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Electrochemical copolymerization of furan and 3-methyl thiophene

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Electrochemical copolymerization of furan and 3-methyl thiophene was performed potentiostatically in a binary solvent system consisting of boron trifluoride-ethyl ether and additional ethyl ether (mole ratio 2:1). The product obtained was characterized by cyclic voltammetry and infrared spectroscopy. The influence of polymerization potential on the synthesis of the copolymer was investigated. The lower potential favored the incorporation of furan units into the copolymer. The conductivities of synthesized homopolymers and copolymers were determined by the four-probe technique. Thermogravimetric analysis (TGA) was also carried out to investigate the properties of the copolymer.

1. Introduction

Conducting polymers have many potential applications, such as new materials for battery electrodes [1], gas sensors [2], chemical sensors [3], ion sieving [4], corrosion protection [5], and microwave shielding [6]. Especially, extensive research has been focused on the polymerization of five-member heterocyclic compounds such as pyrrole and thiophene [1–7]. Copolymerization is an important method to develop the properties of individual polymers. So far copolymers of pyrrole with furan [8], pyrrole with bithiophene [9], pyrrole with aniline [10], 3-methyl thiophene with 3,4-ethylenedioxythiophene [11], have been prepared successfully by electrolytic oxidation of mixtures of the monomers.

However polyfuran (PFu), because of the great difficulty of its synthesis in conventional solvent systems, is rarely copolymerized with other heterocycles. Recently, we successfully prepared and characterized PFu[12, 13] and poly(3-methyl thiophene) (PMth) [14] in a similar solvent system. Therefore it is expected to copolymerize these two monomers via electrochemical oxidation of the monomer mixtures.

In this paper the copolymers obtained have been characterized by Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). In addition, the influence of the applied polymerization potential on the properties of the copolymer is discussed.

2. Experimental

2.1. Materials

Furan (Fluka, Buchs, Switzerland, 99%) and 3-methyl thiophene (Aldrich, 98%) were distilled under a nitrogen atmosphere just prior to use. Ethyl ether (EE) was dried and distilled in the presence of sodium. Boron trifluoride-ethyl ether (BFEE) was freshly distilled before use. Tetrabutylammonium tetrafluoroborate (TBATFB) was dried under vacuum at 80°C for 24 h. Acetonitrile was dried and distilled before use.

2.2. Electrochemical experiments

The electrochemical examinations and polymerizations were performed in a one-compartment, three electrode cell with the use of an EG&G model 283 potentiostat (Princeton, NJ) under the control of a computer at room temperature. The potentiostatical method was used for the electrochemical polymerization. The free standing film were obtained using stainless steel plates (1.5×2 cm^2) as the working electrode and counter electrode, which was polished with abrasive paper and diamond paste and then washed with acetone. Electrochemical behaviors were investigated with a platinum disc electrode (1.96×10^{-3} cm^2) that was polished and cleaned before each experiment. An Ag/AgCl (0.1 M KCl) electrode was used as the reference electrode, and TBATFB was used as an electrolyte in organic solvents in all cases. The solution was deareated by the bubbling of dry argon before each electrochemical experiment and a slight argon overpressure was maintained during the experiment. The platinum disc with precipitates was dried and then put into a monomer-free acetonitrile solution to obtain the cyclic voltammograms.

2.3. Spectroscopy experiments

FTIR spectra were recorded on an IFS-66V spectrometer (Bruker, Germany). Copolymer, PMth and PFu films were deposited onto a stainless steel electrode (1.5×2 cm^2) and they were then stripped off from the electrode. The films were dedoped with 20%

ammonia solution, washed with distilled water and acetone, and then dried under vacuum at 80°C for 24 h before spectroscopic characterization.

2.4. Measurement of thermal and electrical properties

TGA was performed in an SDF2960 thermal analyzer (TA Instruments, U.S.A.). TGA measurements were done under a nitrogen atmosphere at a temperature from 25 to 800°C at a heating rate of 20°C/min. The obtained films were first washed well with acetone before being stripped off the electrode and then dried under vacuum at ambient temperature. The conventional four-probe method was utilized to measure electrical conductivity.

3. Results and discussion

3.1. Electrochemical preparation and characterization

The current-potential curves taken in quiet solution at a potential sweep rate of 20 mV/s are given in Fig. 1. It should be noticed that the background electrolyte is electrochemically silent in the whole potential range. It can be seen that the polymerization threshold (i.e., the lowest potential needed to allow the growth of a polymer layer) of furan is 1.05 V versus Ag/AgCl/0.1 M KCl (curve c) and that of 3-methyl thiophene is 1.26 V versus Ag/AgCl/0.1 M KCl (curve a). The small distinction between the oxidation potential of the two monomers suggests a great possibility of the copolymerization of the two monomers. When a current potential curve was taken in a BFEE + EE (mole ratio 2:1) containing 0.05 M furan and 0.1 M 3-methyl thiophene, curve b was obtained. However the superposition of curve a and curve c does not add up strictly to curve b. The current of curve b is smaller than that of curve a (3-methyl thiophene) but larger than that of curve c (furan). This may be due partly to some change in the electrochemical environment such as electrode roughness caused by successive deposition of the two monomers during the course of current-potential curve measurements and due partly to the influence of the low electric conductivity accompanying the incorporation of furan ring in the copolymer chain. In addition, it should be noticed that the oxidation potential of the mixture of furan and 3-methyl thiophene is about 1.10–1.20 V, which is between the oxidation potentials of two monomers, indicating that the two monomers are oxidized alternately and the copolymer chains are composed of alternate furan and 3-methyl thiophene units.

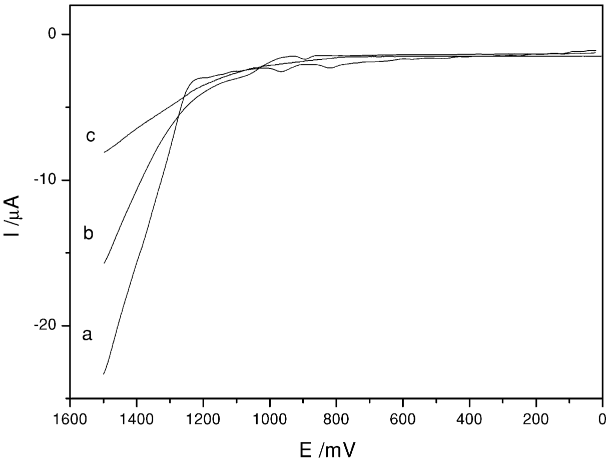

Figure 1 The current-potential curves of (a) 0.1 M 3-methyl thiophene, (b) 0.1 M 3-methyl thiophene and 0.05 M furan and (c) 0.05 M furan in BFEE + EE (mole ratio 2:1). Scan rate: 20 mV/s. Reference electrode: Ag/AgCl/0.1 M KCl.

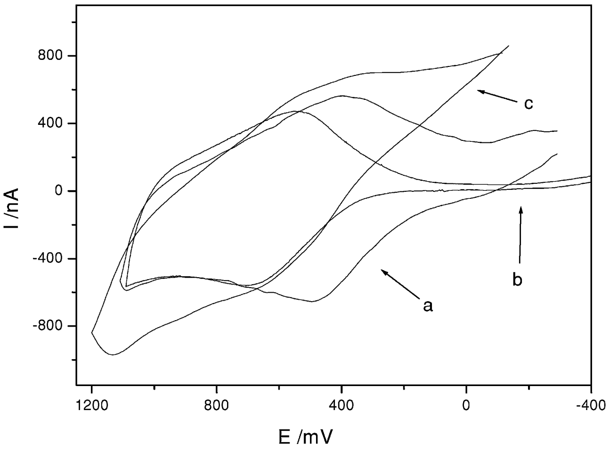

Figure 2 The cyclic voltammograms recorded in acetonitrile + 0.01 M $TBABF_4$ solution of (a) pure PMth, (b) pure PFu prepared from BFEE + EE (mole ratio 2:1) solution containing each monomer and (c) copolymer prepared at 1.2 V from BFEE + EE (mole ratio 2:1) solution containing 0.1 M 3-methyl thiophene and 0.05 M furan. Scan rate: 20 mV/s.

The copolymerization is carried out under different potentiostatic conditions. Fig. 2 shows the cyclic voltammogram of the copolymer prepared at 1.2 V vervus Ag/AgCl/0.1 M KCl, together with those of pure PMth and pure PFu. Only one anodic/cathodic peak current couple appears in the copolymer film, which is different from those of PMth and PFu. The appearance of one redox peak of the copolymer indicates uniform redox properties, which is accordance with the current-potential curve in the solution containing 0.1 M 3-methyl thiophene and 0.05 M furan in Fig. 1b. Furthermore, another noticeable feature is that both the cathodic current and the anodic one are higher than those of pure PMth and pure PFu. This result shows that the electrochemical activity of the copolymers is higher after the same time of polymerization. However, when the preparation potential increases to 1.5 V vervus Ag/AgCl/0.1 M KCl, the copolymer undergoes irreversible oxidation in the acetonitrile solution. It is due to the destruction of the conjugated structure of the copolymer when the polymerization potential is too high [8].

And the cyclic voltammograms of the copolymer film obtained at 1.2 V remain quite steady during the scanning process, as shown in Fig. 3. So it can be concluded that the copolymer film obtained shows good long-term stability of the redox activity in acetonitrile solution.

3.2. Spectroscopy measurements

The FTIR spectra of the copolymers deposited potentiostatically from BFEE + EE (mole ratio 2:1) solution containing 0.1 M 3-methyl thiophene and 0.05 M furan at different polymerization potential are compared with

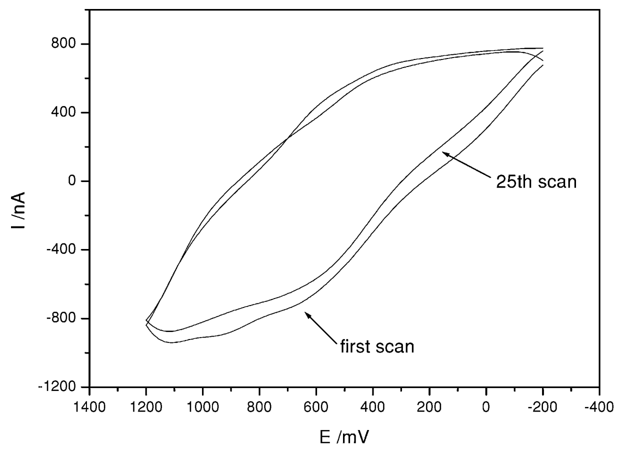

Figure 3 The cyclic voltammograms recorded in acetonitrile + 0.01 M $TBABF_4$ solution of copolymer prepared at 1.2 V from BFEE + EE (mole ratio 2:1) solution containing 0.1 M 3-methyl thiophene and 0.05 M furan. Scan rate: 20 mV/s.

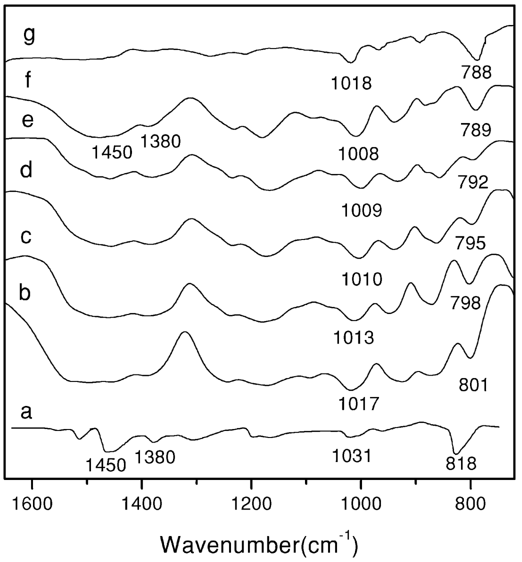

Figure 4 Infrared spectra of (a) pure PMth, (b) copolymer prepared from BFEE + EE (mole ratio 2:1) solution containing 0.1 M 3-methyl thiophene and 0.05 M furan at 1.5 V, (c) at 1.4 V, (d) at 1.3V, (e) at 1.2 V, (f) at 1.1 V and (g) pure PFu.

those of pure PFu and pure PMth in Fig. 4. The characteristic peaks of pure PFu and pure PMth could be found in the spectrum of the copolymer. In the spectrum of PMth the peaks located near 1380 and 1450 cm^{-1} are assigned to the deformation of the CH_3 group [15, 16]. In the spectra of the copolymers there are also two absorption bands located around 1380 and 1450 cm^{-1}, indicating the 3-methyl thiophene units are contained in the copolymer chain.

The evolution of the absorption bands located around 1020 cm^{-1} with the change of the polymerization potential is also interesting. In the spectrum of PFu, the single peak located near 1018 cm^{-1} is ascribed to the in-plane vibration combination of C—O stretching vibration, C—H in-plane bending and ring deformation [12, 17]. In the spectrum of PMth, the band near 1031 cm^{-1} is assigned to the symmetric in-plane C—H deformation [15, 16]. However in the spectra of copolymer deposited at different potential, although the bands seem similar in shape to that of PFu, the absorption peak center shifts gradually from 1008 cm^{-1}(prepared at 1.1 V) to 1017 cm^{-1} (prepared at 1.5 V). The peaks differ apparently from those of PMth in this region. This may be due to the interaction between furan units and 3-methylthiophene units in the copolymer and may be regarded as evidence of copolymerization distinguishing itself from the simple addition of the spectra of pure polymers, for the simple addition of the spectra of pure polymers would imply that the composites of PFu and PMth were formed.

Furthermore, the other noticeable feature in the spectra is an absorption band around 790 cm^{-1}, which is a characteristic of α-substituted five-member heterocyclic compounds [18]. The strong absorption peaks appear at 788 cm^{-1} for pure PFu and 818 cm^{-1} for pure PMth, respectively, which is attributed to the out-of-plane C—H bending of 2,5-disubstituted rings. With the increase of the polymerization potential, the peaks of the copolymer shift from 789 to 801 cm^{-1}, indicating that the amount of 3-methyl thiophene units incorporated into the copolymer increases with the increasing preparation potential. All these features suggest that copolymerization occurs in the potentiostatic electrochemical polymerization of furan and 3-methyl thiophene, which is accordance with the conclusions of the cyclic voltammetry.

3.3. Thermal and electrical analysis

The curves of TGA of PFu, PMth and copolymer are given in Fig. 5. The values of TGA results were also tabulated in Table I. As seen from the table, it is clear that the initial temperature of decomposition of PFu is much lower than that of PMth, implying that PMth is more stable than PFu. However, the copolymer begins to decompose at the temperature, which is the same as the initial decomposition temperature of PFu and with the increase of temperature, the behavior of decomposition is like that of PMth. This may be due to relative short chains of furan units and relative long chains of 3-methyl thiophene units in the copolymer, which can be explained by the difference of the activity of the radical cation as its electrooxidation mechanism [19].

The conductivities of PFu, PMth and the copolymers prepared in different electrochemical polymerization

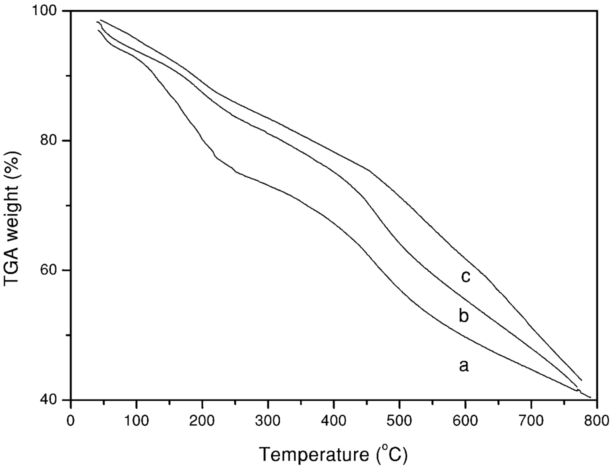

Figure 5 TGA curves of (a) pure PFu, (b) copolymer prepared at 1.2 V from BFEE + EE (mole ratio 2:1) solution containing 0.1 M 3-methyl thiophene and 0.05 M furan and (c) pure PMth.

TABLE I The values of TGA results of polymer

Polymer	Initial decomposition temperature (°C)	Maximum decomposition temperature (°C)	Final decomposition temperature (°C)
Copolymer in 1.2 V	190	330	453
PFu	185	253	312
PMth	228	344	470

TABLE II The conductivities of PFu, PMth and the copolymers prepared in different electrochemical polymerization potential

Polymer	Conductivity (S/cm)
Copolymer in 1.1 V	0.28
Copolymer in 1.2 V	0.36
Copolymer in 1.3 V	0.25
Copolymer in 1.4 V	0.12
Copolymer in 1.5 V	0.07
PFu	0.008
PMth	0.76

potential are listed in Table II. It could be found that the conductivities of the copolymers are between the conductivities of pure PFu and PMth. And it is noticed that when the electrochemical polymerization potential is 1.2 V, the conductivity of copolymer reaches the maximum value, which is much higher than the conductivity of the bipolymer film polyfuran/polythiophene and polythiophene/polyfuran reported by Talu *et al.* [20]. However, when the preparation potential increases to 1.5 V, the conductivity of copolymer decreases to only 0.07 S/cm, which is about five times lower than the maximum. The decrease of conductivities is ascribed to the destruction of the conjugated structure of the copolymer when the potential applied in synthesis is too high [8].

4. Conclusions

Electrochemical copolymerization of furan and 3-methyl thiophene was successfully realized in a binary system consisting of boron trifluoride-ethyl ether and additional ethyl ether (mole ratio 2:1) solution by the potentiostatic method. The electrochemical properties of the copolymer film obtained were investigated using cyclic voltammetry techniques, which indicates that the copolymer has intermediate properties between pure PFu and pure PMth, together with infrared spectroscopy and thermogravimetric analysis. The higher is the applied potential, the more 3-methyl thiophene units are incorporated into the copolymer. While the polymerization potential is too high, it destructs the conjugated structure of the copolymer and decrease the conductivity of the copolymer.

Acknowledgements

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