Effect of Oligomeric Additives and Applied Potential on the Molecular Weight and Structure of Electrochemically Synthesized Poly(3-alkylthiophenes)

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ABSTRACT: Poly(3-*n*-pentylthiophene) and poly(3-*n*-hexylthiophene) have been synthesized using the potentiostatic technique and characterized with cyclic voltammetry and IR, ^{1}H NMR, and electronic absorption spectroscopy. The molecular weight and molecular weight distribution of the undoped polymers have been studied by means of gel-permeation chromatography in a THF solution. The polymers show a bimodal molecular weight distribution. The molecular weight of the polymers increases as the applied potential is increased up to about 1.7 V vs SCE and then levels off and decreases because of chain degradation. The presence of oligomeric additives, 2,2′-bithiophene and 2,2′:5′,2″-terthiophene, in the polymerization system significantly enhances the structure regularity of the polymer chains, which is indicated by a bathochromic shift of the π–π^* transition band in the electronic spectra of the polymers. The molecular weight becomes lower as the amount of the additives is increased. The molecular weight was found to increase rapidly with time in the early stage of the polymerization but to remain almost constant with further reaction. All the changes in the molecular weight are mainly contributed by the high molecular weight fraction of the polymers. The low molecular weight fraction is a minor fraction, which consists of oligomers with less than 10 monomer units and is affected little by the polymerization conditions. All the results strongly support the electrophilic aromatic substitution mechanism for the oxidative polymerization of thiophene monomers.

Introduction

The discovery[1,2] of fusibility and solubility of poly(3-alkylthiophenes), which have side-chain lengths greater than four carbon atoms, has opened a new window for elucidating the conduction mechanism and the relationship between electronic properties and structure of the electroactive polymers. Many research groups have investigated the electronic and mechanical properties of poly(3-alkylthiophenes) in relation to the polymer chain structures and conformations,[3] polymer morphology,[4] and polymerization parameters.[5] Research efforts have also been made to design and synthesize new soluble electroactive polymers with improved physical and chemical properties via various approaches. For examples, new monomers were synthesized by attaching different functional groups to the thiophene ring at the β-position to improve the processibility of the polymers.[6–8] Other monomers or polymers were introduced in the polymerization of the thiophene monomers to form random[9] and graft[10] copolymers. Polymer composites and semiinterpenetrating networks were prepared[11] to enhance the mechanical properties and stability of the electroactive materials. A number of new applications of polythiophenes have also been explored, such as rectifying bilayer electrodes,[12] unipolar thin-film devices,[13] the preparation of Langmuir–Blodgett films,[14] and the fabrication of highly oriented conducting films.[15]

Molecular weight and molecular weight distribution are important parameters in determining the physicochemical properties of a polymer. Furthermore, the changes in these parameters as a function of the polymerization conditions often provide information about the mechanism of polymerization. Taking advantage of the good solubilities of the long-chain alkyl-substituted polythiophenes, many groups have measured the molecular weights of these polythiophenes, which were synthesized by either the chemical or electrochemical method, using gel-permeation chromatography (GPC), light scattering, embulliometry, and/or solution viscometry.[6,8,16–19] The results from the light scattering studies[16] are particularly interesting because this method affords absolute molecular weights. The average molecular weights determined by light scattering were found to be in remarkable agreement with the GPC measurements using polystyrene calibration.[16] However, the effects of polymerization conditions on the molecular weight and molecular weight distribution of poly(3-alkylthiophenes) have not been fully exploited and understood in association with the polymerization mechanism. In our previous work, we have developed a new method for the polymerization of thiophene monomers.[20,21] The polymerization was found to be facilitated significantly by adding a small amount of an oligomer of thiophene, such as 2,2′-bithiophene or 2,2′:5′,2″-terthiophene, to the system. The results were interpreted based on the mechanism that the polymer growth is mainly achieved by electrophilic attack on the neutral thiophene monomer by the radical cation at the growing chain end.[21] Recently, we have carried out a series of systematic studies on the relations of the polymerization conditions with the structure, molecular weight, and molecular weight distribution of poly(3-alkylthiophenes) and other related polymers, in an effort to gain further insights into the polymerization mechanism and to control the structure and molecular weight of the polymers with improved synthetic methodologies.

In the present paper, we report the effects of the applied potential, the presence of the oligomeric additives, and the duration of polymerization on the molecular weight, molecular weight distribution, and chain structure of poly(3-*n*-pentylthiophene) and poly(3-*n*-hexylthiophene). The electrochemical polymerizations were performed using the potentiostatic technique. The polymers were characterized by cyclic voltammetry (CV) and IR, ^{1}H NMR, and electronic absorption spectroscopy. The molecular weights were determined by the GPC method. Mechanistic implications of the experimental results are discussed.

Experimental Section

Materials and Instrumentation. 3-*n*-Pentylthiophene and 3-*n*-hexylthiophene were synthesized by a cross-coupling reaction between the corresponding *n*-alkylmagnesium bromides and 3-bromothiophene in the presence of Ni(dppp)Cl_2, following Tamao's procedure,[22] and were purified by fractional distillation. 2,2′-Bithiophene (97%; Aldrich), 2,2′:5′2″-terthiophene (99%;

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Aldrich), acetonitrile (99.9%; Fisher Scientific), and lithium perchlorate (anhydrous, 99.5%; Alfa) were used as received. The GPC measurements were performed on a Waters GPC Model IIA equipped with a Model 590 programmable solvent delivery module, a differential refractometer detector, and an Ultrastyragel linear column at 35 °C using THF (HPLC grade; Aldrich) as eluant. The molecular weight and molecular weight distribution were calculated based on monodispersed polystyrene standards. An EG&G PAR Model 273 potentiostat/galvanostat was employed for electrochemical polymerization and cyclic voltammetry studies. The cyclic voltammograms were taken from the polymer–THF solution cast film on a platinum electrode in a 0.1 M $LiClO_4$–acetonitrile solution. The electronic absorption spectra of the polymers in a THF solution and of the polymer thin films on an indium–tin oxide (ITO) electrode were recorded on a Perkin-Elmer λ-2 UV/vis/near-IR spectrophotometer. The error range in measuring the maximum absorption wavelength was about ±2 nm. The NMR spectra were collected on an IBM Bruker WM250 FT-NMR spectrometer, using $CDCl_3$ as solvent, and the chemical shifts in ^1H NMR were referenced to the proton signal (7.25 ppm) of residual $CHCl_3$ in the solvent. The diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded on a Perkin-Elmer Model 1600 FT-IR spectrometer with a diffusion refractor accessory.

Electrochemical Polymerization. The electrochemical polymerization of poly(3-*n*-pentylthiophene) and poly(3-*n*-hexylthiophene) was conducted potentiostatically in a one-compartment cell containing about 25 mL of deaerated electrolyte with platinum foil as both working electrodes (area, 3.0 cm^2) and counterelectrodes (6.0 cm^2). A saturated calomel electrode (SCE) was used as the reference electrode. The monomer concentration was generally 0.2 M in the electrolyte. The concentrations of the additives, 2,2′-bithiophene and 2,2′:5′,2″-terthiophene, varied in the range from 0 to 0.02 M as specified in the text. The supporting electrolyte was 0.1 M $LiClO_4$ in acetonitrile. The applied potential for the polymerization was in the range from 1.3 to 2.0 V vs SCE. The amount of polymer deposited on the working electrode was controlled by the total amount of charge consumed by the reaction system, which was generally ~1700 mC unless otherwise specified in the text. After each polymerization, the polymer was reduced by holding the polymer-coated electrode in a monomer-free 0.1 M $LiClO_4$–acetonitrile solution at −0.6 V for about 15 min, until the decrease in the anodic charge became negligible. The polymer film was then washed with acetonitrile and methanol. Upon drying in nitrogen, the polymer film was dissolved in 1.5 mL of THF. The dissolution appeared to be incomplete. The residual solid particles were removed by filtration through a 0.5-μm Teflon filter. The filtrate was used for the GPC and the solution spectroscopic and cyclic voltammetric studies. In the spectroelectrochemical studies of the polymer thin films, the ITO electrode was used as the working electrode in the polymerization. For the IR measurements, the polymer samples were collected from the electrode and were dried under vacuum at room temperature overnight.

Results and Discussion

Figure 1 shows typical cyclic voltammograms of a poly(3-*n*-pentylthiophene) film in a 0.1 M $LiClO_4$–acetonitrile solution at various scan rates. The film was cast from the polymer solution in THF onto a platinum electrode. The polymer was prepared at a constant applied potential of 1.5 V vs SCE in the presence of 0.1% (by mole with respect to the amount of monomer) 2,2′-bithiophene. In the potential region from −0.2 to +1.3 V, the CV traces show one major pair of reversible redox peaks with the anodic peak at ~0.8 V and the cathodic peak at ~0.78 V, which correspond to the oxidation and reduction of the electroactive poly(3-*n*-pentylthiophene) film, respectively. Accompanying the redox process of the polymer, the film color also changed reversibly from dark blue (oxidized) to orange yellow (reduced). Both the anodic and cathodic peaks are broad, which is associated with a multiplicity of redox sites and their interactions in the polymer film.[4,23] The direct proportionality of both anodic and cathodic peak currents to the scan rate (shown as the inset in Figure 1) confirms the surface-confined nature of the redox species.[24] The peak positions and the shape of the redox waves should be related to the film thickness and conductivity of the polymers.[25] Since the thickness and homogeneity of the solution-cast films could not be accurately controlled and evaluated, no definitive data on the conductivity of the polymer films were obtained in this regard. All the poly(3-*n*-pentylthiophene) films have similar CV patterns as shown in Figure 1, regardless of the polymerization conditions under which they were synthesized. However, the redox peaks became significantly broader as the higher applied potentials (e.g., 2.0 V) were employed in the synthesis. The CV traces of the as-synthesized polymer films differ little from those of the corresponding solution-cast films. The electrochemical behavior of poly(3-*n*-hexylthiophene) is practically the same as that of poly(3-*n*-pentylthiophene).

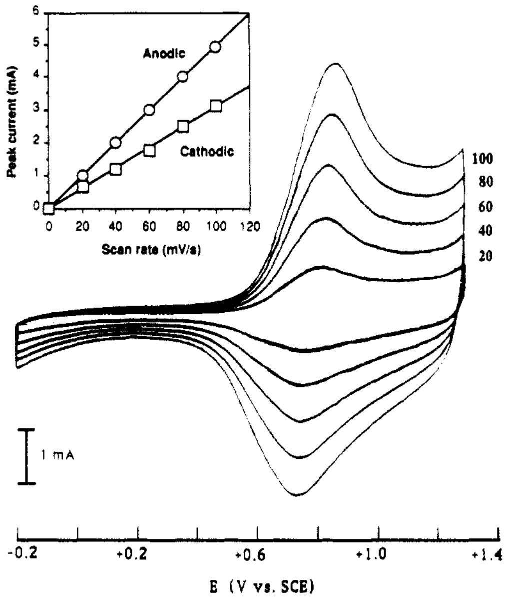


Figure 1. Cyclic voltammograms of a poly(3-*n*-pentylthiophene)–THF-solution-cast film in 0.1 M $LiClO_4$–acetonitrile in the potential range of −0.2 to +1.3 V vs SCE at various scan rates in millivolts per second (as labeled next to the curves). The polymer was synthesized at 1.5 V in the presence of 0.1% 2,2′-bithiophene. The inset shows the dependence of both anodic and anodic currents on the scan rate.

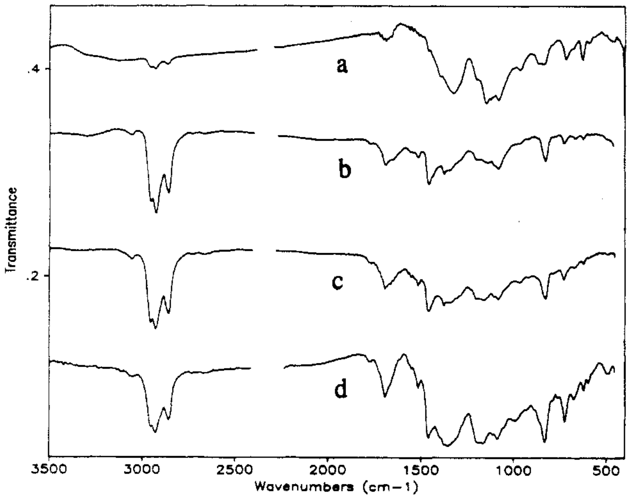


Figure 2. Diffuse reflectance infrared spectra of poly(3-*n*-pentylthiophene) samples prepared at 1.5 V (a) in oxidized form and (b) reduced at −0.6 V for 15 min and (c) prepared at 1.35 V in the presence of 0.1% 2,2′-bithiophene and then reduced and of (d) poly(3-*n*-hexylthiophene) prepared at 1.5 V and then reduced.

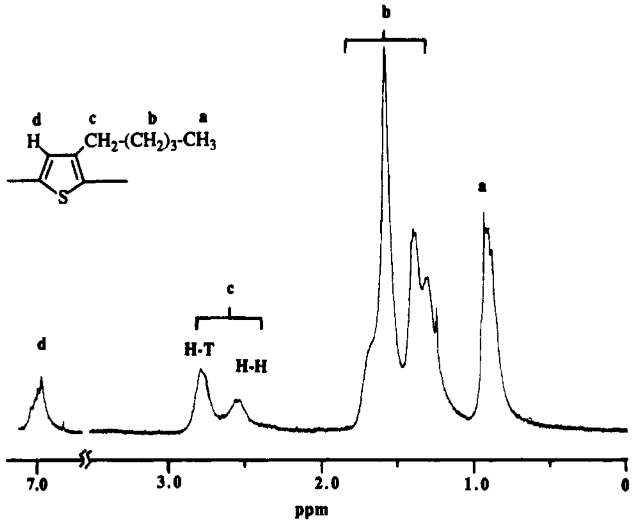


Figure 3. ^{1}H NMR spectrum of poly(3-*n*-pentylthiophene) prepared at 1.5 V in $CDCl_3$.

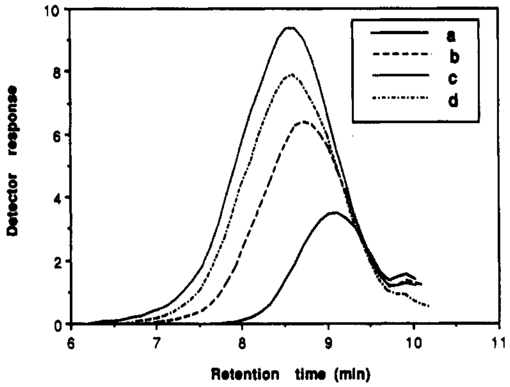


Figure 4. GPC chromatograms of poly(3-*n*-pentylthiophene) synthesized at the applied potential of (a) 1.3, (b) 1.5, (c) 1.7, and (d) 1.9 V vs SCE, in the presence of 0.1% 2,2′:5′,2″-terthiophene.

The diffuse reflectance infrared spectra of the electrochemically synthesized poly(3-*n*-pentylthiophene) and poly(3-*n*-hexylthiophene) are shown in Figure 2. In general, all the poly(3-*n*-pentylthiophene) samples, which were synthesized in the absence or in the presence of 2,2′-bithiophene and 2,2′:5′,2″-terthiophene, have essentially the same IR spectra as long as the polymers are at the same oxidation state (see parts b and c of Figure 2 for typical examples). The same results were obtained for all the poly(3-*n*-hexylthiophene) samples. The characteristic bands in the spectra of poly(3-*n*-hexylthiophene) are also practically identical to those of poly(3-*n*-pentylthiophene) (e.g., comparing parts d and b of Figure 2). The changes in the oxidation states (i.e., doping or undoping) of the polymers appear to have little effect on the absorption bands at 2928, 2926, and 2856 cm^{-1} (aliphatic C–H stretching), at 1688 cm^{-1} (the aromatic ring stretching), at 1082 cm^{-1} (the C–H bending), and at 828 cm^{-1} (aromatic C–H out-of-plane bending). Upon electrochemical reduction, the strong absorption bands at 1324, 1148, 1122, 964, 837, and 719 cm^{-1} for the oxidized polymer (Figure 2a) are replaced by new bands at 1460, 1376, 1200, and 1160 cm^{-1} (Figure 2b). These assignments and observations are in agreement with those reported in the literature.[26]

A typical ^{1}H NMR spectrum of poly(3-*n*-pentylthiophene) in $CDCl_3$ is given in Figure 3. The protons of the methylene group directly attached to the thiophene ring give two separated peaks at 2.58 and 2.80 ppm, which correspond to the polymer backbone with head-to-head and head-to-tail linkages, respectively.[17,18,27,28] The ratio of the integrations of these two peaks is very informative about the polymer backbone structure and the regioselectivity of the polymerization. The head-to-tail placement is usually considered favorable because of the lower steric hindrance in comparison to the head-to-head placement. The addition of 2,2′-bithiophene or 2,2′:5′,2″-terthiophene to the polymerization of 3-alkylthiophenes seems to reduce the number of head-to-head linkages in polymer chains, typically, from 40% to 30% as the amount of the additive was varied from 0% to 10% in the polymerization.

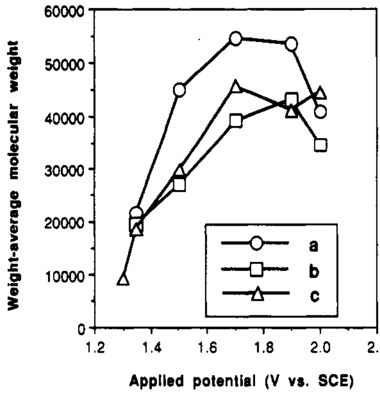
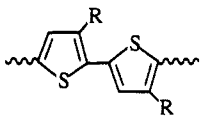
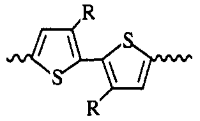


Figure 5. Relationship between the applied potential and the weight-average molecular weight of poly(3-*n*-pentylthiophene) prepared (a) in the absence of additive and in the presence of (b) 0.1% 2,2′:5′,2″-terthiophene and (c) 0.1% 2,2′-bithiophene.



Head-to-tail placement



Head-to-head placement

The molecular weights and molecular weight distributions of the soluble poly(3-alkylthiophenes) were investigated as a function of the polymerization conditions, including the applied potential, the presence and amount of the oligomeric additives, and the reaction time. In general, the gel-permeation chromatograms exhibit a bimodal elution pattern, as exemplified in Figure 4. On the basis of polystyrene calibration, the peak molecular weights (e.g., Figure 4a) are about 6800 and 1200 for the high and low molecular weight fractions, respectively. The peak area of the high molecular weight fraction is usually much greater than that of the low molecular weight fraction.

Figure 4 shows representative GPC curves of poly(3-*n*-pentylthiophene) prepared in the presence of 0.1% 2,2′:5′,2″-terthiophene at various applied potentials. As the applied potential increases from 1.3 V (Figure 4a) to 1.7 V (Figure 4c), the GPC curve moves to the direction of lower retention time (i.e., higher molecular weight). The area ratio of the high to low molecular weight peaks also becomes greater. While the peak molecular weight of the low molecular weight fraction remains essentially unchanged at about 1200, the peak molecular weight of the high molecular weight fraction increases from 6800 (Figure 4a) to 21 000 (Figure 4c). However, further increasing the applied potential to 1.9 V resulted in a decrease in the molecular weight (Figure 4d). These correlations between the applied potential and the molecular weight of the polymer are further demonstrated in Figure 5. As a general trend, the molecular weight of poly(3-*n*-pentylthiophene) increases as the applied potential is increased up to about 1.7 V, then levels off, and decreases significantly at higher potentials. The same trend was also observed in the poly(3-*n*-hexylthiophene) system. These results can be readily

Table I
Molecular Weight and Molecular Weight Distribution of Poly(3-*n*-pentylthiophene) (PPTH) and Poly(3-*n*-hexylthiophene) (PHTH) Prepared Potentiostatically under Various Conditions

		M_n (M_w/M_n) of the polymer prepared at the applied potential (V) of					
polymer	additive[a]	1.30	1.35	1.50	1.70	1.90	2.00
PPTH	none		4700 (4.7)	9500 (4.7)	10 400 (3.6)	13 000 (4.2)	4400 (9.2)
	bithiophene		5100 (3.8)	8200 (3.3)	10 800 (3.6)	13 000 (3.3)	7000 (5.0)
	terthiophene	3900 (2.4)	4400 (4.2)	7700 (3.9)	12 400 (3.7)	8 700 (4.7)	9100 (4.9)
PHTH	none		9500 (3.0)	15400 (2.5)	14 200 (2.7)	9 600 (3.3)[b]	9500 (3.1)
	bithiophene		6400 (2.3)	13600 (2.4)	14 800 (2.9)	12 100 (2.8)	11000 (3.3)

[a] Amount of the oligomeric additive: 0.1% by mole with respect to the amount of monomer. [b] Applied potential: 1.8 V.

interpreted according to the mechanism that we have proposed for the oxidative polymerization of thiophene monomers.[21] In this mechanism, the polymer chain growth is mainly achieved via electrophilic aromatic substitution of the neutral monomers by the chain radical cation intermediates, which are generated from oxidation of (e.g., removal of one electron from) the neutral polymer chains. The cationic charge of the intermediates is stabilized by delocalization through the conjugated polymer backbone. Hence, the electrophilicity of a chain intermediate should become lower as the chain length is increased. However, when more electrons are removed from the polymer chain, the resultant intermediate with multiple cationic charges will have a higher electrophilicity and therefore a higher reactivity toward the incoming monomers, which in turn leads to a greater rate of the chain growth and to higher molecular weight.[21] This is consistent with the observation that the molecular weight increases in the applied potential range of 1.3–1.7 V, because more electrons could be removed at higher potentials. It is known that polythiophene also degrades at high potentials because of overoxidation of the polymer chains.[29] Therefore, as the applied potential is further increased (e.g., to 2.0 V), the degradation of the polymer chains becomes dominant, resulting in the observed decrease in the molecular weight of the polymers as shown in Figures 4 and 5. To further verify such degradation, two poly(3-*n*-pentylthiophene) films were prepared under identical conditions at an applied potential of 1.5 V. After the synthesis, one of the films was treated at a potential of 1.9 V for 30 s in a monomer-free 0.1 M $LiClO_4$–acetonitrile solution. Both polymer films were then reduced to the neutral form for GPC measurements. It was found that the M_w decreased from 45 000 for the as-synthesized polymer to 14 000 for the polymer with the additional treatment at 1.9 V.

As summarized in Table I, the effect of the applied potential on the number-average molecular weight (M_n) is similar to that on M_w of the poly(3-alkylthiophenes). The molecular weight distributions as represented by the polydispersities, M_w/M_n, are also listed in Table I. In general, the M_w/M_n values are in a range of 2–5 except that for the poly(3-*n*-pentylthiophene) prepared at 2.0 V. The polymers prepared at the applied potentials greater than 1.7 V tend to have broader molecular weight distributions. At 2.0 V, the polymers usually give the highest M_w/M_n values. Again, this could be attributed to the degradation of the polymer chains at high potentials.

We have reported[20,21] that the rate of both chemical and electrochemical polymerization of thiophene monomers is greatly increased, when a small amount of oligomeric additives, including 2,2′-bithiophene or 2,2′:5′,2″-terthiophene, is present in the systems. The potential cycling method was employed in the electrochemical polymerization.[20,21] In this work, the same rate enhancement was observed for the polymerization of 3-alkylthiophenes using the potentiostatic method. For example, the rate of polymerization of 3-*n*-pentylthiophene at 1.5 V was increased by about 10% when only 0.1% of the bithiophene was added. The presence of the additives in the polymerization system was also found to affect the molecular weight of the polymers significantly. As shown in Figure 5, poly(3-*n*-pentylthiophene) prepared in the presence of additives tends to have a lower molecular weight in comparison with that in the absence of the additive at the same applied potential. The effect of the oligomeric additives on molecular weight is further demonstrated in Figure 6. When the amount of 2,2′-bithiophene in the polymerization of 3-*n*-pentylthiophene increases from 0% to 10% at an applied potential of 1.5 V, the M_w of the polymer decreases drastically from 45 000 to 2500 (Figure 6a). This decrease in M_w seems to be contributed mainly from the high molecular weight fraction of the polymer in the bimodal molecular weight distribution (Figure 4). The GPC peak molecular weight of the high molecular weight fraction decreases from 19 000 to 2300 (Figure 6b), while that of the low molecular fraction remains nearly unchanged (Figure 6c). These results can be rationalized by the proposed mechanism as illustrated in Scheme I.[21]

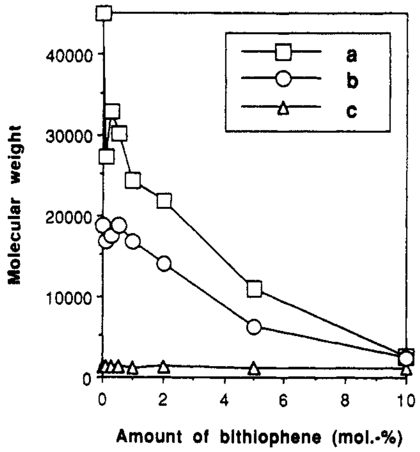
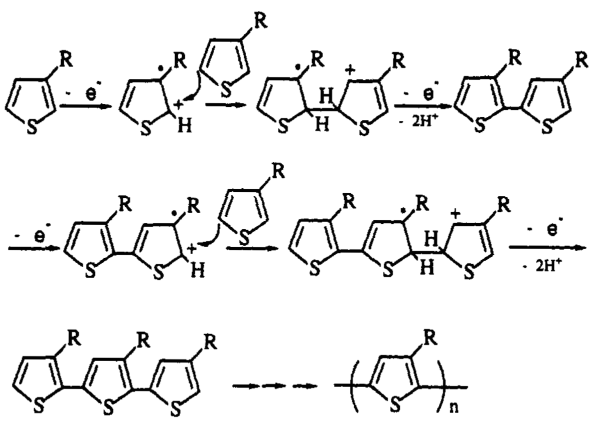


Figure 6. Effect of the amount of 2,2′-bithiophene present in the polymerization of 3-*n*-pentylthiophene at 1.5 V on (a) the weight-average molecular weight, (b) the peak molecular weight of the high molecular weight fraction, and (c) the peak molecular weight of the low molecular weight fraction of the polymer.

In the absence of the additives, the first step (i.e., oxidation of monomer to form a radical cation) is the rate-determining step, because the thiophene monomers have higher oxidation potentials than the subsequent oligomers and polymers.[30] The radical cation undergoes an electrophilic aromatic substitution reaction with a neutral monomer, followed by oxidation and deprotonation to yield a dimer. This oxidation–substitution–deprotonation process proceeds repeatedly, leading to higher oligomers and eventually to the polymer. Introduction of a small amount of the bithiophene or terthiphene into the system could bypass the slowest step and result in a significant increase in the rate of polymerization, because the oxidation

Scheme I



potentials of the bithiophene (1.31 V) and terthiophene (1.05 V) are much lower than that of the thiophene monomers (e.g., 1.8 V for 3-*n*-pentylthiophene). Thus, these oligomeric additives will get oxidized first in the system to form radical-cation intermediates, upon which the polymer chains grow. The number of growing polymer chains in the presence of the additives should be greater than that in their absence. Therefore, the added bithiophene or terthiophene effectively functions as an initiator in the polymerization. Increasing the amount of the initiator results in a greater number of growing polymer chains, which in turn leads to lower average molecular weights of the polymers. This accounts well for the experimental observations. Moreover, the low molecular weight fraction having GPC peak molecular weights of about 1000–1200 (Figure 6c) is attributed to the oligomers with less than 10 monomer units, which are generated in the polymerization. Because these oligomers are soluble in the electrolyte and grow into longer polymer chains once they diffuse to and get oxidized on the electrode surface,[5,31] their amount on the electrode should remain low and their molecular weights should be affected little by the presence of the additives.

We have also studied the effect of the bithiophene and terthiophene additives on the electronic absorption spectra of the polymers, which were measured both in THF solution and as thin films on ITO electrodes. As demonstrated in Figure 7a, poly(3-*n*-pentylthiophene) synthesized and oxidized at a constant potential 1.5 V on an ITO electrode shows a strong absorption band at 426 nm and a broad absorption at 800 nm in the near-IR region. The absorption with a maximum wavelength (λ_{max}) of 427 nm has been characterized as a π–π^* transition, which is related to the conjugation in the polymer backbone.[2,18,32] As the conjugation length increases, this absorption band shifts to higher wavelengths.[27,33] The absorption band at 800 nm is attributed to the oxidation (i.e., doping) of the polymer, and the increase in the doping level leads to the higher intensity of this band.[34] When the polymer was electrochemically reduced (undoped), the band at 800 nm nearly disappeared, while the band at 427 nm remained (Figure 7b). The electronic absorption spectrum of the reduced polymer (Figure 7c) in a THF solution is quite similar to that of the polymer film in the reduced form (Figure 7b). The blue shift of the π–π^* transition absorption in the polymer solution is attributed to the disorder (i.e., random-coil conformation) of the polymer chains in the solution, which shortens the conjugation length.[16,32]

The presence and amount of 2,2′-bithiophene or 2,2′:5′,2″-terthiophene in the polymerization of 3-alkylthiophenes have a significant effect on the π–π^* absorption band of the resultant polymers. In general, the polymers prepared in the presence of the additive have higher λ_{max} values than those prepared in the absence of the additive. In Figure 8, the λ_{max} of poly(3-*n*-pentylthiophene) in a THF solution is plotted against the amount of 2,2′-bithiophene and 2,2′:5′,2″-terthiophene employed in the polymerization. When the amount of the additives is increased to about 2%, the λ_{max} increases sharply by about 15 nm. This bathochromic shift indicates the longer average conjugation length of the polymer backbone, and therefore the higher structural regularity of the polymer chains.[27,33] The improvement in the structural regularity of the polymers probably results from the increase in the overall rate of the polymerization in the presence of a small amount of 2,2′-bithiophene or 2,2′:5′,2″-terthiophene, so that some possible side reactions might be suppressed. As evidenced by the NMR results, the number of the regular head-to-tail placements in the polymer backbone is increased when the bithiophene or terthiophene is present in the polymerization. However, the increase in λ_{max} slows down and levels off at amounts of the additives greater than 2%. This is because the conjugation length depends not only on the structural regularity of the polymer chains but also on many other factors including the molecular weight of the polymer. As shown in Figure 6a, increasing the amount of the additive in the polymerization results in a decrease in the overall molecular weight of the polymer. At 10% of the additive, the M_w and M_n are as low as 2500 and 1400, respectively, which correspond to an average chain length of about 10 monomer units. Thus, the λ_{max} leveling off could be attributed, at

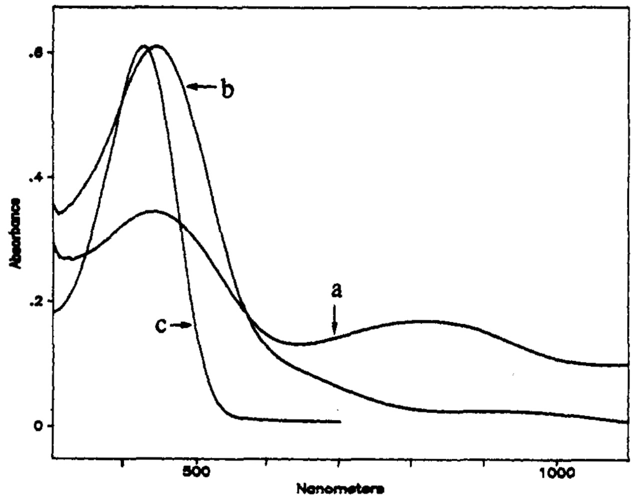


Figure 7. Electronic absorption spectra of poly(3-*n*-pentylthiophene) measured on an ITO electrode (a) in oxidized form and (b) in reduced form and (c) measured in reduced form in a THF solution.

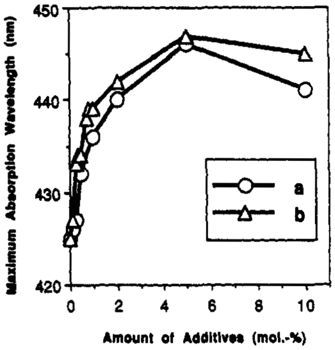


Figure 8. Dependence of the λ_{max} (nm) in the electronic absorption spectra of poly(3-*n*-pentylthiophene) measured in a THF solution on the amount of (a) 2,2′-bithiophene and (b) 2,2′:5′,2″-terthiophene presented in the polymerization at 1.5 V.

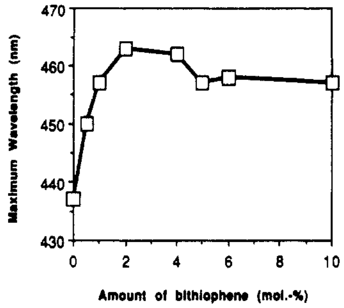


Figure 9. Relation of the λ_{max} (nm) in the electronic absorption spectra of poly(3-*n*-pentylthiophene) measured on an ITO electrode with the amount of (a) 2,2′-bithiophene and (b) 2,2′:5′,2″-terthiophene presented in the polymerization at 1.5 V.

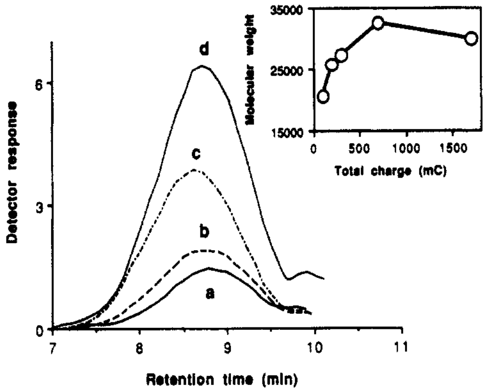


Figure 10. GPC chromatograms of poly(3-*n*-pentylthiophene) synthesized at 1.5 V in the presence of 0.1% 2,2′:5′,2″-terthiophene after consuming a total amount of charge of (a) 100, (b) 300, (c) 700, and (d) 1700 mC. The inset shows the relationship between the weight-average molecular weight and the total charge consumed.

least in part, to lowering the molecular weights. The same trend was observed in the electronic absorption spectra of the polymer films on ITO electrodes. As demonstrated in Figure 9, λ_{max} increases rapidly with the amount of 2,2′-bithiophene up to about 2% and then levels off. It should be noted that the polybithiophene film prepared under identical conditions (i.e., the amount of 2,2′-bithiophene was 100%) shows a λ_{max} of 469 nm. The rate of the λ_{max} increment in the range of 2–100% bithiophene is far smaller than that in the range of 0–2%. The IR spectra of poly(3-alkylthiophenes) prepared in the presence of the additives are essentially the same as those of poly(3-alkylthiophenes) prepared in the absence of the additive but are quite different from those of the homopolymers of the additives (e.g., polybithiophene[20]). Therefore, the observed bathochromic shift should not be caused by the formation of the homopolymers of the additives in the polymerization systems.

The dependence of the molecular weight on polymerization time was investigated. Since the total amount of charge consumed in the potentiostatic polymerization is approximately proportional to the reaction time, we have used the total amount of charge to control and to represent the reaction time. As exemplified in Figure 10, poly(3-*n*-pentylthiophene) exhibits a bimodal GPC elution pattern regardless of the reaction time. The molecular weight of the polymer increases significantly as the total charge is increased up to 700 mC (corresponding to about 130 s in reaction time); then it becomes almost constant as the reaction further proceeds to a total charge of 1700 mC (see the inset in Figure 10). It is noteworthy that such a relationship between the reaction time and molecular weight resembles the behavior of typical chain polymerizations.[35] Again, the observed increment in the molecular weight is mainly contributed by the high molecular weight fraction of the polymer. The peak molecular weight of the low molecular weight fraction remains essentially unchanged at ~1000–1200. The electronic absorption spectra of the polymer show little dependence on the polymerization time under our experimental conditions. These results are consistent with the proposed mechanism.[21] Thus, the polymerization proceeds through the formation of soluble oligomeric intermediates, upon which the polymer chains grow rapidly, leading to high but limited molecular weights at a constant applied potential. The limitation of the molecular weights should be dictated by the applied potential employed. As discussed earlier, the higher applied potential could result in the removal of more electrons from a polymer chain, which in turn increases the reactivity of the chain radical cations, leading to further growth of the polymer to higher molecular weights.

Conclusions

Poly(3-*n*-pentylthiophene) and poly(3-*n*-hexylthiophene) prepared potentiostatically under various conditions have a bimodal molecular weight distribution. In general, the molecular weight of the polymers increases with the applied potential up to about 1.7 V vs SCE. When the potential is further increased, the molecular weight levels off and/or decreases because the degradation of the polymer chains becomes dominant at the higher potentials. The polymerization of the 3-alkylthiophenes is facilitated by introducing a small amount of the oligomeric additives, 2,2′-bithiophene and 2,2′:5′,2″-terthiophene, into the system. The presence of the additives also improves the structural regularity of the resultant polymer chains, which is evidenced by a significant bathochromic shift of the λ_{max} for the π–π^* transition band in the electronic absorption spectra of the polymers. The more additives present in the polymerization result in the polymers with lower molecular weights. The molecular weight was found to increase rapidly with time in the early stage of the polymerization (e.g., ~130 s for the polymerization of 3-*n*-pentylthiophene in the presence of 0.1% 2,2′:5′,2″-terthiophene at 1.5 V). However, as the polymerization proceeds beyond this stage, the molecular weight remains almost constant. All the changes in the molecular weight are mainly contributed by the high molecular weight fraction of the polymers in the bimodal distribution. In contrast, the low molecular weight fraction is a minor fraction, which consists of oligomers with less than 10 monomer units and is not significantly dependent of the polymerization conditions. All the results are interpreted by, and strongly support, the electrophilic aromatic substitution mechanism for the oxidative polymerization of thiophene monomers.

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