Electrochemical Polymerization of Thiophenes in the Presence of Bithiophene or Terthiophene: Kinetics and Mechanism of the Polymerization

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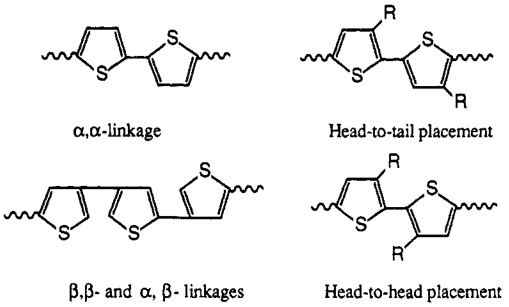
Electrically conductive polythiophene and poly(3-alkylthiophenes) have been prepared by using a new synthetic method, in which a small amount of 2,2′-bithiophene or 2,2′:5′2″-terthiophene is introduced to the system of electrochemical polymerization of thiophene and 3-alkylthiophenes and results in a significant increase in the rate of polymerization and in a lowering of the required applied potentials. The polymers were characterized by infrared spectroscopy, electron scanning microscopy, cyclic voltammetry, and thermogravimetric analysis. In the presence of the additives, the number of nucleation sites of the polymers on the surface of the electrode is much greater, resulting in more uniform polymer films. There is no apparent structural difference between the polymers produced in the absence and in the presence of the additives. Kinetics of the polymerization was also studied. The rate of polymerization was found to be first order in the monomer concentration in the absence of the additives and 0.5 order in the bithiophene and in the terthiophene concentration. A mechanism of polymerization is proposed that the polymer growth is accomplished by electrophilic aromatic substitution of the radical cations to the neutral thiophene monomers.

Introduction

During the past 15 years, electronically conducting polymers such as polyacetylene, polypyrrole, polythiophene, and polyaniline have received considerable attention because of their remarkable electronic, magnetic, and optical properties and their wide range of potential applications in many areas.[1-5] Recently, many novel devices based on conducting polymers such as organic transistors and solar cells were constructed.[6,7] Among all the conducting polymers, polythiophene is particularly interesting because of the recent discovery that polythiophenes with long alkyl chain substituents in the β- (i.e., 3-) position of the thiophene rings were soluble in common organic solvents in both doped and undoped forms.[8] Following this development, a great number of the derivatives of polythiophene have been synthesized, which are soluble in organic solvents[9-15] or even in water.[16] Many polymers with thiophene repeat units of various length being segmented in the polymer backbones were also reported.[17]

Scheme I



Partly because of their good solubility, polythiophenes are among the better characterized conducting polymers. Polymerization of a five-membered heterocyclic rings such as thiophene can occur through the bonding of the monomer at the α- or β- (i.e., 2- or 3-) position (Scheme I). Many theoretical and experimental studies have indicated that the monomer units are incorporated into the polymer chain dominantly through the α,α-linkages because of the much higher reactivity at the α-position than that at the β-position in the monomer.[18] The linkages through the

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β-position may also form during the polymerization and are generally considered undesirable since they could reduce the regularity and the extent of conjugation of the polymer backbone.[19-21] To increase the number of α,α-linkages and therefore to decrease the number of β,β- or α,β-mislinkages in the polymer chains, several approaches have been taken, such as the use of β-position substituted thiophenes (e.g., 3-alkylthiophenes or 3,3′-dialkylthiophenes)[9-16,22] and the dimer or oligomers of thiophenes (e.g., 2,2′-bithiophene and 2,2′:5′,2″-terthiophene)[23,24] as the starting materials for the polymerization. When a β-substituted thiophene is used as the monomer, the regiochemistry of substitution in the resulting polymer chains is of great interest. In principle, the coupling of 3-alkylthiophene monomers can occur by both head-to-head and head-to-tail placements (Scheme I). A series of carefully designed and executed experiments has demonstrated that the head-to-tail placement is dominant over the head-to-head placement and that the regiospecific polymers have improved conductivity and magnetic properties.[9,19,25,26] All the structural characterization results have established unambiguously that the α- (i.e., 2-) position in the thiophene and 3-substituted thiophene monomers is most reactive in the polymerization.

While most of the previous work in the field of polythiophenes has been devoted to the study of the structural, physicochemical, and electronic properties of the polymers and to the exploration of new monomers, the chemistry of the polymerization of thiophene and its derivatives has however received relatively less attention, particularly after the pioneering work on the mechanism of polymerization in the early 1980s.[27-30] Polythiophenes can be prepared by either electrochemical or chemical oxidation of thiophene and its derivatives. The electrochemical polymerization normally requires the applied potentials to be higher than the oxidation potentials of the monomers.[5,31] However, the high applied potentials would facilitate the side reactions (e.g., mislinkages and cross-linking) and possible overoxidation of the polymers, resulting in poor quality of the polymers.[24,32]

Recently, we developed a new synthetic method for preparation of polythiophene and its derivatives.[33] In this new method, a small amount of 2,2′-bithiophene or 2,2′:5′,2″-terthiophene is introduced to the thiophene polymerization system, resulting in a great increase in the rate of polymerization. In the presence of the bithiophene or terthiophene, the applied potentials for the electrochemical polymerization can be significantly lowered to minimize the side reactions without sacrificing the rate of polymerization. In this paper, we present the results on electrochemical polymerization of thiophene, 3-methylthiophene, and 3-*n*-pentylthiophene using the new synthetic method and on kinetics of the polymerization. The resulting polymers are characterized by cyclic voltammetry, Fourier transform infrared spectroscopy, thermogravimetric analysis, and scanning electron microscopy. A mechanism of polymerization is proposed to account for all the observations.

Experimental Section

Materials and Instrumentation. Thiophene (99%, Aldrich) and 3-methylthiophene (99+%, Aldrich) were doubly distilled under reduced pressure. 2,2′-Bithiophene (97%, Aldrich), 2,2′:5′,2″-terthiophene (99%, Aldrich), and lithium perchlorate anhydrous (99.5%, Alfa) were used as received. Acetonitrile (99.9%, HPLC grade, J. T. Baker) was dried and stored over molecular sieves. 3-*n*-Pentylthiophene was prepared by a cross-coupling reaction of *n*-pentylmagnesium bromide with 3-bromothiophene in dry diethyl ether in the presence of a nickel phosphine catalyst, following the procedure reported by Tamao et al.[34] Electrochemical synthesis and cyclic voltammetry (CV) were performed on an EG&G PAR Model 273 potentiostat/galvanostat. A three-electrode cell was employed with a saturated calomel electrode (SCE) as reference and platinum foils as both working and counter electrodes. The working electrode was washed with chromic acid followed by water and was polished to a final smoothness of ca. 0.1 μm with slurries of alumina polishing powder followed by rinsing thoroughly with distilled water and acetonitrile. Infrared spectra of polymer KBr pellets were recorded on a Perkin-Elmer Model 1610 FTIR spectrometer. Electrical conductivities were measured by using standard four-probe techniques on powder-pressed pellets. Gel permeation chromatography was studied on a Waters GPC IIA equipped with an Ultrastyragel linear column at 35 °C using tetrahydrofuran (Aldrich, HPLC grade) as eluant. Thermogravimetric analysis (TGA) was performed on a Du Pont 9900 thermal analysis system with a TGA-950 module under nitrogen. All the experiments were performed at room temperature in a nitrogen atmosphere. All the potentials were referenced against SCE. The electron micrographs were taken on a JEOL-JSM35CF scanning electron microscope (SEM).

Electrochemical Polymerization. Electrochemical polymerization of thiophene monomers can be carried out by using potentiostatic, galvanostatic, or cyclic potential sweep techniques. In the present studies, cyclic potential sweep technique was employed. Although this technique requires longer reaction times to obtain the polymer film as compared with potentiostatic or galvanostatic method, it is advantageous because the electrochemical characteristics of the growing polymer can be monitored during the polymerization process. Hence, it allows a detailed kinetic study of polymerization. Thus, polythiophene, poly(3-methylthiophene), and poly(3-*n*-pentylthiophene) films were deposited on the working electrode (surface area 3.0 cm^2) in an acetonitrile/0.1 M $LiClO_4$ electrolyte (usually 25 mL) containing the appropriate monomer (with or without addition of 2,2′-bithiophene or 2,2′:5′2″-ter-

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thiophene) by using the cyclic potential sweep technique. The concentration range of the monomer was 0.05–0.4 M, and that of 2,2′-bithiophene or 2,2′:5′,2″-terthiophene was 0.1–2 mM. The potential sweep ranges were between −0.2 and 1.5 V (or other up-switch potential values as specified in the text) vs. SCE at a scan rate of 100 mV/s. Before each of the anodic scans, the potential was held at −0.2 V for 10 s. The cyclic voltammograms of polymerization were recorded on a Houston 2000 X–Y chart recorder continuously and coincidentally with the synthesis. In addition, the integrated charges were read directly from the EG&G PAR 273 potentiostat/galvanostat. For comparison, poly(2,2′-bithiophene) and poly(2,2′:5′,2″-terthiophene) were also prepared following the same procedure except 2,2′-bithiophene and 2,2′:5′,2″-terthiophene were employed as the monomers. In most of the syntheses, the total charge was controlled to be ca. 300 mC and the film thickness was ca. 0.6–1 μm. After each electrochemical synthesis, the polymer film was washed thoroughly with acetonitrile. The cyclic voltammogram of the film was then recorded in a monomer-free 0.1 M $LiClO_4$ acetonitrile solution with cycling the potentials between −0.2 and 1.2 V and at various scan rates of 25, 50, 75, and 100 mV/s. The reported oxidation potentials of all the monomers and polymers were measured by cyclic voltammetry in 0.1 M $LiCO_4$ acetonitrile solution at a scan rate of 100 mV/s.

Poly(3-*n*-pentylthiophene) was also prepared for GPC studies using the potentiostat technique. A constant potential of 1.35 V vs. SCE was applied for a period of 20 min. Immediately after the synthesis, the polymer formed on the electrode was reduced to its neutral state by the reversal of cell polarity followed by holding the potential at −0.2 V for 15 min. The polymer was washed thoroughly with acetonitrile and dissolved in THF for GPC analysis. Directly based on polystyrene calibration, $\bar{M}_n$ and $\bar{M}_w$ of the soluble poly(3-*n*-pentylthiophene) were found to be ca. 1400 and 1800, respectively.

Results and Discussion

Electrochemical Polymerization. Figure 1a shows typical cyclic voltammograms of the electrochemical polymerization of 3-methylthiophene in a 0.1 M $LiClO_4$ acetonitrile solution using cyclic potential sweep technique in the potential range of −0.2 to 1.5 V vs. SCE at a scan rate of 100 mV/s. The anodic peak at ca. 0.55 V, corresponding to the oxidation of poly(3-methylthiophene), appeared in the second scan. As the polymerization proceeds, the peak current increases in the successive cycles, indicating the growth of polymer on the surface of the electrode. The anodic peak potential shift gradually to higher values as the thickness of the polymer film increases. This potential shift is attributed to heterogeneous electron-transfer kinetics, the *IR* drop across the film, porosity of the film and hence mobility of counterions,[35] and a decrease in the film conductivity.[36] The cyclic voltammograms of the electrochemical polymerization of 3-methylthiophene (0.2 M) in the presence of a small amount of 2,2′-bithiophene (0.2 mM) are shown in Figure 1b. In the first scan, an anodic peak appears at ca. 1.3 V, which is absent in the bithiophene-free system (Figure 1a). This peak is attributed to the oxidation of 2,2′-bithiophene and is also observed in the subsequent scans (Figure 1b). In the second scan, the anodic peak for the oxidation of the polymer appeared at ca. 0.55 V. The anodic peak current at ca. 0.55 V (Figure 1b) increases more rapidly with lesser peak potential shift than it does in the bithiophene-free system (Figure 1a), indicating a faster polymer growth rate for the polymerization of 3-methylthiophene in the presence of 2,2′-bithiophene and higher conductivity of the resulting polymer film.

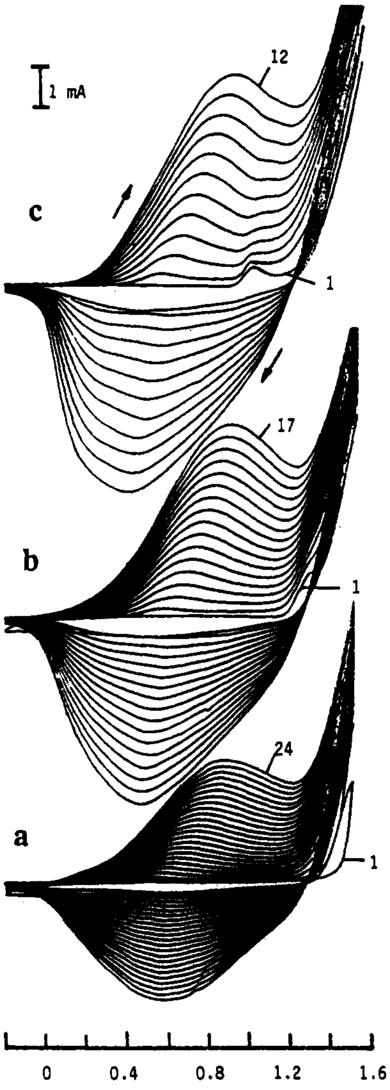
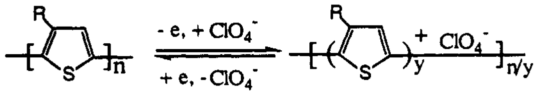


Figure 1. Cyclic voltammograms of polymerization of 3-methylthiophene (0.2 M) in acetonitrile/0.1 M $LiClO_4$ (a) in the absence and in the presence (0.2 mM) of (b) 2,2′-bithiophene and (c) 2,2′:5′,2″-terthiophene, with continuous potential cycling between −0.2 and 1.5 V vs SCE at a scan rate of 100 mV/s.

Cyclic voltammograms of the poly(3-methylthiophene) films resulting from the above polymerizations were measured in a monomer-free $LiClO_4$-acetonitrile electrolyte. Regardless of the polymerization methods, the films exhibit essentially the same electrochemical characteristics with one major redox pair. As a typical example, the CV of poly(3-methylthiophene) prepared in the presence of 2,2′-bithiophene is shown in Figure 2. In general, the redox process of the polymer is chemically reversible because the amount of cathodic charge is essentially the same as that of anodic charge.[3] The reaction can be depicted by the following equation:



where *n* is the degree of polymerization and *y* represents

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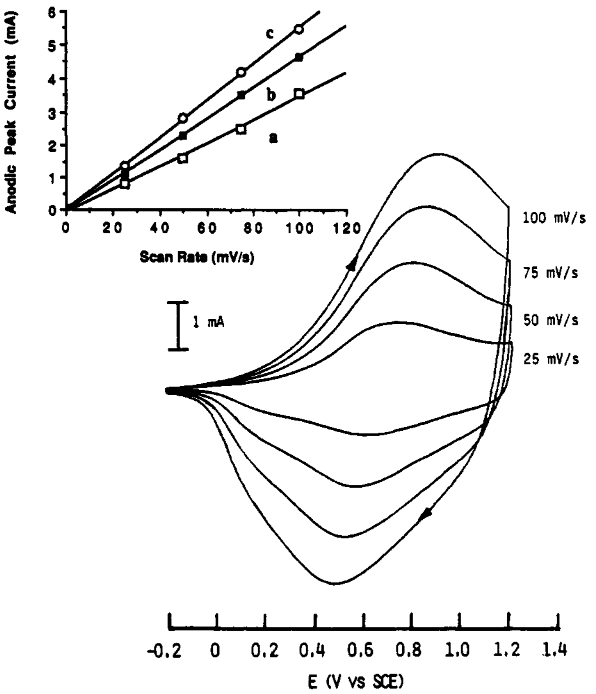

Figure 2. Cyclic voltammograms of poly(3-methylthiophene) measured in a monomer-free MeCN/0.1 M $LiClO_4$ electrolyte at various scan rates (ν). The polymer film was prepared under the conditions given in Figure 1b. The insert shows the dependence of the anodic peak current on ν for the polymer films prepared under the conditions given in Figure 1a–c.

the doping level of the polymer. Both anodic and cathodic peaks are quite broad, which is probably caused by the slow diffusion of the dopant anions in and out of the film. Compared to the anodic peak, the cathodic peak extends over a even larger potential range. This feature is generally related to the reorganization processes of the polymeric chains, accompanied by the expulsion of the anions toward or inclusion of cations from the electrolytic medium.[37] When the poly(3-methylthiophene) film was cycled between the conducting (oxidized) and nonconducting (neutral or reduced) state, it was accompanied by a reversible color change from copperish brown (neutral) to black (oxidized). The cyclic voltammogram of poly(3-methylthiophene) was also measured at various potential scan rates. The height of anodic current peak (i_{pa}) was directly proportional to the scan rate (ν) in the range 25–100 mV/s (the insert in Figure 2). This correlation holds regardless of whether the polymer film was synthesized from 3-methylthiophene alone or from 3-methylthiophene in the presence of 2,2′-bithiophene or 2,2′:5′,2″-terthiophene. The linear i_{pa}–ν plot is characteristic of an electroactive polymer film grafted on an electrode where the current is not diffusion controlled.[3,12] Hence, the electroactive species is effectively localized on the electrode surface.[3,12,38]

Since both the anodic and cathodic charges are related to the amount of electroactive polymers deposited on the electrode, the electrochemical polymerization can be monitored by the cyclic voltammograms of polymerization recorded simultaneously with the synthesis (e.g., Figure 1). In each of the anodic scans, there are two processes that contribute to the total anodic charge. One is the doping charge, i.e., oxidation of the polymer that has already deposited on the electrode; another is the charge consumed for the polymerization process. On the other hand, the cathodic charge only corresponds to the reduction (i.e., dedoping) of the polymer that has already deposited on the electrode and is proportional to the amount of polymer.[3] Therefore, the cathodic charges (Q_c) obtained from the cyclic voltammograms are used as quantitative indications of the amount of polymer deposited on the electrode in this study. Parts a and b of Figure 3 show the plots of the cathodic charge as a function of the number of cycles, which represents the reaction time (t), for the polymerization of 3-methylthiophene in the absence and in the presence of 2,2′-bithiophene. For the system without addition of 2,2′-bithiophene (Figure 3a), there is a long induction period of 7 cycles. This period is significantly reduced to ca. 3 cycles in the system with addition of 2,2′-bithiophene (Figure 3b). After the induction period, the rate of the polymer growth (dQ_c/dt, i.e., the slope of the Q_c–t plots in Figure 3) for the system with 2,2′-bithiophene is much higher than that without 2,2′-bithiophene. Since 2,2′-bithiophene can also be polymerized under the same experimental conditions, the Q_c is plotted against the cycle number in Figure 3d for the polymerization system containing only 2,2′-bithiophene (0.2 mM) as the monomer. As shown in Figures 3a,b,d, the sum of the cathodic charges of poly(3-methylthiophene) and poly(2,2′-bithiophene) generally does not equal that of the polymer produced from the 3-methylthiophene/2,2′-bithiophene system. This indicates that the polymerization of 3-methylthiophene in the presence of 2,2′-bithiophene is not a simple addition of homopolymerizations of the two individual compounds. Further supporting evidence was obtained from the infrared spectroscopic studies of the polymers generated from these three systems. The spectrum of the polymer grown in the solution containing 3-methylthiophene and a small amount of 2,2′-bithiophene is essentially identical with that of poly(3-methylthiophene) but quite different from that of poly(2,2′-bithiophene). The characteristic absorption bands in the IR spectra of both poly(3-methylthiophene) and poly(2,2′-bithiophene) are consistent with those reported in the literature.[3,10]

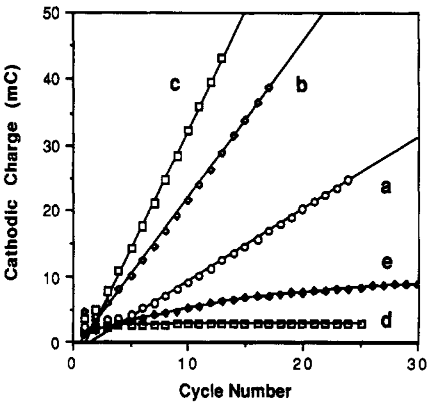

Figure 3. Plots of the cathodic charge against the cycle number for the electrochemical polymerization of 3-methylthiophene (0.2 M) (a) in the absence and in the presence (0.2 mM) of (b) 2,2′-bithiophene and (c) 2,2′:5′,2″-terthiophene and for the polymerization of (d) 2,2′-bithiophene (0.2 mM) and (e) 2,2′:5′,2″-terthiophene (0.2 mM). The polymerization conditions were given in Figure 1.

The effect of 2,2′:5′,2″-terthiophene on the polymerization of 3-methylthiophene is similar to that of 2,2′-bithiophene. Typical cyclic voltammograms of the electrochemical polymerization of 3-methylthiophene with addition of 2,2′:5′,2″-terthiophene are shown in Figure 1c. In

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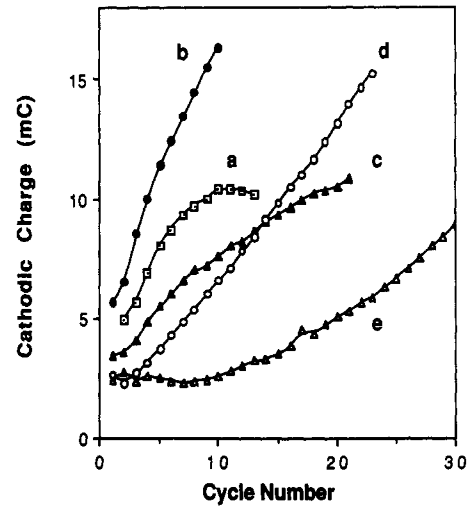

Figure 4. Plots of the cathodic charge against the cycle number for the polymerization of (a) thiophene alone (0.2 M) with a potential cycling range of −0.2 to 2.0 V, for the polymerization of thiophene (0.2 M) in the presence of 2,2′-bithiophene (0.2 mM) with the potential cycling range of (b) −0.2 to 2.0 V and (c) −0.2 to 1.8 V and for the polymerization of *n*-pentylthiophene (0.2 M) with the potential cycling range of −0.2 to 1.5 V (e) in the absence and (d) in the presence of 2,2′-bithiophene (0.2 mM).

comparison with the terthiophene-free system (Figure 1a), this system shows a more rapid increase in the anodic peak current and cathodic charge. There is an anodic peak at ca. 1.1 V in the first scan, which is absent in the terthiophene-free system and is therefore attributed to the oxidation of the terthiophene. Figure 3a,c,e shows that the cathodic charges of the polymer produced from the 3-methylthiophene/terthiophene system is higher than the sum of the cathodic charges of poly(3-methylthiophene) and poly(2,2′:5′,2″-terthiophene). This indicates that the terthiophene also facilitates the polymerization and that the rate enhancement is not due to the homopolymerizations of individual monomers. The extent of rate enhancement of 2,2′:5′,2″-terthiophene appears to be greater than that of 2,2′-bithiophene, as demonstrated by the larger slope of the dQ_c/dt–t plot (Figure 3c as compared with 3b). The polymer is formed more rapidly, and the initial induction period is further reduced.

The rate-enhancement effect of 2,2′-bithiophene and 2,2′:5′,2″-terthiophene was also observed in the electrochemical polymerization of unsubstituted thiophene as demonstrated, for example, in the Q_c–t plots for the polymerization of thiophene in the absence (Figure 4a) and in the presence (Figure 4b) of the bithiophene. The cyclic voltammogram of polythiophene film measured in the monomer-free electrolyte exhibits a similar shape as that of poly(3-methylthiophene) (Figure 2), except that the oxidation potential of polythiophene is higher than that of poly(3-methylthiophene) at the same scan rate. The oxidation potential of thiophene (2.0 V) is higher than that of 3-methylthiophene (1.8 V) because of the electron-donating nature of the methyl substituent.[19,29] Therefore, polymerization of unsubstituted thiophene requires a higher up-switch potential than that of 3-methylthiophene. In the presence of the bithiophene or terthiophene, the up-switch potential can be lowered significantly. For example, polythiophene can be prepared from the thiophene monomer with 0.1% of 2,2′-bithiophene via a potential cycling between −0.2 and 1.8 V (Figure 4c), whereas no polymer formation was observed after cycling the potentials in the same range for 6 h without 2,2′-bithiophene. The similar switch-potential dependence was observed for the electrochemical polymerization of the 3-alkylthiophenes. For the polymerization of 3-methylthiophene in the absence of 2,2′-bithiophene, an up-switch potential of at least 1.4 V is required. In general, the higher the up-switch potential employed, the faster the polymerization (Figure 5). At the up-switch potential of 1.3 V, no noticeable cathodic charge could be measured even after cycling the potentials for 5 h. However, when a small amount of 2,2′-bithiophene (0.2 mM) was added to the system, poly(3-methylthiophene) was produced with a reasonably fast rate at an up-switch potential of 1.3 V as shown in Figure 5a.

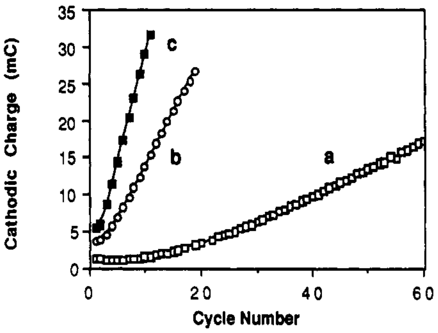

Figure 5. Plots of the cathodic charge against the cycle number for the polymerization of 3-methylthiophene (0.2 M) with the potential cycling range of (a) −0.2 to 1.3 V in the presence of 2,2′-bithiophene (0.2 mM) and with the potential range of −0.2 to 1.6 V (b) in the absence and (c) in the presence of 2,2′-bithiophene (0.2 mM).

Thus, the use of small amount of 2,2′-bithiophene or 2,2′:5′,2″-terthiophene in the polymerization system can effectively shorten the initial induction period and can lower the required up-switch potential. This presents a great advantage in minimizing side reactions such as the formation of mislinkages and degradation as resulted from the overoxidation of the polymers. The higher up-switch potentials generally give a fast polymerization but at the expense of more degradation. As shown in Figure 4a, in the absence of 2,2′-bithiophene, the growth of polythiophene actually slows down and levels off when the cathodic charge reaches about 10 mC. During the polymerization process, a brown-purple coloration in solution was observed around the surface of the electrode. These are attributed to the formation of soluble, low molecular weight degradation products that do not adhere to the electrode surface and diffuse into the solution.[30,39] In the presence of the biothiophene (Figure 4b), the extent of degradation seems to be reduced considerably. The formation of degradation products was sensitive to the up-switch potential used. The higher the up-switch potential, the more colored species observed. The side reactions appear to be more significant in the syntheses of polythiophene than those of poly(3-alkylthiophenes) as manifested by the extent of coloration and the negative deviation in the Q_c–t plots (Figures 3–5). The lower stability of polythiophene could be attributed to the relatively slower polymerization that could not effectively compete with the side reactions. It may also be resulted from the higher content of structural defects (e.g., β-linkages) in the polythiophene chains than that in poly(3-alkylthiophenes).[19,20] The degradation of the polymers at high applied potentials was further confirmed from the CVs of the polymer films measured in the monomer-free electrolyte. When up-switch potentials higher than 1.2 V were employed, there was a significant decrease in the anodic

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(39) Bryce, M. R.; Chissel, A. D.; Smith, N. R. M.; Parker, D.; Kathirgamanathan, P. *Synth. Met.* **1988**, *26*, 153.

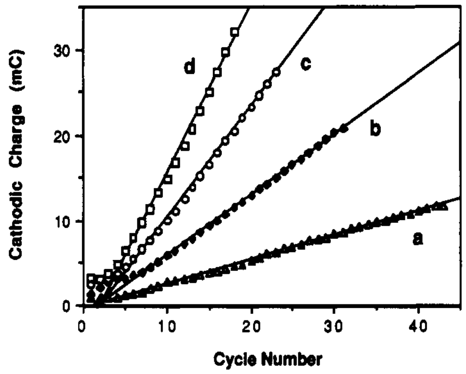

Figure 6. Plots of the cathodic charge (Q_c) against the cycle number (t) for the polymerization of 3-methylthiophene in the absence of the additives, at monomer concentrations of (a) 0.05, (b) 0.1, (c) 0.25, and (d) 0.4 M. The potential cycling range was −0.2 to 1.5 V.

peak current in repetitive cycles accompanied by the coloration of the electrolyte solution.

Similar to the polymerization of 3-methylthiophene, the presence of the bithiophene or terthiophene also increases the rate of polymerization of 3-*n*-pentylthiophene. Since poly(3-*n*-pentylthiophene) was partially soluble in the electrolyte, the values of Q_c recorded may not represent quantitatively the amount of polymer produced. Qualitatively, the rate of the polymer formation in the presence of the additive (Figure 4d) was clearly greater than that in the absence of the additive (Figure 4e), particularly with the assumption of the same solubility of poly(3-*n*-pentylthiophene) produced in both systems.

The films of poly(3-methylthiophene) and polythiophene electrochemically prepared with and without addition of 2,2′-bithiophene or 2,2′:5′,2″-terthiophene were examined by SEM. The thickeness of the films was controlled to be ca. 200 nm by limiting the total charges at ca. 100 mC/cm^2 in each of the syntheses.[36,40] Polythiophene and poly(3-methylthiophene) prepared in the absence of 2,2′-bithiophene gave discontinuous and irregular microislands that reflect the nucleation and initial growth of the polymers.[36,37,40] However, the films of both polymers prepared in the presence of 2,2′-bithiophene (0.1% by mole to the monomer) appeared much more uniform and covered the electrode surface smoothly and continuously. The uniformity of these films was close to that of the poly(2,2′-bithiophene) film. These observations indicate that in the presence of the bithiophene, the number of nucleation sites is greater than that in the absence of the bithiophene. The film morphology was also examined at various reaction times. The polymer nucleation appeared much sooner (within 5 potential cycles) when the bithiophene was present. Similar results were obtained for the systems with addition of the terthiophene.

Kinetic Studies of Polymerization. To gain further insight into the mechanism of polymerization of thiophene monomers, we have studied the effect of concentrations of the monomers ([M]), 2,2′-bithiophene ([M_2]), and 2,2′:5′,2″-terthiophene ([M_3]) on the rate of polymerization. Since polythiophene decomposes readily and poly(3-*n*-pentylthiophene) partially dissolves in the electrolyte solution during the polymerization, 3-methylthiophene was selected as the monomer for more detailed kinetic studies.

For the polymerization of 3-methylthiophene, the increase in cathodic charges (Q_c) is essentially linear with respect to the cycle number (i.e., reaction time t) during polymerization except for the initial induction period, as demonstrated in Figure 6. (The data points in the induction period were discarded in the kinetic treatment). This suggests that the rate of polymerization (dQ_c/dt) is constant and that the increment of accumulation of the polymer on the working electrode is the same in each consecutive scan. It is interesting to note that in this polymerization system, there is no significant autoacceleration effect as observed in electrochemical polymerization of aniline monomers.[41] Thus, the rate of polymerization of 3-methylthiophene is independent of the amount of polymer formed on the electrode. This is further confirmed by the observation that the rate of polymerization measured with a polymer-coated electrode was essentially the same as that measured with an uncoated electrode. As the concentration of 3-methylthiophene was varied in a range 0.05–0.4 M in the absence of 2,2′-bithiophene or 2,2′:5′,2″-terthiophene, the rate of polymerization was found to increase linearly with the monomer concentration (Figure 7), indicating a direct proportionality between the rate and the concentration. Furthermore, a plot of log (dQ_c/dt) vs. log [M] gives a linear line with a slope of 0.90. Hence, the rate of polymerization is approximately first order in the monomer concentration, and the empirical rate expression can be written as

$$\text{rate} = dQ_c/dt = k^{app}[M]$$

where k^{app} is an apparent rate constant. This first-order dependence does not change when the electrolyte containing the monomer was stirred vigorously during the polymerization, indicating that kinetics of the polymerization is not diffusion controlled.

Electrochemical polymerizations of 3-methylthiophene were also performed in which the monomer concentration was kept constant at 0.2 M, and the concentration of 2,2′-bithiophene or 2,2′:5′,2″-terthiophene was varied from 0.1 to 2 mM. In general, the higher the additive concentration, the higher the polymerization rate as demonstrated in Figures 8 and 9. The plots of log (dQ_c/dt) vs. log [M_2], and log (dQ_c/dt) vs. log [M_3] both give a slope of 0.48 (Figure 10). Thus, the rate of polymerization is approximately 0.5 order with respect to 2,2′-bithiophene or 2,2′:5′,2″-terthiophene concentration at the constant monomer concentration. In our experiments, the yield of polymer that formed on the surface of the electrode was

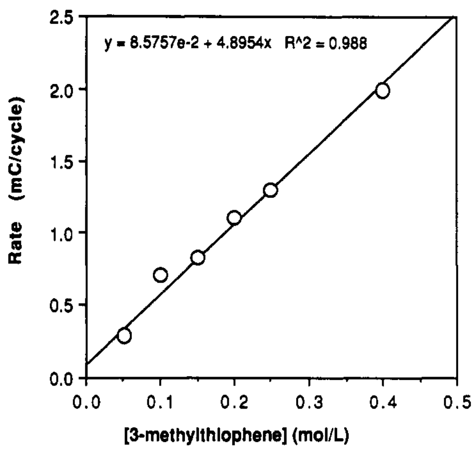

Figure 7. Dependence of the rate (dQ_c/dt, i.e., the slopes in Figure 6) on the concentration of 3-methylthiophene.

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[40] (a) Masuda, H.; Tanaka, S.; Kaeriyama, K. *Synth. Met.* **1989**, *31*, 29. (b) Christensen, L.; Hendrickson, W. A.; Yang, R.; Evans, D. F. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (2), 100.

[41] (a) Wei, Y.; Sun, Y.; Tang, X. *J. Phys. Chem.* **1989**, *93*, 4878. (b) Wei, Y.; Jang, G.-W.; Hsueh, K. F.; Chan, C.-C.; Hariharan, R.; Patel, S. A.; Whitecar, C. K. *J. Phys. Chem.* **1990**, *94*, 7716.

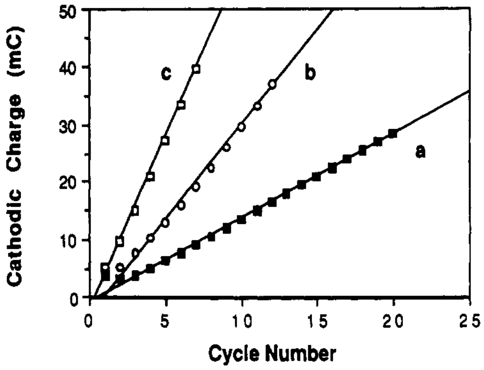


Figure 8. Plots of the cathodic charge (Q_c) against the cycle number (t) for the polymerization of 3-methylthiophene (0.2 M) in the presence of 2,2'-bithiophene at concentrations of (a) 0.1, (b) 0.5, and (c) 2.0 mM. The potential cycling range was −0.2 to 1.5 V.

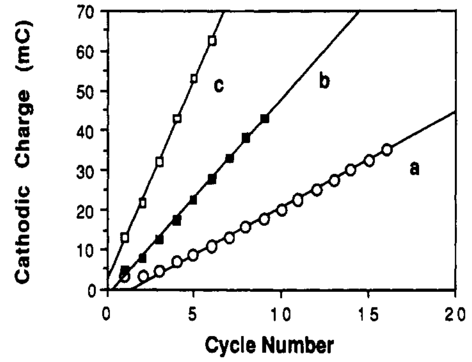


Figure 9. Plots of the cathodic charge (Q_c) against the cycle number (t) for the polymerization of 3-methylthiophene (0.2 M) in the presence of 2,2':5',2''-terthiophene at concentrations of (a) 0.1, (b) 0.5, and (c) 2.0 mM. The potential cycling range was −0.2 to 1.5 V.

very low (<1%). The low conversion of monomer is evidenced by the observation that when the electrolyte containing the monomer after one polymerization process was used again for another process, a similar rate was achieved. Therefore, the concentration of 3-methylthiophene ([M]) is essentially unchanged during the electrochemical polymerization. The intercepts of the double-log plots (Figure 10) represent the values of log ($k^{app'}$[M]) and log ($k^{app''}$[M]) for the polymerization system with addition of the bithiophene and terthiophene, respectively, where $k^{app'}$ and $k^{app''}$ are the apparent rate constants. As shown in Figure 10, the intercept of the plot for the terthiophene system (Figure 10b) is higher than that for the bithiophene system (Figure 10a), reflecting the greater rate enhancement effect of the terthiophene (i.e., $k^{app''} > k^{app'}$). The empirical rate expression for the polymerization in the presence of 2,2'-bithiophene and 2,2':5',2''-terthiophene could be written as

$$\text{rate} = \mathrm{d}Q_c/\mathrm{d}t = k^{app'}[\mathrm{M}][\mathrm{M}_2]^{1/2}$$

$$\text{rate} = \mathrm{d}Q_c/\mathrm{d}t = k^{app''}[\mathrm{M}][\mathrm{M}_3]^{1/2}$$

respectively, at a constant monomer concentration.

Mechanism of Polymerization. It has been well established that the polymerization of thiophene involves removal of two electrons in each of the polymer growth steps (i.e., per monomer unit incorporated into the polymer chain).[27-30] The mechanism of polymerization was proposed to consist of a series of radical coupling reactions,[2,3,27-30] as illustrated in Scheme II. Thus, the electrochemical oxidation of the monomer generates radical cation intermediates, which undergo radical coupling reactions to yield dimer and then oligomers. Subsequent couplings of the monomeric, dimeric, and oligomeric radical cations result in polymer formation. This coupling mechanism was successful in explaining many experimental observations and was suggested to be general and applicable to the polymerization of all the aromatic heterocyclic monomers including thiophene, pyrrole, furan, and their derivatives.[2-5] However, this coupling mechanism could not satisfactorily explain the observed effects of the small amount of 2,2'-bithiophene or 2,2':5',2''-terthiophene on the polymerization of thiophene and 3-alkylthiophenes and the kinetic data obtained. For example, it cannot explain why a small amount of the bithiophene or terthiophene enhances the rate throughout the entire period of polymerization. Thus, if the observed fast reaction were solely due to the polymerization of the added bithiophene, the rate of polymerization should decrease after the consumption of all the bithiophene and the structure of the polymer obtained should be similar to that of poly(2,2'-bithiophene) rather than that of poly(3-methylthiophene). These are inconsistent with the experimental observations. Furthermore, the polymerization of thiophene monomers in the presence of the bithiophene or terthiophene proceeds at the applied potentials significantly lower than the oxidation potentials of the monomers, suggesting the oxidation of the monomers may not be necessary for the polymer growth. Therefore, a different mechanism of polymerization is proposed to account for all the experimental observations as shown in Scheme III.

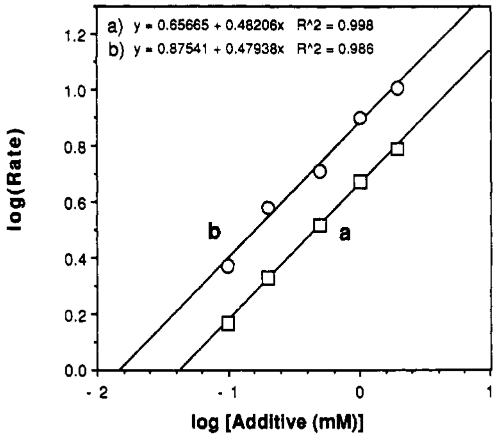
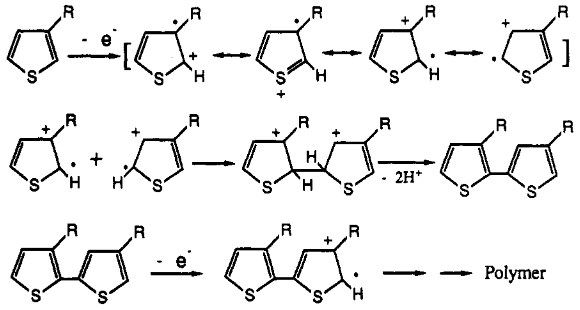


Figure 10. Dependence of log (rate) on (a) log [bithiophene] and (b) log [terthiophene].

Scheme II



In this mechanism, when the bithiophene or terthiophene is not added, the oxidation of monomer to form radical cation is the rate-determining step because of the higher oxidation potential of the thiophene monomers as compared with the subsequently formed dimer, trimer, higher oligomers, and polymer (Table I).[19,29] The radical cation undergoes an electrophilic aromatic substitution

Scheme III

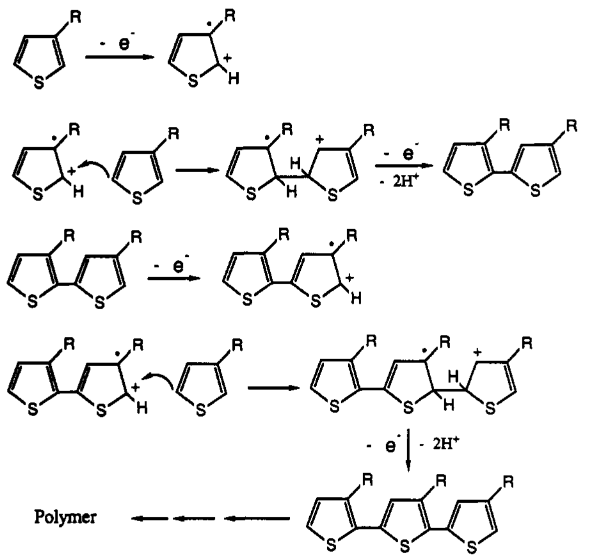
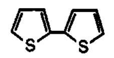
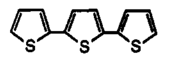
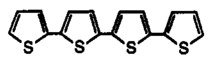
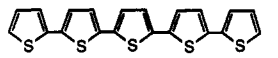
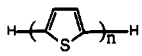


Table I. Oxidation Peak Potentials (E_{ox}) of Thiophene and Its Oligomers and the Probabilities of Polymer Growth upon These Species

	E_{ox},[a] V vs SCE	probability
	2.07	1
	1.31	1
	1.05	2/3
	0.95	2/4
	0.83	2/5
	0.7	2/n

[a] Diaz, et al. *J. Electroanal. Chem.* **1981**, *121*, 355.

reaction with a neutral thiophene monomer followed by oxidation and deprotonation to yield a dimer. This dimer will be oxidized immediately after its formation to a dimeric radical cation that attacks another neutral monomer leading to the formation of a trimer. These reactions proceed repeatedly, leading to higher oligomers and eventually to the polymer. Since the oxidation of the monomer to form the dimer is the slowest step, introduction of a small amount of 2,2′-bithiophene into the polymerization system could bypass this step and result in a decrease in the induction period and a significant increase in the rate of polymerization. The number of growing polymer chains in the presence of the bithiophene should be greater than that in the absence of the bithiophene. Therefore, there are more nucleation sites on the surface of the electrode, leading to the formation of more uniform polymer films as observed in SEM. The added bithiophene essentially functions as an initiator in the polymerization, and the consumption of the bithiophene during the entire period of polymerization is much smaller than that of the monomer. These account for the observations that the rate-enhancement effect by the bithiophene lasts throughout the entire polymerization process and that the IR spectra of poly(3-methylthiophene) are identical regardless whether the polymer was prepared in the presence or in the absence of the bithiophene. The effects of the terthiophene can be explained in a similar manner. The greater rate enhancement of the terthiophene is attributed to its lower oxidation potential than the bithiophene.

According to this mechanism, the required up-switch potential for polymerization of the thiophene monomers in the presence of 2,2′-bithiophene or 2,2′:5′,2″-terthiophene could be significantly lowered to the level of the oxidation potential of the bithiophene (1.3 V) or the terthiophene (1.1 V) since the oxidation of the monomers is no longer necessary. Indeed, polymerization of 3-methylthiophene proceeds at 1.3 V when 2,2′-bithiophene or 2,2′:5′,2″-terthiophene is present. However, the presence of the polymer, which was formed and accumulated on the electrode during the polymerization, does not facilitate the rate of polymerization significantly, although the oxidation potential of the polymer is even lower, e.g., 0.77 V for poly(3-methylthiophene), than that of the terthiophene. In addition, the kinetic data demonstrate that the rate of polymerization is 0.5 order in the bithiophene or terthiophene concentration but essentially independent of the amount of the polymer formed on the electrode. To explain these results, we will further examine the factors that influence the rate of polymerization and will explore the possible termination mode of the polymerization.

The dimer (i.e., 2,2′-bithiophene), trimer (i.e., 2,2′:5′,2″-terthiophene), and higher oligomers have to be oxidized to a radical cation in order to accomplish the growth steps in the polymerization. To simplify the discussion, we define p as the probability of polymer chain growth upon a radical cation of the monomer or any oligomeric species, assuming that the radical cation is delocalized in *only* one thiophene ring (this assumption is *not* needed as discussed later in this paper on the nature of p). For example, when one electron is removed from either one of the two thiophenyl rings in the dimer, a radical cation is formed and is capable of undergoing an electrophilic attack at a neutral monomer, leading to formation of the trimer. We assign a probability of 1 to this process. In the case of oxidation of the trimer, one electron can be removed from either (i) the central thiophene ring or (ii) one of the two end thiophenyl rings. The radical cation formed from (i) may not contribute to the chain growth because of the fact that the α,α-linkage is the major constituent of the thiophene polymers.[9,25,26] The chain growth is, therefore, mainly achieved via the radical cation formed from (ii). The probability for the oxidation that could lead to chain growth can be assigned as 2/3 for the trimer. Likewise, $p = 2/4$ for tetramer, $p = 2/5$ for pentamer, and $p = 2/n$ for the oligomer or polymer having n thiophene units (Table I). It is quite clear that the probability of the chain growth decreases continuously as n increases. In contrast, as n increases, the oxidation potential decreases,[19,29] promoting the rate of oxidation reactions. However, the decrease in oxidation potential as n increases is very fast from the monomer to tetramer but slows down as n further increases and eventually levels off as the polymer forms as depicted in Figure 11. Therefore, introduction of the dimer or trimer into the polymerization system greatly facilitates the polymerization because the effect of oxidation potential prevails over that of p. The presence of the polymer does not facilitates the polymerization because the effect of p is dominant. As the polymerization proceeds, p decreases gradually. However, p would decrease drastically if a radical coupling reaction occurs between two oligomer radical cations. For example, see Scheme IV, where p decreases from 2/3 for the trimer to 1/3 for the hexamer. In addition, the number of possible growing chains also decreases from two to one. As the consequence of the coupling reactions, the polymerization

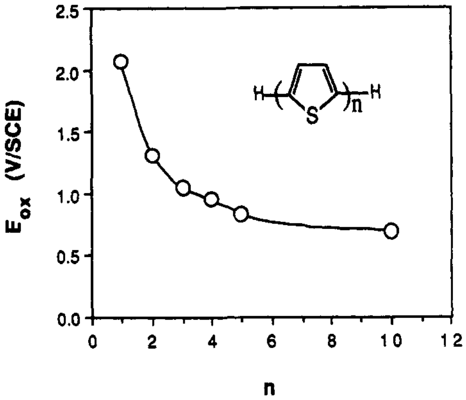
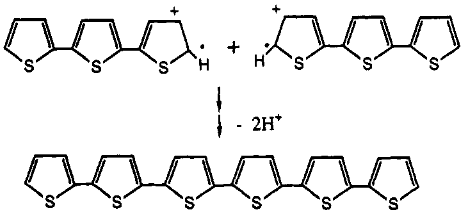


Figure 11. Dependence of the oxidation peak potential (E_{ox}) of the oligomers of thiophene on the number of the thiophene units (n). The data are taken from ref 29. Polythiophene is taken arbitrarily as $n = 10$.

Scheme IV



could slow down drastically, if not terminate. Taking these concepts into consideration, we can readily interpret all the kinetic results obtained under our reaction conditions.

Thus, the polymerization of thiophene monomer can be described by the following equations, where M and M* represent the monomer and oxidized monomer (i.e., monomer radical cation); M_2 and $M_2{}^*$ represent the dimer and oxidized dimer, etc.:

$$\mathrm{M} \rightarrow \mathrm{M}^* \qquad k_i \text{ initiation}$$

$$\mathrm{M}^* + \mathrm{M} \longrightarrow \mathrm{M}_2 \qquad k_{p1} \text{ propagation } (p = 1)$$

$$\mathrm{M}_2 \rightarrow \mathrm{M}_2{}^* \qquad k_{r2} \text{ reinitiation}$$

$$\mathrm{M}_2{}^* + \mathrm{M} \longrightarrow \mathrm{M}_3 \qquad k_{p2} \text{ propagation } (p = 1)$$

$$\mathrm{M}_3 \rightarrow \mathrm{M}_3{}^* \qquad k_{r3} \text{ reinitiation}$$

$$\mathrm{M}_3{}^* + \mathrm{M} \longrightarrow \mathrm{M}_4 \qquad k_{p3} \text{ propagation } (p = 2/3)$$

$$\mathrm{M}_4 \rightarrow \mathrm{M}_4{}^* \qquad k_{r4} \text{ reinitiation}$$

$$\mathrm{M}_4{}^* + \mathrm{M} \longrightarrow \mathrm{M}_5 \qquad k_{p4} \text{ propagation } (p = 2/4)$$

$$\vdots$$

In general

$$\mathrm{M}_m \rightarrow \mathrm{M}_m{}^* \qquad k_{rm} \text{ reinitiation}$$

$$\mathrm{M}_m{}^* + \mathrm{M} \longrightarrow \mathrm{M}_{m+1} \qquad k_{pm} \text{ propagation } (p = 2/m)$$

In the absence of added dimer or trimer, the first reaction (i.e., oxidation of the monomer, which has the highest oxidation potential) is the rate-determining step. Therefore, the rate of polymerization can be expressed as

$$\text{rate} = k_i[\mathrm{M}]$$

which is consistent with the experimental results.

In the presence of added dimer ($m = 2$) or trimer ($m = 3$), the first step is avoided and the general rate expression for the polymer growth can be written as[42]

$$\text{rate} = k_{pm}[\mathrm{M}_m{}^*][\mathrm{M}]$$

The steady-state assumption is made that the rate of formation of $\mathrm{M}_m{}^*$ equals the rate of termination of $\mathrm{M}_m{}^*$, i.e., $d[\mathrm{M}_m{}^*]/dt = 0$. The rate of formation of $\mathrm{M}_m{}^*$ is $k_{rm}[\mathrm{M}_m]$. On the basis of the concepts discussed earlier, the "termination" of $\mathrm{M}_m{}^*$ could take place when a coupling reaction between two $\mathrm{M}_m{}^*$ species occurs:

$$\mathrm{M}_m{}^* + \mathrm{M}_m{}^* \rightarrow \mathrm{M}_{2m} \qquad k_t \text{ "termination"}$$

Thus, the rate of "termination" is $k_t[\mathrm{M}_m{}^*]^2$. It should be noted that this "termination" is different from the conventional concept of termination of a polymerization, such as termination of a free-radical polymerization by combination or disproportionation,[42] because the "terminated" chain M_{2m} could be reinitiated to continue the chain growth at, however, a much slower rate. Therefore, we have

$$k_{rm}[\mathrm{M}_m] = k_t[\mathrm{M}_m{}^*]^2$$

$$[\mathrm{M}_m{}^*] = (k_{rm}[\mathrm{M}_m]/k_t)^{1/2}$$

Substitution of the latter equation into the equation, rate $= k_{pm}[\mathrm{M}_m{}^*][\mathrm{M}]$, yields

$$\text{rate} = k_{pm}(k_{rm}/k_t)^{1/2}[\mathrm{M}][\mathrm{M}_m]^{1/2}$$

This rate expression is consistent with those determined experimentally at $m = 2$ and 3.

The mechanism that we have presented above satisfactorily accounts for all the experimental observations. In this mechanism, the major modes for propagation and termination are considered to be electrophilic aromatic substitution and radical coupling reactions, respectively. The proposed propagation mode is further supported by the results, reported by Hotta et al.,[11] that polythiophenes were successfully synthesized via a chemical dehydrohalogenation of 2-halogenothiophenes in the presence of a Friedel–Crafts catalyst such as $\mathrm{AlCl_3}$. It should be noted that in our earlier discussion about the probability (Table I), we considered the cases that only one electron was removed from the monomer or the subsequent oligomers up to the polymer. If two or more electrons could be removed, the probability for chain growth should be higher. It is apparent that removal of two electrons from the monomer or dimer to form dications would be unlikely because the second ionization potentials could be too high. When the higher oligomers or polymer are oxidized, it is certainly possible to remove two or more electrons from the chain. However, the number of electrons that can be removed from one chain is still limited by the energy required for a minimum charge separation and is reflected in the doping level of the polymer. Strongly depending on reaction conditions and structure of the polymers, the doping level varies greatly for polythiophene and poly(3-alkylthiophenes) and is typically in a range of ca. 1 charge/12 thiophene rings to ca. 1 charge/3 rings.[2-6] Under the polymerization conditions of this study with the up-switch potential of 1.5 V vs SCE, the doping level of poly(3-methylthiophene) was ca. 1 charge/8 rings as estimated by elemental analysis and thermogravimetric analysis (TGA), in which the amount of dopant can be estimated from the weight loss at ca. 200 °C because of thermal dedoping process.[14e,43] Furthermore, our preliminary study of molecular weight by gel permeation chromatography showed that poly(3-*n*-pentylthiophene), which was synthesized by using the potentiostat technique with an applied potential being fixed at 1.35 V for 20 min, has $\bar{M}_n$ of approximately 1.4×10^3, corresponding to ca. 10 monomer units, based on polystyrene calibration.

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Therefore, the value of p based on removal of one electron should be valid at least up to $n \leq 8$ in this study. When a higher up-switch potential is employed, the doping level and therefore p become greater, leading to a faster rate of polymerization as observed experimentally.

Another important factor that affects the p values is extensive delocalization of the radical cation along the oligomer chains. Unlike *trans*-polyacetylene, polythiophenes have nondegenerate ground states. The effective delocalization of a radical cation extends to a few thiophene rings.[3,29,44,45] Although the charge distribution along the oligomer chains could be quite uneven, the cationic character of the α-carbons in the thiophenyl rings at chain ends decreases because of the delocalization.[29,45] As the chain length (i.e., the n value) increases, the cationic character at chain ends and therefore the reactivity of the radical cation decrease, resulting in lower reaction rate.[2,21] Furthermore, we can discuss the relationship between n and the reactivity from a different perspective. For example, since the formation of the bithiophene radical cation is more difficult than that of the terthiophene (as manifested by their oxidation potentials, Table I), the stability of the latter radical cation should be greater than the former. Therefore, the reactivity of the latter should be lower than the former in the subsequent electrophilic aromatic substitution. Likewise, the reactivity of the tetramer radical cation should be lower than that of the trimer radical cation, and so on. The general tendency that the reactivity of a radical cation decreases as n increases is the same as that with the simplified probability argument. Thus, the value of p depends on the radical cation reactivity, which in turn depends on the extent of cationic character, at the α-carbon of the thiophenyl chain ends. If one assumes that the radical cation were evenly distributed on every atom in the monomer or oligomers, the p values could be assigned as $2/5$ to the monomer, $2/10$ to the dimer, $2/15$ to the trimer, ..., and $2/5m$ to the m-mer radical cations. Furthermore, if only one of the two chain ends were accessible for chain growth (as a referee suggested), the corresponding p values would be $1/5$, $1/10$, $1/15$, ..., and $1/5m$. The general tendency remains unchanged in all cases. Further theoretical and experimental work will be needed to obtain the specific numeric values of p quantitatively.

Conclusions

We have described a new method for electrochemical polymerization of thiophene and 3-alkylthiophenes. In this method, a small amount of 2,2′-bithiophene or 2,2′:5′2″-terthiophene is introduced to the otherwise conventional polymerization system. In the presence of the bithiophene or terthiophene, the overall rate of polymerization is significantly increased and the required applied potentials can be reduced considerably to the values lower than the oxidation potentials of the monomers. The rate enhancement of the terthiophene is still greater than that of the bithiophene. In the presence of these additives, both the number of nucleation sites and the rate of nucleation of the polymers on the surface of electrode are greatly increased, resulting in more uniform polymer films. There is no apparent structural difference between the polymers produced in the absence and in the presence of the additives as indicated by FTIR and CV results. Kinetic studies of the polymerization of 3-methylthiophene demonstrate that the rate of polymerization is approximately first order in the monomer concentration in the absence of the additives and is 0.5 order in the bithiophene and in the terthiophene concentration. The rate is essentially independent of the amount of polymer already deposited on the electrode. A mechanism of polymerization is proposed that the polymer growth is mainly accomplished by electrophilic aromatic substitution of the radical cations to the neutral thiophene monomers and that the radical coupling reaction between two oligomeric radical cations results in a drastic decrease in the probability for further chain growth and therefore in the rate of polymerization. This mechanism satisfactorily accounts for all the experimental observations under our reaction conditions.

There are many implications resulting from this mechanism. For example, the oxidative polymerization of other heterocyclic monomers such as pyrrole is believed to follow the similar mechanism to that of thiophene.[2-5] Indeed, we have found that a small amount of 2,2′-bipyrrole greatly increases the rate of polymerization of pyrrole.[46] Furthermore, the chemical polymerization of thiophene or pyrrole is also affected by the additives, such as the bithiophene or bipyrrole, as manifested by a significant increase in the yield of the polymer.[43,46] The details of these results will be presented in our forthcoming articles. Further investigation is in progress to evaluate the effects of applied potential and other experimental parameters on the molecular weights of poly(3-alkylthiophenes) and polypyrrole and to explore the possibility of the preparation of graft and block copolymers by reinitiating an already formed polymer chain in the presence of different monomers.

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Registry No. Thiophene, 110-02-1; thiophene (homopolymer), 25233-34-5; 3-methylthiophene, 616-44-4; 3-methylthiophene (homopolymer), 84928-92-7; 2,2′-bithiophene, 492-97-7; 2,2′:5′,2″-terthiophene, 1081-34-1; 3-*n*-pentylthiophene, 102871-31-8; 3-*n*-pentylthiophene (homopolymer), 110851-62-2.

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