

Electrochemical Copolymerization of Indole and 3-Methylthiophene

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Received 2 August 2006; accepted 14 November 2006

DOI 10.1002/app.25861

Published online 5 March 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The copolymerization of indole (In) and 3-methylthiophene (3MeT) was successfully achieved electrochemically in boron trifluoride diethyl etherate (BFEE) by direct anodic oxidation of the monomer mixtures on stainless steel electrodes although their respective oxidation potentials were quite different. The electrochemical properties of the copolymers were studied by cyclic voltammetry. As-formed free-standing insoluble copolymers owned both the advantages of polyindole (PIn) and poly(3-methylthiophene) (P3MeT), i.e., good thermal stability, good electrochemical activity, and high conductivity. The insert of 3MeT units in PIn was helpful to improve the conductivity of PIn and the insert of In units in P3MeT was also beneficial to improve the electrochemical and thermal stability of P3MeT. The influ-

ence of applied polymerization potential on the synthesis of copolymer was investigated. The higher potential favored the incorporation of 3MeT units into the copolymers. 1.3 V vs. SCE was tested to be the best potential for the electrochemical copolymerization of In and 3MeT. The structure and morphology of the copolymers were investigated by UV-vis spectroscopy, infrared spectroscopy, thermal analysis, and scanning electron microscopy (SEM), respectively. Polymerization mechanism studies showed that the polymerization of indole ring occurred at 2,3 position. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3129–3136, 2007

Key words: conducting polymers; poly(3-methylthiophene); polyindole; copolymerization; electrochemistry

INTRODUCTION

Inherently, conducting polymers with π -conjugated electronic structures have been widely investigated since the late 1970s^{1–3} because of their wide fundamental interest and potential industrial applications based on their high conductivity and good environmental stability. Among these polymers, polyindole (PIn)^{4–7} and poly(3-methylthiophene) (P3MeT)^{8–11} have been received a significant share of attention. PIn owns several advantages, especially fairly good thermal stability because of the incorporation of benzene rings on the polymer backbone⁶ and high redox activity and stability.^{12,13} Therefore, PIn may be a good candidate for applications in various domains like electronics, electrocatalysis, and anticorrosion coatings. However, PIn has relatively low electrical conductivity, close to 10^{-1} S cm⁻¹ in the doped state,^{14–16} which

may inhibit its applications. On the other hand, P3MeT, as an important derivative of polythiophene, has led to numerous applications in the areas of microelectronics,¹⁷ optoelectronics, and sensors¹⁸ owing to its high conductivity and high tensile strength and flexibility. However, the thermal property of P3MeT films is relatively poor in contrast to PIn film, which also brings some obstacle to its applications.

Recently, research works have been focused on the copolymerization to prepare conducting polymers with better properties and to overcome the limitation of the rarity of new monomers. By means of the electrochemical copolymerization, some new conducting copolymers have been prepared with obvious advantages, such as variations of conductivity, enhancements of electrochemical activity, and thermal stability. Up to now, 3MeT-based copolymers^{19–27} have been prepared successfully by direct electrochemical oxidation of the mixtures of 3MeT with other corresponding monomers. On the other hand, electroactive copolymers with improved physical and chemical properties obtained from In with different monomers have also been electrochemically synthesized.^{13,28,29}

It is well known that high quality free-standing films of P3MeT³⁰ and PIn¹⁶ can be produced by direct anodic oxidation of corresponding monomers in boron trifluoride diethyl etherate (BFEE). The interactions between the middle strong Lewis acid, BFEE,

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Contract grant sponsor: New Century Excellent Talents in University; contract grant number: NCET-04-0649.

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20275020.

Contract grant sponsor: Special Project of Qingdao for Generalship of Science and Technology; contract grant number: 05-2-JC-80.

Journal of Applied Polymer Science, Vol. 104, 3129–3136 (2007)
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and the aromatic monomers lower their oxidation potentials and the catalytic effect of BFEE facilitates the formation of high quality freestanding P3MeT and PIn films. Under these circumstances, BFEE serves not only as the solvent but also as the supporting electrolyte and no other supporting electrolyte is needed.³¹ However, freestanding PIn films with relatively poor conductivity obtained from BFEE are brittle in contrast to P3MeT films. According to the strategy of electrochemical copolymerization mentioned earlier, copolymers of In and 3MeT would extend the applications of PIn and P3MeT. On the basis of the traditional view of electrocopolymerization, the success of copolymerization is mainly because of the closeness of the oxidation potentials of two monomers. Unfortunately, the oxidation potentials of 3MeT and In are quite different, which make it a challenge to achieve the electrochemical copolymerization of 3MeT and In. To the best of our knowledge, electrochemical copolymerization of In with 3MeT in BFEE has not been reported so far. In addition, there were two main opinions on the electrochemical polymerization mechanism of indole, 1,3 position or 2,3 position (Scheme 1). Copolymerization of In and 3MeT may be helpful to interpret the debating of polymerization mechanism. On the basis of these considerations, it would be interesting to copolymerize In with 3MeT electrochemically so that as-formed copolymer may have both the advantages of high conductivity of P3MeT and good environmental stability of PIn.

In this article, In and 3MeT were copolymerized successfully by direct electrochemical oxidation of the monomer mixtures. The electrochemistry of PIn, P3MeT, and copolymers were studied. In addition, the thermal stability, spectroscopic properties, conductivity, and morphology of the copolymer were also investigated in detail.

EXPERIMENTAL

Materials

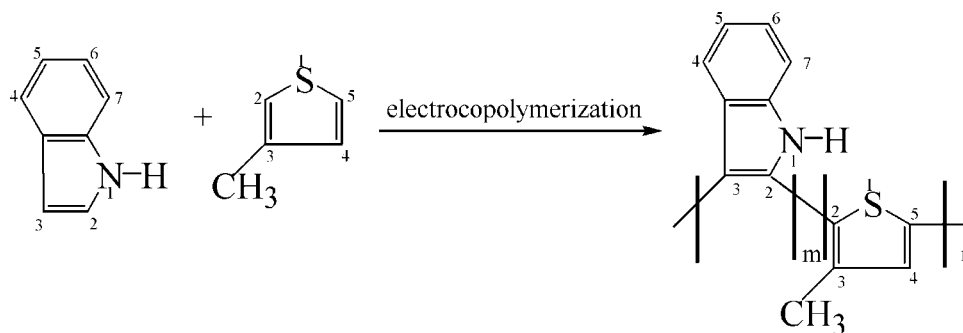
3MeT (99%, Acros Organics, Fair Lawn, NJ) was used as received without further purification. In (Shanghai

Laize Fine Chemical Plant, Shanghai, China) was purified by recrystallization from methanol and distilled water. BFEE (Beijing Changyang Chemical Plant, Beijing, China) was distilled and stored at -20°C before use. Ammonia (25%), made by Jinan Chemical Reagent Company (Jinan, China), was used as received.

Electrochemical experiments

Electrochemical syntheses and examinations were performed in a one-compartment cell with the use of a Model 263 potentiostat-galvanostat (EG and G Princeton Applied Research, Oak Ridge, TN) under computer control at room temperature. The working and counter electrodes for cyclic voltammetry experiments were stainless steel wires with diameter of 1 mm placed 0.5 cm apart. To obtain a sufficient amount of polymer for characterization, stainless steel sheets with a surface area of 10 and 12 cm^2 each were employed as the working and counter electrodes, respectively. Electrodes mentioned earlier were carefully polished with abrasive paper (1500 mesh), and cleaned by water and acetone successively before each examination. The polymers were deposited on indium-tin-oxide (ITO) coated glass for UV-vis spectral measurements. The electrochemical dedoping of polymer films was performed at a constant potential of 0 V in a monomer-free BFEE solution until the current density was close to zero. All potentials were referred to a saturated calomel electrode (SCE).

All the samples were grown in BFEE without any supporting electrolyte. All solutions were deaerated by a dry argon stream and maintained at a slight argon overpressure during experiments. The amount of polymer deposited on the electrode was controlled by the integrated charge passed through the cell. PIn films were prepared at 1.1 V vs. SCE in BFEE containing 0.01 mol L^{-1} In, and P3MeT films were obtained at 1.4 V vs. SCE in BFEE-containing 0.15 mol L^{-1} 3MeT monomer. To remove the electrolyte and oligomers/monomers, the polymer films were rinsed with water and acetone. For spectral analysis, the polymer was dried *in vacuo* at 60°C for 2 days.



Scheme 1 Electrochemical copolymerization route of In and 3MeT.

Characterizations

The conductivity of as-formed polymer films was measured by the conventional four-probe technique. UV-vis spectra were taken by using a Cary 500 UV-vis-NIR spectrophotometer. Infrared spectra were recorded using a Nicolet 510P FTIR spectrometer with KBr pellets. The thermogravimetric analysis (TGA) was performed with a thermal analyzer of NETZSCH TG209. All thermal analysis was performed under a nitrogen stream in the temperature range of 25–800°C with a heating rate of 10°C/min. Scanning electron microscopy (SEM) measurements were taken by using a JEOL JSM-6700F SEM.

RESULTS AND DISCUSSION

Electrochemical copolymerization

To ensure the copolymerization of In and 3MeT in BFEE, the electrochemical experiments were classified into different groups on the basis of feed ratios of the two monomers. The similar results obtained from earlier different experiments were that the oxidation potential of 3MeT was much higher than that of In ($\Delta E > 0.3$ V), where ΔE is the difference of the oxidation potentials between In and 3MeT. It is well known that successful electrochemical copolymerization of different monomers is because of the fact that the oxidation potentials of the monomers are close to each other.³² From this point, it seems that it is impossible to achieve the electrochemical copolymerization of In and 3MeT. To realize the copolymerization successfully, we tried this study by the strategy of diffusion method established by Kuwabata et al.³³ Under diffusion limited conditions 3MeT oxidation occurred, which implied that the copolymerization was feasible. For this reason, after a series of experiments with different feed ratios of In and 3MeT, the concentration of In was chosen as 0.01 mol L⁻¹, while that of 3MeT was 0.15 mol L⁻¹.

Figure 1 shows the typical anodic polarization curves taken in BFEE at a potential scanning rate of 20 mV s⁻¹. It should be noted here that the background electrolyte was electrochemically silent in the whole potential range.³⁴ The oxidation onset of 0.15 mol L⁻¹ 3MeT was initiated at 1.18 V [Fig. 1(a)] and that of 0.01 mol L⁻¹ In was 0.86 V [Fig. 1(b)]. When the electrolytic solutions contained 0.01 mol L⁻¹ In and 0.15 mol L⁻¹ 3MeT, the anodic curve [Fig. 1(c)] was different from the curves a and b. It can be seen that the oxidation onset of the mixture of two monomers was initiated at 0.96 V, which was intervenient between In and 3MeT. This may be partly because of some changes of the electrochemical environment caused by successive deposition of the two monomers during the anodic polarization,^{19,32} or partly because of the influence of the low electric conductivity accom-

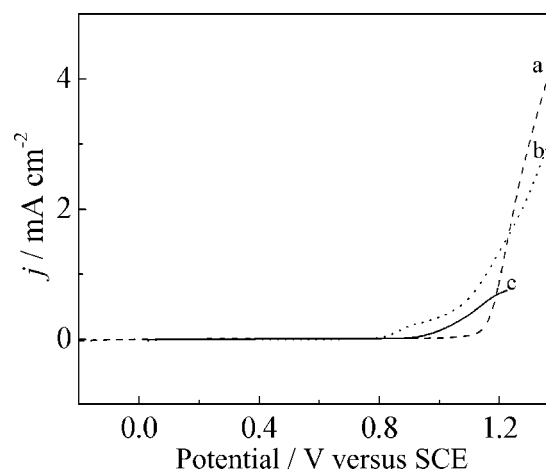


Figure 1 Anodic polarization curves of (a) 0.15 mol L⁻¹ 3MeT, (b) 0.01 mol L⁻¹ In, and (c) 0.01 mol L⁻¹ In + 0.15 mol L⁻¹ 3MeT in BFEE, respectively. Scanning rates: 20 mV s⁻¹.

panied by the incorporation of In unit into the copolymer chain. In addition, the fact that the oxidation potential of the mixture of In and 3MeT was between that of the two monomers suggested that the two monomers were oxidized alternately and the copolymer chains were composed of alternate In and 3MeT units, indicating the occurrence of copolymerization.^{13,35}

Electrochemistry of the copolymer films

The films of PIn, P3MeT, and copolymer of In and 3MeT were electrodeposited potentiostatically from BFEE after the same polymerization time. The successive cyclic voltammograms (CVs) of PIn, P3MeT, and copolymer recorded in monomers-free BFEE were given in Figure 2, respectively. As illustrated in this figure, only one anodic/cathodic wave-current couple appeared in the CVs of copolymer film, which was different from those of PIn and P3MeT. In each case, five CVs were recorded to ensure reproducibility. The appearance of one redox peak of copolymer indicated uniform redox properties,¹⁹ which was also in accordance with the anodic polarization curve in the solutions containing 0.01 mol L⁻¹ In and 0.15 mol L⁻¹ 3MeT [Fig. 1(b)]. In addition, another noticeable characteristic was that the anodic and cathodic current densities of copolymer lay between PIn and P3MeT. This result implied that the electrochemical activity of copolymer film was higher than pure PIn,¹³ partly because of the influence of the high electric conductivity by the incorporation of 3MeT units into the copolymer chain. The PIn film was very stable in monomers-free BFEE while there was obvious degradation of P3MeT. This implied the electrochemical stability of PIn was better than P3MeT. As was shown in Figure 2(c), there was degradation of the copolymer obtained at 1.3 V in comparison with PIn during cycling

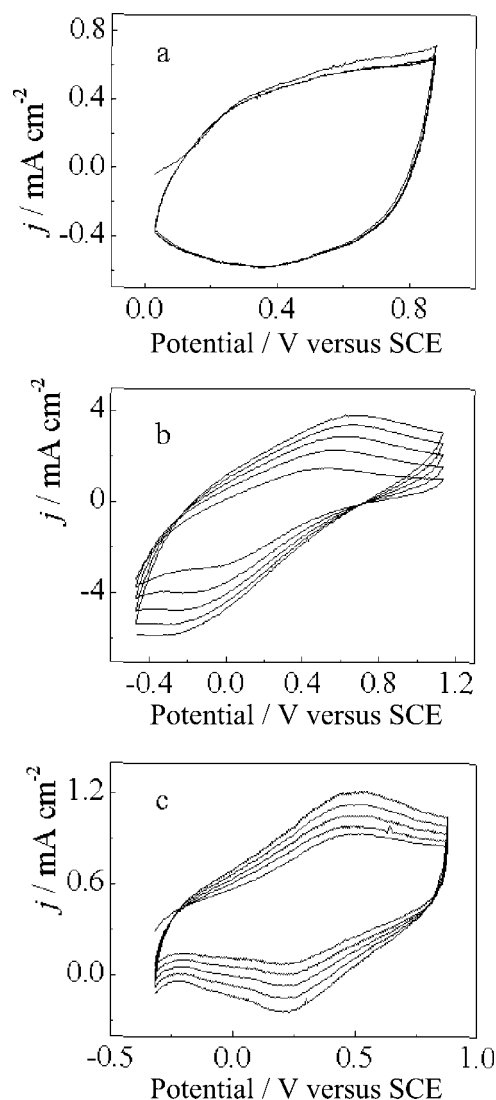


Figure 2 Cyclic voltammograms recorded in monomers-free BFEE of (a) PIn, (b) P3MeT, and (c) copolymer prepared from BFEE solution containing 0.01 mol L^{-1} In and 0.15 mol L^{-1} 3MeT. Scanning rates: 50 mV s^{-1} .

because of the incorporation of 3MeT units into the copolymer chain. However, according to the wave-current density, the degree of degradation of the copolymer was less than that of P3MeT, which indicated that the insert of In units in P3MeT was also beneficial to improve the electrochemical properties of P3MeT in some degree.

To investigate deeper the electrochemical activity of copolymer films, the CVs of copolymer films prepared at different potentials were recorded in monomers-free BFEE, as shown in Figure 3. It should be noted that the growth profiles of CVs of copolymer films obtained at 1.2 and 1.4 V were similar to those of 1.1 and 1.5 V, respectively. The redox wave values of the copolymers were listed in Table I. It can be seen from Table I that the redox potentials shifted more negatively with the increase of the applied potentials. For

example, the copolymer obtained at 1.1 V showed a couple of redox waves at 0.55 and 0.32 V, which was similar to PIn [Fig. 3(a)]. When the applied potential became 1.3 V, the redox peaks located at around 0.45 and 0.18 V, close to P3MeT. Moreover, according to the CVs in Figure 3, the difference of wave-current density was also interesting. According to Figure 3b, the anodic/cathodic wave-current densities of the copolymer prepared at 1.3 V were much higher than those obtained at other potentials, which implied that there was a distinct capacitive feature of the charge storage.³⁶ In Figure 3(b), there was an increase in the current density during the process of potential scan followed by a plateau, while the reverse course showed the discharge of the stored charge as the capacitor returned to its original state. As was shown in Figure 3, the electrochemical activity and capacitive property of the copolymer prepared at 1.3 V were better than those obtained at 1.1 and 1.5 V after the same polymerization time. This difference also confirmed the occurrence of copolymerization.²⁹

Structural characterizations

In this study, PIn, P3MeT, and copolymers were all freestanding films. As a result, they were all insoluble in strong polar solvents such as water and also insoluble in weak polar or nonpolar solvent such as acetone, tetrahydrofuran, and acetonitrile, which made it hard to take more complete characterizations.

PIn film was golden yellow in the dedoped state and dark green in the doped form, which was in accordance with the literature.^{12,16} P3MeT film changed its color from pale-blue in the doped state to red in the dedoped form. For the copolymer, its color changed from yellow green in the doped state to darkish red-brown color in the dedoped state. The UV-vis spectra

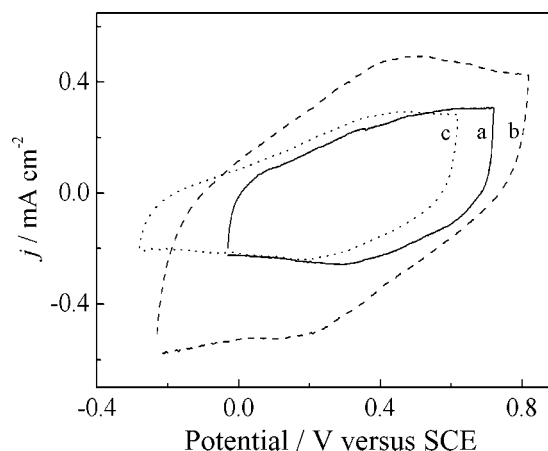


Figure 3 The cyclic voltammograms recorded in monomers-free BFEE of the copolymers prepared at (a) 1.1, (b) 1.3, and (c) 1.5 V obtained from BFEE solution containing 0.01 mol L^{-1} In and 0.15 mol L^{-1} 3MeT, respectively. Scanning rate: 100 mV s^{-1} .

TABLE I
Redox Peak Values and Conductivities of Copolymers Prepared From BFEE Solution Containing 0.01 mol L⁻¹ In and 0.15 mol L⁻¹ 3MeT at Different Polymerization Potentials

Polymerization potential (V)	1.1	1.2	1.3	1.4	1.5
Polymerization time (s)	150	150	150	150	150
Anodic potential (V)	0.55	0.51	0.45	0.47	0.42
Cathodic potential (V)	0.32	0.32	0.18	0.16	0.13
Anodic current density (mA cm ⁻²)	0.31	0.28	0.51	0.25	0.28
Cathodic current density (mA cm ⁻²)	-0.26	-0.23	-0.53	-0.20	-0.24
Conductivity (S cm ⁻¹)	0.01	0.39	1.18	0.17	0.21

of the copolymer films deposited at various potentials, pure PIn, and P3MeT were shown in Figure 4. The broadening of the absorbance peaks in comparison with the monomers implied the wide molar mass distribution of as-prepared films during the electrosyntheses. As predicted theoretically,³⁰ the spectra of the P3MeT films showed a much broader absorption at around 500 nm [Fig. 4(a)]. On the other hand, the spectra of the PIn films showed a characteristic absorption at about 398 nm [Fig. 4(b)]. The spectral profiles of the copolymers were also related to each other. Nevertheless, in contrast to PIn, there was a little bit red shift on the location of absorption maximum of copolymers because of the incorporation unit of 3MeT, further certifying the occurrence of copolymerization. Their absorption maxima ranged from 410 nm of the copolymer obtained at 1.2 V to 425 nm prepared at 1.3 V. These copolymers with different optical properties may be helpful to widen the range of PIn in fabricating electrochromic devices.¹⁸

Vibrational spectra can provide the structural information of the dedoped conducting polymers, especially for those insoluble and infusible. P3MeT, PIn, and copolymers prepared potentiostatically from BFEE

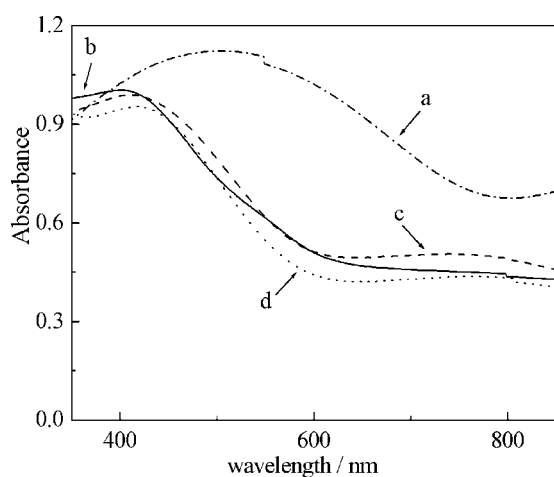


Figure 4 UV-vis spectra of dedoped (a) PIn, (b) P3MeT and copolymer films coated on an optically transparent ITO electrode at 1.2 V (c), and 1.3 V (d), respectively. The polymer films were prepared from BFEE solution containing 0.01 mol L⁻¹ In and 0.15 mol L⁻¹ 3MeT.

solution containing 0.01 mol L⁻¹ In and 0.15 mol L⁻¹ 3MeT at different applied potentials were analyzed by FTIR spectroscopy, as shown in Figure 5. The spectra of PIn and P3MeT homopolymers had several characteristic peaks at 740, 1112, 1232, 1459, 1560, 1628, 2920, and 3407 cm⁻¹ and 820, 880, 1380, 1435, 1515, 1640, 2850, 2920, 2966, and 3059 cm⁻¹, respectively. These characteristic peaks of PIn and P3MeT homopolymers can also be found in the copolymers [Fig. 5(b-f)]. From the literatures, there are two main opinions on the electrochemical polymerization mechanism of indole, 1,3 position or 2,3 position (Scheme 1). The presence or not of N-H vibration mode in the spectrum of dedoped PIn is the key factor for determining the polymerization whether happened on one position. In the case of PIn [Fig. 5(g)], the strong and broader peak at 3407 cm⁻¹ was characteristic absorp-

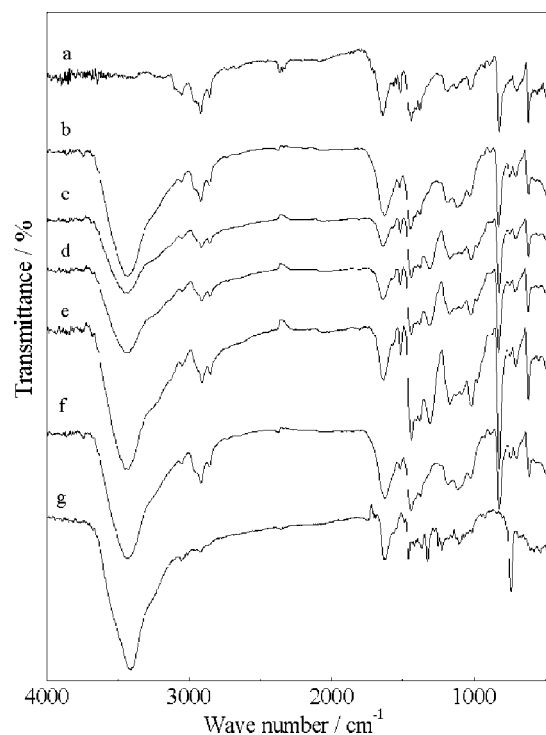


Figure 5 Infrared spectra of (a) P3MeT, (g) PIn and copolymers prepared at (b) 1.1, (c) 1.2, (d) 1.3, (e) 1.4, and (f) 1.5 V from BFEE solution containing 0.01 mol L⁻¹ In and 0.15 mol L⁻¹ 3MeT, respectively.

tion of the N—H bond. This band together with the bands at 1560 cm^{-1} can be ascribed to be the elongation and the deformation vibrations of the N—H bond, respectively.³⁷ This result implied that there were still N—H bonds on the dedoped copolymer backbone. Thus, nitrogen species cannot be the polymerization site and polymerization should happen at the two and three positions (Scheme 1). Furthermore, the peaks at 1628 , 1459 , and 740 cm^{-1} are assigned to the stretching and bending modes of benzene ring, which could be found in the copolymers [Fig. 5(b–f)]. This implied that the In units were incorporated into the copolymer chain. As is shown in Figure 5(a–f), some characteristic bands of 2,5-disubstituted 3MeT unit clearly appears: the aromatic ring stretching bands at 1515 cm^{-1} , the aliphatic C—H stretching bands at 2966 , 2920 , and 2850 cm^{-1} , the aromatic C—H stretching bands at 3053 cm^{-1} , and the aromatic C—H out of plane band at 820 cm^{-1} . In addition, the peaks located near 1380 and 1443 cm^{-1} were assigned to the deformation of the CH_3 group.¹⁹ These peaks can also be seen in the spectra of copolymers although there was some change in the absorption intensity. As mentioned earlier, this implied that the 3MeT units were incorporated into the copolymer chain. All these features indicated that copolymerization happened during the potentiostatic electrocopolymerization of In and 3MeT, which was consistent with the results of the cyclic voltammetry.

Thermal analysis

To investigate the thermal stability of copolymers of In and 3MeT, the thermal properties of PIn, P3MeT, and copolymers obtained at 1.3 V were investigated, as shown in Figure 6. It can be clearly seen from this figure that PIn started to lose weight when the temperature reached 475°C [Fig. 6(a)]. In comparison, there were two evident decomposition processes during the thermal degradation of P3MeT [Fig. 6(c)], and these two decomposition occurred at 265 and 445°C , respectively. This indicated that PIn had better thermal stability than P3MeT. However, there was an obvious degradation located at about 460°C for the copolymer obtained at 1.3 V [Fig. 6(b)], which was higher than that of P3MeT. This may be ascribed to the incorporation of In units into the polymer main chain. All these results described earlier implied that the incorporation of In units into P3MeT contributed to the improvement of the thermal property of P3MeT.

Conductivity and morphology

The conductivities of P3MeT, PIn, and the copolymers obtained potentiostatically from BFEE solutions containing 0.01 mol L^{-1} In and 0.15 mol L^{-1} 3MeT at different polymerization potentials were shown in Table

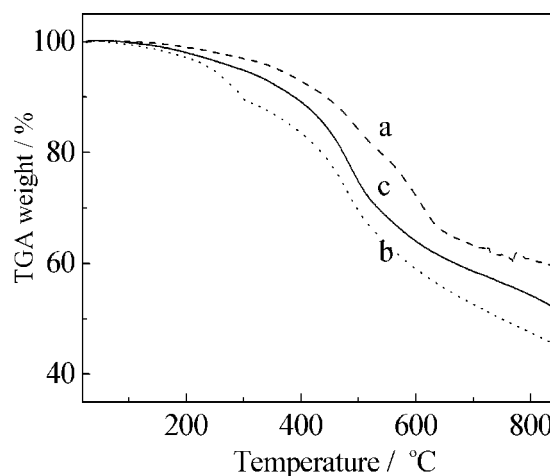


Figure 6 TGA curves of (a) PIn, (b) P3MeT, and (c) copolymer film prepared at 1.3 V from BFEE solution containing 0.01 mol L^{-1} In and 0.15 mol L^{-1} 3MeT, respectively.

I. Pure P3MeT exhibited good conductivity, 2.82 S cm^{-1} , while the conductivity of PIn was 0.16 S cm^{-1} . It can be clearly seen from Table I that the conductivities of the copolymers were between those of pure P3MeT and PIn. This indicated that the insert of 3MeT units into PIn was helpful to improve the conductivity of PIn, which may be beneficial to extend the applications of PIn. Among the copolymers prepared at different potentials, those electro synthesized at 1.3 V showed the highest conductivity, 1.18 S cm^{-1} . This was in accordance with the electrochemical and thermal analysis results. Therefore, 1.3 V was the best potential suitable for the electrocopolymerization of 3MeT and In.

The properties of conducting polymers are strongly dependent on their morphology and structure. PIn, P3MeT, and copolymers were all freestanding films, which can be peeled off the stainless electrode directly. However, the freestanding PIn film was brittle in contrast to P3MeT film. The scanning electron micrographs (SEM) of PIn, P3MeT, and copolymers obtained at 1.3 V were examined, as illustrated in Figure 7. As predicted theoretically,^{35,38} the morphology depends on the preparation conditions, counter ion, and nature of solvent. In this case, the morphology of pure P3MeT was compact and very regular with a growth of aggregates shaped as blossoms [Fig. 7(a)]. Pure PIn resembled ordered arrangements of the branched dendritic morphology and the growth of the nuclei was in the form of clusters, which may be ascribable to the brittle property [Fig. 7(b)]. Meanwhile, the morphology of the copolymer obtained at 1.3 V showed a cauliflower-shape structure as shown in Figure 7(c,d).

CONCLUSIONS

Electrochemical copolymerization of 3MeT and In was successfully realized in BFEE containing 0.01 mol L^{-1}

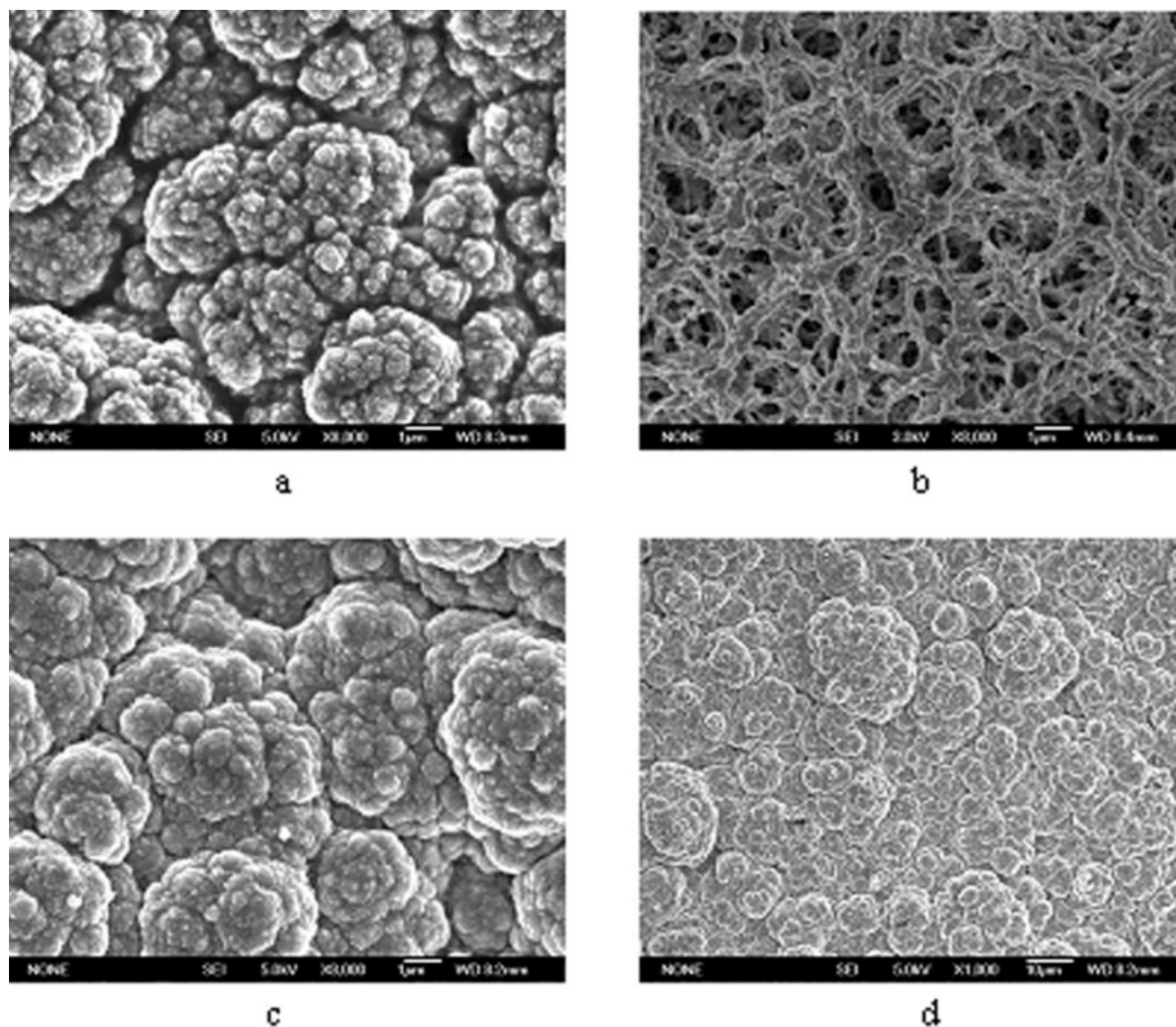


Figure 7 SEM of (a) P3MeT, (b) PIn, and (c, d) copolymer films prepared at 1.3 V from BFEE solution containing 0.01 mol L^{-1} In and 0.15 mol L^{-1} 3MeT, respectively.

In and 0.15 mol L^{-1} 3MeT by the potentiostatic method. The influences of polymerization potential and feed ratio of monomers on the properties of as-formed copolymers were studied in detail and 1.3 V was proved to be the best potential suitable for the electrocopolymerization of In and 3MeT. According to IR spectra, the existence of N—H bond implied the coupling between the monomer units occurred at the C_2 and C_3 positions of indole ring. The copolymers of PIn and P3MeT showed good redox activity, capacitive property, electrical conductivity, and thermal stability. These properties of copolymers would extend the applications of both PIn and P3MeT.

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