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Electrochemical fabrication of novel fluorescent Poly(pyrene-*co*-3-methylthiophene) polymeric film

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Poly(pyrene-*co*-3-methylthiophene), a new copolymer, was successfully synthesized by the direct electrochemical oxidation of a monomer mixture of pyrene and 3-methylthiophene in boron trifluoride diethyl etherate. The electrochemical performance of the copolymers was characterized by cyclic voltammetry. Ultraviolet visible (UV-vis) and Flourier transform infrared (FI-TR) were used to characterize the structure of the copolymers. In addition, the resulting copolymers were found to partially dissolve in some organic solvents (e.g., dimethyl sulfoxide). Fluorescence spectroscopy revealed that not only can the copolymers emit different photoluminescence under 365 nm UV light in the dimethyl sulfoxide solution, but also their emitting properties can be controlled by changing the monomer feed ratios.

Keywords: Electrochemical copolymerization, Conducting polymers, Poly(3-methylthiophene), Polypyrene.

1. INTRODUCTION

Alterations in the form, structure, and properties of conductive polymers (CPs) are still one of the main intentions of CPs synthesis and application. Pyrene is an aromatic monomer with distinct fluorescence performance, which can be employed as a radical fluorescent probe, a sensor indicator, or a press-sensitive material [1-4]. Oligopyrene, which has a longer delocalized p-electron chain sequence, is anticipated to have superior fluorescent and electroluminescent performance compared to its monomer. In addition, crystalline oligopyrene nanowires with pleochroic emission, which are synthesized by the electrochemical template polymerization of the pyrene monomer [5], have potential applications in the fabrication of multicolour fluorescent labels, nanodevices, organically electronic displays, and electroluminescent devices. However, the preparation of high-quality polypyrene films by the electrochemical method is still challenging. Copolymerization is a feasible method to address this problem because the properties of copolymers are usually intermediate between the individual polymers, thus overcoming the limitations associated with homopolymer preparation and producing better materials with controlled performance [6]. In general, boron trifluoride diethyl etherate (BFEE) is an excellent solvent and electrolyte that can significantly lower the oxidation potentials of monomers. For example, free-standing poly (3-methylthiophene) (PMeT) films, which have excellent flexibility and high tensile strength, can be easily prepared by direct oxidation of the corresponding monomers in the BFEE system [7, 8]. To date, studies on 3-methylthiophene (3MeT) based copolymers which have been successfully synthesized by the electrochemical oxidation of mixtures between 3MeT and other homologous monomers have been heavily reported [9-20]. However, little research has been conducted on the free-standing PMeT films, the polypyrene prepared in the BFEE system is always oligopyrene. Therefore, synthesizing the copolymer containing pyrene and 3MeT monomer units has been found beneficial for improving its performance.

In this work, we report a copolymer which was successfully copolymerized from the monomer mixture of pyrene and 3MeT through electrochemical oxidation in BFEE. The electrochemistry, structure spectroscopic performance, and electrical conductivity of polypyrene, PMeT, and their copolymers was studied in detail.

2. EXPERIMENTAL

2.1. Materials

BFEE was purchased from Changyang Chemical Plant in Beijing, which was distilled and stored at -20 ^{o}C before use. Pyrene (99%) and 3MeT (99%) were acquired from Acros Organics. Acetone (analytical grade) and dimethyl sulfoxide (analytical grade) were purchased from Tianjin Bodi Chemical Co., Ltd.

2.2 Electrochemical Measurement

Electrochemical polymerization and testing were performed in a common three-electrode system using a 263 potentiostat/galvanostat (EG & G Princeton Applied Research, Oakridge, Tennessee) at room temperature. A platinum electrode (diameter: 0.5 mm) was used as the working electrode. Prior to each experiment, its surface was carefully polished and thoroughly cleaned with water and acetone. A stainless-steel wire and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. BFEE was used as the solvent and electrolyte. Polypyrene, PMeT and the copolymer films were synthesized at the same polymerization potential with different feed ratios. Prior to each experiment, the solution was degassed with a stream of dry argon and maintained under a slight argon overpressure. Prior to polymerization, the anodic polarization curves with different feed ratios (pyrene: 3MeT = 1:0, 1:5, 1:15: 1:30, 0:1) were explored at a scan rate of 20 mV s^{-1}. Thereafter, the successive CV curves of different feed ratios were tested at a scan rate of 100 mV s^{-1}. The nano-copolymer films were grown on the platinum electrode surface at a constant potential of 1.2 V. In addition, produce obtain sufficient polymer for the test, two stainless steel plates with surface areas of 10 and 12 cm^2 were used as the working and counter electrodes, respectively. Before each experiment, the samples were polished carefully with sandpaper (1500 mesh) and thoroughly cleaned with water and acetone. The integrated charge of the cell could control amount of the deposited polymer on the electrode. After electropolymerization, the polymers were scraped from the electrode and washed with acetone to remove the residual electrolytes and monomers. The polymers were dried for 2 days at 60 °C in vacuum to facilitate the spectral analysis.

2.3 Characterization

The electrical conductivity of the polymer films was measured using the routine four-probe technique. The UV-Vis spectra were obtained using a PerkinElmer Lambda 900 ultraviolet-visible-near-infrared spectrometer. The FT-IR spectrograms of the samples were obtained using a Bruker Vertex 70 FT-IR spectrometer. The fluorescence spectra of the samples were measured using an F-4500 fluorescence spectrophotometer (Hitachi).

3. RESULTS AND DISCUSSION

3.1 Electrochemical Copolymerization

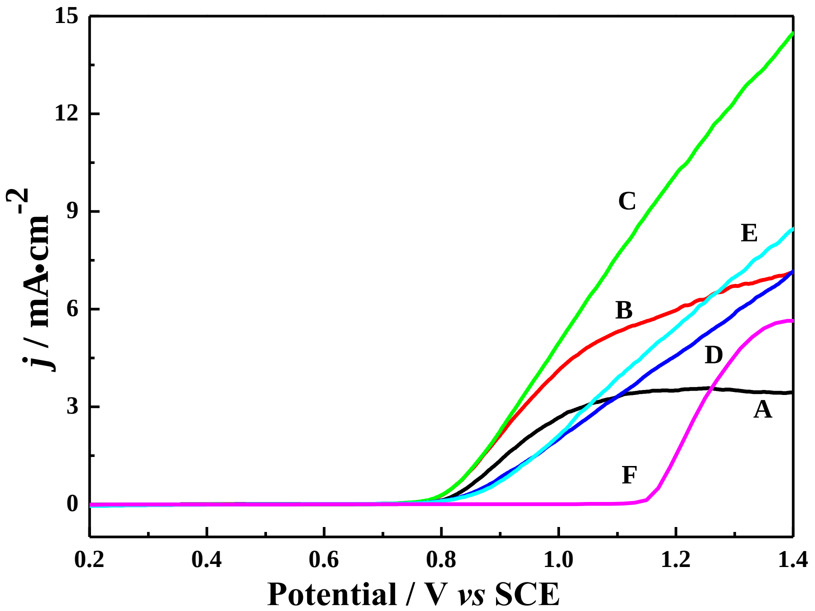


Figure 1. Anodic polarization curves of (A) 0.025 mol L^{-1} pyrene, (B) 0.01 mol L^{-1} pyrene and 0.01 mol L^{-1} 3MeT, (C) 0.01 mol L^{-1} pyrene and 0.05 mol L^{-1} 3MeT, (D) 0.01 mol L^{-1} pyrene and 0.15 mol L^{-1} 3MeT, (E) 0.01 mol L^{-1} pyrene and 0.3 mol L^{-1} 3MeT and (F) 0.05 mol L^{-1} 3MeT in BFEE. The scanning rates are 20 mV s^{-1}.

Previous reports show that, if the oxidation potential of the starting monomers is fairly close, the copolymer chain with alternating monomer units can be more easily prepared [21, 22]. The anodic oxidation of pyrene and 3MeT was first inspected to confirm the initial oxidation potential (E_{ox}) of pyrene and 3MeT in BFEE, which were 0.80 and 1.17 V, respectively [Fig. 1 (A) and (F)]. Evidently, E_{ox} of 3MeT was higher than that of pyrene, indicating the difficulty of electrochemical copolymerization for these two monomers.

The diffusion method proposed by Kuwabata et al. is a good strategy to address this problem [23]. That is, while 3MeT oxidizes, pyrene can be oxidized under diffusion-limited circumstances, achieving the copolymerization of the two monomers. Various feed ratios of the monomers were tested to determine the appropriate stoichiometry for the copolymer formation. As the feed ratios of pyrene to 3MeT are 1:1, 1:5, 1:15 and 1:30, E_{ox} of the copolymer are 0.77, 0.77, 0.80, and 0.80 V, respectively [Fig. 1 (B-E)]. Clearly, the copolymer E_{ox} was different from that of the two monomers, indicating that they can be oxidized together.

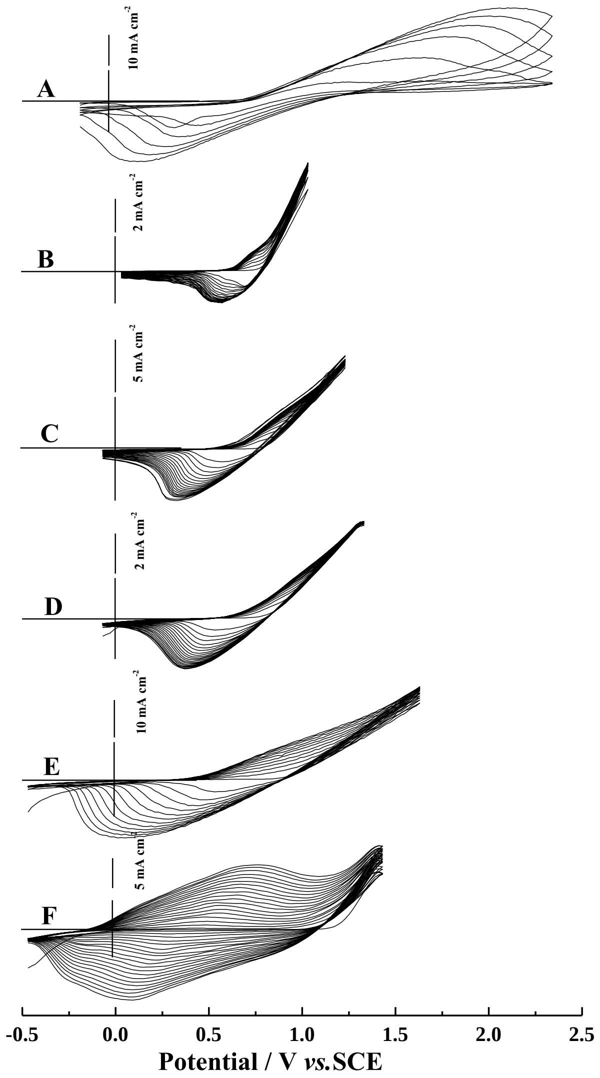
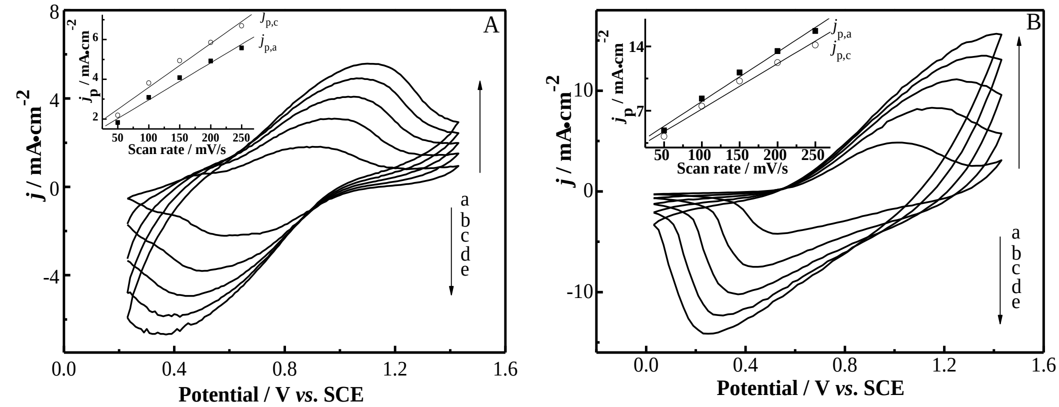


Figure 2. CVs of (A) 0.025 mol L^{-1} pyrene, (B) 0.01 mol L^{-1} pyrene and 0.01 mol L^{-1} 3MeT, (C) 0.01 mol L^{-1} pyrene and 0.05 mol L^{-1} 3MeT, (D) 0.01 mol L^{-1} pyrene and 0.15 mol L^{-1} 3MeT, (E) 0.01 mol L^{-1} pyrene and 0.3 mol L^{-1} 3MeT and (F) 0.05 mol L^{-1} 3MeT in BFEE. The scanning rates are 100 mV s^{-1}.

At 100 mV s^{-1} scan rate, the cyclic voltammograms (CVs) of pyrene, 3MeT, and the mixed monomers with diverse feed ratios (pyrene to 3MeT = 1:1, 1:5, 1:15, 1:30) in BFEE were revealed in Fig. 2. Conducting polypyrene films were generated on the surface of the stainless-steel plate during the continuous CV scans [Fig. 2(A)]. The changes in the redox wave currents show that the mass of the polymer on the electrode was increasing. The potential shift of the peak current density indicates the increased electrical resistance and the necessarily surmountable resistance of the overpotential for the polymer film. These indicated the formation of a polymer film on the electrode. Alike conditions were also discovered in the CV diagram of 3MeT in BFEE [Fig. 2(F)]. Pyrene and polypyrene may be oxidized and reduced between 2.30 and 0.16 V [Fig. 2(A)]. In contrary, 3MeT CVs showed the broad redox waves whose oxidation and reduction peaks were at 0.73 and 0.07 V, respectively [Fig. 2(F)]. The CVs of the mixed monomers with different feed ratios of pyrene to 3MeT (1:1, 1:5, 1:15, and 1:30) are also illustrated in Fig. 2 (B–E). The CV curves of pyrene to 3MeT (1:1) mixtures are alike to those of polypyrene, showing that pyrene units are the majority in the copolymer [Fig. 2(B)]. With the increased 3MeT concentration, the CVs changed significantly [Fig. 2(C-D)]. While the 3MeT concentration increased to 0.3 mol L^{-1}, the CV curve of the copolymer was similar to that of PMeT, elucidating that more 3MeT units are incorporated into the copolymer film [Fig. 2(E)]. It is different that the oxidation peaks of the copolymers shifted toward positive regions compared to those of homopolymers. Besides, the reduction peaks of the mixture appeared between those of pyrene and 3MeT, and the changes in the peak potentials were different from those of the homopolymers, suggesting a successful copolymerization of pyrene and 3MeT [24].

3.2 Electrochemistry of the Copolymer Films



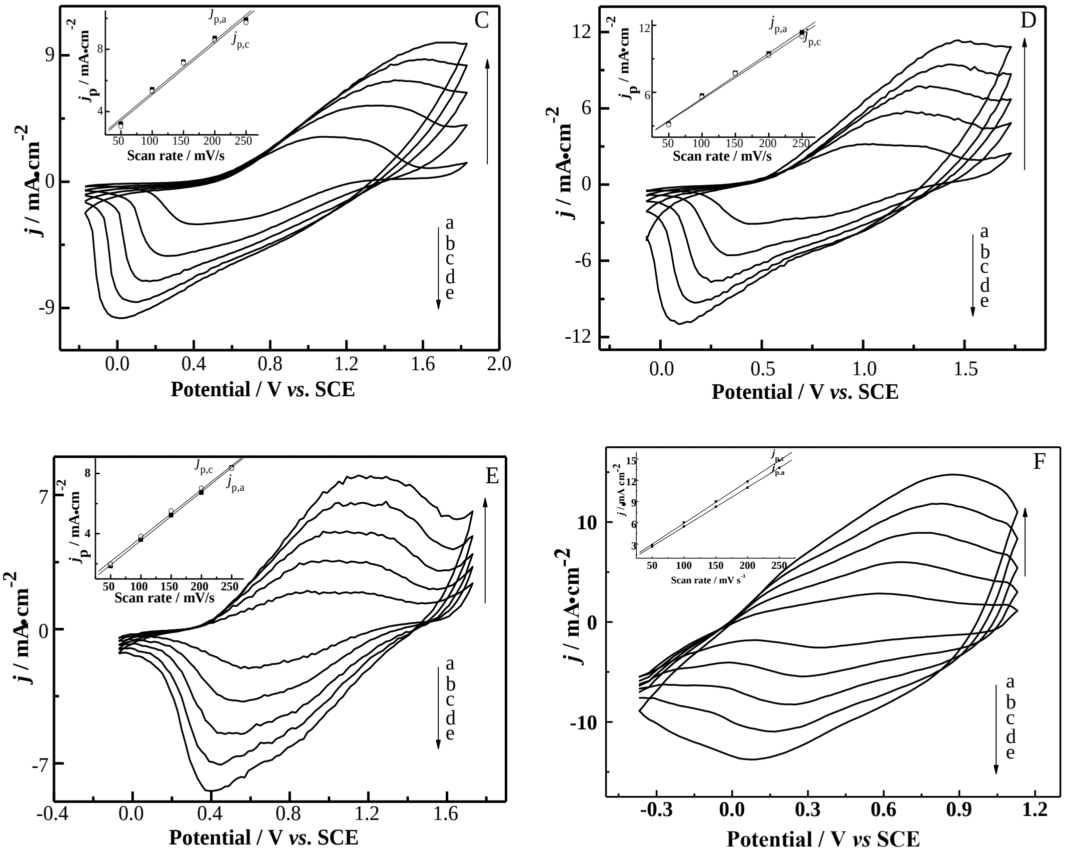


Figure 3. CVs of (A) Polypyrene films, (B) poly(pyrene-*co*-3MeT=1:1) films, (C) poly(pyrene-*co*-3MeT=1:5) films, (D) poly(pyrene-*co*-3MeT=1:15) films, (E) poly(pyrene-*co*-3MeT=1:30) films, (F) PMeT films recorded in BFEE The scanning rates are 50, 100, 150, 200 and 250 mV s^{-1}. $j_{p.a}$, $j_{p.c}$ are defined as the anodic peak current densities, and the cathodic peak current densities, respectively.

Farther studying the electrochemical behaviors of polypyrene, PMeT and copolymer films were synthesized with different feed ratios at an identical 1.2 V potential. Fig.3 shows the electrochemical performance of the polymer films measured by CVs in BFEE. At the scanning rate of 50 mV s^{-1}, the anodic and cathodic peak potentials of the polypyrene film appear at 0.91 and 0.59 V [Fig. 3(A)], respectively, and those of the PMeT film appeared at 0.61 and 0.38 V, respectively [Fig. 3(F)]. The anodic peak potentials of the copolymer films prepared with the feed ratios of pyrene to 3MeT at 1:1, 1:10, 1:15, and 1:30 are 1.01, 0.52, 1.01, and 0.46 V, respectively. Additionally, their cathodic peak potentials were 1.09, 0.40, 0.88, and 0.56 V, respectively [Fig. 3(B, C, D and E)]. All of the peak current densities were proportional to the scan rates of the potentials (inset of Fig. 3), declaring that the electrochemical processes of all films are not limited by the diffusion [25]. The copolymer films can be repeatedly cycled between the conducting (oxidized) and insulating (neutral) states in pure BFEE, which does not undergo obvious material decomposition, showing that the polymer has good stability.

3.3 Structural Characterization

The color of the solutions gradually changed from colorless to black along with the process of polymerization, indicating the possible formation of soluble oligomers during the anodic oxidation. Thereafter, the fractional oligomers became insoluble and were deposited on the stainless-steel plate, showing that the polymer backbone is growing. However, a small number of oligomers were still able to diffuse from the electrode into the solution, resulting in the darkening of its color. Oligopyrenes can easily dissolve in some organic solvents, such as methanol, dimethyl sulfoxide (DMSO) and so on. In contrast, because of its poor solubility, the electrochemically prepared PMeT is barely dissolved in any organic solvent. As the copolymers possess the combined performance of oligopyrene and PMeT, they may dissolve in DMSO and diethyl ether.

As shown in Fig.4, the doped polypyrene, PMeT, and copolymer films were characterized by UV-vis spectroscopy. There are two characteristic absorptions of the polypyrene film at 307 and 390 nm. The absorption peak from 340 to 440 nm is related to the transition of the valence band and conduction band for polypyrene.

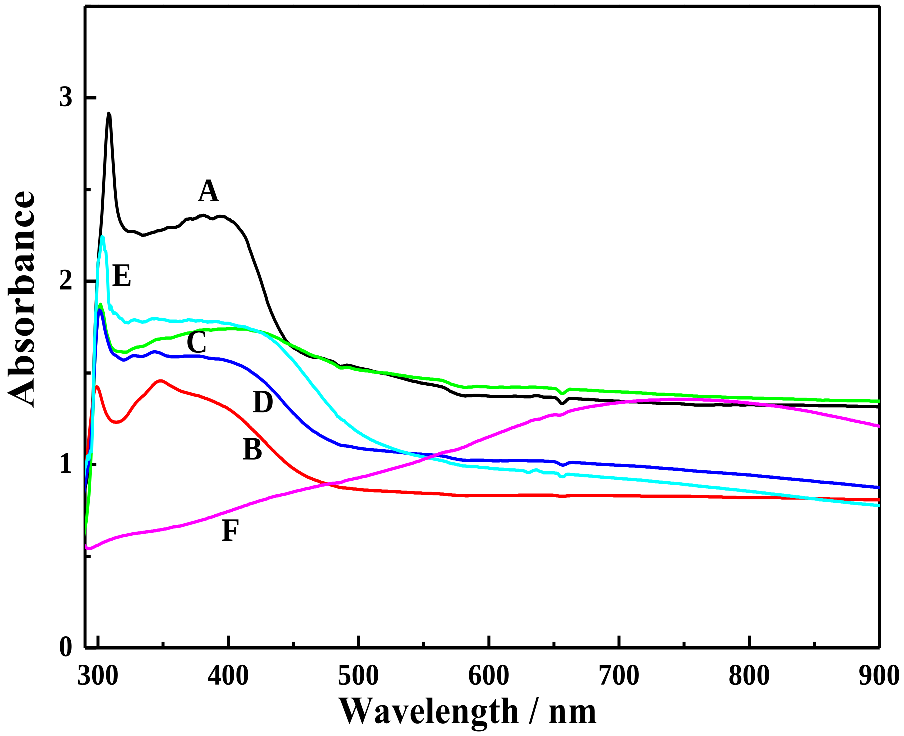


Figure 4. UV–visible spectra of (A) Polypyrene, (B) poly(pyrene-*co*-3MeT=1:1), (C) poly(pyrene-*co*-3MeT=1:5), (D) poly(pyrene-*co*-3MeT=1:15), (E) poly(pyrene-*co*-3MeT=1:30) , (F) PMeT coated on an ITO electrode in the doped states.

A wide absorption of the doped PMeT film was located from 650 to 860 nm [Fig. 4 (F)], indicating the presence of characteristic carriers (e.g. polarons and bipolarons) in the doped state. During the doping process, the originally filled PMeT valence band gradually became partly empty. The Fermi level dropped down to the valence band ensuring the metallic behavior of PMeT. As for copolymer film, it displayed similar characteristic absorptions as the polypyrene and PMeT films [Fig. 4 (B-E)]. Nevertheless, compared to the polypyrene film, the main absorption of the copolymer film showed a slight red shift which may be relevant to the introduction of 3MeT units, further proving that the occurrence of copolymerization.

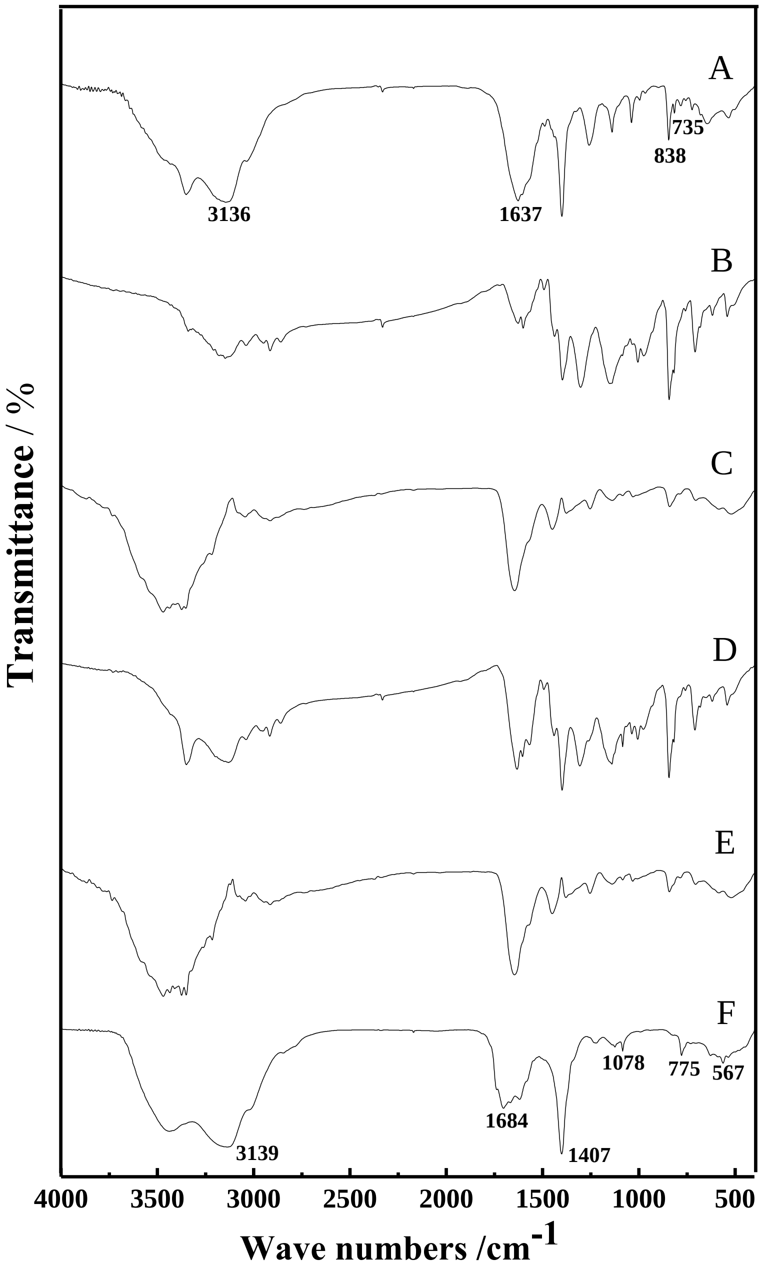


Figure 5. Infrared spectra of (A) Polypyrene, (B) poly(pyrene-*co*-3MeT=1:1), (C) poly(pyrene-*co*-3MeT=1:5), (D) poly(pyrene-*co*-3MeT=1:15), (E) poly(pyrene-*co*-3MeT=1:30), (F) PMeT.

Fig. 5 shows the FI-TR spectra of polypyrene, PMeT and copolymers with diverse feed ratios of pyrene to 3MeT. The band of the polypyrene spectrum at 735 cm^{-1} was derived from the out-of-plane vibration of the three adjacent C–H bonds of pyrene rings [Fig. 5(A)], and the band at 838 cm^{-1} was derived from the two adjacent C–H bonds of pyrene rings. The peaks located at 1637 and 3136 cm^{-1} correspond typically to the stretching vibration peaks of C=C and C–H bonds in the pyrene rings. For the PMeT spectrum, the bands at 1684 and 1078 cm^{-1} were derived from the C=C bond stretching mode of the thiophene ring [26], and the band at 775 cm^{-1} is specified as the out-of-plane vibration of the C–H bond. As shown in Fig. 5(F), the characteristic peaks of the 2,5-disubstituted 3MeT are evident. The C–H stretching bands of the aromatic ring were located at 3139 cm^{-1}. The band of the deformation for the methyl group were located at ~1407 cm^{-1} [27, 28]. The characteristic peak of the C–S bond was located at 567 cm^{-1}. The copolymers spectra showed the uniform characteristic bands of polypyrene and PMeT [Fig. 5 (B-E)], indicating that the potentiostatic copolymerization occurred between pyrene and 3MeT.

3.4 Fluorescence Properties

It is well known that polypyrene, which can easily dissolve in a majority of organic solvents, is a well-blue-light emitter. However, P3MeT has almost no emission over the entire wavelength range. P3MeT, which is synthesized by direct anodic oxidation, can be easily electrodeposited to prepare free-standing films which has excellent mechanical performance and high electrical conductivity. If their advantages can be combined, it can be prepared with both light-emitting, flexible, and highly conductivity of the new copolymer as a light-emitting material. The fluorescence spectra of polypyrene and copolymers are examined in DMSO. Under a 295 nm excitation wavelength, polypyrene showed strong and weak emission peaks at ~460 and ~340 nm, respectively [Fig. 6 (A)].

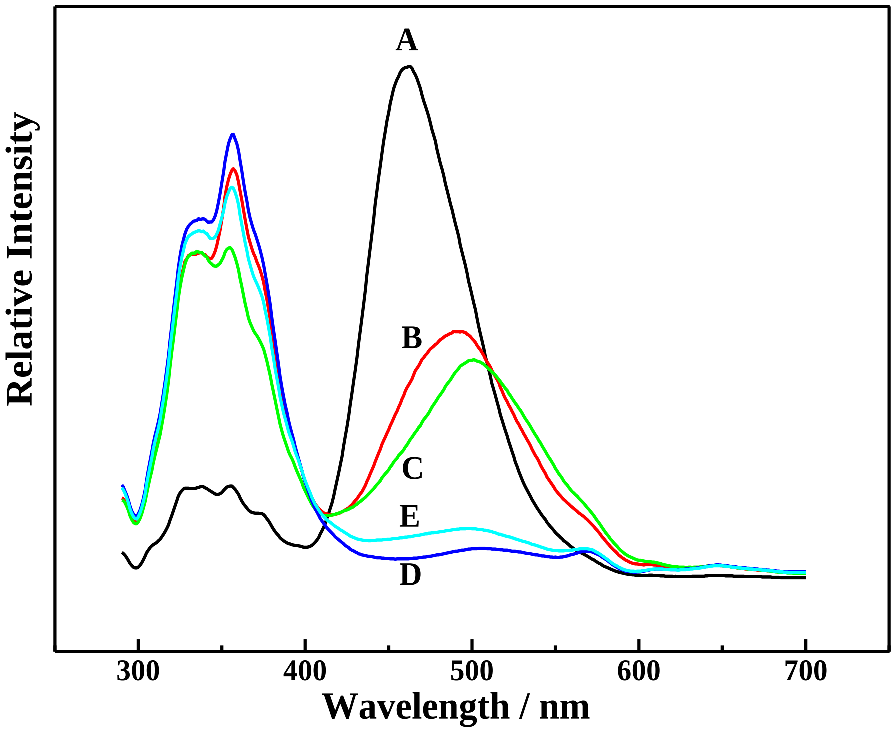


Figure 6. Fluorescence spectra of (A) Polypyrene, (B) poly(pyrene-*co*-3MeT=1:1), (C) poly(pyrene-*co*-3MeT=1:5), (D) poly(pyrene-*co*-3MeT=1:15), (E) poly(pyrene-*co*-3MeT=1:30). Solvent: DMSO.

For the copolymers, there were three emission peaks located at 335, 355, and 490 nm and the corresponding fluorescence spectra showed a slight red shift [Fig. 6 (B-E)]. Compared to the polypyrene, the increased concentration of 3MeT during the copolymerization can cause the increased intensity of emission peak at 355 nm and the decreased intensity of emission peak at 490 nm [Fig. 6 (B-E)]. With the introduction of 3MeT into the polypyrene chains, DMSO solutions containing the copolymers showed the different color under 365 nm UV irradiation. As the feed ratios of pyrene to 3MeT were 1:1 and 1:5, the color of the solutions was green, but while the feed ratios of pyrene to 3MeT are 1:15 and 1:30, the color of solutions gradually turned yellow-green, which may be ascribed to the incorporation of 3MeT units into the polymer chains [Fig. 7]. Therefore, it is possible to control the fluorescence performance of copolymers by changing the feed ratios of the mixed monomers.

3.6 Electrical Conductivity

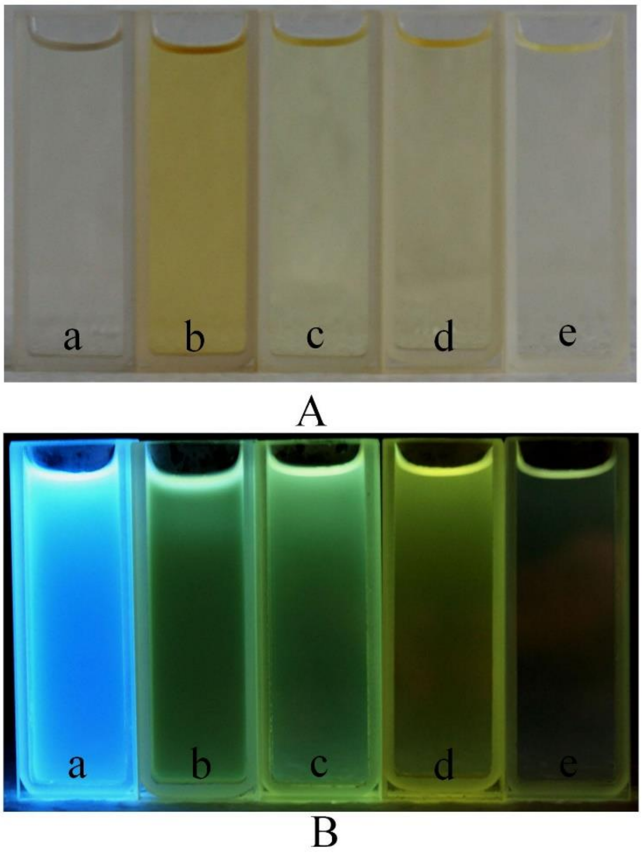


Figure 7. A: Photographs of (a) Polypyrene, (b) poly(pyrene-*co*-3MeT=1:1), (c) poly(pyrene-*co*-3MeT=1:5), (d) poly(pyrene-*co*-3MeT=1:15), (e) poly(pyrene-*co*-3MeT=1:30) dissolved in DMSO under nature light. B: Photographs of (a) Polypyrene, (b) poly(pyrene-*co*-3MeT=1:1), (c) poly(pyrene-*co*-3MeT=1:5), (d) poly(pyrene-*co*-3MeT=1:15), (e) poly(pyrene-*co*-3MeT=1:30) dissolved in DMSO under UV irradiation (365 nm).

As shown in Table 1, the electrical conductivities of the all samples were investigated. PMeT showed good electrical conductivity (56.2 S cm^{-1}), but that of polypyrene was ~1.0×10^{-3} S cm^{-1}. The electrical conductivities of the copolymers lied between those of the PMeT and the polypyrene, indicating that inserting 3MeT into polypyrene is very effective in improving the electrical conductivity of polypyrene. This is beneficial for the applications of polypyrene.

Table 1. The electrical conductivities of Polypyrene, P3MeT, and copolymers films.

Samples	Conductivity (S cm^{-1})
Polypyrene	0.001
Poly(pyrene/ 3MeT = 1:1)	0.032
Poly(pyrene/ 3MeT = 1:10)	0.089
Poly(pyrene/ 3MeT = 1:20)	0.17
Poly(pyrene/ 3MeT = 1:50)	0.31
Poly(3MeT)	56.2

4. CONCLUSIONS

In summary, we report a new copolymer which was prepared by the direct anodic oxidation of pyrene and 3MeT mixed monomers in BFEE. The performance of poly(pyrene-*co*-3MeT) films can be regulated and controlled by the feed ratios of the mixed monomers. The introduction of 3MeT into the polypyrene chain can improve the mechanical performance and electrical conductivity of the polypyrene film. The characterization of fluorescence indicated that the copolymer is a great blue-green-light emitter which has two emission peaks at 383 and 523 nm, respectively. Besides, the copolymer emission intensity can be readily adjusted by the feed ratios of the mixed monomers.

ACKNOWLEDGEMENTS

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