ELSEVIER

Journal of Electroanalytical Chemistry 453 (1998) 107–112

JOURNAL OF ELECTROANALYTICAL CHEMISTRY

Electrochemical gelation of poly(3-hexylthiophene) film

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Received 20 January 1998; received in revised form 18 May 1998

Abstract

When the chemically synthesized poly(3-hexylthiophene) film was oxidized electrochemically in acetonitrile for 1 h, it showed three times a volume change after being transferred into chloroform solution to yield a permanent gel. The swelling increased as the potential was more positive. The absorbance at ca 302 nm, attributed to the $n\rightarrow\pi^*$ transition in the conjugated chain, increased with the longer and more positive electrolysis, indicating development of the conjugation. In contrast, the absorbance at 765 nm, responsible for the electric conduction, decreased with the electrolysis. Both solubility of the polymer in chloroform and the electric conductance also decreased. The volume change was related quantitatively to the solubility with the help of Flory's theory of the swelling, in which the swelling ratio is proportional to the fifth power of the volume per crosslinked polymer molecule. FTIR spectra suggested that =C–H in the thiophene ring was more highly decomposed with application of the more positive potential to yield the crosslinking. The electrochemically synthesized film showed variations similar to those of the chemically synthesized film although the variations were less specific. The electrochemical gel was different from the gel initiated by benzoyl peroxide, which results in crosslinking between the hexyl chains.

Keywords: Crosslinking; Electric conduction; Flory's theory; FTIR; Gel; Poly(3-hexylthiophene); Solubility

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1. Introduction

Conducting polymers such as polyaniline are characterized by the exhibition of electronic conduction in the doped state [1,2]. Since the conduction is ascribed to the long extended conjugation on the backbone, chemical modification of the backbone frequently decreases the conductivity. Thus, modification has often been made to the substituents of the backbone, exemplified by poly(3-alkylthiophene). Various functionalities of poly(3-alkylthiophene) have been used to improve the solubility in various organic solvents [3], fusibility at low temperature [4], crystallinity [5], conductivity [6], and photosensitivity [7]. In the course of the modification, gelation of poly(3-alkylthiophene) has attracted attention to the volume change [8–10].

Volume transition of gels occurs as a result of change in temperature, ionic strength, compositions of solvents, electric field, and mechanical pressure [11]. It also responds to electrode processes [12], in which the phase transition is associated with the change of mass transfer rate of the electroactive species in the gel [13,14]. Unfortunately, the effect of electrode processes is not so specific as variations of temperature or ionic strength, and no remarkable volume change has been reported yet, to our knowledge. This is partly because the electric field relevant to the volume change is restricted to the double layer in the vicinity of the electrode rather than the gel bulk, partly because the electrochemically generated species which causes volume change is localized near the electrode surface [14], and partly because the usual electrochemical systems include a high concentration of ions which makes the change of the ionic strength insignificant. If a gel made of conducting polymers shows a volume change between the conducting state and the insulating state, the electrochemical

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PII S0022-0728(98)00238-1

switching might cause a rapid volume response extended over the whole polymer. Rapidity is expected even for films as thick as a few millimeters because the electrochemical switching provides almost homogeneous redox states [15–23] in spite of the inherently heterogeneous reaction. The homogeneity is ascribed to the propagation of a conducting zone [15–19] and the electric percolation [20–23].

In this report, electrochemical gelation of poly(3-hexylthiophene) is described in the context of the dependence of volume change, solubility, conductance, UV-vis and FTIR spectra on the electrode potential. This is found in the course of voltammetric variation of poly(3-methylthiophene) with the temperature [24], in which an apparent negative activation energy has been observed.

2. Experimental

Three kinds of working electrodes were used: (A) an indium tin oxide (ITO) plate (9 × 55 mm^2); (B) a glass-shielded platinum disk 0.5 mm in diameter; and (C) a platinum plate (40 × 9.2 mm^2). The counter electrode was a platinum coil. The reference electrode was a silver wire in 0.01 M (mol dm^{-3}) $AgNO_3$ + 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) + acetonitrile. All the electrochemical measurements were made in the acetonitrile solution including 0.1 M TBATFB + molecular sieves at room temperature.

Two types of poly(3-hexylthiophene) films were prepared either by chemical or electrochemical oxidation. The chemical oxidation of 3-hexylthiophene was made using anhydrous $FeCl_3$ in chloroform [25] to yield a dark red polymer. The polymer dissolved in chloroform was cast on electrodes (A) and (B) to be dried in air. Then it was treated electrochemically in 0.1 M TBATFB + acetonitrile solution or used for voltammetric measurements. On the other hand, the electrochemical preparation was made galvanostatically (3 mA cm^{-2}) at electrode (B) or (C) for 100 s at 5°C in 0.1 M 3-hexylthiophene + 0.1 M TBATFB + nitrobenzene. The film on electrode (C) was rinsed three times with acetonitrile and was then peeled off from the electrode. It was cast on electrode (A) by dissolving it slightly in acetone.

In order to make crosslinking chemically in the polymer, benzoyl peroxide (BPO) dissolved in chloroform was added dropwise to the film. Then the yellow film became orange and was swollen. 20 min after the addition, the film was immersed in chloroform for 4 h to remove the soluble part. Then the polymer became dark red, and the volume was twice that of the original film.

The in situ UV-vis spectrometry and time scan were performed in a one-compartment cell with electrode (A). The ITO plate in acetonitrile + 0.1 M TBATFB solution was used for a reference for the absorption. FTIR spectra were taken with a PROTAGE System 460 (Nicolet) by mounting a 1 mg sample in a KBr pellet.

The conductance of the film was measured by casting the film on the ITO, drying it in air, pressing a copper rod on the film, and measuring the dc current between the rod and the ITO.

3. Results and discussion

The chemically synthesized film was oxidized at various potentials ($E > 0.6$ V) for 1 h and then was reduced at -0.6 V for 5 min. The film turned dark red. When it was transferred into chloroform, it was swollen immediately and partly dissolved in the chloroform. The film kept in the oxidized state did not exhibit any volume change when transferred into chloroform. Thus reduction after the long term oxidation is required for the swelling. When the film was inserted into ethanol solution, it curled up without any volume change. Even if chloroform was removed from the swollen film by evaporation, the film remained the same size. The film transferred back to the acetonitrile solution did not change in volume. Therefore, the volume change is irreversible even with change of solvent; that is, the electrochemically treated film is a permanent gel. The swelling was almost independent of the kind of cation (tetraethylammonium, lithium and tetrabutylammonium) in solution as well as the kind of electrode material (ITO and Pt).

As a measure of the swelling, we measured the side length of the rectangular cut film 1 × 1 mm^2 through a microscope 30 s after the transfer into chloroform. 95% of the swelling was completed within 20 s. Fig. 1 shows the dependence of the ratio of the swollen length on the oxidation potential. The ratio was independent of the reduction time if it was over 60 s as well as of the reduction potential (from -0.9 to -0.1 V) after the oxidation. Since the swelling is irreversible, each plot in Fig. 1 was obtained at a new film. The scatter of the data points for different films was within 15%. The swelling began at 0.65 V and increased linearly with the potential. The initiation potential 0.65 V is close to the peak potential of the cyclic voltammogram of the cast film ((a) in Fig. 2). Films oxidized for a time less than 5 min did not show the swelling, whereas the swelling was saturated at oxidation times longer than 1 h. The current in the cyclic voltammogram decreased with the potential cycle in the domain from 0.65 to 1.0 V, indicating that the swelling is associated with electrochemical deactivation.

We measured the conductance of the dried film after electrochemical oxidation for 1 h. Fig. 3 shows the

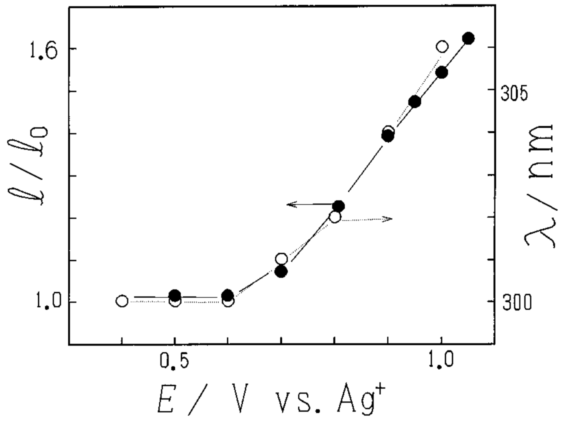

Fig. 1. Variations of the ratio of the side length of the film (filled circle) and wavelength of UV spectra around 300 nm (open circle) with the applied potential, E. The chemically synthesized film was cast on the ITO, to which E was applied in 0.1 M TBATFB + acetonitrile solution for 1 h, and then reduced at − 0.6 V for 5 min. For the measurement of the swollen length, the film was detached from the ITO, rinsed with acetonitrile three times, cut in a rectangular form (1 × 1 mm^2), transferred into chloroform solution, and mounted on a microscope.

dependence of the conductance on the applied potential, which was varied in the positive direction and then reversed. The conductance had a maximum at 0.7 V. Once a potential more positive than 0.7 V was applied, the electric conductance was lost and could not be recovered by any potential change. This big hysteresis accords with the irreversible variation of the swelling.

Fig. 4 shows UV-vis spectra at various potentials for electrode (A). With the positive increase in the potential, the absorbance at ca 300 nm, which has been assigned to an $n \rightarrow \pi^*$ transition [26], increased. This is associated with a red shift from 300 nm at 0.6 V to 306 nm at 1.0 V. The increase and the red shift have been ascribed to the development and stabilization of the conjugation [26]. The variation of the red shift is akin to that of ℓ/ℓ_0, as shown in Fig. 1 although the quantitative comparison of the intensity (ℓ) with the energy (λ) has no meaning. The similarity indicates a similar participation in the conjugation. The absorbance increased not only with the applied potential but also with the time, as shown in Fig. 5. The gradual increase and the saturation of the absorbance demonstrate that long time (1 h) electrolysis is crucial to make the gel. The other feature of the potential-dependent spectra is the broad absorption band at ca 770 nm. It has been assigned to the transition of the bipolaron [27], which is thought to be responsible for the electronic conduction [28]. Fig. 5 also shows the potential dependence of the absorption at 765 nm. The dependence is similar to the variation of the conductance (Fig. 3). It resembles the degradation of the film by over-oxidation. The degradation occurs, however, reportedly at potentials greater than 1.2 V [29].

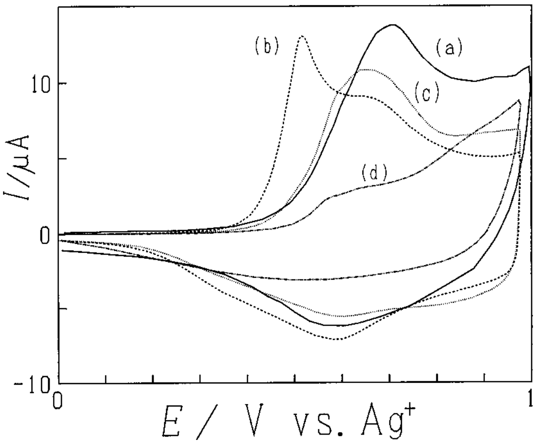

Fig. 2. Cyclic voltammogram (a) of the chemically synthesized and cast film in 0.1 M TBATFB + acetonitrile at the sweep rate 50 mV s^{-1} at electrode (B). Cyclic voltammograms at 50 mV s^{-1} of the electrochemically synthesized films immediately after the synthesis (b), after 0.8 V (c) and 1.0 V (d) oxidation for 20 min.

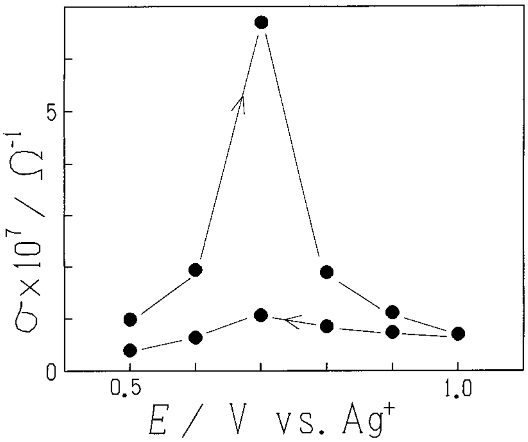

Fig. 3. Variation of the conductance of the film with the potential applied for 1 h to the film before the conductance measurement. The arrow is the order of the measurement.

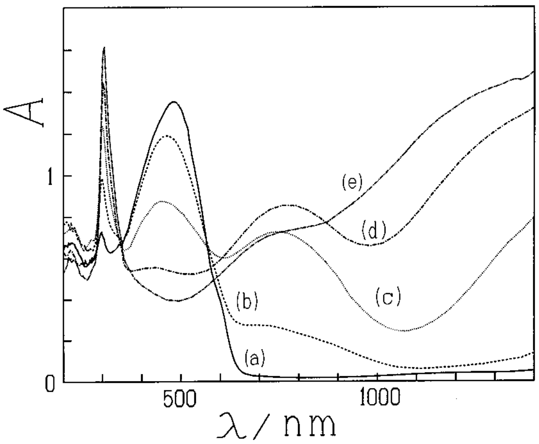

Fig. 4. UV-vis spectra of the film without oxidation (a), with oxidation at (b) 0.3; (c) 0.5; (d) 0.7; and (e) 0.9 V.

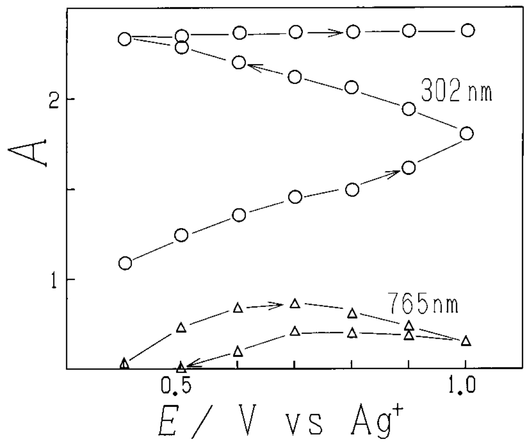

Fig. 5. Variations of absorbances at 302 nm (circle) and 765 nm (triangle) with the applied potential. Each point was taken successively after 5 min potential application.

The higher is the crosslinking level, generally the poorer is the solubility of a polymer. We determined the solubility of the chemically synthesized poly(3-hexylthiophene) film in chloroform at various oxidation potentials. When the film was oxidized electrochemically and transferred into chloroform solution, it showed actually no solubility. If it was reduced for a short time in acetonitrile, it had finite solubility in chloroform. Thus we oxidized the film at various potentials for 1 h in 0.1 M TBATFB + acetonitrile solution, reduced it at -0.5 V for 5 min followed by rinsing it with acetonitrile, and immersed it for 3 h in chloroform, which was then analyzed spectroscopically at 436 nm ($\pi \rightarrow \pi^*$ transition). Fig. 6 shows dependence of the insolubility, $1 - A/A_0$, on the oxidation potential, where A_0 is the absorbance without the oxidation. Films oxidized at $E < 0.3$ V were completely dissolved in chloroform. The film became insoluble with a positive shift of the potential. The film oxidized at $E > 0.9$V took on a gel form which was insoluble. Although the insolubility should be related with the swelling in conjunction with crosslinking and molar mass, it does not have a simple relation with ℓ/ℓ_0, as shown in Fig. 6.

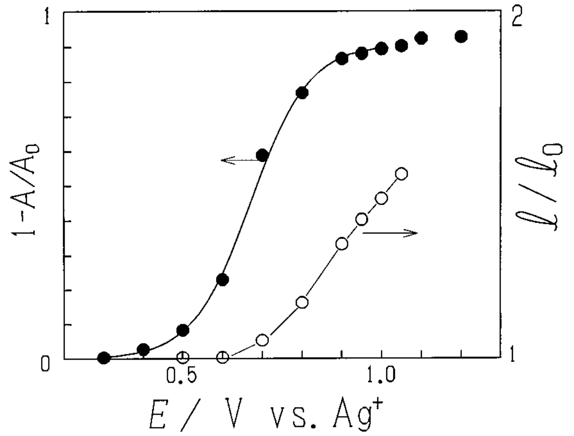

Fig. 6. Dependence of the insolubility of the film to chloroform on the potential, which was applied to the film for 1 h in acetonitrile solution. The insolubility is defined as $1 - A/A_0$, where A is the absorbance of the dissolved polymer in chloroform at 436 nm, and A_0 is the absorbance without the electrochemical oxidation. The right abscissa shows the swollen length which was displayed in Fig. 1. The solid curve on the plot of $1 - A/A_0$ was calculated by combination of the Nernst equation and the mass balance for $E^{\circ\prime} = 0.67$ V and $\alpha = 0.35$.

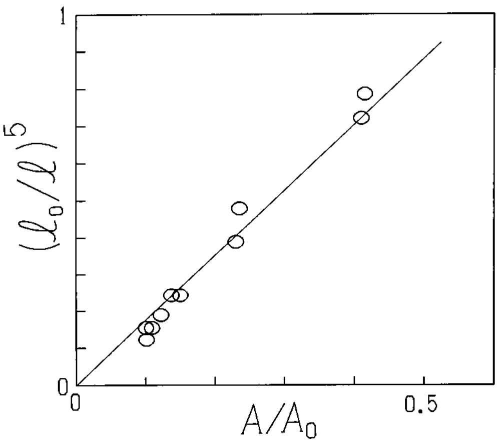

Fig. 7. Dependence of $(\ell/\ell_0)^5$, indicating the number of crosslinked polymers in the film, on the solubility A/A_0 of the film that was oxidized electrochemically.

We consider in more detail the relation between the solubility, the swelling, the crosslinking and the oxidation potential. Intuitively the crosslinking increases the insolubility and the swelling ratio unless it occurs so highly as to block the penetration of solution. The solubility decreases generally with an increase in the molar mass. As the molar mass increases by crosslinking polymer chains, the amount of uncrosslinked polymer decreases. For the simplest case, the solubility may be proportional to the amount of polymer, v_e, that is $A/A_0 = kv_e$. The relation between the swelling and v_e reminds us of Flory's theory of the swelling of gels [30]. According to the theory, the one-dimensional swollen length is given by

$$\frac{\ell}{\ell_0} = \left[\frac{V_0}{v_e}\left(\frac{1}{2} - \chi_1\right)v_1\right]^{1/5} \qquad (1)$$

where V_0 is the volume of the film before the swelling, χ_1 is the interaction parameter between the solvent and the polymer, and v_1 is the volume fraction of the solvent in the gel. Substitution of $A/A_0 = kv_e$ into Eq. (1) gives

$$\left(\frac{\ell_0}{\ell}\right)^5 = k'\left(\frac{A}{A_0}\right) \qquad (2)$$

We plotted in Fig. 7 values of $(\ell/\ell_0)^5$ against A/A_0 corresponding to the same potential as $(\ell/\ell_0)^5$. Except for the domain of the sufficiently dissolved film, the plot fell on a straight line through the origin. The excellent proportionality may be ascribed to weak dependence of χ_1 and v_1 on the oxidation. However, the present analysis does not always justify Flory's theory because it includes ambiguity in the parameters.

The insolubility caused by the oxidation suggests electrochemically irreversible crosslinking, which may be expressed by the electrode reaction: $M \rightarrow M^+ + e^-$ followed by a chemical chain reaction: $nM^+ \rightarrow M_n$. The equilibrium concentration of M^+ is represented by the Nernst equation: $[M^+] = 1/[1 + \exp(\alpha F(E - E^{\circ\prime})/RT)]$, where α is a fractional number of electrons per electroactive site, usually ranging from 0.2 to 0.5 [16,23,31,32]. The mass balance leads to $[M^+] + n[M_n] = \text{const}$. Since M_n is scarcely soluble, its concentration is proportional to $1 - A/A_0$. Thus $1/[1 + \exp(\alpha F(E - E^{\circ\prime})/RT)]$ should have a linear relation with $1 - A/A_0$. Unfortunately, the relation includes the unknowns α and $E^{\circ\prime}$. We attempted to find the linearity by inserting various values of α and $E^{\circ\prime}$. Then the best linearity was obtained with $E^{\circ\prime} = 0.67$ V and $\alpha = 0.35$. From these values, values of $1 - A/A_0$ were calculated. The result is shown as a solid curve in Fig. 6. Agreement of the simulation is excellent, indicating that the insolubility can be explained by the simple EC mechanism.

In order to interpret the macroscopic swelling with a discussion at the molecular level, we measured FTIR spectra of the oxidized film. Fig. 8 shows FTIR spectra of the poly(3-hexylthiophene) chemically synthesized (A), and electrochemically treated at 0.8 (B) and 1.0 V (C) for 1 h. Strong absorption bands at 2957, 2918 and 2856 cm^{-1} have been assigned, respectively, to the asymmetric C–H stretching vibrations in $-CH_3$ and $-CH_2-$, and the symmetric C–H stretching vibration in $-CH_2-$ [33]. They are ascribed to the hexyl-side chain. Since the methyl group is not electroactive in the present potential domain, we regarded the absorbance at 2957 cm^{-1} as a reference for normalizing the other absorbances. The bands at 3057 and 828 cm^{-1} have been assigned, respectively, to the stretching vibration of CH in the aromatic =C–H and the =C–H out-of-phase deformation of aromatic =C–H. Both should be ascribed to the 4-position of the thiophene ring. The ratio of absorbance A at 828 cm^{-1} for the film with potential applied to that for the film before the potential application decreased with the positive potential shift, as shown in Fig. 9. The variation is very similar to that of $(\ell/\ell_0)^5$ although the direction of the variation is opposite. This correspondence indicates that the swelling is due to the loss of the aromatic =C–H. If the relation between $A_{828}/(A_{828})_0$ and $(\ell/\ell_0)^5$ is combined with the proportionality depicted in Fig. 7, it turns out that A_{828} should be proportional to V_0/v_e. In other words, the number of the decomposed thiophene rings has a linear relation with the volume of a crosslinked polymer, or the decomposition causes the crosslinking by an equivalent amount. Thus a possible mechanism of the electrochemical oxidation is the oxidation at the sulfur of the thiophene ring, and stabilization by resonance followed by the activation at the 4-position of the thiophene ring, which causes coupling with other rings to generate a crosslinked network.

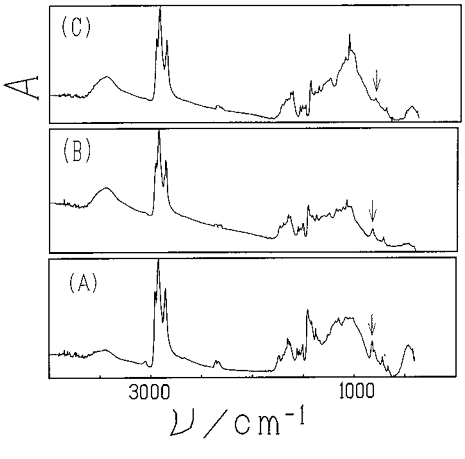

Fig. 8. FTIR spectra of the chemically prepared films (A), potential-applied films at 0.8 V (B) and 1.0 V (C) for 1 h. The arrow is at 828 cm^{-1}.

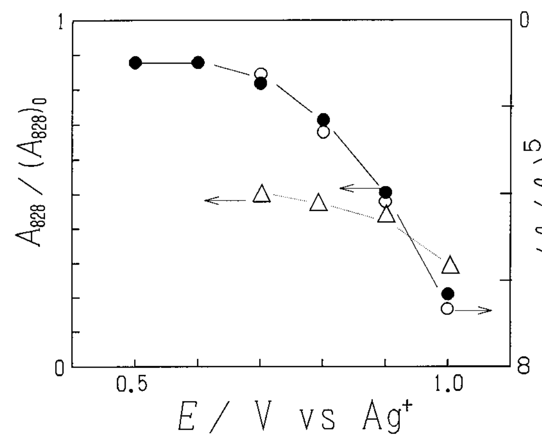

Fig. 9. Variation of the FTIR absorbance A (on the left ordinate) at 828 cm^{-1} for the chemically synthesized films (circle) and the electrochemically synthesized films (triangle) which were oxidized at various potentials. The plots were normalized by the absorption A_0 at 828 cm^{-1} of the film without electrochemical treatment. They agree with variation of $(\ell/\ell_0)^5$ on the right ordinate (with an increase downward).

All the discussion above was for crosslinking by the electrochemical oxidation of the chemically synthesized film. A question arises on the crosslinking of an electrochemically native-born film, because the synthesized film must include the electrochemical crosslinking simultaneously. Since the galvanostatic polymerization started at 3.5 V, the film should be subjected to the crosslinking. Indeed, FTIR spectra showed the appearance of the band at 828 cm^{-1}. When the film was further oxidized for 1 h in a solution of 0.1 M TBATFB + acetonitrile, the absorbance at 828 cm^{-1} decreased with the positive shift of the potential, as shown in Fig. 9. Consequently, the electrochemically synthesized film has been partially crosslinked. Cyclic voltammograms (b,c,d in Fig. 2) of the electrochemically synthesized film lost the electrochemical activity gradually with a longer oxidation time. This is consistent with the loss of conductance in Fig. 3.

Crosslinking is usually a result of radical formation by benzoyl peroxide (BPO). We compared FTIR spectra of the electrochemically oxidized gel with those of the crosslinked polymer by BPO [3–8]. When the BPO-crosslinked film was transferred into ethanol, it shrank into half the volume. Therefore it is a kind of gel. It showed the same absorbance at 828 cm^{-1} as the film without the electrochemical oxidation. Thus the aromatic =C–H is retained in the BPO-crosslinked film whereas it disappeared owing to the gelation in the electrochemical oxidation. The absorbances at 2918 and 2856 cm^{-1} were 15% less than those for the film without the electrochemical oxidation. Consequently, the crosslinking occurs in the hexyl chain. This is quite different from the gelation by the electrochemical oxidation.

4. Conclusion

The electrochemical oxidation of poly(3-hexylthiophene) films caused crosslinking to yield a permanent gel, which was swollen in chloroform. Further, it caused a red shift of the $n \rightarrow \pi^*$ transition, a decrease in the electric conductance, a decrease in solubility in chloroform in the short term reduced state, and a decrease in the amount of =C–H group. The variation of the solubility was related to the oxidation through the reaction $n\mathrm{M} + n\mathrm{e}^- \rightarrow \mathrm{M}_n$. It was also correlated with the volume change through Flory's theory. The long term oxidation decomposed a 4-position of the thiophene ring to cause the red-shift of the lone pair at the sulfur of the thiophene ring. Thus it blocks the resonance on the original polythiophene chains, and hence both conductance and electrochemical activity of voltammetry decreased with the oxidation. Thus, most observations can be explained consistently.

The electrochemical crosslinking is different from the crosslinking by BPO in that the conjugation by polythiophene chains is destroyed. Therefore it is unsuitable to produce an electronic conducting gel. However, it generates a gel with a large volume change.

Acknowledgements

This work was supported by Grants-in-Aid for Scientific Research (Grant 09237228) from the Ministry of Education in Japan.

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