur and quenched with chloroacetone to afford (3-thienylthio)acetone.[39] (See eq 2.)



(2)

Ring closure of this derivative to the desired product was facilitated using AlCl$_3$ as a catalyst in carbon disulfide.

Polymers **4a** and **4b** were prepared from the monomers by chemical oxidation with FeCl$_3$ in chloroform.[40] A solution of the desired monomer was stirred at ambient temperature until the reaction was shown to be complete by consumption of the monomer (TLC, silica, hexanes). The polymer had precipitated from the reaction solution at that time. Isolation and purification of the polymer was achieved through a series of washings in methanol, acetone, and water to remove the inorganic salts. The polymers were obtained as reddish-gold powders which were insoluble in all solvents investigated. The powders were pressed into pellets at 15 000 psi for approximately 2 min to obtain samples for conductivity measurements.

The same monomers were electrochemically polymerized in acetonitrile with tetrabutylammonium hexafluorophosphate as the supporting electrolyte to afford polymers **5a** and **5b**. The potential was held constant at the oxidation potential of the monomer, resulting in the formation of a polymer film on the anode (ITO glass).

Table II
Thermal Data for Poly(2,5-ethynylenethiophenediylethynylenes) (1a–f) and Related Analogues 2 and 3

		DSC		TGA, % wt loss	
polymer	R	T_{exo_1}, °C (kcal/mol)[a]	T_{exo_2}, °C (kcal/mol)[a]	400 °C	700 °C
1a	H	179 (15.75)		0	13
1b	CH_3	206 (15.57)	352 (4.04)	0	12
1c	n-C_4H_9	210 (12.29)	375 (10.62)	7	29
1d	n-C_6H_{13}	218 (5.14)	373 (6.22)	8	39
1e	n-C_8H_{17}	219 (17.94)	382 (1.45)	8	50
1f	Ph	174 (11.76)	451 (2.68)	0	12
2		125 (8.64)	231 (1.44)	0	19
3		141 (10.93)		0	24

[a] $\Delta H_{reaction}$ based on kcal/mol of recurring unit.

These films were readily removed from the electrode for further investigation, including electrical conductivity measurements. The materials prepared by electrochemical polymerization were obtained in a partially oxidized state.

Polymers **1a–f**, **2**, and **3** were subjected to thermal cross-linking via the ethynyl moiety at moderate temperatures[41] (Table II). Polymers **1a–f** exhibit a sizable reaction exotherm by differential scanning calorimetry (DSC) at approximately 200 °C. To determine the structure of the cross-linked product, solid-state ^{13}C CP/MAS data were obtained on representative samples of unreacted and of cross-linked materials.[19] The spectrum of **1b** showed five absorption peaks due to CH_3 (16 ppm), acetylenic carbons (78–80 ppm), the 2- and 5-ring carbons (122 ppm), the 4-ring carbon (136 ppm), and the 3-ring carbon (145 ppm). Thermolysis of **1b** was effected upon heating the polymer at 200 °C for 10–15 min. The material changed in appearance from dark red to black. The ^{13}C CP/MAS for this material, **12b**, was quite different from that of the unreacted polymer. The virtual disappearance of the absorption in the sp region for acetylenic carbons and the absence of absorption in the allenic carbon region (~200 ppm) suggested that the structure of **12b** corresponds to highly cross-linked material containing all sp^2-hybridized carbons in the polymer backbone. Three structures that have been proposed as the products of the polymerization of conjugated diynes are shown in Scheme I.[42] The allenic and dienyne representations of cross-linked product do not correspond well to the spectral data. Also, the absence of a new absorption at 50–60 ppm suggested the lack of [4 + 2] cycloaddition into the thiophene ring since the bridgehead carbons thus formed would appear in this region. The spectrum of the cross-linked material required a significantly longer acquisition time (10 vs 2 h), probably due to a significant concentration of free radicals. The materials exhibited a broad EPR signal centered at $g \approx 1.9$. The fact that the cross-linking reaction goes to completion was determined by thermal analysis (DSC). The first reaction exotherm was absent in the DSC of the thermolyzed polymer.

All of the polymers except **1a** (Table II) exhibited a second, smaller exotherm (T = 350–450 °C). One possible origin of this second process is thermal decomposition of the alkyl side chains that may be occurring at these temperatures. To this end, the phenyl derivative **1f** was prepared. If the second reaction exotherm were due to thermal decomposition, it would be expected to be absent in the DSC of **1f** due to the greater thermal stability of the phenyl substituent over the saturated alkyl chains (**1b–e**). The fact that a second reaction exotherm exists in the DSC of **1f** makes this result somewhat ambiguous because the exotherm, while present, occurs at a significantly higher temperature than for the other polymers. The small amount of weight loss exhibited (TGA) by the polymers **1c–e** up to 400 °C under argon is not consistent with thermal decomposition of the alkyl side chain. Alternatively, a second cross-linking reaction may have occurred, where the remaining sp carbons observed in the solid-state ^{13}C NMR spectrum of **12b** may correspond to carbon atoms that experienced a misalignment of orbital overlap during the initial cross-linking process (~200 °C). Additional thermal excitation may allow further cross-linking of such acetylenic groups. A sample of the brick-red polymer **1b** was heated to 375 °C for 10 min to obtain a sample of completely thermolyzed material which exists as a very crusty black powder. A ^{13}C CP/MAS spectrum was obtained and showed mostly sp^2 carbons, and, again, the spectrum required a long acquisition time probably due to a high concentration of free radicals. Also, only a small peak in the region of the methyl carbon was evident, indicating that some decomposition of the aliphatic chain had taken place. Due to enhancement resulting from relaxation through dipole–dipole interaction of carbon with attached protons, a methyl carbon should exhibit a much higher intensity than was observed in the CP/MAS experiment.

The size of the alkyl substituent (**1a–f**) has a small effect on the onset of the cross-linking reaction (~200 °C). In general, the temperature increased linearly with the size of the substituent, but no obvious correlation between the substituent and ΔH of the reaction was deduced. An unmistakable trend in the thermal stabilities of **1a–f** is evident from the TGA data in Table II. Polymers **1a**, **1b**, and **1f** exhibited no weight loss up to 400 °C and only marginal loss up to 700 °C (12–13%). In contrast, the more highly alkylated derivatives **1c–e** demonstrated slight weight loss by 400 °C (7–8%) and significantly greater weight loss by 700 °C (29, 39, and 50%, respectively).

Thermal analysis (DSC) of **2** indicated the presence of two reaction exotherms, T_{exo} = 125 °C (8.64 kcal/mol) and T_{exo} = 231 °C (1.44 kcal/mol) and a thermal stability (TGA) analogous to polymers **1** (Table II). No weight loss was exhibited by **2** up to 400 °C, and 19% weight loss was observed by 700 °C. Polymer **3** exhibited only one reaction exotherm, T_{exo} = 141 °C (10.93 kcal/mol) (DSC), was thermally stable to 400 °C, and experienced a weight loss of 24% by 700 °C (Table II). Attempts to obtain satisfactory elemental analysis on polymers **1a–f**, **2**, and **3** demonstrated the thermal stability of the materials. The analysis data was not considered to be reliable due to the considerable variability obtained in duplicate samples.

The differential mechanical analysis (DMA) data on a film of poly(2,5-diethynylene-3-hexylthiophenylene) (**1d**) cast from solution were obtained. The polymer exhibited a T_g of 106 °C (maximum in tan δ) which was not observable in the DSC and a room temperature storage modulus $E' = 2.2 \times 10^9$ Pa. The cross-linking reaction occurred at approximately 200 °C and was accompanied by a decrease in the storage modulus of the polymer. After the completion of the cross-linking reaction, the storage modulus increased until at approximately 225 °C cracks appeared in the film. Cross-linked films of **1d** were very brittle, and no mechanical data could be obtained from these films.

The electrical conductivities of all polymers were measured by the four-probe method described by Wnek[43] and are reported in Table III. For the insoluble polymers **1a**, **1b**, and **1f** (R = H, CH_3, and Ph, respectively), **2** and **3**, the measurements were obtained on pellets which had been pressed at 15 000 psi for 2 min. Measurements for

Table III
Conductivity Data on Poly(2,5-ethynylenethiophenediylethynylenes) (1a–f), Related Analogues 2 and 3, and Poly(thieno[3,2-*b*]thiopheneylenes) 4a and 4b and 5a and 5b

polymer	σ (intrinsic), S/cm	σ (doped with I_2[a]), S/cm	σ (doped with AsF_5[b]), S/cm
1a	1.6×10^{-13}	5.4×10^{-11}	3.9×10^{-8}
1b	1.4×10^{-12}	2.2×10^{-8}	2.2×10^{-6}
1c	3.7×10^{-11}	2.7×10^{-8}	8.1×10^{-7}
1d	1.2×10^{-12}		7.8×10^{-9}
1f	5.4×10^{-13}		1.1×10^{-8}
2	2.9×10^{-13}		1.3×10^{-8}
3	5.1×10^{-13}		3.0×10^{-7}
4a	2.4×10^{-6}		0.57
4b	9.4×10^{-8}		0.91
5a			0.73
5b			2.46
cross-linked			
12a	1.3×10^{-8}		2.0×10^{-8}
12b	1.1×10^{-9}		4.0×10^{-8}
12c	6.4×10^{-11}		6.9×10^{-6}
12d	2.1×10^{-12}		2.4×10^{-9}
12f	6.1×10^{-13}		2.0×10^{-10}
13	4.1×10^{-14}		1.5×10^{-8}
14	4.8×10^{-13}		2.5×10^{-8}

[a] Iodine vapor. [b] 400 Torr of AsF_5; conductivity values reported are for 24–72-h exposures.

the other materials **1c**, **1d**, and **1e** (R = n-C_4H_9, n-C_6H_{13}, and n-C_8H_{17}, respectively) were made on solution-cast films (chloroform or tetrachloroethane). All materials exhibited conductivities of less than 10^{-10} S/cm before doping. Polymers **1a–c** were doped with iodine vapor, and moderate increases in conductivity were realized, but the materials remained insulating. A stronger oxidant, arsenic pentafluoride, was also used to dope the polymers, and larger gains in conductivity were observed.

Polymers **1a–f**, **2**, and **3** each exhibited an increase in conductivity upon exposure to arsenic pentafluoride to afford semiconductive materials. The conductivities reported are at the lower end of the semiconductive region. Increased conductivity was expected for the cross-linked polymers, **12a–f**, **13**, and **14**. The thermolyses of **1a–f** were carried out at 200 °C to give cross-linked materials, and polymers **2** and **3** were thermolyzed at 150 °C. The intrinsic conductivities of **12a–f**, **13**, and **14** were several orders of magnitude greater than those observed for the unreacted polymers. Upon doping with arsenic pentafluoride, only slight increases in conductivity were observed for the pelleted materials. A significant increase in the conductivity was observed only for **12c** (R = n-C_4H_9) which was a thermolyzed film that had been cast from tetrachloroethane. Polymers **1b** and **1d** were doped with sodium naphthalide to afford an n-doped material. The conductivities obtained in these experiments were σ_d (**1b**, R = CH_3) = 1.6×10^{-6} S/cm (pellet) and σ_d (**1d**, R = n-C_6H_{13}) = 1.6×10^{-5} S/cm (film). The increased polarizability or decreased oxidation potential expected for polymers **2** and **3** was not demonstrated by an increased conductivity of the polymers. The conductivity of the cross-linked counterparts **12a–f** was in the same range or was slightly decreased from polymers **1a–f**.

Several reasons for the lower than expected conductivities of polymers **1a–f**, **2**, and **3** may exist. Primarily, a lack of interaction of the dopant with the polymer was observed by measuring the weight increase in a polymer pellet or film after exposure to arsenic pentafluoride. Only small increases in weight, approximately 5%, occurred for polymers **1**. A weight increase of approximately 2% was observed for a pellet of **2** upon doping with arsenic pentafluoride. Nontheless, these oxidation levels should be sufficient to generate an adequate concentration of charge carriers for conductivity to be observed.[44] The lack of a larger extent of dopant uptake might be due to the decreased polarizability of polydiacetylenes relative to polyenes, which, in general, causes polydiacetylenes to exhibit lower conductivities than their polyene analogues.[45] The lack of polarizability usually corresponds to a greater band width and higher oxidation potential, therefore making oxidation of the polymer backbone more difficult.

A polarizable polymer containing an aromatic moiety usually experiences a greater contribution of the quinoid resonance structures which, in turn, allows for electron delocalization over the extended conjugation length.[46] For example, the quinoid structure of a polythiophene may be expected to contribute significantly to the delocalization of electrons. The quinoid structure of a poly(diethynylenethiophenylene) may be expected to be much less favorable and of much higher energy than the aromatic representation, due a number of cumulated double bonds. The delocalization of the π-electrons is related to the carrier mobility within the polymer. The observed conductivity is a function of carrier mobility, $\sigma = ne\mu$, which is related to not only electron delocalization but also interchain hopping mechanisms. In addition to limited delocalization, any lack of structural order would thereby decrease the efficiency of electron transport between chains.

Electrochemical oxidation of films of **1d** that had been cast from solution onto the surface of a glassy carbon electrode showed a single irreversible oxidation peak at approximatly 1.55 V vs SCE (acetonitrile/$TBAPF_6$). This potential is significantly more positive than would be expected if long-range charge delocalization were occurring along the polymer chain. Electrochemical studies of the bis(trimethylsilyl)-protected monomer **6e** indicated that the oxidation electrochemistry is qualitatively identical to that of the above-mentioned polymer films. All of these electrochemical results argue strongly that there is little or no charge delocalization occurring through the ethynyl linkage in the polymers. These results are also consistent with the apparent failure of the polymers to dope (given their very positive oxidation potentials) and, as a consequence, their low conductivity.

Another factor which may be important is the hardness of the materials, as determined from Young's moduli. In a recent report, Whitesides et al. discussed the hardness of hyper-cross-linked organic solids, including polymer **12c**.[21] This material was reported to exhibit a Young's modulus which closely resembled that of glassy carbon, which could be scratched by steel but not by aluminum. Hence, it is possible that the lack of incorporation of the dopant arises from the inability of the counterions (AsF_6^-) to become intercalated into the polymer matrix. Without such interaction, there is no stabilization of the cationic charge carriers (holes) and very little electrical conductivity.

The electrical conductivities of **4a** and **4b** and **5a** and **5b** are included in Table III. Measurements were obtained on pellets of poly(thieno[3,2-*b*]thiophenes) **4a** and **4b** that were pressed at 15 000 psi for 2 min at ambient temperature. Films of **5a** and **5b** were used in the conductivity measurements as formed from the electrochemical polymerization. The conductivities of **4a** and **4b** were intrinsically in the semiconductor region. Upon doping with arsenic pentafluoride, conductive materials were obtained with σ = 0.57 and 0.91 S/cm. Intrinsic conductivities for **5a** and **5b** are not reported because the polymers were isolated from the electrochemical polymerization as the more stable partially oxidized films. The initial conductivity values of these films were 0.012 and 0.034

S/cm for **5a** and **5b**, respectively. The polymers exhibited the expected change of color upon cycling from conducting to neutral films, forming as a purple, conductive film on the anode that could be reduced to a red, neutral film by reversing the potential. The partially oxidized polymer films were exposed to arsenic pentafluoride, increasing the conductivity of the films by almost 2 orders of magnitude to $\sigma = 0.73$ and 2.46 for **5a** and **5b**, respectively.

Conclusion

The novel class of polymers poly(2,5-ethynylenethiophenediylethynylenes) (**1a–f**) and related materials **2** and **3** undergo a cross-linking reaction at moderate temperatures. The thermal reactivity of the polymers containing a diethynyl moiety provided substantial insight into the solid-state cross-linking reaction of polymeric conjugated diacetylenes. Solid-state ^{13}C CP/MAS data showed that the principal structure of the cross-linked material may be represented as a diene-containing material.[19]

The intrinsic conductivities of the poly(2,5-ethynylenethiophenediylethynylenes) were in the insulating region. Upon doping with strong oxidants such as arsenic pentafluoride or the strong reducing agent sodium naphthalide, the conductivity increased only into the semiconducting regime. The unreacted and the cross-linked materials exhibit similar electrical conductivities. Explanations for these results involve, principally, the lack of interaction between the polymer and the dopant due to a relatively high oxidation potential of the polymer. Subsequent investigations of the electrical conductivities of poly(5,5′-ethynylene-2,2′-bithiophenediylethynylene) and poly[2,5-ethynylene(thieno[3,2-*b*]thiophenediyl)ethynylene] were carried out to afford materials which upon doping were also semiconductive. New syntheses of poly(2,5-thieno[3,2-*b*]thiopheneylene) and poly[2,5-(3-methylthieno[3,2-*b*]thiopheneylene)] by both $FeCl_3$ oxidation and electrochemical polymerization of the respective monomers afforded conductive materials upon doping.

Experimental

Instrumentation. Melting points reported are uncorrected and were performed in a Mel-Temp laboratory device. Infrared spectra were obtained on a Beckman Model 4250 infrared spectrometer or a Perkin-Elmer 1600 Series FTIR spectrophotometer. Proton and carbon NMR spectral analyses were performed on an IBM–Bruker WP270-SY, an IBM–Bruker WP200-SY, or a Bruker AC300P spectrometer. NMR spectra were obtained in deuteriochloroform solutions with tetramethylsilane (proton) or deuteriochloroform (carbon) internal standards unless otherwise noted. Gas chromatographic analyses were performed on a Varian Instruments Model 3700 gas chromatograph equipped with a thermal conductivity detector and a $^1/_4$-in. Supelco SP2100 column. Thermal analyses (DSC, TGA, and DMA) were obtained employing a Du Pont Instruments 9900 thermal analysis system. Polymer viscosities were measured in dilute chloroform or tetrachloroethane solutions using a Cannon-Ubbelohde microdilution viscometer (size 50 for $CHCl_3$, size 75 for TCE). Molecular weight determinations were done by size-exclusion chromatography on a Waters Model 150C liquid/gel permeation chromatograph with a refractive index detector vs polystyrene standards in chloroform.

Materials. Tetrahydrofuran and ether solvents were distilled from sodium–benzophenone. Chloroform and tetrachloroethane were distilled from phosphorus pentoxide. All other solvents were distilled from calcium hydride unless otherwise noted. Azobis(isobutyronitrile) (AIBN), copper(I) chloride, *p*-diaminobenzene, *N*-bromosuccinimide (NBS), and triphenylphosphine were purified by standard methods.[47] Copper(I) iodide was dried under vacuum at 100 °C. All chemicals were purchased from Aldrich Chemical unless otherwise noted and were used as received unless otherwise stated. The halothiophenes, 2-bromothiophene, 3-bromothiophene, 2,5-dibromothiophene, and 2-iodothiophene were distilled at reduced pressures if not freshly opened. All alkyl halides were filtered through basic alumina prior to use.

The following transition-metal catalysts were prepared by literature procedures: tetrakis(triphenylphosphine)palladium,[48] bis(triphenylphosphine)palladium(II) dichloride,[49] bis(acetonitrile)palladium dichloride,[50] and [1,3-bis(diphenylphosphino)propane]nickel(II) dichloride ($NiCl_2dppp$).[51]

(Trimethylstannyl)acetylene[25] was prepared by a literature procedure. (Trimethylsilyl)acetylene was also prepared by a literature procedure[52] or was purchased from Farchan Laboratories. The alkylation of 3-bromothiophene to afford the series of derivatives 3-butyl-, 3-hexyl-, 3-octyl-, and 3-phenylthiophenes was done by the Grignard reaction as outlined by Kumada et al.[31]

Procedures. Monomer Synthesis. Synthesis of 3-Alkyl-2,5-dibromothiophenes. The 3-methyl and 3-butyl derivatives were prepared upon treatment of the 3-alkylthiophene with 2.1 equiv of bromine in glacial acetic acid.[30] The reactions were monitored by gas chromatography for consumption of starting material. The remaining dibromothiophenes were prepared from the reaction of *N*-bromosuccinimide (NBS) with the appropriate 3-alkylthiophene in glacial acetic acid.

Synthesis of Thieno[3,2-*b*]thiophene.[36] **Methyl (2-Formyl-3-thienylthio)acetate.** To 0.500 g (6.84 mmol) of DMF under argon was added dropwise 0.880 g (5.75 mmol) of $POCl_3$. The mixture was allowed to stir at room temperature for 45 min, and 0.940 g (5.0 mmol) of methyl (3-thienylthio)acetate was then added dropwise. A clear yellow solution resulted which was stirred at room temperature for 8 h and at which time TLC (silica, hexanes) confirmed consumption of the starting material. Ice was added to the reaction mixture, and a waxy yellow solid appeared in 2 h. The reaction mixture was extracted into ether and washed with water, 10% HCl, saturated $NaHCO_3$, and water. The ethereal solution was dried over $MgSO_4$, filtered, and concentrated to leave a yellow oil. The crude product was chromatographed (silica, 5% ethyl acetate/benzene) followed by Kugelrohr distillation (0.30 Torr, 65 °C). A colorless oil which weighed 0.81 g (73%) was obtained and crystallized slowly at 0 °C to give a white solid melting at 39–40 °C (lit.[37] mp 40 °C).

Methyl Thieno[3,2-*b*]thiophenecarboxylate. To a solution of 0.152 g (0.70 mmol) of methyl (2-formyl-3-thienothio)acetate in 30 mL of methanol was added 54 mg (1.0 mmol) of sodium methoxide. The reaction was heated to reflux for 6 h and then cooled to ambient temperature. Quenching was accomplished by the addition of 2 mL of water, at which time a white precipitate formed. Further addition of water (10 mL) resulted in a heavy solid mass. The crude product was collected by filtration and recrystallized from ethanol/water to yield 103 mg (73%) of white needles: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.97 (s, 1 H), 7.57 (d, 1 H, $J = 5.26$ Hz), 7.26 (d, 1 H, $J = 5.26$ Hz), 3.90 (s, 3 H); mp 96–97 °C. Anal. Calcd for $C_8H_6O_2S_2$: C, 48.45; H, 3.05; S, 32.30. Found: C, 48.30; H, 2.99; S, 32.23.

Thieno[3,2-*b*]thiophene-2-carboxylic Acid. To a solution of 0.63 g (0.48 mmol) of methyl thieno[3,2-*b*]thiophenecarboxylate in a solvent mixture of 10 mL of THF, 1 mL of water, and 2 mL of ether was added 0.20 g (3.64 mmol) of $LiOH\cdot H_2O$. The reaction was stirred at ambient temperature for 3 days, and the organic solvents were evaporated. Acidification of the aqueous solution with 0.5 mL of concentrated HCl resulted in precipitation of the product. Recrystallization of the crude product from water/ethanol gave 0.45 g (73%) of the acid: mp 218–220 °C (lit.[37] mp 219–221 °C).

Thieno[3,2-*b*]thiophene. To a solution of 1.62 g (8.8 mmol) of thieno[3,2-*b*]thiophene-2-carboxylic acid in 19 mL of quinoline was added 47 mg of copper bronze powder. The resulting suspension was heated to 160 °C under argon for 8 h, after which time complete reaction was evidenced by TLC (2% ethyl acetate/hexanes). The solution was allowed to cool to room temperature, diluted with 40 mL of ether, and filtered through Celite. The organic solution was copiously washed with 10% aqueous HCl to remove residual quinoline. The solution was dried over $MgSO_4$, filtered, and concentrated to afford a brown oil. Chromatography on silica (hexanes) and trituration with cold methanol

(20 mL) gave 0.95 g (78%) of a white solid: mp 56–57 °C (lit.[37] mp 55–56 °C).

Preparation of 3-Methylthieno[3,2-*b*]thiophene.[39] **Synthesis of (3-Thienylthio)acetone.** To a solution of 3.19 g (18.4 mmol) of 3-bromothiophene in 60 mL of dry ether was added 17.5 mL of 1.08 M n-butyllithium (in hexanes). The solution was stirred for 1 h at −78 °C, and 0.71 g (22.0 mmol) of sulfur was added. The reaction was allowed to warm to −30 °C, at which time 2.30 g (24.0 mmol) of chloroacetone was added. The resulting solution was allowed to warm to ambient temperature and stirred overnight. Quenching with 20 mL of saturated NH_4Cl, the layers were separated and the organic phase was diluted with 70 mL of ether. The organic layer was washed with water, followed by saturated NH_4Cl. Concentration at reduced pressure gave a brown oil which was chromatographed on silica (5% ethyl acetate/benzene). The product, (3-thienylthio)acetone, was obtained in 69% (2.19 g) as a light-yellow oil which is unstable at room temperature: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.19 (dd, J = 0.8 and 0.54 Hz, 1 H), 7.09 (m, 1 H), 6.90 (d, J = 0.80 Hz, 1 H), 3.45 (s, 2 H), 2.13 (s, 3 H); IR (neat) 3071, 2905, 1643, 774 cm^{-1}.

Synthesis of 3-Methylthieno[3,2-*b*]thiophene. To a mixture of 2.0 g (15 mmol) of $AlCl_3$ in 50 mL of carbon disulfide was added 2.0 g (11.6 mmol) of (3-thienylthio)acetone in 15 mL of CS_2. The resulting dark-red solution was stirred at room temperature for 8 h. At that time, water was added, and the organic layer was recovered and washed again with water. The solvent was removed under reduced pressure to give a brown oil which was chromatographed on silica (pentane). A 26% yield (0.474 g) of 3-methylthieno[3,2-*b*]thiophene was obtained as a colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.34 (m, 1 H), 6.97 (m, 1 H), 2.36 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.83, 138.56, 129.59, 126.72, 122.40, 120.07, 14.91; IR (neat) 3087, 2973, 1508, 1450, 1357, 791, 751 cm^{-1}. Anal. Calcd for $C_7H_6S_2$: C, 54.50; H, 3.92; S, 41.57. Found: C, 54.41; H, 3.93; S, 41.50.

Synthesis of 5,5′-Dibromo-2,2′-bithiophene. 2,2′-Bithiophene was treated with NBS in glacial acetic acid to afford product in 88% yield after recrystallization from 95% ethanol/chloroform:[38] mp 147–148 °C (lit. mp[54] 149–151 °C); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.95 (d, 2 H, J = 3.83 Hz), 6.84 (d, 2 H, J = 3.83 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.78, 130.65, 124.14, 115.53. Anal. Calcd for $C_8H_4Br_2S_2$: C, 29.60; H, 1.24; S, 2.01. Found: C, 29.67; H, 1.26; S, 19.85.

Synthesis of 2,5-Dibromothieno[3,2-*b*]thiophene. This compound was prepared according to a literature procedure whereby thieno[3,2-*b*]thiophene was treated with NBS in glacial acetic acid.[38]

Synthesis of 3-Alkyl-2,5-bis[2-(trimethylsilyl)ethynyl]thiophenes (6a–f). All derivatives **6a–f** were prepared from the reaction of (trimethylsilyl)acetylene with the dibromothiophene in the presence of amine bases and palladium and copper catalysts. A representative procedure is given below, followed by pertinent reaction and characterization data for each derivative.

2,5-Bis[2-(trimethylsilyl)ethynyl]thiophene (6a). To a solution of triethylamine (16 mL) and pyridine (10 mL) in a flame-dried three-neck 50-mL flask were added 45 mg (0.17 mmol) of triphenylphosphine, 22 mg (0.115 mmol) of copper(I) iodide, 1.1 g (22 mmol) of (trimethylsilyl)acetylene, and 5.0 g (20 mmol) of 2,5-dibromothiophene. The flask was flushed with argon, and $(Ph_3P)_2PdCl_2$ (22 mg, 0.06 mmol) was added. The reaction was allowed to proceed for 12 h at 80 °C. The solution was cooled to room temperature and was filtered to remove the precipitated amine hydrobromide salts, followed by dilution with chloroform (40 mL) and washing with water. The organic phase was dried over $MgSO_4$, filtered, and concentrated. The crude product was dissolved in ether (50 mL), and the removal of residual amines was accomplished by copious washings with saturated $CuSO_4$. The ether solution was dried over $MgSO_4$, filtered, and concentrated at reduced pressure. A red solid occurred and was sublimed to yield 0.9 g (68% yield) of pale-yellow product (0.2 Torr, 100 °C): mp 79–80 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.02 (s, 2 H), 0.23 (s, 18 H); IR ($CDCl_3$ solution) 2950, 2880, 2120, 1500, 1425, 1400, 1240, 1160, 835 cm^{-1}. Anal. Calcd for $C_{14}H_{20}Si_2S$: C, 60.80; H, 7.30; S, 11.59. Found: C, 60.66; H, 7.35; S, 11.51.

2,5-Bis[2-(trimethylsilyl)ethynyl]-3-methylthiophene (6b). The reaction mixture was heated at 60 °C with stirring for 8 h, after which time starting material was shown to be consumed by gas chromatography (GC). After isolation of the product, a yellow solid was obtained. Purification of this material by sublimation (90 °C, 0.2 Torr) afforded a 70% yield of a white solid: mp 86–87 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.90 (s, 1 H), 2.21 (s, 3 H), 0.23 (s, 9 H), 0.216 (s, 9 H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 142.92, 134.19, 122.98, 120.34, 99.58, 97.36, 77.01, 76.49, 42.27, −0.06, −0.22. Anal. Calcd for $C_{15}H_{23}SSi_2$: C, 62.0; H, 7.63; S, 11.03. Found: C, 61.95; H, 7.65; S, 10.96.

2,5-Bis[2-(trimethylsilyl)ethynyl]-3-butylthiophene (6c). The reaction mixture was heated at 60 °C for 11 h and was monitored by GC. Isolation of the product left a yellow oil. Purification of the oil was accomplished by Kugelrohr distillation (110 °C, 0.2 Torr). A 79% yield of the desired product as a colorless oil was obtained: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.95 (s, 1 H), 2.61 (t, 2 H), 1.56 (m, 2 H), 1.31 (m, 2 H), 0.91 (t, 3 H), 0.24 (s, 9 H), 0.23 (s, 9 H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 148.30, 133.41, 123.10, 120.13, 99.47, 97.56, 97.09, 77.48, 32.07, 29.11, 22.24, 13.68. Anal. Calcd for $C_{18}H_{28}SSi_2$: C, 64.99; H, 8.49; S, 9.64. Found: C, 64.52; H, 8.43; S, 9.50.

2,5-Bis[2-(trimethylsilyl)ethynyl]-3-hexylthiophene (6d). The reaction mixture was heated at 60 °C for 20 h and was monitored by GC. The product was isolated as a yellow oil, which was purified by Kugelrohr distillation (110 °C, 0.2 Torr) to afford a 88% yield of a colorless oil: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.95 (s, 1 H), 2.59 (t, 2 H), 1.55 (m, 2 H), 1.27 (m, 6 H), 0.88 (t, 3 H), 0.24 (s, 9 H), 0.23 (s, 9 H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 148.36, 133.40, 122.99, 120.02, 101.88, 99.41, 97.51, 96.98, 31.57, 29.90, 29.43, 28.80, 22.56, −0.14, −0.13. Anal. Calcd for $C_{20}H_{32}Si_2S$: C, 66.60; H, 8.94; S, 8.87. Found: C, 66.43; H, 9.19; S, 8.85.

2,5-Bis[2-(trimethylsilyl)ethynyl]-3-octylthiophene (6e). The reaction mixture was heated at 60 °C with stirring and was allowed to proceed for 46 h, at which time the starting materials were shown by TLC (silica, hexanes) to be consumed. The product was dissolved in hexanes (40 mL) and extracted with saturated $CuSO_4$ solution. Purification of the product was achieved by chromatography on silica (hexanes) followed by two sequential Kugelrohr distillations (180 °C, 0.2 Torr) to afford a 73% yield of a colorless oil: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.93 (s, 1 H), 2.57 (t, 2 H), 1.52 (br, 2 H), 1.25 (br, 10 H), 0.86 (t, 3 H), 0.23 (s, 9 H), 0.21 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.66, 133.73, 122.03, 118.87, 83.88, 81.62, 77.40, 75.98, 34.14, 31.89, 30.02, 29.34, 29.23, 22.68, 22.36, 14.95. Anal. Calcd for $C_{22}H_{36}Si_2S$: C, 67.97; H, 9.34; S, 8.25. Found: C, 68.03; H, 9.43; S, 8.32.

2,5-Bis[2-(trimethylsilyl)ethynyl]-3-phenylthiophene (6f). The reaction mixture was heated at 60 °C for 24 h, at which time TLC (silica, hexanes) showed consumption of the starting material. Initial isolation of the product gave a tan oil which was chromatographed on silica (4% ethyl acetate/hexanes). The yellow oil obtained was by Kugelrohr twice distilled at 110 °C (0.4 Torr) to afford a 80% yield of a colorless, viscous oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.75 (dd, 2 H), 7.37 (br, 3 H), 7.29 (s, 1 H), 0.27 (s, 9 H), 0.23 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.98, 134.44, 132.87, 128.29, 127.93, 127.84, 123.32, 119.07, 102.32, 100.18, 97.63, 96.90, −0.21, −0.35. Anal. Calcd for $C_{20}H_{24}SSi_2$: C, 68.12; H, 6.86; S, 9.09. Found: C, 68.69; H, 6.93; S, 9.24.

Synthesis of 5,5′-Bis[2-(trimethylsilyl)ethynyl]-2,2′-bithiophene. To a flame-dried 50-mL round-bottomed flask was added 13.4 mg (0.05 mmol) of triphenylphosphine, 6.4 mg (0.003 mmol) of copper(I) iodide, 10 mL of triethylamine, and 4 mL of pyridine. The resulting mixture was then treated with 0.486 g (1.5 mmol) of 5,5′-dibromo-2,2′-bithiophene and 0.324 g (3.30 mmol) of (trimethylsilyl)acetylene under argon. After addition of $PdCl_2(PPh_3)_2$ (6 mg, 0.0087 mmol), the reaction mixture was heated at 60 °C for 9 h, at which time completion was indicated by TLC (silica, hexanes). The flask was allowed to cool to room temperature, and the solution was filtered. Evaporation of the filtrate left a yellow solid, which was dissolved in ether (50 mL) and was washed with saturated $CuSO_4$, water, and saturated NaCl. The solution was dried over $MgSO_4$, filtered, and concentrated at reduced pressure to give a yellow solid which was chromatographed on silica with 4% ethyl acetate/hexanes to afford 0.38

g (71%) of a yellow crystalline material: mp 173–175 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.11 (d, 2 H, J = 3.76 Hz), 6.99 (d, 2 H), 0.24 (s, 18 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.94, 133.43, 123.73, 122.55, 100.48, 97.19, −0.19. Anal. Calcd for $C_{18}H_{22}Si_2S$: C, 60.30; H, 6.20; S, 17.88. Found: C, 60.36; H, 6.19; S, 17.80.

Synthesis of 2,5-Bis[2-(trimethylsilyl)ethynyl]thieno[3,2-*b*]thiophene. To a flame-dried 50-mL round-bottomed flask was added 45 mg (0.18 mmol) of triphenylphosphine, 21 mg (0.11 mmol) of copper(I) iodide, 15 mL of triethylamine, and 10 mL of pyridine. To this solution was added 1.49 g (5.0 mmol) of 2,5-dibromothieno[3,2-*b*]thiophene and 1.08 g (11.0 mmol) of (trimethylsilyl)acetylene. The system was flushed with argon, and 20 mg (0.03 mmol) of $PdCl_2(PPh_3)_2$ was added. The resulting solution was heated to 60 °C for 10 h. Completion was shown by disappearance of the starting material by TLC (silica, hexanes). The reaction was allowed to cool to room temperature, and the solution was filtered. The filtrate was concentrated at reduced pressure to afford an orange oil. The crude product was dissolved in chloroform, and the solution was washed with saturated $CuSO_4$, water, and saturated NaCl. After drying over $MgSO_4$, filtering, and concentrating, the resulting orange oil was chromatographed on silica (hexanes). A yellow solid was obtained and recrystallized twice from methanol/chloroform to afford 1.06 g (61%) of a pale-yellow crystalline solid: mp 220–222 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.28 (s, 2 H), 0.26 (s, 18 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.75, 126.71, 124.60, 101.68, 97.62, −0.22. Anal. Calcd for $C_{16}H_{20}Si_2S$: C, 57.77; H, 6.06; S, 19.28. Found: C, 58.69; H, 6.08; S, 19.20.

Synthesis of 2,5-Diethynylthiophene Monomers 7a–f. The monomers **7a–f** were prepared from the bis(trimethylsilyl)-protected derivatives **6a–f** by hydrolysis in caustic methanol.[29] Two representative procedures are given below, followed by physical and spectral data for each monomer. NOTE: The monomers were unstable in their pure states even at 0 °C and rapidly turned orange upon standing. If not used immediately in the polymerization reaction, monomers were stored as dilute solutions (5%) in pentane at 0 °C.

2,5-Diethynylthiophene (7a). To a solution of 0.54 g (2 mmol) of 2,5-bis[2-(trimethylsilyl)ethynyl]thiophene in 12 mL of methanol was added 4 mL of 1 N KOH. The solution was stirred at room temperature under an argon atmosphere. The reaction was shown to be complete after 6 h by TLC. Partial removal of the methanol allowed the product to be extracted into ether (10 mL). The ether extract was washed with saturated NaCl and dried over $MgSO_4$. The inorganics were removed by filtration, and the filtrate was carefully concentrated at reduced pressure to give 0.28 g (94% yield) of product: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.97 (s, 2 H), 3.22 (s, 2 H).

Synthesis of 2,5-Diethynyl-3-methylthiophene (7b). To a stirred solution of 1.475 g (5 mmol) of bis[2-(trimethylsilyl)ethynyl]-3-methylthiophene in 70 mL of methanol was added 2.0 mL of 1 N KOH dropwise. Stirring was continued at room temperature for 6 h, after which time analysis by GC indicated consumption of the starting material. The product was extracted into pentane (50 mL), and the organic solution was extracted with water (100 mL). The layers were separated, and the organic layer was dried over $MgSO_4$, filtered, and concentrated at reduced pressure. The resulting yellow oil was immediately chromatographed on flash-grade silica (pentane) as the eluent to yield 0.44 g (61%) of a clear oil: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.96 (s, 1 H), 3.44 (s, 1 H), 3.30 (s, 1 H), 2.25 (s, 3 H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 143.7, 134.9, 122.5, 119.8, 84.4, 82.1, 76.9, 76.4, 15.05.

Synthesis of 3-Butyl-2,5-diethynylthiophene (7c). The reaction solution was stirred at room temperature for 4 h, after which time analysis by GC indicated consumption of the starting material. Isolation of the product as described above afforded a yellow oil which was immediately chromatographed on flash-grade silica (pentane) to yield a clear oil in 90% yield: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.00 (s, 1 H), 3.43 (s, 1 H), 3.31 (s, 1 H), 2.64 (t, 3 H), 1.56 (m, 2 H), 1.33 (m, 2 H), 0.92 (t, 3 H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 148.57, 133.71, 122.24, 119.06, 83.84, 81.55, 76.73, 76.10, 32.12, 29.05, 22.2, 13.68.

Synthesis of 2,5-Diethynyl-3-hexylthiophene (7d). The reaction was allowed to proceed at room temperature for 7 h, at which time analysis by GC indicated completion of the reaction. The product was isolated as a yellow oil, which was immediately chromatographed on flash-grade silica with hexane as the eluent to yield a clear oil in 99% yield: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.99 (s, 1 H), 3.42 (s, 1 H), 3.30 (s, 1 H), 2.62 (t, 2 H), 1.57 (m, 2 H), 1.29 (m, 6 H), 0.87 (t, 3 H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 148.68, 133.76, 122.03, 118.88, 83.95, 81.69, 76.61, 76.00, 31.59, 29.99, 29.32, 28.84, 22.4, 14.09.

Synthesis of 2,5-Diethynyl-3-octylthiophene (7e). The reaction was stirred at ambient temperature for 45 h, and after isolation of the product as described above a yellow oil was obtained. Purification of the oil was achieved by chromatography on silica with pentane to afford 90% yield of a colorless oil: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 6.99 (s, 1 H), 3.41 (s, 1 H), 3.30 (s, 1 H), 2.62 (t, 2 H), 1.57 (m, 2 H), 1.26 (m, 8 H), 0.87 (t, 3 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 148.66, 133.73, 122.03, 118.87, 83.88, 81.62, 77.40, 75.98, 34.14, 31.89, 30.02, 29.34, 29.23, 22.68, 22.36, 14.05.

Synthesis of 2,5-Diethynyl-3-phenylthiophene (7f). The reaction mixture was stirred at room temperature for 10 h, after which time completion was indicated by TLC (silica, pentane). The product was isolated as a yellow oil, which was purified by chromatography on silica with pentane as the eluent to afford a 99% yield of a colorless oil: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.67 (d, 2 H, J = 6.8 Hz), 7.35 (br, 3 H), 7.28 (s, 1 H), 3.37 (s, 1 H), 3.33 (s, 1 H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 145.58, 134.28, 133.42, 128.49, 128.12, 127.90, 122.70, 84.03, 82.29, 76.64, 76.25.

Synthesis of 5,5′-Diethynyl-2,2′-bithiophene (9). To a solution of 0.358 g (1.0 mmol) of 5,5′-bis[2-(trimethylsilyl)ethynyl]-2,2′-bithiophene in a 1:1 solvent mixture of methanol/THF (25 mL) was added 1 mL of 1 N KOH with stirring. The reaction mixture was allowed to stir for 15 h at room temperature, after which time completion was indicated by TLC (silica, hexanes). Approximately half the volume of methanol was evaporated, resulting in the precipitation of the product as a crystalline solid. The suspension was diluted with ether (40 mL) to dissolve the solid. The ethereal solution was then washed with water followed by brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated at reduced pressure. The crude product was chromatographed on silica with methylene chloride as eluent. A 99% yield (0.212 g) of yellow solid was realized. Material darkened slowly upon standing at atmospheric and reduced pressure: mp 105–110 °C (dec); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.16 (d, 2 H, J = 3.74 Hz), 7.02 (d, 2 H, J = 3.74 Hz), 3.41 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.90, 133.94, 123.89, 121.47, 82.61, 76.63.

Synthesis of 2,5-Diethynylthieno[3,2-*b*]thiophene (11). A stirred solution of 0.664 g (2.0 mmol) of 2,5-bis[2-(trimethylsilyl)ethynyl]thieno[3,2-*b*]thiophene in a solvent mixture of 1:1 methanol/THF (25 mL) was treated with 2 mL of 1 N KOH. Completion of the hydrolysis was shown by TLC (silica, CH_2Cl_2) in 24 h. At that time half the volume of the solvents was evaporated. The residual solution was diluted with CH_2Cl_2 (40 mL), and the solution was washed with water. The layers were separated, and the organic phase was washed with saturated NaCl and dried over $MgSO_4$. The solution was filtered and concentrated to leave 0.370 g (98%) of a yellow crystalline solid. This material slowly darkened upon standing at atmospheric and reduced pressure: mp 85 °C (dec; sealed tube); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 7.35 (s, 2 H), 3.50 (s, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.06, 133.92, 123.88, 121.43, 82.58.

Procedures. Polymer Synthesis. Synthesis of Poly(2,5-ethynylenethiophenediylethynylene) (1a). To a solution of 0.35 g (2.65 mmol) of diethynylthiophene in 15 mL of pyridine was added 26 mg (1 mmol) of CuCl with stirring. A stream of oxygen was bubbled through the solution for 5 min, and stirring at room temperature was continued for 2.5 h. The color of the reaction solution turned from bright yellow to dark green within 45 min, and a brown precipitate was noticed after 1.5 h. Consumption of the starting material was indicated by TLC (silica, pentane). Evaporation of the solvent left a brown powdery residue which was twice stirred in 20 mL of 5% NH_4OH for 2 h. Decantation of the aqueous solvent left a brown insoluble powder (0.24 g, 66%). Shiny, dark pellets of **1a** were pressed at 15 000 psi for 2 min. A reaction exotherm was observed (DSC) at 179 °C (121 cal/g), and the material exhibited no weight loss up to 400 °C and only 13% weight loss at 700 °C.

Synthesis of Poly(2,5-ethynylene-3-methylthiophenediylethynylene) (1b). To a solution of 0.44 g (3.0 mmol) of 2,5-

diethynyl-3-methylthiophene in 20 mL of pyridine was added 94 mg (0.095 mmol) of CuCl with stirring. The flask was fitted with a balloon filled with oxygen and small quantities of O_2 were periodically bubbled through the solution. Within 2 min, the reaction solution had changed color from bright yellow to dark orange. After stirring for 3 h at room temperature, the color of the solution was dark brown and contained a large amount of precipitate. TLC (silica, pentane) indicated consumption of the starting material after 3 h. The solvent was removed at reduced pressure, and the dark-red solid residue was stirred in 50 mL of 10% NH_4OH for ~1 h. The residue was isolated by filtration and dried under vacuum to give 0.40 (89%) of polymer. Slight solubility characteristics of the polymer were observed in tetrachloroethane and chloroform. However, a sufficient concentration of a significant fraction of the polymer was not sustained to allow solution characterization. Shiny, dark pellets were prepared by subjecting the polymer to a hydraulic press at 15 000 psi for 2 min. Thermal analysis of the material indicated the presence of two reaction exotherms (DSC): T_{exo_1} 206 °C (108 cal/g) and T_{exo_2} 352 °C (28 cal/g). Thermal stability was obtained (TGA) with no weight loss up to 400 °C and a 12% weight loss at 700 °C.

Synthesis of Poly(2,5-ethynylene-3-butylthiophenenediylethynylene) (1c). To a solution of 0.30 g (1.6 mmol) of 3-butyl-2,5-diethynylthiophene in 10 mL of pyridine was added 15.8 mg (0.016 mmol) of CuCl with stirring. The flask was fitted with a balloon filled with oxygen, and small quantities of oxygen were periodically bubbled through the solution. Within 5 min, the solution changed color from bright yellow to dark orange. The reaction was monitored by TLC (silica, pentane) for consumption of the starting material, and after 3 h of stirring at room temperature the reaction was complete. Violet–black rubbery material had precipitated, and solvent was removed at reduced pressure. The dark-purple residue was pulverized at -196 °C using a SPEX 6700 freezer/mixer. The resulting fine powder was stirred in 20 mL of 10% NH_4OH for ~1 h to extract the copper salts, resulting in a blue aqueous solution. After filtration and drying under vacuum, 0.210 g (40%) of polymer was obtained. Concentrated solutions of the polymer in tetrachloroethane were anisotropic: ^1H NMR ($PhNO_2$-d_5, 120 °C, 200 MHz) (all peaks are very broad) δ 7.20 (1 H), 2.77 (2 H), 1.67 (2 H), 1.32 (2 H), 0.98 (3 H). Molecular weight determination on **1c** by GPC vs polystyrene standards in chloroform gave M_w = 22 000, M_n = 4500, and D = 4.96. The polymer was approximately 65% soluble in tetrachloroethane and slightly more soluble in hot nitrobenzene and hot chlorobenzene. Thermal analysis (DSC) gave T_{exo_1} 210 °C (66 cal/g) and T_{exo_2} 375 °C (57 cal/g). A 7% weight loss at 400 °C (TGA) and a 29% weight loss by 700 °C were obtained.

Synthesis of Poly(2,5-ethynylene-3-hexylthiophenediylethynylene) (1d). This polymer offered much improved solubility over the previous materials **1a–c**. For this reason, several different polymerization procedures were investigated for this material in order to optimize desirable characteristics such as solubility and molecular weight.

Method A. To a solution of 1.50 g (7.0 mmol) in 50 mL of pyridine was added 70 mg (0.71 mmol) of CuCl with stirring. The flask was fitted with a balloon filled with oxygen, and small quantities of oxygen were periodically bubbled through the solution. Within 5 min, the solution changed color from bright yellow to dark orange. The reaction was monitored by TLC (silica, pentane) for consumption of the starting material, and after 4 h at room temperature the reaction was complete and a blackish rubbery material had precipitated. The solvent was removed at reduced pressure, and the dark purple residue was pulverized at -196 °C using a SPEX 3700 freezer/mixer. The resulting fine powder was stirred in 60 mL of 10% NH_4OH for 1 h. After filtration and drying under vacuum, 1.40 g (96%) of polymer was obtained. The polymer exhibited $[\eta]$ = 2.95 dL/g ($CHCl_3$) and a broad molecular weight distribution by GPC with M_w = 23 100, M_n = 6200, and D = 3.72. The polymer was approximately 70% soluble in tetrachloroethane and chloroform, and films could be cast from solution. Thermal analysis of this material demonstrated two reaction exotherms (DSC) T_{exo_1} 218 °C (7 cal/g) and T_{exo_2} 373 °C (29 cal/g). The thermal stability of **1d** was noticeably less than polymers **1a–c** with 8% weight loss at 400 °C and 39% weight loss at 700 °C: ^1H NMR ($CDCl_3$, 270 MHz) (all peaks were extremely broad) δ 7.07 (1 H), 2.65 (2 H), 1.58 (2 H), 1.29 (6 H), 0.87 (3 H).

Method B. To a solution of 0.500 g (2.27 mmol) of 2,5-diethynyl-3-hexylthiophene in 16 mL of pyridine was added 23 mg (0.23 mmol) of copper(I) chloride with stirring. The solution was aerated periodically with O_2, and a film of polymer formed on the sides of the flask. After stirring for 8 h at room temperature, the polymerization was complete as indicated by TLC and the mixture was poured into methanol. Precipitate had formed and was collected to yield 0.48 g (96%) of polymer. The material exhibited slightly better solubility characteristics than that of method A, and the characteristic reaction exotherms (DSC) were T_{exo_1} 211 °C (73 cal/g) and T_{exo_2} 400 °C (18 cal/g). As determined from a solution in tetrachloroethane, the polymer has an intrinsic viscosity $[\eta]$ = 3.7 dL/g.

Method C. To a solution of 75 mg (0.75 mmol) of copper(I) chloride in a solvent mixture of 4.0 mL of DMF, 1.0 mL of pyridine, and 0.04 mL of TMEDA was added a solution of 0.550 g (2.5 mmol) of 2,5-diethynyl-3-hexylthiophene in 1.0 mL of DMF with stirring. Periodically, oxygen was bubbled through the system, and, after 2 h at room temperature, precipitate had formed (as a film on the sides of the flask). The polymerization was complete in 4 h as evidenced by TLC (silica, hexanes), and the mixture was poured into methanol. Separation of the polymer film from the methanol gave 0.54 g (98%) of material after drying. This material is approximately 70% soluble in TCE and slightly less soluble in $CHCl_3$. Thermal analyses (DSC and TGA) were consistent with previous descriptions. Intrinsic viscosities were slightly increased from methods A and B, $[\eta]$ = 6.7 dL/g (TCE) and $[\eta]$ = 6.3 dL/g ($CHCl_3$). The molecular weight of the soluble fraction was determined by GPC vs polystyrene standards with M_w = 37 600, M_n = 6600, and D = 5.69; IR (film) 2954, 2926, 2856, 2181, 2137, 1654, 1465, 844 cm^{-1}.

Synthesis of Poly(2,5-ethynylene-3-octylthiophenediylethynylene) (1e). The polymerization was carried out in a three-neck 50-mL round-bottomed flask designed to disperse air or gas through the solution via a specialized stirring mechanism. The flask was wrapped in aluminum foil, and 0.488 g (2.0 mmol) of 2,5-diethynyl-3-octylthiophene and 30 mL of pyridine were added. The flask was fitted with a balloon filled with oxygen, and 20 mg (0.2 mmol) of CuCl was added to the flask. The reaction was monitored by TLC (hexanes) for disappearance of the starting material and was complete after 12 h of stirring at room temperature. A film of polymer formed on the sides of the flask through the duration of the reaction. The solution was filtered. The precipitate (film) was soaked in methanol for 3 days and powdered at -196 °C. An 80% (0.189 g) yield of material was obtained. The material was soluble in chloroform and TCE, and films could be cast. GPC analysis vs polystyrene standards indicated M_w = 21 900, M_n = 7400, and D = 2.96. Differential scanning calorimetry (DSC) of the polymer gave T_{exo_1} 220 °C (75 cal/g) and a small second exotherm T_{exo_2} 382 °C (6 cal/g). This polymer was the least thermally stable of all the polymers **1a–e** and exhibited 8% weight loss at 400 °C and 50% weight loss at 700 °C.

Synthesis of Poly(2,5-ethynylene-3-phenylthiophenediylethynylene) (1f). This material was prepared by the previously described method of polymerization in pyridine or in a mixture of DMF and pyridine.

Method A. To a solution of 0.200 g (0.57 mmol) of 2,5-diethynyl-3-phenylthiophene in 3 mL of pyridine was added 6 mg (0.06 mmol) of CuCl with stirring. The reaction was conducted in the dark, and the solution was periodically aerated with O_2. After 5 h at room temperature, a red precipitate had formed. After 8 h, completion of the reaction was indicated by TLC (silica, pentane) and the mixture was poured into methanol. The precipitated polymer was allowed to stand in methanol for 1 h and collected by filtration. The polymer was dried under vacuum to leave 0.16 g (80%) of red powder. The material was approximately 20% soluble in chloroform or TCE.

Method B. A solution of 15 mg (0.15 mmol) of CuCl in 1.5 mL of dry DMF and 0.5 mL of pyridine was treated with a solution of 0.200 g (0.568 mmol) of 2,5-diethynyl-3-phenylthiophene in 1 mL of pyridine. The color of the reaction mixture darkened immediately and stirring was continued for 2 h in the absence of light with periodic bubbling of oxygen into solution. The monomer had been consumed as evidenced by TLC, and a red precipitate had formed. The mixture was poured into methanol and allowed to stand for approximately 1 h. After filtration, the red solid was dried under vacuum to afford 0.190 g (95%) of polymer. Comparison of the physical characteristics of the polymers by method A or B was consistent. Thermal analysis showed two reaction exotherms present in the DSC, T_{exo_1} 174 °C (57 cal/g) and T_{exo_2} 451 °C (13 cal/g). The polymer exhibited better thermal stability than the alkyl derivatives **1a–e** with no weight loss observed at 400 °C and only 12% weight loss at 700 °C.

Synthesis of Poly(5,5′-ethynylene-2,2′-bithiophenediylethynylene) (2). To a solution of 0.160 g (0.75 mmol) of 5,5′-diethynyl-2,2′-bithiophene in 1.3 mL of DMF and 1.5 mL of pyridine was added 11.8 mg (0.12 mmol) of CuCl. Stirring at room temperature with periodic bubbling of oxygen through the solution for 1 h, a red precipitate formed. The solution also became viscous. Dilution of the reaction by addition of 1.0 mL of pyridine and 1.0 mL of DMF was initiated. The monomer was consumed (TLC, silica, CH_2Cl_2) after 4 h, and the mixture was poured into methanol. After filtration, an orange solid was obtained, which was dried under vacuum to afford 0.154 g (96%) of material. This material was completely insoluble in all common solvents. Shiny, dark pellets of the polymer could be formed at 15 000 psi for 2 min. Thermal analysis of **2** demonstrated the presence of two reaction exotherms T_{exo_1} 125 °C (48 cal/g) and T_{exo_2} 231 °C (8 cal/g) (DSC). The thermal stability observed was good up to 400 °C with 0% weight loss, and 19% weight loss was observed by 700 °C.

Synthesis of Poly[2,5-ethynylene(thieno[3,2-*b*]thiophenediyl)ethynylene] (3). To a stirred solution of 282 mg (1.5 mmol) of 2,5-diethynylthieno[3,2-*b*]thiophene in 3 mL of DMF and 3 mL of pyridine was added 24 mg of CuCl. Within 30 min a precipitate had formed. Stirring was continued until the monomer was shown to be consumed by TLC (silica, hexanes) for a total of 2 h. The mixture was poured into methanol, and after filtration an orange solid was obtained in 100% yield (0.281 g). The material was completely insoluble in common solvents but was able to be pressed into shiny, dark pellets at 15 000 psi for 2 min. One reaction exotherm was observed, T_{exo} 141 °C (71 cal/g) (DSC). No weight loss was observed up to temperatures of 700 °C.

Synthesis of Poly(2,5-thieno[3,2-*b*]thiopheneylene) and Poly[2,5-(3-methylthieno[3,2-*b*]thiopheneylene)] (4a,b and 5a,b). Polymerizations of thieno[3,2-*b*]thiophene and 3-methylthieno[3,2-*b*]thiophene were performed according to literature procedures.[40]

Poly(2,5-thieno[3,2-*b*]thiopheneylene) (4a). To a solution of 70 mg (0.500 mmol) thieno[3,2-*b*]thiophene in 5.0 mL of chloroform was added 325 mg (2.00 mmol) of ferric chloride. The solution was stirred at room temperature for 2 h, after which time TLC (silic, hexanes) indicated consumption of the monomer. The reaction formed a precipitate during the course of the polymerization and was poured into methanol, filtered, and stirred in water for several hours to remove inorganic salts. The filtered solids were washed with methanol and acetone, followed by drying under high vacuum, affording 66 mg (95%) of a brown powder. This material was insoluble in all solvents but could be pressed into shiny, dark pellets at 15 000 psi for 3 min.

Poly[2,5-(3-methylthieno[3,2-*b*]thiopheneylene)] (4b). The polymer was obtained following the procedure described above in 92% yield and was also an insoluble powder that was pressed into pellets at 15 000 psi for 3 min.

Poly(2,5-thieno[3,2-*b*]thiopheneylene) (5a) and Poly[2,5-(3-methylthieno[3,2-*b*]thiopheneylene)] (5b). The polymerizations were effected at 10% solution of the appropriate monomer in acetonitrile using tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. The potential was scanned in the positive direction until a substantial current for the oxidation of the thieno[3,2-*b*]thiophene was observed. The potential was held constant through the duration of the polymerization. Polymer **5a** or **5b** formed as a film on the anode (ITO glass) and was removed from the electrode for further investigation. An earlier report by other workers had described the electrochemical synthesis of poly(thieno[3,2-*b*]thiopheneylene) to give a semiconductive material coated on an SiO_2 wafer.[36]

Thermal Cross-Linking of the Polymers. The procedures used to effect the cross-linking reaction of the polymers involved heating a polymer sample at or around T_{exo_1} for 10 min. Cross-linking was determined by DSC analysis, and the above conditions afforded materials no longer containing a T_{exo_1}. Pellets of **1a** and **1b** were preformed at 15 000 psi for 5 min and then placed in a hydraulic press at 30 000 psi. The temperature was ramped from 100 to 200 °C and held at 200 °C for 10 min. Films of **1c** and **1d** were placed between pieces of glass fiber filter paper and sandwiched between microscope slides. The slides were placed in a jacketed drying pistol over refluxing ethylene glycol for approximately 1 h to effect the cross-linking reaction. These films were checked for the absence of the reaction exotherm to verify that cross-linking had occurred. The longer thermolysis time was necessary to ensure the completeness of the reaction. Films of **1c** and **1d** could be cross-linked upon heating in a DMA oven with the motor off. Polymers **1d** and **1f** were also thermolyzed in this manner upon heating to 220 and 175 °C, respectively. Polymers **2** and **3** were thermolyzed as pressed pellets in the DMA oven at 130 and 150 °C, respectively, for 10 min.

Representative Conductivity Experiment. Conductivity data were obtained and doping experiments performed as described by Wnek.[43] For the insoluble polymers **1a**, **1b**, **1f**, **2**, and **3** measurements were obtained in pressed pellets for both the initial polymers and the corresponding cross-linked materials. Polymers **1c**, **1d**, and **1e** were cast from solution of tetrachloroethane or chloroform to form free-standing films. Conductivity measurements were obtained on these films before and after cross-linking.

Briefly, a polymer film **1d** was measured for thickness upon taking an average of 10 measurements, and films typically were 0.04–0.06 mm. The width of the film was analogously determined and ranged from 0.4 to 0.6 cm. The film was attached to the four-probe apparatus with Electrodag (Acheson Colloids) to maintain electrical and mechanical contact. The distance between the center two probes was measured and usually was ~0.2 cm. The initial resistance of the material was measured across the inner two probes. The system was evacuated, and arsenic pentafluoride (400 Torr) was released from a gas bulb and allowed to contact the polymer sample. The maximum increase in conductivity was usually observed within 24 h, although some samples were observed for up to 5 days. The conductivity was calculated from the following equation: $\sigma = l/(twR)$ where l = distance between the center two probes, t = thickness of the film, w = width of film, and R = sample resistance. For samples that offer a resistance of less than 10^5 ohm upon doping, it is necessary to measure the resistance of the sample by the four-probe method to render the contact resistance between the sample and probe to be negligible. Hence, the sample resistance is calculated by $R_s = (V_s/V_r)R_r$.

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References and Notes

(1) Skotheim, T. A., Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986.

(2) Heeger, A. J. Reference 1, p 769.

(3) Qiem, R. *Makromol. Chem., Macromol. Symp.* **1990**, *33*, 327.

(4) (a) Frommer, J. E.; Chance, R. R. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1986; Vol. 5, p 462. (b) Reynolds, J. R. *J. Mol. Electron* **1986**, *2*, 1.

(5) (a) Shirakawa, H.; Ikeda, S. *Polymer* **1971**, *2*, 231. (b) Ito, T.; Shirakawa, H.; Ikeda, S. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 11.

(6) (a) Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chaing, C. K.; Heeger, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 578. (b) Chaing, C. K.; Park, Y. W.; Heeger, A. J.; Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G. *Phys. Rev. Lett.* **1977**, *39*, 1098.

(7) Ivory, D. M.; Miller, G. G.; Sowa, J. M.; Shacklette, L. W.; Chance, R. R.; Baughman, R. H. *J. Chem. Phys.* **1979**, *71*, 1506.

(8) Kanazawa, K. K.; Diaz, A. F.; Gill, W. D.; Grant, P. M.; Street, G. B.; Gardini, G. P.; Kwak, J. F. *Synth. Met.* **1980**, *1*, 329.

(9) (a) Baughman, R. H.; Brédas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* **1982**, *82*, 209. (b) Bloor, D.; Monkman, A. P.; Stevens, G. C.; Cheung, K. M.; Righ, S. *Mol. Cryst. Liq. Cryst.* **1990**, *187*, 231. (c) Campbell, D. K. *Mol. Cryst. Liq. Cryst.* **1990**, *189*, 65. (d) Bulka, B. R. *Mater. Sci.* **1988**, *14*, 133.

(10) (a) Street, G. B. Reference 1, p 265. (b) See: Proceedings of International Conference on the Science and Technology of Synthetic Metals. *Synth. Met.* **1989**, *28*, C1–C269.

(11) (a) Tourillion, G. Reference 1, p 293. (b) See: Proceedings of the International Conference on the Science and Technology of Synthetic Metals. *Synth. Met.* **1989**, *28*, C275–C545.

(12) (a) Wellinghoff, S. T.; Kedrowski, T.; Jenekhe, S.; Tshida, T. *J. Phys., Colloq.* **1983**, *677*, C3. (b) Jenekhe, S.; Wellinghoff, S.; Reed, J. *Mol. Cryst. Liq. Cryst.* **1984**, *105*, 175.

(13) (a) Tunney, S. E.; Suenaga, J.; Stille, J. K. *Macromolecules* **1983**, *16*, 1398. (b) Tunney, S. E.; Suenaga, J.; Stille, J. K. *Macromolecules* **1987**, *20*, 258.

(14) (a) Inabe, T.; Kannewurf, C. R.; Lyding, J. W.; Mogel, M. K.; Marles, T. J. *Mol. Cryst. Liq. Cryst.* **1983**, *355*, 93. (b) Inabe, T.; Lomac, J.; Lydine, J.; Kannewurf, C.; Wynne, K. *Macromolecules* **1984**, *17*, 260.

(15) Townsend, P. D.; Baker, G. L.; Schlotter, N. E.; Etemad, S. *Synth. Met.* **1989**, *28*, D633.

(16) Brédas, J. L.; Chance, R. R.; Baughman, R. H. *J. Chem. Phys.* **1982**, *76*, 3673.

(17) (a) Bloor, D.; Hubble, C. L.; Ando, D. J. In *Molecular Metals*; Hatfield, W. E., Ed.; *NATO Conference Series VI*; Plenum: New York, 1979; Vol. 1, p 243. (b) Seiderheld, U.; Baessler, H. *Solid State Commun.* **1983**, *47*, 391.

(18) (a) Hay, A. S. *J. Org. Chem.* **1960**, *25*, 1275. (b) Hay, A. S. *J. Polym. Sci., Polym. Chem. Ed.* **1969**, *7*, 1625. (c) Hay, A. S.; Bolon, D. A.; Leimer, K. R.; Clark, R. F. *J. Polym. Sci., Part B* **1970**, *8*, 97.

(19) Rutherford, D. R.; Stille, J. K. *Macromolecules* **1988**, *21*, 3530.

(20) Rutherford, D. R.; Stille, J. K.; Elliott, C. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31*, 643.

(21) Neenan, T. X.; Callstrom, M. R.; Scarmoutzos, L. M.; Stewart, K. R.; Whitesides, G. M.; Howes, V. R. *Macromolecules* **1988**, *21*, 3525.

(22) Cernia, E.; D'Ilario, L.; Ortaggi, G.; Scarsella, M.; Scialis, R.; Sleiter, G. *Gazz. Chim. Ital.* **1989**, *119*, 309.

(23) Ortaggi, G.; Sleiter, G.; D'Ilario, L.; Piozzi, A.; Bolasco, A.; Chimenti, F. *Gazz. Chim. Ital.* **1989**, *119*, 395.

(24) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

(25) West, R.; Kraihanzel, C. S. *Inorg. Chem.* **1962**, *1*, 967.

(26) Eschavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478.

(27) Trumbo, D. L.; Marvel, C. S. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 2231, 2311.

(28) (a) *Stephens*, R. D.; Castro, C. E. *J. Org. Chem.* **1963**, *28*, 3313. (b) Austin, W. B.; Bilow, N.; Kelleghan, W. J.; Lau, K. S. Y. *J. Org. Chem.* **1981**, *46*, 2280.

(29) Harris, S. J.; Walton, D. R. M. *Tetrahedron* **1978**, *34*, 1037.

(30) Meth-Cohn, O.; Gronowitz, S. *Acta Chem. Scand.* **1966**, *20*, 1577.

(31) (a) Tamao, K.; Sumitami, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374. (b) Tamao, K.; Kumada, S.; Nakajima, I.; Kumada, M. *Tetrahedron* **1982**, *38*, 3347.

(32) For a discussion of the bromination of thiophenes, see: Taylor, R. In *Heterocyclic Compounds*; Gronowitz, S., Ed.; Wiley: New York, 1986; Vol. 44, Part 2, p 82.

(33) Brédas, J. L.; Street, G. B.; Thémans, B.; André, J. M. *J. Chem. Phys.* **1985**, *83*, 1323.

(34) Wu, X.; Dirlikov, S. K. *Polym. Mater. Sci. Eng.* **1989**, *60*, 762.

(35) (a) Krische, B.; Hellberg, J.; Lilja, C. *J. Chem. Soc., Chem. Commun.* **1987**, 1476. (b) Waltman, R. J.; Bargon, J.; Diaz, A. F. *J. Phys. Chem.* **1983**, *87*, 1439.

(36) Lazzaroni, R.; Dujardin, S.; Boutique, J.-P.; Mousty-Desbuquoit, C.; Riga, J.; Verbiot, J. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 249.

(37) (a) Goldfarb, Y. L.; Litvinov, V. P.; Ozolin, S. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1965**, 510. (b) Litvinov, V. P.; Goldfarb, Y. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1963**, 2183. (c) Bugge, A. *Acta Chem. Scand.* **1968**, *22*, 63.

(38) Bugge, A. *Acta Chem. Scand.* **1969**, *23*, 2704.

(39) Lazzaroni, R.; Dujardin, S.; Boutique, J.-P.; Mousty-Desbuquoit, C.; Riga, J.; Verbiot, J. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 249.

(40) (a) Österholm, J.-E.; Laakso, J.; Nyholm, P.; Isotalo, H.; Stubb, H.; Inganäs, O.; Salanek, W. R. *Synth. Met.* **1989**, *28*, C435. (b) Sugimoto, R.; Takeda, S.; Gu, H. B.; Yoshino, K. *Chem. Express* **1986**, *1*, 635.

(41) (a) Wegner, G. *Makromol. Chem.* **1971**, *145*, 85. (b) Wegner, G. *Makromol. Chem.* **1970**, *134*, 219. (c) Hay, A. S.; Bolon, D. A.; Leimer, K. R.; Clark, R. F. *Polym. Lett.* **1970**, *8*, 97. (d) Patel, G. N.; Walsh, E. K. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 203. (e) Newkirk, A. E.; Hay, A. S.; McDonald, R. S. *J. Polym. Sci., Part A* **1964**, *2*, 2217. (f) White, D. M.; Quin, C. B. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2595.

(42) (a) Tieke, B. *Adv. Polym. Sci.* **1985**, *71*, 79. (b) Chance, R. R. *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1987; Vol. 10; pp 670–683.

(43) Wnek, G. E. Ph.D. Dissertation, University of Massachusetts, 1980; p 71.

(44) Shacklette, L. W.; Eisenbaumer, R. L.; Chance, R. R.; Eckhardt, H.; Frommer, J. J.; Baughman, R. H. *J. Chem. Phys.* **1981**, *75*, 1919.

(45) Brédas, J. L.; Dory, M.; André, J. M. *J. Chem. Phys.* **1985**, *83*, 5242.

(46) Brédas, J. L.; Dory, M.; Thémans, B.; Delhalle, J.; André, J. M. *Synth. Met.* **1989**, *28*, D533.

(47) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Permagon Press: New York, 1980.

(48) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

(49) Tayim, H. A.; Bouldoukian, A.; Awad, F. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3799.

(50) Doyle, J. R.; Slade, P. G.; Jonassen, H. B. *Inorg. Synth.* **1960**, *6*, 216.

(51) Van Hecke, G. R.; Horrocks, W. D., Jr. *Inorg. Chem.* **1966**, *5*, 1968.

(52) Holmes, A. B.; Sporikou, C. N. *Organic Syntheses*; Vedejs, E., Ed.; Wiley: New York, 1987; Vol. 65; p 61.

(53) Rennekamp, M. E.; Perry, W. O.; Cooks, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 4985.

(54) Kellogg, R. M.; Schaap, A. P.; Wynberg, H. *J. Org. Chem.* **1969**, *34*, 343.