Grignard Synthesis of π-Conjugated Poly(3-alkylthiophenes): Controlling Molecular Weights and the Nature of Terminal Units

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ABSTRACT: Poly(3-hexylthiophene) has been polymerized by polycondensation of a reaction mixture consisting of 2,5-diiodo-3-hexylthiophene and mono- and di-Grignard reagents thereof. Molecular weights, molecular weight distributions, and the nature of the terminal units were dependent on the percentage compositions of the polymerization mixture. Terminal thienyl units of the polymers possessed Grignard functionality when the initial mixture consisted largely of the di-Grignard reagent. The addition of H_2O, D_2O, and I_2 to this polymer produced hydrogen-, deuterium-, and iodine-terminated polymer chains, as indicated by ^1H NMR. Both 2- and 5-terminal ring protons could be detected upon conversion of the Grignard termini with water.

Introduction

Thiophene can be polymerized to yield materials which possess extended π-orbital conjugation along the main chain.[1-3] As a result of conjugation these polymers are often highly colored, exhibit significant third-order nonlinear optical responses, and can be easily oxidized so as to impart electronic conductivity. Early work in this field focused on polymers obtained from electrochemical polymerization of thiophene and 3-methylthiophene monomers.[4-9] Polymers produced in this manner form insoluble films on electrodes which can be removed from the surface for further analysis. Chemical routes for synthesizing polythiophenes have also been devised, namely, polycondensation between heterocyclic di-Grignard reagents and dihalogenated heterocycles[1,10,11] and oxidative coupling of thiophenes using Lewis acids such as ferric chloride, molybdenum pentachloride, and ruthenium trichloride.[12] The materials produced are intractable solids irrespective of the synthetic route.

Significant effort has been directed to tailoring the physical properties polythiophenes. The impetus is the realization of processable and application-specific electronically conducting polymers. It is now known that derivatization of the thienyl ring at the 3-position with long alkyl chain, methoxy, alkylmercapto, or ether functionality[13-20] yields polymers which are soluble in common organic solvents. The advantage of preparing soluble polymers is their ease of characterization, which also affords detailed investigation of the effect of polymerization conditions on the physicochemical properties of the polymer. For example, Leclerc et al. have shown that electropolymerization leads to bimodal molecular weight distributions of poly(alkylthiophenes).[21] The fraction of the higher molecular weight component increases with polymerization time. ^1H NMR studies indicate that the lower molecular weight component contains branched polythiophenes due to irregular 2,4-coupling of thienyl units. Branching was also observed for poly(alkylthiophenes) produced by chemical polymerization using ferric chloride, although the polymers possessed a higher percentage of 2,5-coupling compared to electrochemically prepared polymers, as evidenced by a higher degree of crystallinity, higher levels of conductivity, and ^{13}C NMR studies.

Condensation of 2,5-di-Grignard-3-alkylthiophenes should provide linear polymers if the starting materials are sufficiently free from 4-Grignard isomers. Although this method has been reported by several workers,[10,11,19,20] studies relating reaction conditions to the intrinsic properties of the polymer are lacking. Our studies on poly(3-alkylthiophenes) reveal that the polymerization mixture comprises three thienyl monomers and that the initial composition determines molecular weights, molecular weight distributions, and nature of the terminal units of the resulting polymer. The results for poly(3-hexylthiophene) (P3HT), described in this paper, are typical for poly(3-alkylthiophenes). Our investigation of the Grignard polycondensation of thiophenes also stems from an interest in preparing telechelic π-conjugated polythiophenes which can be used as intermediates for higher polymers and polymer blends.[22] We have, therefore, investigated the chemical nature of the termini with the intent of finding a suitable procedure for preparing telechelic poly(3-alkylthiophenes).

Experimental Section

Preparation of Diiodo-3-hexylthiophene (I). 3-Hexylthiophene was synthesized by coupling the Grignard reagent of 3-bromothiophene (Aldrich) with 1-bromohexane using [1,3-bis(diphenylphosphino)propane]nickel(II) chloride ($Ni(dppp)_2Cl_2$) as catalyst.[33] The product was purified by fractional distillation under reduced pressure. 3-Hexylthiophene (7.8 g, 46 mmol) and 12.2 g (48 mmol) of I_2 (BDH Chemicals Ltd.) were added to a mixture comprising 18 mL of chloroform, 3 mL of concentrated HNO_3, and 3 mL of H_2O. The mixture was refluxed for 16 h, and the composition of thiophene products was monitored by gas chromatography (GC). The product, I, was purified through a silica gel column using hexane as eluant. After workup, the yield was 71%, and the purity was >99% as determined by GC.

Polymerization of Diiodo-3-hexylthiophene. Magnesium metal (0.29 g, 12 mmol) was reacted with 4.2 g (10 mmol) of I in ether to prepare the corresponding Grignard reagent. The composition of the Grignard mixture was determined periodically by quenching aliquots of the mixture with water and analyzing the resulting products by GC. The response of the detector was calibrated using pure compounds in order to obtain quantitative information. Following formation of the Grignard reagents, the polymerization was initiated by the addition of $Ni(dppp)_2Cl_2$. The polymerization was complete after 0.5–2 h. The reaction was quenched by the addition of water, iodine, or heavy water. The reaction mixture was poured into 5% HCl in methanol to precipitate poly(3-hexylthiophene). Yields were 60–70%.

Instrumentation. Infrared spectra were recorded on a Bomem Michelson FTIR (120 Series). UV–vis absorption spectra were recorded on a Perkin-Elmer Lamda 3A UV–vis spectrophotomer at 25 °C. ^1H NMR were recorded with a 400-MHz Bruker AMX400 in $CDCl_3$. Gas chromatography was performed on a Hewlett-Packard 5890A gas chromatograph.

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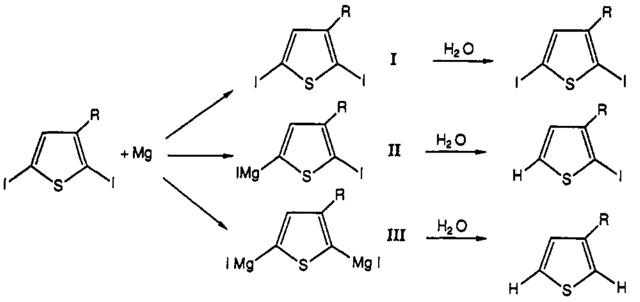
Scheme I



Molecular weight distribution curves of polymers were determined by size exclusion chromatography (SEC) using 10^5-, 10^4-, and 10^3-Å μ-Styragel columns at 25 °C. Polymers were eluted with tetrahydrofuran and detected using a UV–vis spectrophotometer (Spectra-Physics, Model SP8000) and a refractive index detector (Waters, Model R400). Data were acquired, stored, and analyzed using an IBM personal computer and custom-written software.

Polystyrene standards (Polymer Labs. Inc.) of molecular weights ranging from 233 000 to 750 were used for calibrating GPC columns for hydrodynamic volume versus elution volume. The polystyrene calibration curve was converted to a P3HT-based calibration using the following Mark–Houwink constants: $K_{\mathrm{P3HT}} = 2.28 \times 10^{-3}$ cm^3/g, $a_{\mathrm{P3HT}} = 0.96$, $K_{\mathrm{PS}} = 1.29 \times 10^{-2}$ cm^3/g, and $a_{\mathrm{PS}} = 0.713$.[24,25]

Results and Discussion

Grignard Polymerization of 2,5-Diiodo-3-hexylthiophene. The reaction of magnesium with 2,5-diiodo-3-hexylthiophene initially yields a Grignard reagent possessing one IMg substituent. If the reaction is left for a sufficient time, the second iodo group on the ring is converted to a Grignard functionality. The composition of the polymerization mixture can, therefore, vary widely. The fraction of mono- and di-Grignard species which form in the reaction mixture upon the addition of magnesium can be followed by GC by quenching the reaction with water so that IMg substituents are replaced by hydrogen (see Scheme I). After quenching, the reaction typically contains the starting reagent, 2,5-diiodo-3-hexylthiophene (I), 2(or 5)-iodo-3-hexylthiophene, which corresponds to the presence of the mono-Grignard species (II),[26] and 3-hexylthiophene, which implies the presence of the di-Grignard species (III) prior to quenching.

Figure 1 shows the evolution or depletion of I, II, and III as the reaction with Mg proceeds. As expected, the starting compound I initially decreases rapidly with concurrent formation of the mono-Grignard, II. Further reaction yields the di-Grignard, III, at the expense of both I and II. The reaction time shown in Figure 1 is only indicative of the system since the reaction rate varies from experiment to experiment due to the nature of the heterogeneous reaction. Furthermore, the relative composition varies slightly between experimental runs. In using the data shown in Figure 1 to interpret polymerization data, only the fractional composition of the reaction mixture is emphasized, irrespective of the time required for its formation. To aid explanation of the effect of monomer composition on the polymers produced, it is convenient to divide the compositional diagram into three zones. Zone A comprises reaction mixtures which consist largely of the diiodo compound, I, with a smaller but variable amount of the mono-Grignard II. Zone B consists largely of II with a lesser quantities of I and the di-Grignard III. Zone C consists mainly of II and III with lesser quantities of I.

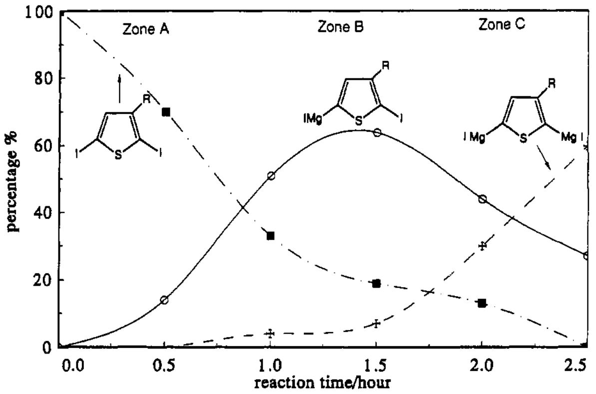


Figure 1. Plot of the evolution or depletion of I, II, and III during reaction of I with magnesium. Solvent = diethyl ether, 25 °C. I:magnesium molar ratio = 1:2.

It is well-known that a hydrogen–metal exchange mechanism interferes with the formation of Grignard reagents of thiophene and that possible rearrangement products include thiophenes with iodo or Grignard species in the 4-position.[27] The presence of such molecules would cause irregular 2,4- or 4,5-linkages in the resulting polymer. However, rearrangement did not occur due to the fact that the 4-thienyl hydrogen is insufficiently acidic to take part in the exchange mechanism. Care should be taken, however, when using lithiated halothiophenes since these readily rearrange by the base-catalyzed halogen dance mechanism to yield β-halothiophenes.[28]

Molecular Weights and Molecular Weight Distributions. Polycondensation of Grignard and iodo monomers proceeds upon addition of Ni(dppp)$_2$Cl$_2$ catalyst. Polycondensation is very rapid. The reaction was usually complete after 40 min, and no additional increase in molecular weight was observed even after an additional 24 h of reaction time. The molecular weights, molecular weight distributions, and nature of the terminal groups of the resultant polymers depend on the composition of the mixture at the time catalyst is added and from which polymerization proceeds. Relatively short polymers were produced when catalyst was added to zone A compositions, having number-average molecular weights of <2500. Molecular weight distributions were in the range 1.6–1.9. These are considerably narrower compared to those of polymers produced by other methods.[17,20,21] A size exclusion chromatogram for a polymer obtained from a compositional mixture of 61% I, 25% II, and 14% III is shown in Figure 2a. The wavelength of maximum absorption of this polymer was 422 nm (in CHCl$_3$). Molecular weights for various compositions are shown in Table I.

Molecular weights of polymers obtained from zonc C compositional mixtures were slightly lower, on average 1100–2000, compared to those obtained from zone A, and the molecular weight distributions were even narrower (see Table I). Molecular weight distributions of 1.07 make then the most monodispersed polythiophenes reported to date; however, the degree of polymerization was only ~8. Figure 2c shows a size exclusion chromatogram for a polymer obtained from an initial mixture 2% I, 17% II, and 81% III ($\lambda_{\max}$ = 390 nm, CHCl$_3$). Low molecular weights are due to the presence of an excess of iodo or Grignard functionality. The polymerization terminates prematurely, therefore, when one of the reactive groups is depleted.

In principle, the polymerization should proceed most effectively when the polymerization mixture contains only the mono-Grignard reagent, II, due to the fact that this

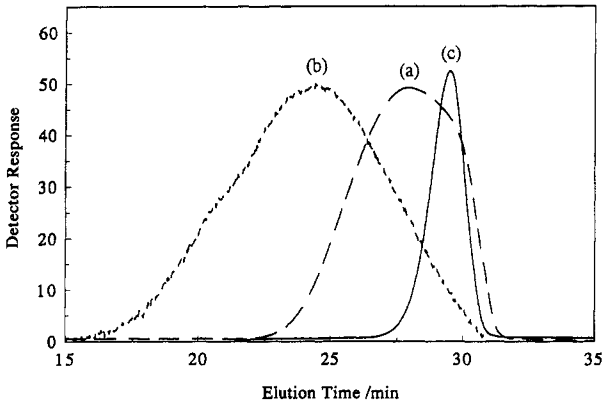


Figure 2. Size exclusion chromatograms for poly(3-hexylthiophene) prepared from a polymerization mixture comprising (a) 61% I, 25% II, and 14% III (zone A); (b) 10% I, 58% II, and 32% III (zone B); and (c) 2% I, 17% II, and 81% III (zone C). Eluant = THF (1 mL/min).

Table I
Effect of Composition of Polymerization Mixture on Molecular Weights

composition,[a] %							compositional
I	II	III	M_w^b	M_n^b	MWD[c]	$\overline{DP}^d$	zone
61	25	14	4600	2400	1.92	14	A
45	26	29	3100	1900	1.63	11	
32	59	9	15100	4900	3.08	29	B
10	58	32	18400	5200	3.54	31	
16	39	45	5800	3500	1.66	21	C
11	42	47	3100	2000	1.55	12	
2	17	81	1500	1400	1.07	8	

[a] Determined by gas chromatography. [b] Determined by size exclusion chromatography. [c] Molecular weight distribution. [d] Number-average degree of polymerization.

species possesses one reactive iodo group and one reactive Grignard functionality. Compositions falling within zone B are the closest to ideal polymerization conditions. However, it is impossible to produce large quantities of II in the absence of the diiodo species I or the di-Grignard III. Even so, polymerization of zone B compositions resulted in polymers which were significantly different from those produced from zones A and C. Molecular weights and molecular weight distributions of these polymers were significantly larger. A size exclusion chromatogram is shown for poly(3-hexylthiophene) polymerized from a reaction mixture composed of 10% I, 58% II, and 32% III (Figure 2b) (λ_{max} = 438 nm, $CHCl_3$).

Sole formation of mono-Grignard reagents might possibly be achieved using a 1:1 molar ratio of magnesium to 2,5-diiodo-3-hexylthiophene (I). However, experimentally this was not observed. An ~1:1 stoichiometry yielded a reaction mixture comprising 34% 2,5-diiodo-3-hexylthiophene (I), 23% of the mono-Grignard species (II), and 43% di-Grignard species (III). The weight-average and number-average molecular weights of polymers resulting from this composition were 2800 and 1800, respectively.

Nature of the Thienyl Termini. The reaction mixture consists of monomers, I, II, and III, and thus uncertainty exists concerning the nature of the termini for the polymers produced (Scheme II). Since our motive in studying this polymerization is to prepare telechelics, we decided to investigate this further.

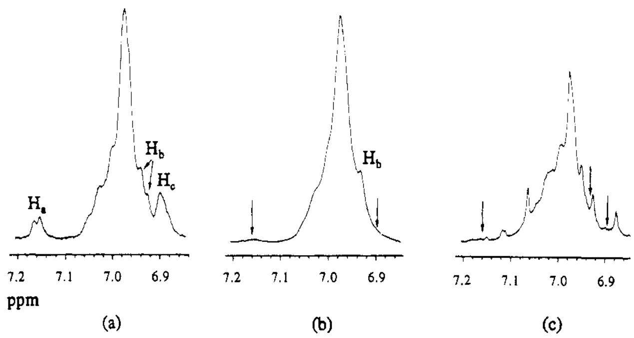


Figure 3. Expanded ^1H NMR spectra for several poly(3-hexylthiophenes) prepared from zone C compositions: (a) after quenching with water; (b) after quenching with D_2O; (c) after quenching with iodine. Arrows refer to the presence or absence of signals corresponding to terminal thienyl protons (see text).

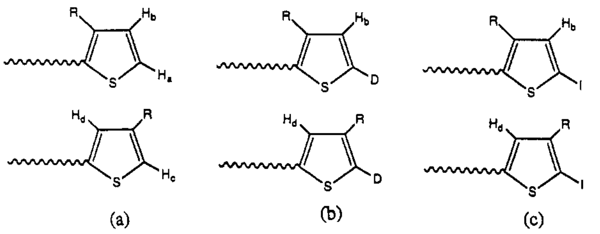
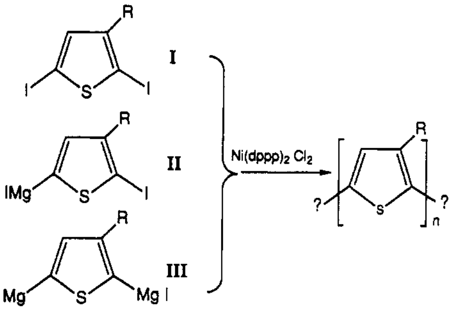


Figure 4. Terminal ring configuration for poly(3-hexylthiophene) prepared by polycondensation of Grignard reagents under conditions described by zone C: (a) after quenching with water; (b) after quenching with D_2O; (c) after quenching with iodine.

Scheme II



^1H NMR was particularly useful in explaining the chemical composition of polymers obtained under different compositional conditions. Figure 3 shows ^1H NMR spectra for several poly(3-hexylthiophenes) prepared from conditions corresponding to zone C, in which the reaction was quenched with various reagents. The spectral range chosen corresponds to β-protons (4-position) and terminal protons (2- and 5-positions) on the thienyl rings. Figure 3a shows a spectrum of a polymer obtained from a zone C mixture after the reaction was quenched with water. IMg termini on the polymer chain are converted to terminal hydrogens under these circumstances. The signal in the region 6.92–7.10 ppm is dominated by β-protons associated with nonterminal thienyl rings. The complexity of the spectra results from HT–HT, TT–HT, HT–HH, and TT–HH triad configurations, respectively. Here, HT, TT, and HH represent head-to-tail, tail-to-tail, and head-to-head diads, respectively.[27] Fine structure associated with these peaks is due to 4-protons in pentad sequences. Little information can be obtained from comparing these peaks since they reflect configurational tendencies rather than chemical differences. Of importance to us in the latter context are the absence, presence, and shifting of the other, smaller, signals. The terminal ring protons of interest to us are illustrated in Figure 4.

The doublet centered at 7.15 ppm (J = 5.1 Hz) and the broad signal at 6.9 ppm in Figure 3a are assigned 5- and 2-terminal ring protons, i.e., protons a and c, respectively.

The terminal 4-proton will have two chemical shifts depending on whether the terminal ring is connected to the main chain by the 2- or 5-position (protons b and d), respectively. The 4-proton labeled b can be observed as a doublet centered at 6.93 ppm ($J = 5.1$ Hz). The terminal 4-proton labeled d is shifted downfield compared to proton b and is, therefore, masked by the large signals due to the 4-protons located on nonterminal thienyl rings. These assignments are based on ^{1}H NMR data reported for poly(3-hexylthiophene),[21,29] dimethyl-2,2′-bithiophenes,[30] and 3-substituted terthiophenes.[31]

Figure 3b shows a ^{1}H NMR spectrum of a polymer obtained from a zone C mixture after the reaction was quenched with D_2O, whereupon any IMg functionality is replaced by deuteriums. The 5- and 2-terminal protons (a and c) at 7.15 and 6.9 ppm are absent. However, proton b can be observed at 6.93 ppm (see arrows). It is no longer a doublet but is a singlet as expected for a deuterium-terminated polymer. This is direct evidence of deuterium-terminated polythiophenes.

The NMR spectrum of iodine-quenched polymer polymerized from zone C (Figure 3b) also does not show doublets at 7.15 and 6.93 or a signal at 6.9 ppm as previously observed in Figure 3a. This is explained by the fact that the polymer possesses terminal 2- and 5-iodines rather than 2- and 5-terminal protons. The proton labeled b experiences deshielding due to the neighboring iodine and moves to lower fields than in the case where the terminal atom is hydrogen or deuterium. It is, therefore, no longer observed at 6.93 ppm. Proton d will be virtually unaffected by the terminal iodine but cannot be observed due to masking.

Poly(3-hexylthiophene) was also obtained from zone A mixtures in which the reaction was quenched with water. Under these conditions terminal IMg is converted to terminal hydrogen. The ^{1}H NMR spectrum (not shown), however, showed no signal at 7.15, 6.93, and 6.9 ppm and was in every respect similar to that shown in Figure 3c. Thus, the two polymers are similar in chemical composition, and both polymers can be considered to possess terminal iodines at the 2- and 5-positions. It is evident that polymers obtained from zone A compositions possess terminal iodines at the 2- and 5-positions whereas polymerization of zone C compositions yields polymers which possess terminal Grignard functionality. The latter can be further converted to terminal hydrogen, deuterium, or iodine by treatment with water, heavy water, or iodine.

Polymers produced from zone B compositions possess both iodine and IMg termini. The ratio of iodine to IMg groups depends on the composition of the polymerization mixture and on the polymerization time. ^{1}H NMR analysis of these polymers, quenched with water, shows complex spectra due to the presence of 2- and 5-terminal iodines, 2- and 5-terminal protons, and the corresponding 4-terminal ring protons.

It is evident that the preparation of polymers possessing terminal IMg functionality is possible when a large fraction of the di-Grignard reagent, III, exists in the polymerization mixture (zone C). This is due to the fact that Grignard reagents cannot couple with themselves. Further evidence for this was obtained by following the fraction of the diiodo, mono-Grignard, and di-Grignard species during the course of polymerization. For an initial composition comprising 16% I, 39% II, and 45% III (zone C) the fraction of monomers I and II had decreased to 6% and <1%, respectively, compared to 94% of III, after only 1 h of reaction time. After 2 h of polymerization time I and II could not be detected, and only III existed in solution. Even after an additional 24 h the solution did not change composition, nor did the molecular weight of the resultant polymer increase.

The polymers described in this study have small but significant differences compared to those obtained by other polymerization techniques. NMR indicates unequivocally that both 2- and 5-terminal protons are present under certain polymerization conditions, i.e., zone C compositions and quenching with H_2O. Sato and Morii have carried out NMR studies of a chemically similar polymer, poly(3-dodecylthiophene), prepared electrochemically.[29] While they assigned doublets at 7.16 and 6.93 ppm to 5- and 4-protons on the terminal ring (protons a and b, Figure 4), they were unable to detect peaks due to other terminal units, i.e., 2- and 4-protons on the terminal ring (protons c and d, Figure 4). It is true that the latter proton would be masked by the large signal due to nonterminal protons but the 2-terminal proton should have been observed at ~6.9 ppm. The fact that it is not observed infers that during electrochemical polymerization the polymer is initiated or terminated in such a manner as not to produce a terminal thienyl ring possessing a 2-proton. We have also performed NMR studies on poly(3-hexylthiophene) synthesized chemically using the oxidant ferric chloride. As in the case of electrochemically polymerized polymer, only the protons at the 4- and 5-positions of a terminal unit were observed. The terminal thienyl ring probably does not possess a proton in the terminal 2-position in electrochemical or Lewis acid promoted polymerizations since these are electrophilic aromatic substitutions involving an attack on a cationic thiophene by a second thiophene molecule. The most stable cation is at the 2-position due to the inductive effect of the alkyl substituent. Similarly, a higher electron density exists at the 2-position of the second thiophene. Thus coupling at the 2-positions of the thiophenes will prevail preferentially over the 5-position. The Grignard polycondensation method does not involve cationic systems. This insight will have little effect on the physical properties of the polymer, but it provides further insight into the initiation and termination of electrochemical and oxidative coupling polymerization of thiophenes.

Conclusion

The molecular weights of poly(3-alkylthiophenes) synthesized via Grignard reagents can be controlled by choice of the initial polymerization conditions. The molecular weights obtained using Grignard reagents are significantly lower than those obtained by electrochemical and Lewis acid promoted polymerization due to the buildup of iodine or IMg terminal groups which, while being reactive with one another, are unreactive with themselves. Higher molecular weight poly(3-alkylthiophenes) can be achieved by ensuring mono-Grignard species are present in excess. However, this is difficult to achieve in a one-pot process. Higher molecular weights are obtained at the expense of narrow molecular weight distributions which become relatively broad. Furthermore, the chemistry of the terminal rings can be controlled so as to produce functional termini. Grignard termini groups can be subject to additional manipulative chemistry from which telechelic and functional electronically conducting polymers can be synthesized.[22]

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References and Notes

(1) Yamamoto, T.; Sanechika; K.; Yamamoto, A. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *56*, 9.

(2) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1982**, *135*, 173.

(3) Skotheim, B., Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986; Vols. 1 and 2.

(4) Hotta, S.; Hosaka, T.; Shimotsuma, W. *Synth. Met.* **1983**, *6*, 69.

(5) Hotta, S.; Hosaka, T.; Shimotsuma, W. *Synth. Met.* **1983**, *6*, 317.

(6) Tanaka, K.; Shichira, T.; Yoshizawa, K.; Yamabe, T.; Hotta, S.; Shimotsuma, T. W.; Yamauchi, J.; Deguchi, Y. *Solid State Commun.* **1984**, *51*, 565.

(7) Tourillon, G.; Gourier, D.; Garnier, F.; Vivien, D. *J. Phys. Chem.* **1984**, *88*, 1049.

(8) Garnier, F.; Tourillon, G.; Barraud, J. Y.; Dexpert, H. *J. Mater. Sci.* **1985**, *20*, 2687.

(9) Funt, B. L.; Lowen, S. V. *Synth. Met.* **1985**, *11*, 129.

(10) Kobayashi, M.; Chen, J.; Chung, T.-C.; Moraes, F.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1984**, *9*, 77.

(11) Monteheard, J. P.; Pascal, T.; Seytre, G.; Steffan-Boiteux, G.; Douillard, A. *Synth. Met.* **1984**, *9*, 389.

(12) Yoshino, K.; Hayashi, S.; Sujimoto, R. *Jpn. J. Appl. Phys.* **1984**, *23*, L899.

(13) Elsenbaumer, R. L.; Jen, K. Y.; Oobodi, R. *Synth. Met.* **1986**, *15*, 169.

(14) Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* **1986**, 873.

(15) Blankesmoor, R. L.; Miller, L. L. *J. Chem. Soc., Chem. Commun.* **1985**, 90.

(16) Bryce, M. R.; Chissel, A.; Kathirgamanathan, P.; Parker, D.; Smith, N. R. *J. Chem. Soc.*, Chem. *Commun.* **1987**, 466.

(17) Yoshino, K.; Nakajima, S.; Sujimoto, R. *Jpn. J. Appl. Phys.* **1987**, *26*, L1038.

(18) Hotta, S.; Rughooputh, S. D. V.; Heeger, A. J. *Synth. Met.* **1987**, *22*, 79.

(19) Ruiz, J. P.; Gielselman, M. B.; Nayak, K.; Marynick, D. S.; Reynolds, J. R. *Synth. Met.* **1989**, *28*, C481.

(20) Nilsson, J.-O.; Gustafsson, G.; Inganas, O.; Uvdal, K.; Salaneck, W. R.; Laakso, J.; Osterholm, J.-E. *Synth. Met.* **1989**, *28*, C445.

(21) Leclerc, M.; Diaz, F. M.; Wegner, G. *Makromol. Chem.* **1989**, *190*, 3105.

(22) Mao, H.; Holdcroft, S., manuscript in preparation.

(23) Tamao, K.; Kodama, S.; Nakajima, J.; Kumada, M. *Tetrahedron* **1982**, *38*, 3347.

(24) Tung, L. H.; Moore, J. C. *Fractionation of Synthetic Polymers*; Tung, L. H., Ed.; Marcel Dekker: New York, 1977.

(25) Holdcroft, S. *J. Polym. Sci., Polym. Phys. Ed.*, in press.

(26) The iodo group could occupy the 2- and 5-position. Schemes I and II show only one isomer in order to maintain pictoral clarity.

(27) Reinecke, M. G.; Pedaja, P. *The Chemistry of Heterocyclic Compounds*; Wiley: New York, 1977; Vol. 44 (2), p 358.

(28) Frohlich, H.; Kalt, W. *J. Org. Chem.* **1990**, *55*, 2993.

(29) Sato, M.-A.; Morii, H. *Macromolecules* **1991**, *24*, 1196.

(30) Krische, B.; Hellberg, J.; Lilja, C. *J. Chem. Soc., Chem. Commun.* **1987**, 1476.

(31) Beny, J.-P.; Dhawan, S. N.; Kagan, J.; Sundlass, S. *J. Org. Chem.* **1982**, *47*, 2201.

Registry No. I, 113736-20-2; I (homopolymer), 113736-21-3; 3-hexylthiophene, 1693-86-3.