A gel permeation chromatography study of electrochemically synthesized poly(3-alkylthiophene)s

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Poly(3-n-pentylthiophene) and poly(3-n-hexylthiophene) were prepared using a potentiostatic method and were characterized by gel permeation chromatography in tetrahydrofuran. In general, the molecular weight of the polymers increased as the applied potential was increased in the range of 1.3–1.7 V (*versus* saturated calomel electrode). The presence of 2,2′-bithiophene in the polymerization system resulted in a slight decrease in molecular weight but the polymer chains had a higher regularity as evidenced by longer π-conjugation length. At potentials of >1.9 V, the molecular weight decreased because of polymer degradation. The results strongly support the electrophilic aromatic substitution mechanism for electrochemical polymerization of thiophene monomers.

(Keywords: conducting polymers; molecular weight; poly(3-alkylthiophene)s; gel permeation chromatography; 2,2′-bithiophene)

Introduction

Among all the conductive polymers, polythiophene and its derivatives are particularly interesting because of the recent discovery that polythiophenes with long alkyl chain substituents in the 3-position of the thiophene rings have good solubilities in common organic solvents in both doped and undoped forms[1–3]. A great deal of research on poly(3-alkylthiophene)s has been devoted to studying the physico-chemical properties, to the design and synthesis of new soluble derivatives[4–18], and to the exploration of new applications of the soluble and processible poly(3-alkylthiophene)s such as the preparation of Langmuir–Blodgett films[15–17] and the fabrication of highly oriented conducting films[18]. It is well known that molecular weight and molecular weight distribution are of prime importance in determining the properties of a polymer and in elucidating the polymerization mechanism. Although the molecular weights of many soluble polythiophenes have been measured[4–14], there is still a general lack of systematic knowledge of the effects of polymerization conditions on molecular weight and molecular weight distribution of the polymers. Recently, we have found that a small amount of 2,2′-bithiophene greatly facilitates the rate of polymerization of thiophene monomers[19,20] and proposed an electrophilic aromatic substitution mechanism for electrochemical polymerization of thiophene monomers[20]. Based on the proposed mechanism, we can predict that the molecular weight of polythiophenes is dependent on the applied potentials in the electrochemical syntheses. In an effort to further establish the polymerization mechanism and to gain the knowledge and therefore the control of molecular weight and molecular weight distribution of the polymers, we have carried out a series of gel permeation chromatography (g.p.c.) studies on electrochemically synthesized poly(3-alkylthiophene)s.

In this communication, we present our preliminary results on the effects of the applied potential and the presence of 2,2′-bithiophene on the molecular weight and the structure of electrochemically prepared poly(3-n-pentylthiophene) and poly(3-n-hexylthiophene). The data are discussed in relation to the proposed polymerization mechanism.

Experimental

3-n-Pentylthiophene and 3-n-hexylthiophene were prepared by cross-coupling reactions between the corresponding n-alkylmagnesium bromides and 3-bromothiophene following Tamao's procedure[21]. Electrochemical synthesis of poly(3-n-pentylthiophene) and poly(3-n-hexylthiophene) were performed using a potentiostatic method[22–24] in a single-compartment cell on an EG&G PAR model 273 potentiostat/galvanostat. Platinum foils were used as both the working electrode (area 3 cm^2) and the counter electrode (6 cm^2). A saturated calomel electrode (SCE) was used as the reference electrode. The monomer concentration was 0.2 M in 0.1 M $LiClO_4$ acetonitrile solution. Concentration of the additive, 2,2′-bithiophene, varied from 0 to 2 mM as specified in the text. The applied constant potential for the polymerization was in the range of 1.3–2.0 V *versus* SCE. The amount of polymer formed on the working electrode was controlled by accumulating the total anodic charge to ~ 1.7 C in all the polymerizations, which corresponds to the reaction time of, for example, ~ 30 min at 1.35 V and ~ 2 min at 1.7 V. Immediately after each polymerization, the polymer film was dedoped in a monomer-free 0.1 M $LiClO_4$ acetonitrile solution by maintaining a constant potential of -0.6 V for ~ 15 min until the current was reduced to a negligible level. The film was then washed with acetonitrile and dried in air followed by dissolution in tetrahydrofuran (THF, 1 ml). After filtering through a 0.5 μm Teflon filter, the solution of polymers was used for g.p.c. measurements, which 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

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column at 35°C using THF as eluant. The molecular weight and molecular weight distribution were calibrated with monodispersed polystyrene standards. The electronic absorption spectra of the poly(3-alkylthiophene)s in THF solution were recorded on a Perkin-Elmer Lambda-2 u.v.–vis. spectrophotometer.

Results and discussion

Figure 1 shows representative g.p.c. elution patterns of poly(3-n-pentylthiophene) prepared at various potentials without addition of 2,2′-bithiophene. In general, a bimodal type of molecular weight distribution can be identified with the high and low molecular weight peaks at the retention times of ~8–9 and ~9.8 min, respectively. As the potential increases, the peak area of the low molecular weight fraction appears to be reduced with respect to that of the high molecular weight fraction but the peak position (i.e. the peak molecular weight) remains essentially unchanged. Since it is difficult to determine precisely the molecular weight of the low molecular weight fraction, the following discussion will concentrate on the high molecular weight fraction only. It is clearly demonstrated in *Figure 1* that as the applied potential increases, the molecular weight of the high molecular weight fraction increases significantly. Based on the polystyrene calibration, poly(3-n-pentylthiophene) prepared at 1.35 V (*Figure 1a*) has a number-average molecular weight ($\bar{M}_n$) of 4700 and a weight-average molecular weight ($\bar{M}_w$) of 21 000, while the polymer prepared at 1.5 V (*Figure 1b*) has $\bar{M}_n$ and $\bar{M}_w$ values of 9500 and 45 000, respectively.

The relationship between the molecular weight and the applied potential is further illustrated in *Figure 2a* with $\bar{M}_w$ ($\bar{M}_n$ yields a similar plot). As the potential increases, the molecular weight increases rapidly in the lower applied potential range, then levels off at higher potentials followed by a significant decrease at 2.0 V. According to the mechanism that we have proposed[20], the polymer chain propagation in the oxidative polymerization of thiophene monomers is mainly achieved via electrophilic aromatic substitution of the neutral monomers by the chain radical cation intermediates that are generated from oxidation of (i.e. removal of one or more electrons from) the neutral oligomer or polymer chains. Removal of more electrons from an oligomer or a polymer chain will result in the chain radical cation intermediate with higher electrophilicity and therefore higher reactivity, which in turn leads to greater rate of the chain growth and higher molecular weight[20]. This is consistent with the observation that $\bar{M}_w$ increases as the applied potential is increased from 1.35 to 1.7 V (*Figure 2a*) because more electrons could be removed at higher potentials. As the potential is further increased, the molecular weight levels off and eventually decreases (e.g. at 2.0 V), mainly because the degradation of the polymer chains resulting from over-oxidation becomes dominant at higher potentials[25,26]. To verify such degradation at higher potentials, the poly(3-n-pentylthiophene) films, which were all prepared under identical conditions at 1.5 V, were subjected to an applied potential of 1.6 or 1.9 V in a monomer-free 0.1 M $LiClO_4$ acetonitrile solution for 30 s. The polymer was then reduced to the neutral form for g.p.c. measurements. It was found that the $\bar{M}_w$ decreased to ~25 000 and 14 000 for the polymer samples after holding potentials at 1.6 and 1.9 V, respectively.

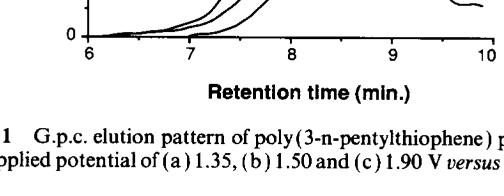

Figure 1 G.p.c. elution pattern of poly(3-n-pentylthiophene) prepared at an applied potential of (a) 1.35, (b) 1.50 and (c) 1.90 V *versus* SCE

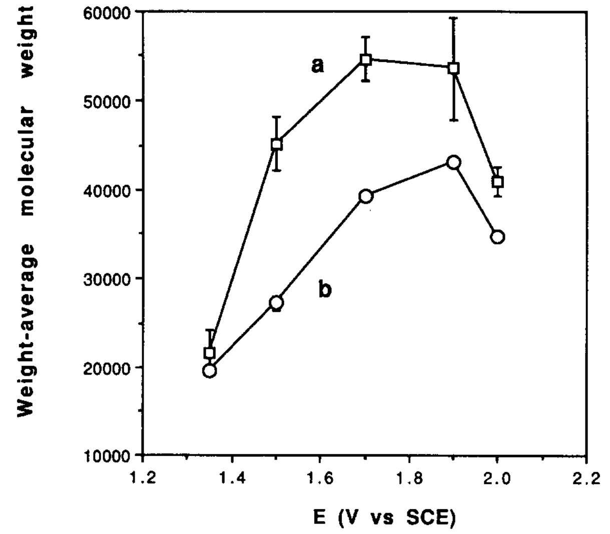

Figure 2 Plots of the weight-average molecular weight of poly(3-n-pentylthiophene) prepared (a) in the absence and (b) in the presence of 0.1 mol% (with respect to the monomer) 2,2′-bithiophene against the applied potential used for the synthesis

Similar effects of the applied potential on the molecular weight of poly(3-n-pentylthiophene) prepared in the presence of 0.2 mM (i.e. 0.1 mol% with respect to the monomer) 2,2′-bithiophene were also observed as demonstrated in *Figure 2b*. The presence of 2,2′-bithiophene also significantly increases the overall rate of polymerization. However, the polymers generally have lower molecular weights than those prepared without the bithiophene (*Figure 2a*). As the amount of the 2,2′-bithiophene increases at a fixed potential (e.g. 1.5 V), the molecular weight decreases slightly. These results are also in good agreement with the proposed mechanism[20]. Since the oxidation potential of the bithiophene (1.2 V) is much lower than that of 3-n-pentylthiophene (1.5 V), the bithiophene molecules will be oxidized first to generate the radical cation intermediates that will undergo electrophilic attack at neutral monomers, leading to the growing polymer chains. Therefore, the added 2,2′-bithiophene functions as an initiator in the polymerization system[20]; the more initiator present, the greater the number of growing polymer chains, resulting in lower average molecular weight.

Poly(3-n-pentylthiophene) samples prepared under various conditions were also studied by u.v.–vis.

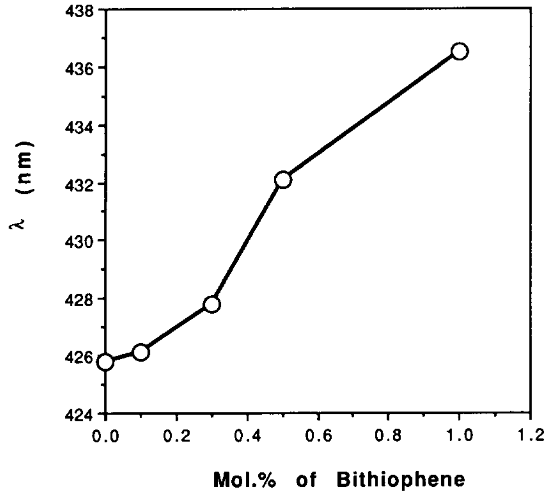

Figure 3 Effect of the amount (mol% with respect to the monomer) of 2,2′-bithiophene added to the polymerization system on the absorption peak maximum in the u.v.-vis. spectra of poly(3-n-pentylthiophene) in THF solution. The applied potential for the syntheses was 1.5 V *versus* SCE

spectroscopy in THF. The polymers prepared in the absence of 2,2′-bithiophene exhibited a maximum absorption (λ_{max}) peak at around 426 nm, which is generally insensitive to the applied potential employed in the synthesis. However, the polymers prepared in the presence of 2,2′-bithiophene showed a significant red shift in this absorption maximum; the more 2,2′-bithiophene added, the greater the red shift. As depicted in *Figure 3*, the λ_{max} increases from 426 to 437 nm as the amount of 2,2′-bithiophene varies from 0 to 1.0 mol% with respect to the amount of monomer. Since this well-understood absorption band is assigned to the π–π^* transition for the conjugated polymer backbones$^{4,27-30}$, the observed red shift indicates that the polymer chains have a longer conjugation length. Thus, the polymers prepared in the presence of bithiophene should have less structural defects and therefore better electronic properties such as higher conductivities as observed previously^{20}. The improved structure regularity could be attributed probably to the increase in the overall rate of polymerization when the bithiophene is present so that many possible side reactions were relatively suppressed. Poly(3-n-hexylthiophene) exhibited essentially the same behaviour as poly(3-n-pentylthiophene).

In summary, we have found that the molecular weight of electrochemically prepared poly(3-alkylthiophene)s increased as the applied potential was increased in the range of 1.3–1.7 V and that the addition of 2,2′-bithiophene to the polymerization system led to a slight decrease in molecular weight but to a significant increase in the π-conjugation length of the polymer chains. All the results can be interpreted by and strongly support the electrophilic aromatic substitution mechanism which we have proposed for electrochemical polymerization of thiophene monomers. Further investigation is in progress in our laboratory to evaluate the effect of other synthetic parameters, such as the reaction time and temperature, and different monomers and additives, on the molecular weight and molecular weight distribution of these polymers.

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