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Electrochemical copolymerization of indole and 3,4-ethylenedioxythiophene

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The copolymerization of indole and 3,4-ethylenedioxythiophene (EDOT) was achieved electrochemically in acetonitrile containing lithium perchlorate as supporting electrolyte by direct anodic oxidation of the monomer mixtures on platinum and stainless steel electrodes. As-formed copolymers own both the advantages of polyindole (PIn) and poly (3,4-ethylenedioxythiophene) (PEDOT), i.e., good thermal stability, good electrochemical behavior, high conductivity and excellent ambient stability. The structure and morphology of the copolymer were investigated by UV-vis, infrared spectroscopy, thermal analysis and scanning electron microscopy (SEM), respectively.

1. Introduction

Inherently conducting polymers with π-conjugated electronic structures have been widely investigated since the late 1970s [1–3] due to their potential industrial applications based on their high conductivity and good environmental stability. Among these polymers, polyindole (PIn) and poly (3,4-ethylenedioxythiophene) (PEDOT) have been received considerable attention. PIn owns several advantages, especially fairly good thermal stability due to the incorporation of benzene rings on the polymer backbone [4–6] and high redox activity and stability [7]. PIn can be a good candidate for applications in various domains like electronics, electrocatalysis and pharmacology. Moreover, it can also be a model for certain biopolymer like melanines [8], which may facilitate the applications of PIn in biological area. However, its relatively low electrical conductivity, close to 0.1 S cm^{-1} in doped state [9], together with poor mechanical property [10], may inhibit its applications. On the other hand, PEDOT contains heterocyclic aromates as monomeric units and has become one of the most popular conducting polymers being studied by many scientific research groups [11–15] owing to its high conductivity, excellent environmental stability, relatively low bandgap, good chemical and electrochemical properties. Like other polythiophene derivatives, PEDOT begins to decompose at relatively low temperature. Is it possible to prepare a polymer that owns both the advantages of PIn and PEDOT?

Recently, research works have been focused on the copolymerization in order to prepare conducting polymers with better properties and to overcome the limitation of the rarity of new monomers. So far, copolymers of funan with pyrrole [16], funan with 3-methyl thiophene [17], pyrrole with indole [18–20], EDOT with pyrrole [21, 22], EDOT with bithiophene [23], etc., had been prepared successfully by direct electrochemical oxidation of mixtures of the corresponding monomers. The successful copolymerization can be ascribed to the fact that the oxidation potential onsets of the corresponding monomers are close to each other. By means of the electrochemical copolymerization as mentioned above, several new conducting polymers had been prepared with obvious advantages, such as variation of conductivity, enhancement of electrochemical activity and thermal stability. However, to the best of our knowledge, electrochemical copolymerization of indole with EDOT has not been reported so far. The closeness of the threshold oxidation potential of indole

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and EDOT implies the possibilities for their electrochemical copolymerization. Therefore, it would be interesting to copolymerize indole with EDOT electrochemically so that as-formed copolymer may have both the advantages of high conductivity and environmental stability of PEDOT and good thermal stability of PIn.

In this paper, indole and EDOT were copolymerized successfully by electrochemical oxidation of the monomer mixtures. The electrochemistry of PIn, PEDOT and copolymers of indole with EDOT were studied. In addition, the thermal stability, spectroscopic properties and morphology of the copolymer were investigated in detail.

2. Experimental

2.1. Materials

EDOT (Aldrich) was used as received without further purification. Indole (Shanghai Laize Fine Chemical Plant) was purified by recrystrallization from methanol and distilled water. Lithium perchlorate ($LiClO_4$, Beijing Baili Chemical Plant) was dried in vacuum at 353 K for 24 h before use. Commercial HPLC grade acetonitrile (ACN, made by Shanghai Chemical Reagent Company) was dried and distilled before use.

2.2. Electrochemical experiments

Electrochemical syntheses and examinations were performed in a one-compartment cell with the use of a Model 263 potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control at room temperature. The working and counter electrodes for cyclic voltammetric experiments were platinum wires with a diameter of 0.5 mm placed 0.5 cm apart. They were polished and cleaned by water and acetone successively before each examination. 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 working and counter electrodes, respectively. Stainless steel electrodes were carefully polished with abrasive paper (1500 mesh), subsequently cleaned by water and acetone successively before each examination. A platinum wire was used as the quasi-reference electrode. It was calibrated using the ferrocene (Fc/Fc^+) redox couple which has a formal potential $E_{1/2} = +0.35$ V vs. platinum wire in this medium. The polymers were deposited on an indium-tin-oxide (ITO) coated glass for UV-visible spectral measurements.

All the samples were grown in an ACN solution containing 0.1 M $LiClO_4$ as a 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. In order to remove the electrolyte and oligomers/monomers, the polymer films were rinsed with water and acetone. For spectral analysis, the polymer was dried under vacuum at 333 K for 2 days.

2.3. Characterizations

The conductivity of as-formed polymer films was measured by conventional four-probe technique. UV-visible spectra were taken by using Cary 500 UV-Vis-NIR spectrophotometer. Infrared spectra were recorded using Nicolet 510P FT-IR spectrometer with KBr pellets. The thermogravimetric analysis (TGA) were performed with a thermal analyzer of NETZSCH TG209. All thermal analysis was performed under a nitrogen stream in the temperature range of 303–1073 K with a heating rate of 10 K/min. Scanning electron microscopy (SEM) measurements were taken by using a JEOL JSM-6700F scanning electron microscopy.

3. Results and discussion

3.1. Electrochemical copolymerization

In order to ensure the copolymerization of indole with EDOT, the electrochemical experiments were classified into different groups on the basis of feed ratios of the two monomers. According to the method of Kuwabata *et al.* [24], the concentration of indole was chosen as 0.05 M, while that of EDOT was 0.025 M. Fig. 1 shows the typical anodic polarization curves taken in ACN containing 0.1 M $LiClO_4$ at a potential scanning rate of 20 mV s^{-1}. It should be noted here that the background electrolyte is electrochemically silent in the whole potential range. The oxidation onset of indole is initiated at 0.85 V (Fig. 1A) and that of EDOT is 0.77 V (Fig. 1B). The small distinction (0.08 V) between the oxidation onset of the two monomers implies that the copolymerization is feasible. When the electrolytic solutions contain 0.05 M indole and 0.025 M EDOT, the anodic curve (Fig. 1C) is different from curve (A) and (B). It can be seen that the oxidation onset of the mixture of two monomers is initiated at 0.81 V, which is intervenient between indole and EDOT. This may be partly due to some changes of the electrochemical environment caused by successive deposition of the two monomers during the anodic polarization [16, 17], or partly due to the influence of the low electric conductivity accompanied by the incorporation of indole unit into the copolymer chain. In addition, the fact that the oxidation potential of the mixture of indole and EDOT is between

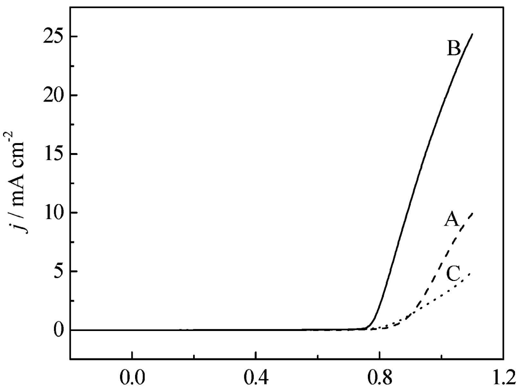


Figure 1 Anodic polarization curves of (A) 0.05 M indole, (B) 0.025 M EDOT, and (C) 0.05 M indole+0.025 M EDOT in ACN+0.1 M $LiClO_4$. Scanning rates: 20 mV s^{-1}.

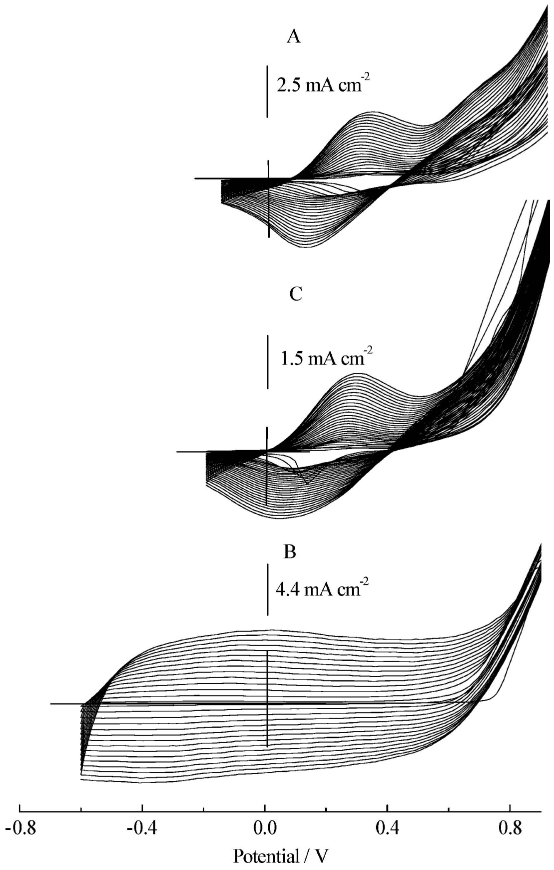


Figure 2 Cyclic voltammograms of (A) 0.05 M indole, (B) 0.025 M EDOT and (C) 0.05 M indole + 0.025 M EDOT in ACN + 0.1 M $LiClO_4$. Scanning rates: 100 mV s^{-1}.

that of the two monomers suggests the two monomers are oxidized alternately and the copolymer chains are composed of alternate indole and EDOT units, indicating the occurrence of copolymerization.

The successive cyclic voltammograms (CVs) of 0.05 M indole, 0.025 M EDOT and the mixture of the two monomers taken in ACN containing 0.1 M $LiClO_4$ at a potential scanning rate s of 100 mV s^{-1}are illustrated in Fig. 2. As can be seen from this figure, the CVs show characteristic features as other conducting polymers such as polythiophene and polypyrrole during potentiodynamic syntheses. As the CV scan continues, a polymer film is also formed on the working electrode surface. The increase in the redox wave currents implies that the amount of the polymer on the electrode is increasing. PIn can be reduced and oxidized between 0.13 and 0.35 V (Fig. 2A). The CVs of EDOT show broad redox waves, similar to the literature [25]. PEDOT can be reduced and oxidized between 0 and −0.4 V. When the CVs are taken in the electrolytic solutions containing 0.05 M indole and 0.025 M EDOT, great differences in the CVs can be easily observed (Fig. 2C). In sharp contrast to pure indole, the oxidation and reduction potentials of the mixture both shift negatively, which lie at 0.28 V and 0.04 V, respectively. The evolution of a new wave at a potential different from the potentials of both pure indole and EDOT suggests the formation of a copolymer [18]. In addition, the shape of Fig. 2C is similar to Fig. 2A, which may be ascribable to the higher concentration of indole in this media.

3.2. Electrochemistry of copolymer films

The films of PIn, PEDOT and copolymers of indole and EDOT with different feed ratios were electrodeposited potentiostatically at 1.0 V after the same polymerization time. The CVs of PIn, PEDOT and copolymers with different EDOT monomer concentrations from 0.025 M to 0.1 M were given in Fig. 3A–E, respectively. In each case, five cyclic voltammograms were recorded to ensure reproducibility. The redox wave values of the copolymers obtained from different feed ratios are listed in Table I. It can be seen from Table I that the redox potentials shift more negatively with the increases of EDOT concentration. For example, when the feed ratio is 0.05:0.025, the copolymer shows a couple of redox waves at 0.22 V and 0.1 V, which is similar to PIn. When the feed ratio becomes 0.05:0.1, the redox peaks locate at around 0.16 V and 0.07 V, close to PEDOT. Moreover, according to the CVs in Fig. 3B, D and E, the CVs shapes of the copolymer become similar to PEDOT when the concentration of indole is less than EDOT. This indicates that at high concentrations of EDOT, EDOT sequences dominate in the copolymer structure. From this point of view, the concentrations of indole and EDOT for copolymerization were chosen as 0.05 and 0.025 M, respectively, in accordance with Fig. 1. It should be noted here that the CVs of the bilayer (PEDOT-PIn composite), prepared by successive polymerization of PEDOT and PIn, are only the sum of the voltammograms of PEDOT and PIn, as shown in Fig. 3F. It is quite different from those of the copolymers, which further confirms the occurrence of copolymerization [20].

It is well known that PEDOT can be used as stable conducting material in tantalum capacitors owing to its pretty good redox properties [26, 27]. According to Fig. 3B, it is obvious that there is a distinct capacitive feature of the charge storage. In Fig. 3B, a rapid increase in current density occurs during the process of potential scan followed by a plateau, while the reverse course shows the discharge of the stored charge as the capacitor returns to its original state. As shown in Fig. 3, the electrochemical activity and capacitive property of the copolymers are much higher after the same polymerization time than that of pure PIn due to the incorporation of EDOT unit into the copolymers (Fig. 3A). For instance, when the feed ratio is 0.05:0.025 (Fig. 3C), the copolymer waves shows greater redox activity compared with pure PIn (Fig. 3A). The values of cathodic and anodic current density are −1.7 and 1.76 mA cm^{-2} (Fig. 3C), much higher than those of pure PIn (−0.04 and 0.05 mA cm^{-2}, respectively). These results indicate that the incorporation of EDOT units has improved the electrochemical activity and capacitive property of pure PIn.

3.3. Structural characterizations

During the potentiostatistic process, the color of solutions around the electrode became darker progressively. This indicates that soluble oligomers may be formed during anodic oxidation. With the polymerizing propagation, part soluble oligomers became insoluble and

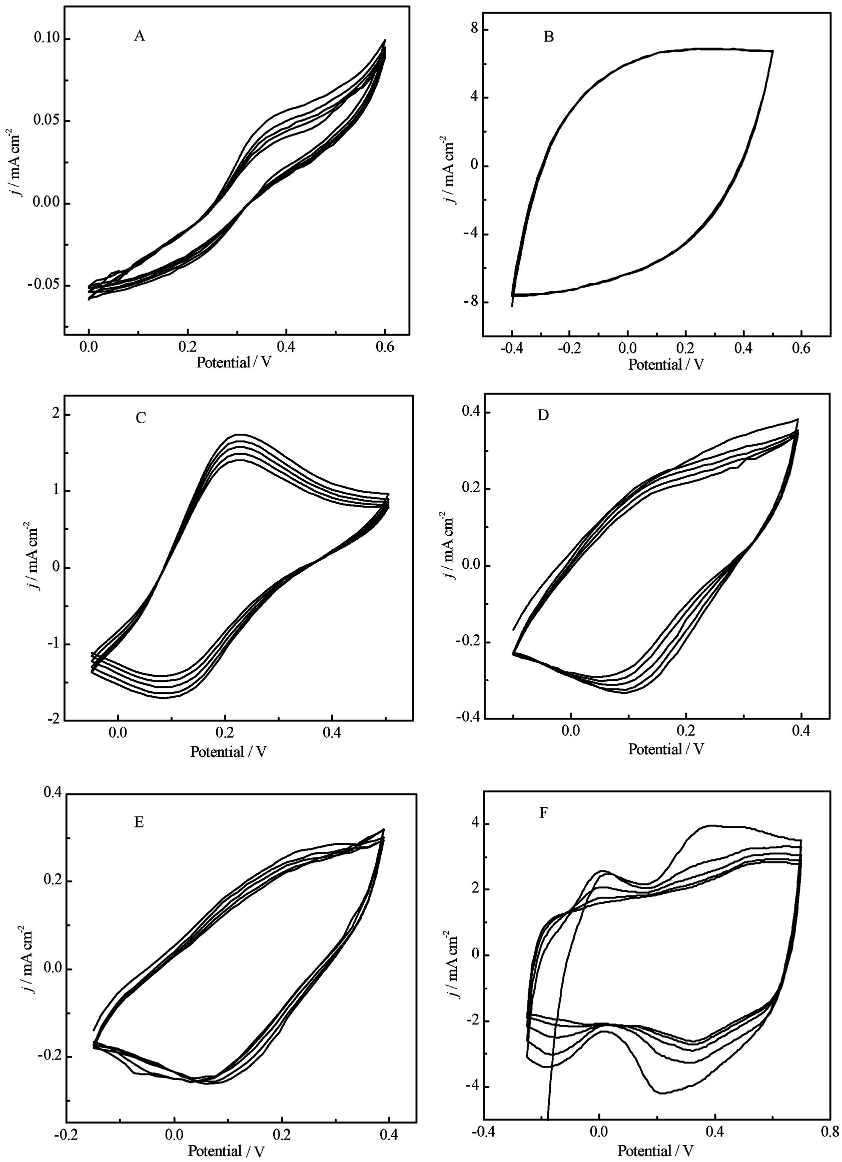


Figure 3 Cyclic voltammograms recorded in ACN+0.1 M $LiClO_4$ solution of (A) pure indole (0.05 M), (B) pure EDOT (0.025 M), indole:EDOT = (C) 2:1, (D) 1:1, (E) 1:2 (mol, indole = 0.05 M), and (F) bilayer (PIn-PEDOT) (0.05 M In-0.025 M EDOT). Scanning rates: 25 mV s^{-1}. Polymerization potential: 1.0 V.

deposited on the working electrode with the elongation of the polymer main chain. However, there are still part oligomers, which diffuse from the electrode into the bulk solution. As a result, the color of the bulk solution became darker. PIn film is golden yellow in dedoped state and dark green in doped form, which is in accordance with the literature [7, 28]. As predicted theoretically [13], PEDOT film changes its color from transparent pale blue in doped state to opaque red in dedoped form. For the copolymer, its color changes from yellow green in doped state to darkish color in dedoped state. The UV-visible spectra of the copolymer films deposited at various potentials, pure PIn and PEDOT are shown in Fig. 4. It should be noted here that the absorption decreases in the spectra around 800 nm was due to the transition of the lamp. The spectra of the PIn films show a characteristic absorption at about 395 nm (Fig. 4A). On the other hand, the spectra of the

TABLE I Redox peak values of copolymers prepared from ACN+0.1 M $LiClO_4$ solution containing 0.05 M indole and different amounts of EDOT

Feed ratio (indole:EDOT)	Indole (0.05 M)	0.05:0.025	0.05:0.05	0.05:0.1	EDOT (0.025 M)
Polymerization potential (V)	1.0	1.0	1.0	1.0	1.0
Polymerization time (s)	300	300	300	300	300
Anodic potential (V)	0.35	0.22	0.18	0.16	0.08
Cathodic potential (V)	0.15	0.10	0.10	0.07	−0.30
Anodic current density (mA cm^{-2})	0.05	1.76	0.25	0.23	6.60
Cathodic current density (mA cm^{-2})	−0.04	−1.70	−0.33	−0.25	−7.60

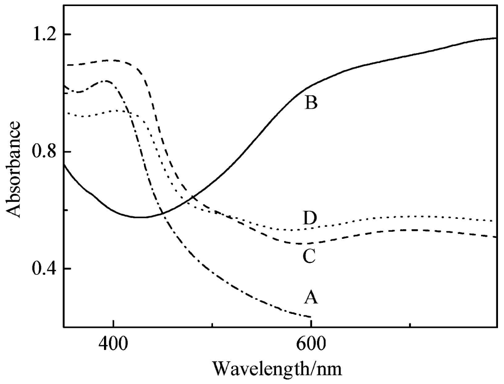


Figure 4 UV-vis spectra of the (A) PIn, (B) PEDOT and copolymer film coated on an optically transparent ITO electrode at (C) 0.9 V and (D) 1.0 V. The polymer films were prepared from ACN+0.1 M $LiClO_4$ solution containing 0.05 M In and 0.025 M EDOT.

PEDOT films show a much broader absorption from 430 to about 600 nm (Fig. 4B). Similar to pure PIn and PEDOT, the spectra of copolymer show characteristic absorptions of both PIn and PEDOT (Fig. 4C and D), in accordance with those published previously [18]. However, there is a little bit red shift of the main absorption of copolymer film in contrast to pure PIn due to the incorporation unit of EDOT, further certifying the occurrence of copolymerization. Moreover, there is a small increase in absorbance in the visible region with the increase of the applied potential during copolymerization.

PEDOT, PIn and copolymers prepared potentiostatically from ACN + 0.1 M $LiClO_4$ solution containing 0.05 M indole and 0.025 M EDOT at different applied potentials were analyzed by FT-IR spectroscopy, as shown in Fig. 5. The spectra of PIn and PEDOT homopolymers have several characteristic peaks at 740, 1113, 1249, 1320, 1405, 1453, 1566, 1608, 2923, 3400 cm^{-1} and 687, 838, 1092, 1107, 1197, 1335, 1394, 1515, 2924 cm^{-1}, respectively. The bands at 1209, 633 cm^{-1} of PIn (Fig. 5A) and 1197, 630 cm^{-1} of PEDOT (Fig. 5B) indicate the presence of perchlorate dopant [18]. These characteristic peaks of PIn and PEDOT homopolymers can also be found in the copolymers (Fig. 5C–F). In the case of PIn (Fig. 5A), the peaks at 1608, 1566, 1453 and 740 cm^{-1} are assigned to the stretching and bending modes of benzene ring, which could be found in the copolymers (Fig. 5C–F). This implies that the indole units were incorporated into the copolymer chain. The single peak at 1320 cm^{-1} (Fig. 5A, C–F) induced by the stretching C—N of amine indicates the participation of the nitrogen atoms of indole in the copolymerization [29]. It should be noted that the presence of band at 1638 cm^{-1} indicates the presence of carbonyl group in PEDOT while this band disappears in the spectra of copolymers.

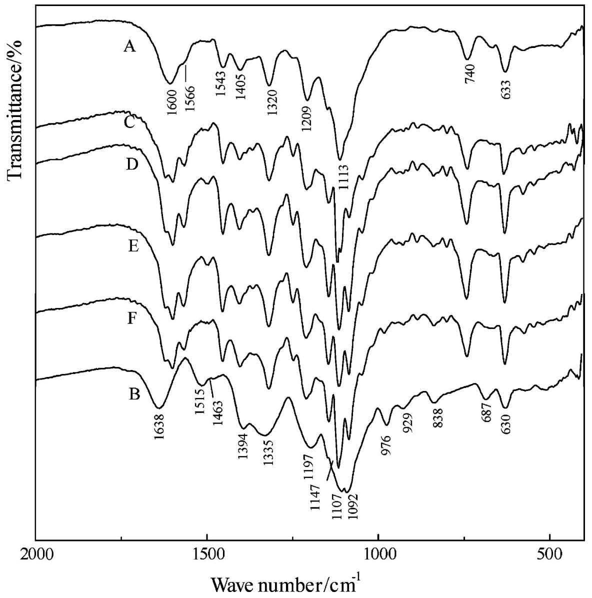


Figure 5 Infrared spectra of (A) pure PIn, (B) pure PEDOT and (C—F) copolymer prepared at 0.9 V, 1.0 V, 1.1 V, 1.2 V from ACN + 0.1 M $LiClO_4$ solution containing 0.05 M In and 0.025 M EDOT, respectively.

According to the spectrum of pure PEDOT (Fig. 5B), the bands at 1515, 1463, 1394 and 1335 cm^{-1} originate from the stretching modes of C═C and C—C in the thiophene ring [30]. In this region, the absorptions shifts happened in the spectra of copolymers due to the interaction of benzene ring and thiophene ring during the electrochemical copolymerization. The bands at 1147 and 1092 cm^{-1} (Fig. 5B) are assigned to the stretching of the C—O—C bond [31], which shift downwards to 1145 and 1086 cm^{-1} and become more obvious in the spectra of the copolymer with the increase of the polymerization potential (Fig. 5C–F). This suggests that EDOT units were incorporated into the main chain of the copolymers and higher potentials may favor the incorporation of EDOT units into the copolymer. Furthermore, vibrations from the C—S bond in the thiophene ring of PEDOT are shown at 976, 929 and 838 cm^{-1}[31], which also could be observed in the copolymer. All these features imply that copolymerization happens during the potentiostatic electropolymerization of EDOT and indole, which is consistent with the results of the cyclic voltammetry.

3.4. Thermal analysis

In order to investigate the thermal stability of copolymers of EDOT and indole, the thermal properties of PIn, PEDOT and copolymers obtained under different applied potentials were investigated, as shown in Fig. 6. It

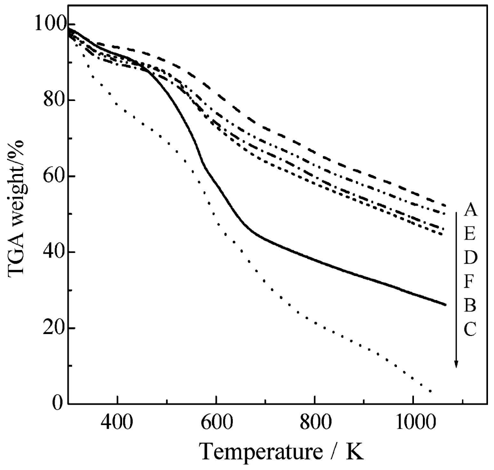


Figure 6 TGA curves of (A) pure PIn, (B) pure PEDOT copolymer prepared at (C) 0.9 V, (D) 1.0 V, (E) 1.1 V, (F) 1.2 V from ACN+0.1 M $LiClO_4$ solution containing 0.05 M In and 0.025 M EDOT.

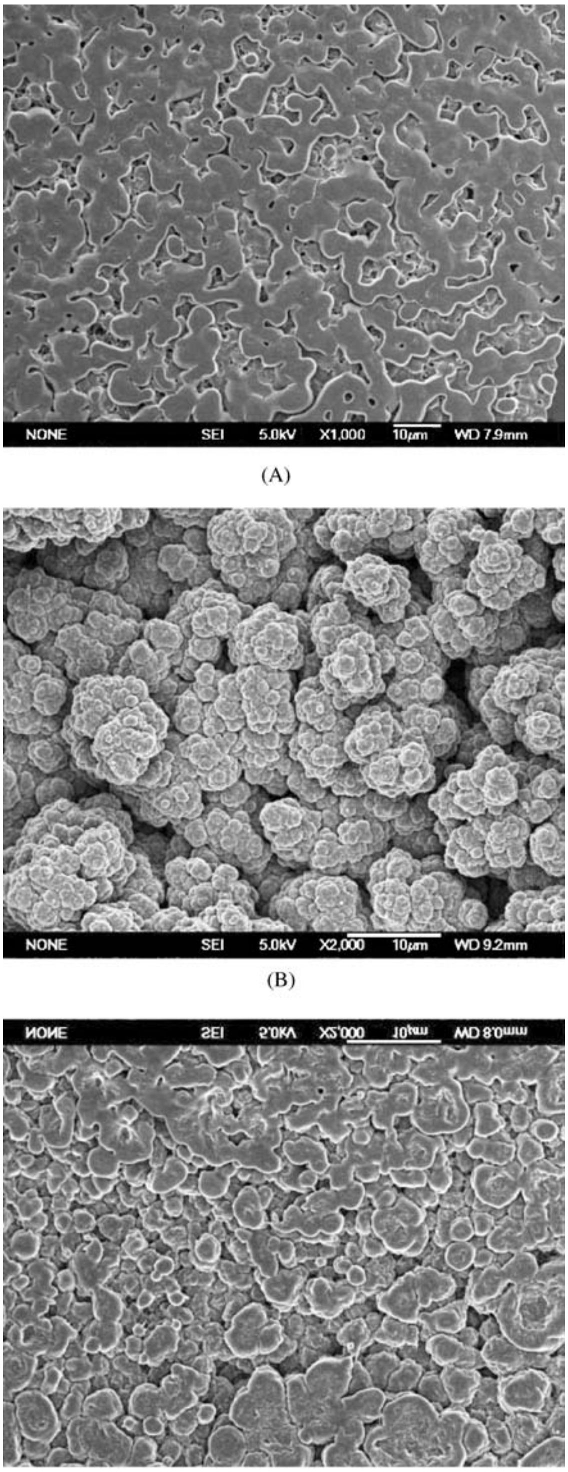
can be clearly seen from this figure that PIn starts to lose weight when the temperature reaches 525 K (Fig. 6A), while the prominent decomposition of PEDOT happens at about 452 K (Fig. 6B). Their corresponding maximum decomposition rates occurred at 610 and 563 K for PIn and PEDOT, respectively. This indicates the thermal stability of PIn is better than that of PEDOT. The reason for this phenomenon is mainly the incorporation of benzene ring into the polymer backbone. Moreover, it can be seen clearly from Fig. 6 that the thermal properties of copolymers prepared at different applied potentials are quite different. The copolymer obtained at 0.9 V undergoes decomposition in several steps (Fig. 6C). The first weight loss occurs at about 410 K, inferior to PIn and PEDOT. This may be correlated to the shorter chains formed at lower applied potential. On the other hand, the thermal properties of copolymers obtained at 1.0, 1.1 and 1.2 V are similar to each other, better than that of pure PEDOT. They start degradation at 485, 488 and 505 K, respectively (Fig. 6D–F). It can also be seen from this figure that copolymers prepared at 1.1 V shows the slowest degradation rate, indicating that the quality of copolymer prepared at 1.1 V is the best. The differences may be ascribable to the differences of the activity of the radical cation as its electrooxidation mechanism [17] or the different composition of the polymer backbone. All these results described above imply that the incorporation of indole units into PEDOT contributes to the improvement of the thermal property of PEDOT.

3.5. Conductivity and morphology

The conductivities of PEDOT, PIn and the copolymers obtained potentiostatically from ACN+0.1 M $LiClO_4$ solution containing 0.05 M indole and 0.025 M EDOT at different polymerization potential are shown in Table II. Pure PEDOT exhibits excellent conductivity, which is up to 89 S cm^{-1}, while the conductivity of PIn is about 0.56 S cm^{-1}. It can be clearly seen from Table II that the conductivities of the copolymers are between those of pure PEDOT and PIn. This indicates that the insert of EDOT units into PIn is helpful to improve the conductivity of PIn, which may be beneficial to extend the applications of PIn. Among the copolymers prepared under different potentials, those electrosynthesized at 1.1 V show the highest conductivity, 26.74 S cm^{-1}. This is in accordance with the thermal analysis results. Therefore, 1.1 V is the best potential suitable for the electrocopolymerization of indole and EDOT.

TABLE II The conductivities of PIn, PEDOT and the copolymers prepared at different polymerization potentials

Polymer	Conductivity (S cm^{-1})
Copolymer at 0.9 V	1.55
Copolymer at 1.0 V	9.63
Copolymer at 1.1 V	26.74
Copolymer at 1.2 V	9.50
PIn	0.56
PEDOT	89.30



(A)

(B)

(C)

Figure 7 SEM photos of (A) pure PIn, (B) pure PEDOT and (C) copolymers prepared at 1.1 V from the solution ACN + 0.1 M $LiClO_4$ solution containing 0.05 M In and 0.025 M EDOT.

The properties of conducting polymers are strongly dependent on their morphology and structure. Therefore, the scanning electron micrographs (SEM) of PIn, PEDOT and copolymers obtained at 1.1 V were examined, as illustrated in Fig. 7. As predicted theoretically[18, 28], the PIn morphology depends on the preparation conditions, counter ion and nature of solvent and a cauliflower shape in the most commonly observed morphology. In this case, pure PIn looks like the branched dendritic morphology (Fig. 7A). On the other hand, the morphology of pure PEDOT is very regular with a growth of aggregates shaped as blossoms (Fig. 7B). Meanwhile, the morphology of the copolymer obtained at 1.1 V shows a grain structure as shown in Fig. 7C. This morphology is between PEDOT and PIn, further confirming the occurrence of copolymerization. Furthermore, the grain structure is more similar to the PIn morphology in some extent due to the higher concentration of indole in this system.

4. Conclusions

Electrochemical copolymerization of indole and EDOT was successfully realized in ACN+0.1 M $LiClO_4$ solution containing 0.05 M indole and 0.025 M EDOT 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 1.1 V was proved to be the best potential suitable for the electrocopolymerization of indole and EDOT. The copolymers of PIn and PEDOT show good redox activity, capacitive property, electrical conductivity and thermal stability. These properties of copolymers would extend the applications of both PIn and PEDOT.

Acknowledgements

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References

1. T. A. SKOTHEIM, in "Handbook of Conducting Polymers" (Marcel Dekker, New York, 1986).
2. T. A. SKOTHEIM, R. L. ELSEMBAUMER and J. R. REYNOLDS, in "Handbook of Conducting Polymer, 2nd edn.," (Marcel Dekker, New York, 1998).
3. P. BERNIER, S. LEFRANT and G. BIDAN, in "Advances in Synthetic Metals: Twenty Years of Progress in Science and Technology" (Elsevier, New York, 1999).
4. D. BILLAUD, E. B. MAAROUF and E. HANNECART, *Synth. Met.* **69** (1995) 571.
5. P. C. PANDEY and R. J. PRAKASH, *J. Electrochem. Soc.* **145** (1998) 4103.
6. P. S. ABTHAGIR, K. DHANALAKSHMI and R. SARASWATHI, *Synth. Met.* **93** (1998) 1.
7. E. B. MAAROUF, D. BILLAUD and E. HANNECART, *Mat. Res. Bull.* **29** (1994) 637.
8. H. TALBI, J. GHANBAJA and D. BILLAUD, *Polymer* **38** (1997) 2099.
9. R. LAZZARONI, A. DEPRYCK, C. H. DEBRAISIEUX, J. RIGA, J. VERBIST, J. L. BREDAS, J. DELHALLE and J. M. ANDRE, *Synth. Met.* **21** (1987) 198.
10. G. TOURILLON and F. GARNIER, *J. Electroanal. Chem.* **135** (1982) 173.
11. D. DELONGCHAMP and P. H. HAMMOND, *Adv. Mater.* **13** (2001) 1455.
12. D. HOHNHOLZ, A. G. MACDIARMID, D. M. SARNO and W. E. JONES, *Chem. Commun.* (2001) 2444.
13. J. A. IRVIN, I. SCHWENDEMAN, Y. LEE, K. A. ABBOUD and J. R. REYNOLDS, *J. Polym. Sci. Part A: Polym. Chem.* **39** (2001) 2164.
14. S. C. J. MESKERS, J. K. J. VAN DUREN, R. A. J. JANSSEN, F. LOUWET and L. GROENENDAAL, *Adv. Mater.* **15** (2003) 613.
15. L. B. GROENENDAAL, G. ZOTTI, P.-H. AUBERT, S. M. WAYBRIGHT and J. R. REYNOLDS, *ibid.* **15** (2003) 855.
16. X. B. WAN, W. ZHANG, S. JIN, G. XUE, Q. D. YOU and B. CHE, *J. Electroanal. Chem.* **470** (1999) 23.
17. L. LI, W. CHEN, N. XU, Z. G. XIAO and G. XUE, *J. Mater. Sci.* **39** (2004) 2395.
18. K. DHANALAKSHMI and R. SARASWATHI, *ibid.* **36** (2001) 4107.
19. F. KÖLELI, Y. ARSLAN and M. DÜDÜKCÜ, *Synth. Met.* **129** (2002) 47.
20. F. WAN, L. LI, X. B. WAN and G. XUE, *J. Appl. Polym. Sci.* **85** (2002) 814.
21. G. SÖNMEZ and A. S. SARAÇ, *Synth. Met.* **135/136** (2003) 459.
22. A. S. SARAÇ, G. SÖNMEZ and F. Ç. CEBECI, *J. Appl. Electrochem.* **33** (2003) 295.
23. N. M. ALPATOVA, E. V. OVSYANNIKOVA, F. JONAS, S. KIRCHMEYER, E. YU. PISAREVSKAYA and M. YU. GROSHEVA, *Russian J. Electrochem.* **38** (2002) 576.
24. S. KUWABATA, S. ITO and H. YONEYAMA, *J. Electrochem. Soc.* **135** (1988) 1691.
25. M. ŁAPKOWSKI and A. PROŃ, *Synth. Met.* **110** (2000) 79.
26. L. B. GROENENDAAL, F. JONES, D.FREITAG, H. PIELARTZIK and J. R. REYNOLDS, *Adv. Mater.* **12** (2000) 481.
27. J. D. STENGER-SMITH, C. K. WEBBER, N. ANDERSON, A. P. CHAFIN, K. ZONG and J. R. REYNOLDS, *J. Electrochem. Soc.* **149** (2002) A973.
28. D. BILLAUD, E. B. MAAROUF and E. HANNECART, *Mat. Res. Bull.* **29** (1994) 1239.
29. K. M. CHOI, C. Y. KIM and K. H. KIM, *J. Phys. Chem.* **96** (1992) 3782.
30. K. I. SEO and I. J. CHUNG, *Polymer* **41** (2000) 4491.
31. C. KVARNSTRÖM, H. NEUGEBAUER, S. BLOMQUIST, H. J. AHONEN, J. KANKARE and A. IVASKA, *Electrochim. Acta* **44** (1999) 2739.

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