



Electrochemical Copolymerization of Cross-Linkable Polythiophene and 9H-Fluorene

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The copolymerization of poly-3-ethyl-3-([6-(3-thienyl)hexyl]oxy)-methyl)oxetane (PTO) and 9H-fluorene was successfully achieved electrochemically in CH_2Cl_2 containing 25 % boron trifluoride diethyl etherate (BFEE) (by volume) as supporting electrolyte by direct anodic oxidation of the monomer mixtures on platinum or an optically transparent ITO electrode. As-formed copolymer own the advantages of PTO, such as good electrochemical behaviours and excellent ambient stability. The structure of the copolymer were investigated by UV-VIS, fluorescence spectra and thermal analysis, respectively. The fluorescence spectra indicate that PPTOF films are yellow-light emitters. Thermal analysis studies confirmed PPTOF has a good thermal stability.

Key Words: Polythiophene, Electrochemical polymerization, Ring-opening, Boron trifluoride diethyl etherate, Copolymerization.

INTRODUCTION

Inherently conducting polymers with π -conjugated electronic structures have been widely investigated¹⁻³ due to their potential industrial applications based on their high conductivity and organic light-emitting. Conducting polymers are currently the subject of a board research area, especially for the applications in electronic and electrochemical devices such as organic field-effect transistors (OFETs)⁴, organic light-emitting diodes (OLEDs)⁵, polymer solar cells (PSCs)⁶ and sensors⁷. Among these polymers, poly(thiophenes) and poly(fluorene) have been received considerable attention, such as poly(thiophenes) have been used in the development of electronic⁸, energy storage batteries⁹, photochromic devices¹⁰ and nonlinear optical devices¹¹.

It is well known that copolymerization is one of efficient approaches to modify the properties of conducting polymers, which can produce copolymers with properties being intermediate between individual polymers. By means of the electrochemical copolymerization, some new conducting polymers have been prepared with several obvious advantages, such as variation of electrical conductivity, enhancement of electrochemical activity and improvement of thermal stability.

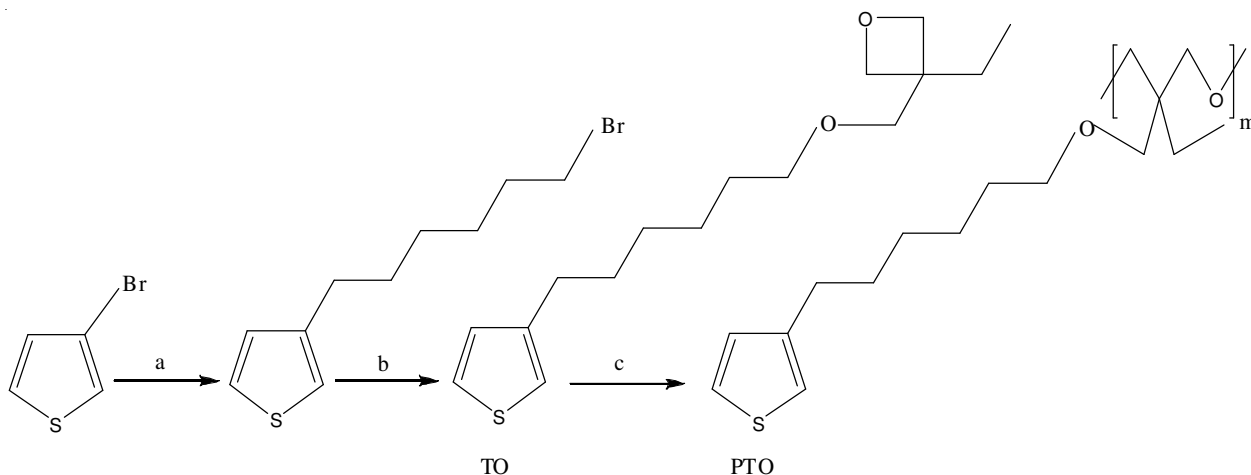
Poly(fluorene) have great fluorescence properties, however, the poor mechanical properties and the low electrical conductivity which limits its application. Poly(thiophenes) have great mechanical properties and lower fluorescence properties than poly(fluorene).

In this paper we report on the use of oxetane-functionalized cross-linkable conjugated polythiophene (PTO) and 9H-fluorene (F) were copolymerized successfully by direct electrochemical oxidation in CH_2Cl_2 containing additional 25 % (by volume) boron trifluoride diethyl etherate (BFEE). The electrochemistry of copolymers (PPTOF) were studied. In addition, the spectroscopic properties and thermal stability of the copolymer were also investigated in detail.

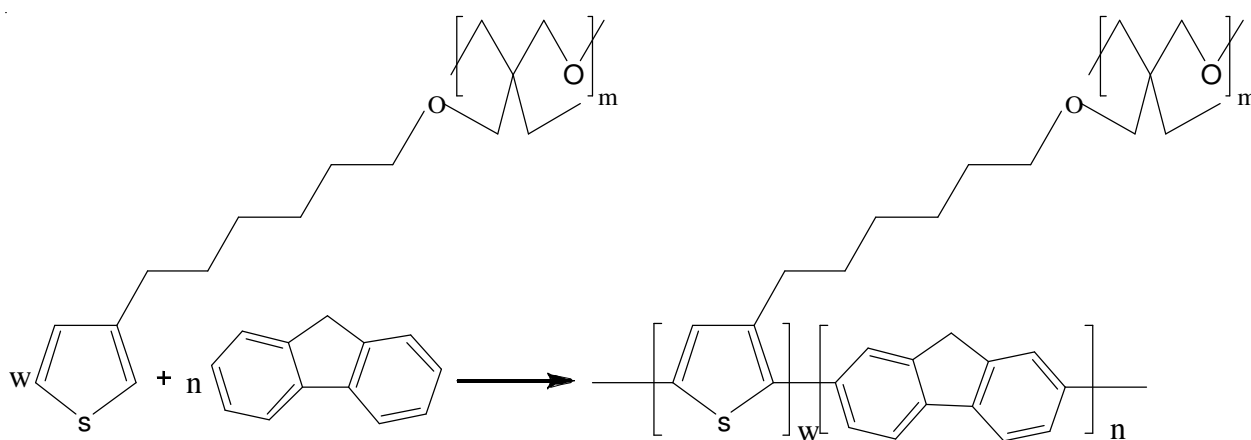
EXPERIMENTAL

General consideration: All reactions were carried out under a dry nitrogen atmosphere. CH_2Cl_2 were distilled over calcium hydride. All solvents were distilled under nitrogen and saturated with nitrogen prior to use. UV-visible spectra were taken by using Perkin Elmer Lambda 900 UV-VIS-NIR spectrophotometer. ^1H NMR spectrum was recorded on a Bruker AV 400 NMR spectrometer and CDCl_3 was used as the solvent. The thermogravimetric analysis (TGA) was performed with a thermal analyzer of Netzsch TG 209. The fluorescence properties were determined with Hitachi F-4500 fluorescence spectrophotometer.

3-(6-Bromohexyl)thiophene (BHT) was synthesized by reaction of 3-bromothiophene (aladdin) with 1,6-dibromohexane (aladdin) in hexane solution using BuLi (aladdin) as reducing agent under the atmosphere of N_2 as illustrated in **Scheme-I**. Boron trifluoride diethyl etherate (BFEE), Sinopharm Chemical Regagent Co., Ltd) was distilled and stored at -20°C before use. Anhydrous sodium acetate was prepared by Guangcheng of Tianjin.



Scheme-I: (a) BuLi, hexane, THF, reflux, 1,6-dibromohexane, THF; (b) 3-ethyl-3-oxetanemethanol, NaOH, toluene, reflux, 8 h; (c) BFEE, CH₂Cl₂



Scheme-II: Copolymerization

Preparation of 3-ethyl-3-((6-(3-thienyl)hexyl)methyl)oxetane (TO): The oxetane-substituted conjugated polymer was prepared by **Scheme-I**¹². ¹H NMR (CDCl₃, d (ppm)): 7.25 (t, 1H), 6.92 (t, 2H), 4.46 (d, 2H), 4.36 (d, 2H), 3.53 (s, 2H), 3.47 (t, 2H), 2.64 (t, 2H), 1.78 (m, 2H), 1.61 (m, 4H), 1.39 (m, 4H), 0.90 (t, 3H).

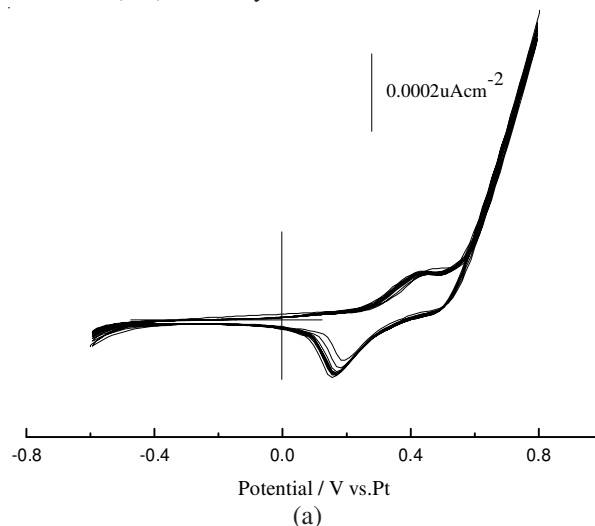
Chemical polymerization: Poly-3-ethyl-3-((6-(3-thienyl)hexyl)methyl)oxetane (PTO) *via* boron trifluoride diethyl etherate (BFEE) to chemical ring opening¹³. 0 °C, C1 (1.2 × 10⁻² mol, 2.976 g), CH₂Cl₂ 9.6 mL, BF₃O (C₂H₅)₂ (3 × 10⁻³ mol, 0.768 mL). After 48 h, ethanol end the reaction, then extracted with CH₂Cl₂ and washed with water (3 × 200 mL). The organic layer was dried over anhydrous MgSO₄, filtered and concentrated.

Copolymerization: High quality freestanding PPTOF network films were synthesized successfully in CH₂Cl₂ containing additional 25 % (by volume) boron trifluoride diethyl etherate by direct anodic oxidation.

RESULTS AND DISCUSSION

Electrochemistry copolymerization: The successive cyclic voltammograms (CVs) of mixtures of the two monomers with various feed ratios on a Pt electrode in BFEE were shown in Fig. 1. 9H-Fluorene (F) could be reduced and oxidized between 0.35 and 0.55 V (Fig. 1 a). On the other hand, CVs of

PTO:F (3:1 mass ratio) showed broad redox waves with reduction and oxidation peaks at -0.50 and 0.50 V (Fig. 1b), CVs of PTO:F (1:1) showed broad redox waves with reduction and oxidation peaks at -0.28 and 0.60 V (Fig. 1c), cyclic voltammograms of PTO:F (1:3) showed broad redox waves with reduction and oxidation peaks at -0.40 and 0.50 V (Fig. 1d). Film of 9H-fluorene was very unstable in the air, the same phenomenon was found in PTO:F (3:1) and PTO:F (1:3), however PTO:F (1:1) was very stable.



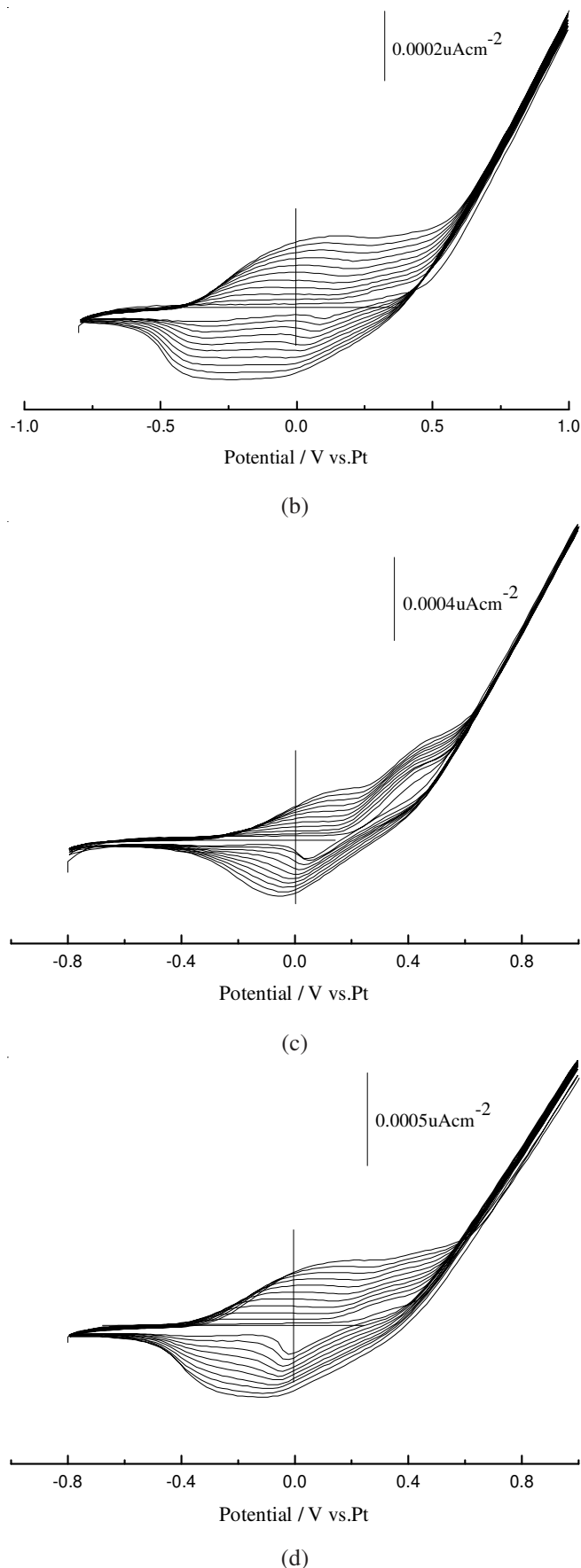


Fig. 1. Cyclic voltammograms of 9H-fluorene (F) (a), PTO:F (3:1) (b), PTO:F (1:1) (c), PTO:F (1:3) (d), in CH_2Cl_2 containing 25 % BFEE (by volume) BFEE. Potential scan rate: 100 mV s^{-1}

It is clearly shown that on the first cyclic voltammograms cycle, the current on the reverse scan was higher than that on the forward scan. The formation of this loop was characteristic of nucleation processes and only appeared on the first cyclic voltammograms cycle. At the same time, with the potential scans continues, a polymer film was formed on the electrode surface. The increases of the redox wave currents implied that the amount of the polymer on the electrode surface has increasing. The potential shift of this maximum provided information about the increase of the electrical resistance in the polymer film and the over-potential was needed to overcome the resistance. All these phenomena indicated that high-quality PPTOF films were formed on the anode surface.

UV-VIS and fluorescence spectra: The UV-vis spectra of 9H-fluorene, PTO prepared from CH_2Cl_2 , PPTOF prepared from CH_2Cl_2 containing 25 % BFEE (by volume) BFEE are shown in Fig. 2. The UV spectrum of the monomer F shows peaks at 264, 290, 300 nm. PTO shows peaks at 236 nm. On the contrary, the spectra of the copolymer have a much broader absorption at 336 nm. The longer wavelength in the spectra indicated a longer polymer sequence. These spectral results also confirmed a conjugated copolymer formation with a broad molarmass distribution.

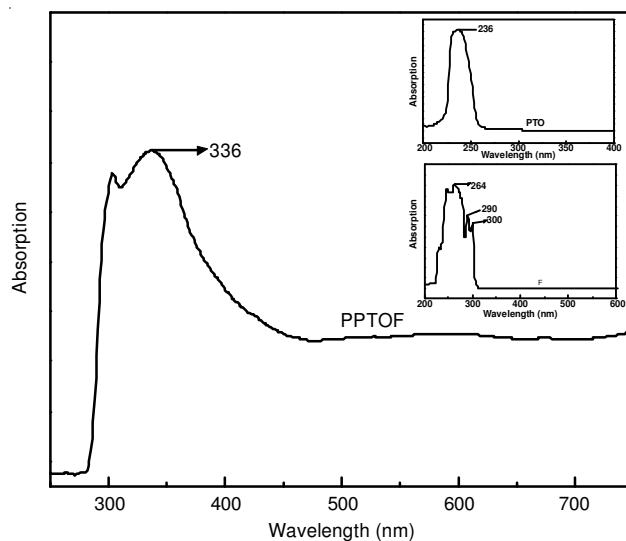


Fig. 2. UV-visible spectra of F, PTO, PPTOF

The fluorescence spectra of the 9H-fluorene, PTO, PPTOF as shown in Fig. 3. As shown in the figure, an obvious emission peak was found at 314 and 336 nm for PTO and 9H-fluorene, while the emission peak of the PPTOF films was found at 377, 400, 547 nm. The red shift of emission peak indicated that longer conjugation PPTOF was formed. These results imply that PPTOF may be used in yellow blue light-emitting material.

Thermal analysis: The polymer films prepared electrochemically by using CH_2Cl_2 containing 25 % BFEE (by volume) thermal analysis of PPTOF was shown in Fig. 4. The thermal analysis of PPTOF was tested under a nitrogen stream from 300 to 1000 K with a heating rate of 10 K/min. There are two steps in weight loss. The first one is from 300 to 400 K, up to 10 %, which can be ascribed to water evaporation or

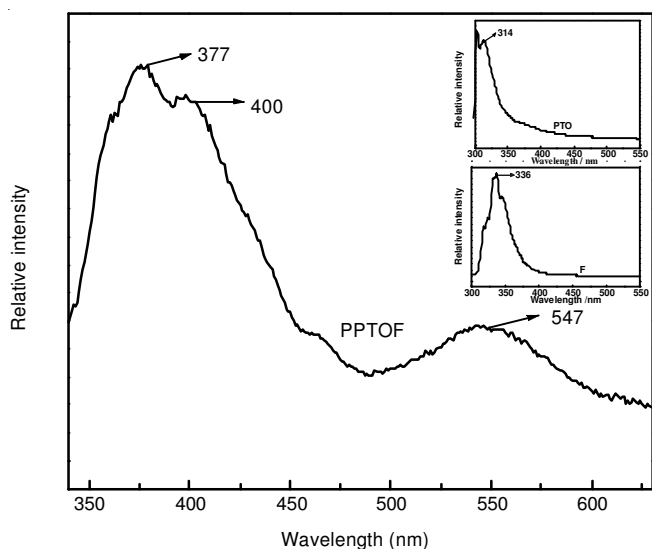


Fig. 3. Fluorescence spectra of F, PTO in CH_2Cl_2 and the PPTOF films coated on an optically transparent ITO electrode

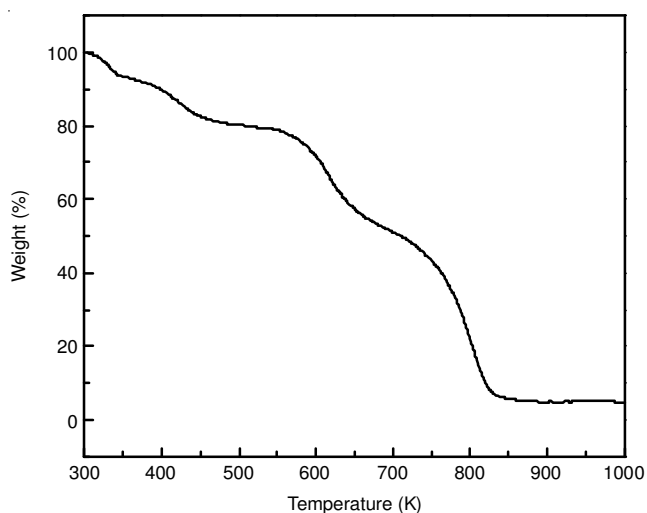


Fig. 4. TGA curves of PPTOF films obtained potentiostatically at 1 V vs. Pt from CH_2Cl_2 containing 25 % BFEE (by volume) BFEE

other moisture trapped in the polymer. The second occurred from 400 to 580 K with a weight loss 15 %. This was mainly due to the ions doped polymer degradation and the degradation

of the polymer contained in the oligomers. The main one occurred from 580 to 750 K, up to 33 %, which was attributed to the degradation radiation of the PPTOF. The main weight loss of PPTOF was found from 750 to 1000 K with a weight loss of 34 %, which results from the degradation of the PPTOF main backbone. All these results indicate that PPTOF has a good thermal stability.

Conclusion

The electrochemical copolymerization of PTO and 9H-fluorene successfully realized in CH_2Cl_2 containing 25 % BFEE (by volume) by direct anodic oxidation of PTO and 9H-fluorene monomer mixtures. The copolymers showed many advantages, such as good electrochemical behaviour, good mechanical properties and favourable thermal stability. Fluorescence studies revealed that the copolymer was good yellow blue light emitter. Under these conditions, copolymer films PPTOF may meet the application in light emitting diodes as light-emitting films.

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