

Electrochemical and electrochromic properties of a novel copolymer based on perylene and EDOT

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ABSTRACT

Copolymer of perylene (PE) with 3,4-ethylenedioxythiophene (EDOT) was electrochemically synthesized and characterized. The resultant copolymer film not only has orange-light emitter property, but also possesses distinct electrochromic properties. It shows four colors at different doped states (from red–brown to light-green). Double potential step chronoamperometry experiment reveals that the copolymer film has high optical contrast (25% at 516 nm, 42% at 1100 nm) and fast switching time (2 s). Cyclic voltammograms indicate that the polymer has reasonable stability because of the existence of EDOT units.

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1. Introduction

Conducting polymers containing conjugated bonds have attracted great interest due to their good environmental stability, ease of fabrication and modified architecture which can control their optical and electrical properties [1–4]. Thanks to these outstanding advantages, these polymers are considered as the good candidates for use in polymer light-emitting diodes [5], electrochromic devices [6], polymer solar cells [7] and sensors [8]. Conjugating polymers can be synthesized by either chemical or electrochemical polymerization. Though a great deal of products can be obtained by chemical route, polymers are difficult to be purified because of the residues of catalyst, which will affect their performance for applications [9]. Comparing with chemical route, electrochemical polymerization can gain polymers under appropriate potential directly without expensive catalyst, and the residues of electrolyte can be eliminated by undoping under negative potential. Moreover, conjugated polymer film can be acquired on the electrode directly. This not only enlarges the scope of polymers, but also omits the procedure of the film coating [10,11].

Perylene (PE) and its derivatives perylenediimides (PDIs) have been widely used in the fields of photovoltaic cells [12], organic transistors [13] and electrochromic devices [14] due to their high fluorescence quantum yield and intense absorption in near-infrared region. However, only a few articles reported its polymer or copolymer by electrochemical polymerization [15,16]. The reason

may be that PPE gets degraded easily under electrochemical environment. Fortunately, this problem can be resolved by copolymer with a co-monomer of better electrochemical stability [17,18]. PEDOT is a low band gap material with outstanding electrochemical stability [19–22]. It is expected that fine-tuning copolymer can be obtained due to the introduction of EDOT units and the copolymer may possess some useful properties.

In this paper, we successfully synthesized the copolymer consisting of PE and EDOT via the electrochemical method. The obtained copolymer films are investigated by cyclic voltammetry (CV), FT-IR, UV–vis absorption and fluorescence spectra. The electrochromic properties of copolymer are also studied in details. The synthesize route of copolymer is illustrated in Scheme 1.

2. Experimental

2.1. Materials

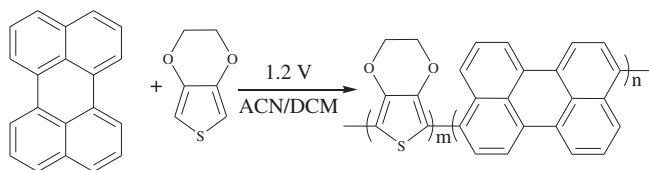
Perylene (PE, Energy Chemical, 99%). 3,4-ethylenedioxythiophene (EDOT, Aldrich, 98%). Tetrabutyl ammonium perchlorate (TBAP, Acros Organics, 95%) was dried in vacuum at 80 °C for 24 h. Commercial HPLC grade acetonitrile (ACN, Shanghai Chemical Reagent Company) and Dichloromethane (DCM, Hangzhou Shuanglin Chemical Reagent Company) were used without further purification. All other reagents were commercial products used as received.

2.2. Equipments

A Nicolet 6700 Fourier-transform infrared spectrometer (FTIR) (Thermo Fisher Nicolet, USA) were used to measure the infrared

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Scheme 1. Electrochemical copolymerization route of PE and EDOT.

spectra. A CHI 660C electrochemical analyzer (CH Instruments, China) were used to perform the electrochemical measurements. UV-vis spectra were recorded on a Varian Cary 100 UV-vis spectrophotometer (Varian, USA). Thermal analysis were performed by a Diamond TG/DTA 6300 under a nitrogen stream in the temperature range of 60–400 °C with a heating rate of 10 °C min⁻¹. SEM measurements were taken by using a Hitachi S-4800 scanning electron microscopy (Hitachi, Japan).

2.3. Electrochemistry

The electro-syntheses and measurements were performed in a conventional three-electrode cell with an ITO-coated glass (CSG holding Co. LTD, $R_s \leq 10 \Omega \text{ cm}^{-1}$, the active area: 1.0 cm × 2.0 cm) as working electrode which was sequentially washed with ethanol, acetone and deionized water under ultrasonic before use, a platinum sheet and a double-junction Ag/AgCl electrode (silver wire coated with AgCl in saturated KCl solution, 0.1 M TBAP in ACN/DCM (1:1, by volume) solution as the second junction) were applied as the counter electrode and the reference electrode, respectively. All the electrochemistry experiments were carried out at 25 °C under N₂ atmosphere.

All electrochemical polymerization and CV tests were investigated in ACN/DCM (1:1, by volume) solution containing 0.1 M TBAP as a supporting electrolyte. The concentration of PE, PE/EDOT and EDOT used for polymerization were all 5 mM. The polymer films were prepared via potentiostatic electrolysis on ITO/glass electrode. Before characterized, the films were electrolyzed at negative potential for several minutes in monomer-free electrolytic solution, then the films were washed with clean ACN for several times to remove the residual supporting electrolyte and the monomers.

3. Results and discussion

3.1. Electrochemical polymerization

Fig. 1 displays the cyclic voltammogram (CV) curves of PE, EDOT and the mixture of two monomers in ACN/DCM solution containing 0.1 M TBAP at a potential scan rate of 100 mV s⁻¹. As the CV scan continued, polymer films are formed on the working electrode surface. The increase in the current implies that the amount of conducting polymers deposited on the electrode is increasing [23]. As shown in Fig. 1a, the CV of PE presents an obvious oxidation peak at +1.13 V and a reduction peak at +0.8 V. The pure EDOT (Fig. 1c) reveals a broad oxidation and reduction peak between +0.3 V and -0.6 V. Compared with PE and EDOT, the CV of PE/EDOT (Fig. 1b) is different from that of PE and EDOT, which only shows a reduction wave at +0.6 V, indicating the formation of new polymer [24]. However, the CV response of homo-polymer blends could also give similar behaviors. Therefore, the further evidence is needed.

3.2. Electrochemistry of polymer films

The films of PPE, P (PE/EDOT) and PEDOT were prepared via potentiostatic polymerization on ITO/glass electrodes in ACN/DCM solution containing 0.1 M TBAP. And then, they were undoped at negative potential in monomer-free solution except

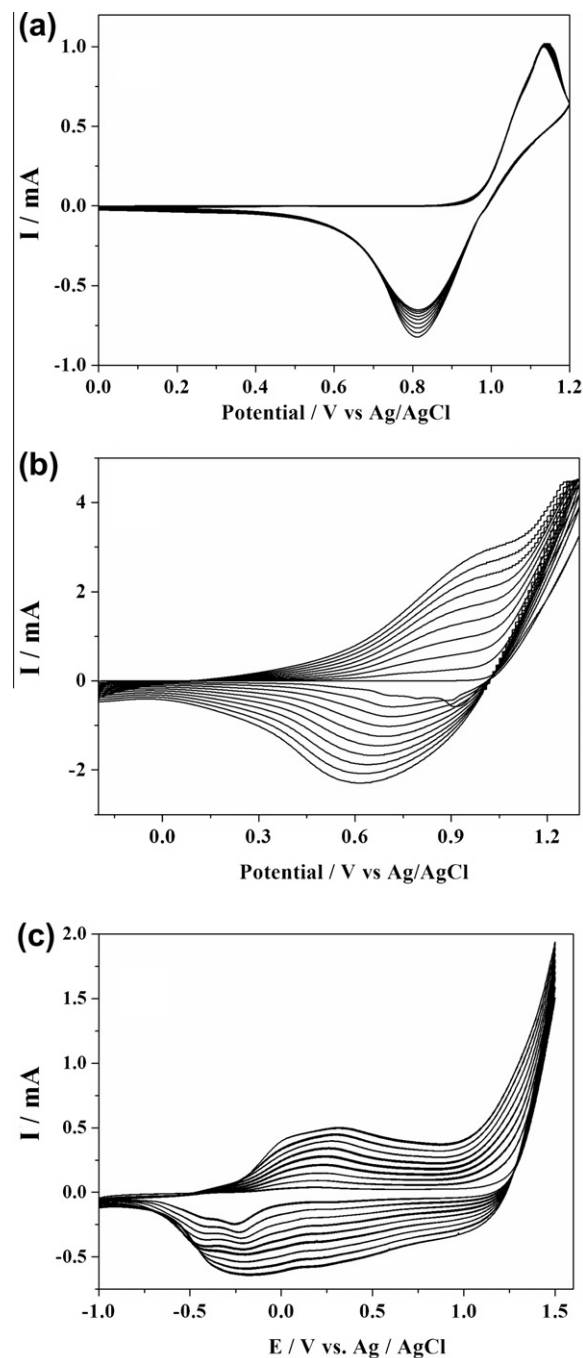


Fig. 1. Cyclic voltammogram curves of (a) 5 mM PE, (b) the mixture of 5 mM PE and 5 mM EDOT, (c) 5 mM EDOT in 0.1 M TBAP/(ACN:DCM = 1:1) solutions at a scan rate of 100 mV s⁻¹.

PPE which was only washed with ACN for several times (for PPE is unstable and easy to fall off the ITO electrode due to its poor adhesion). The CVs of films in monomer-free solution are illustrated in Fig. 2. It is obvious that copolymer film performs an intermediate response with an oxidation peak at +0.95 V and a reduction peak at +0.6 V, which can be attributed to the existence of both PE and EDOT units.

Fig. 3a exhibits the CV curves of P (PE/EDOT) film at different scanning rates ranging from 50 to 250 mV s⁻¹ in monomer-free solution. Well-defined oxidation and reduction peaks confirm the good electro-activity of polymer film. The peak current densities are proportional to the potential scan rate (Fig. 3b), indicating that the electrochemical processes of polymer are not diffusion limited [25,26].

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