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Electrochemical Copolymerization of Two Novel Polythiophene

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The copolymerization of poly-3-ethyl-3-({[6-(3-thienyl)hexyl]oxy}-methyl)oxetane (PTO) and poly[3-(hexyl methacrylate)] thiophene (PMT) was successfully achieved electrochemically in CH_2Cl_2 containing 25 % boron trifluoride diethyl etherate (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 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 PPOMT films are yellow-light emitters. Thermal analysis studies confirmed PPOMT has a good thermal stability.

Key Words: Electrochemical, Copolymerization, Polythiophene.

INTRODUCTION

Light-emitting conjugated polymers continue to attract great attention because of their potential display applications. 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)[1], organic light-emitting diodes(OLEDs)[2], polymer solar cells(PSCs)[3] and sensors[4]. Among these polymers, poly(thiophenes) and poly(fluorene) have been received considerable attention. Such as poly(thiophenes) have been used in the development of electronic[5], energy storage batteries[6], photochromic devices[7] and nonlinear optical devices[8].

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 advantages, such as variation of electrical conductivity, enhancement of electrochemical activity and improvement of thermal stability.

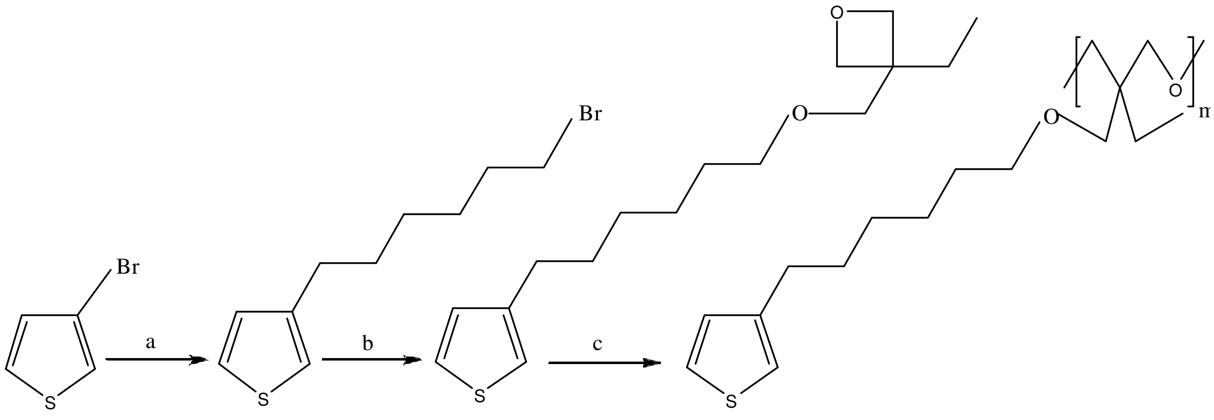
In this paper we report on the use of oxetane-functionalized cross-linkable conjugated polythiophene (PTO) and poly[3-(hexyl methacrylate)]thiophene(PMT) were copolymerized successfully by direct electrochemical oxidation in CH_2Cl_2 containing additional 25 % (by volume) boron trifluoride diethyl etherate (BFEE). The electrochemistry of copolymers (PPOMT) 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. The ^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 Reagent Co. Ltd.) was distilled and stored at -20 ºC before use. Anhydrous sodium acctate was maded by Guangcheng of Tianjin.

Preparation of TO: The oxetane-substituted conjugated polymer was prepared by **Scheme-I**[9]. ^1H NMR ($CDCl_3$), δ (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).



Scheme-I: (a) BuLi, hexane, THF, reflux, 1,6-dibromohexane, THF; (b) 3-ethyl-3-oxetanemethanol, NaOH, toluene, reflux, 8 h; (c) BFEE, CH_2Cl_2

Chemical ploymerization: PTO *via* BFEE to chemical ring opening[10]. 0 ºC, TO (1.2×10^{-2} mol, 2.976 g), CH_2Cl_2 9.6 mL, $BF_3O(C_2H_5)_2$ (3×10^{-3} mol, 0.768 mL). After 48 h, ethanol end the reaction, then extracted with CH_2Cl_2 and washed with water (3 × 200 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated.

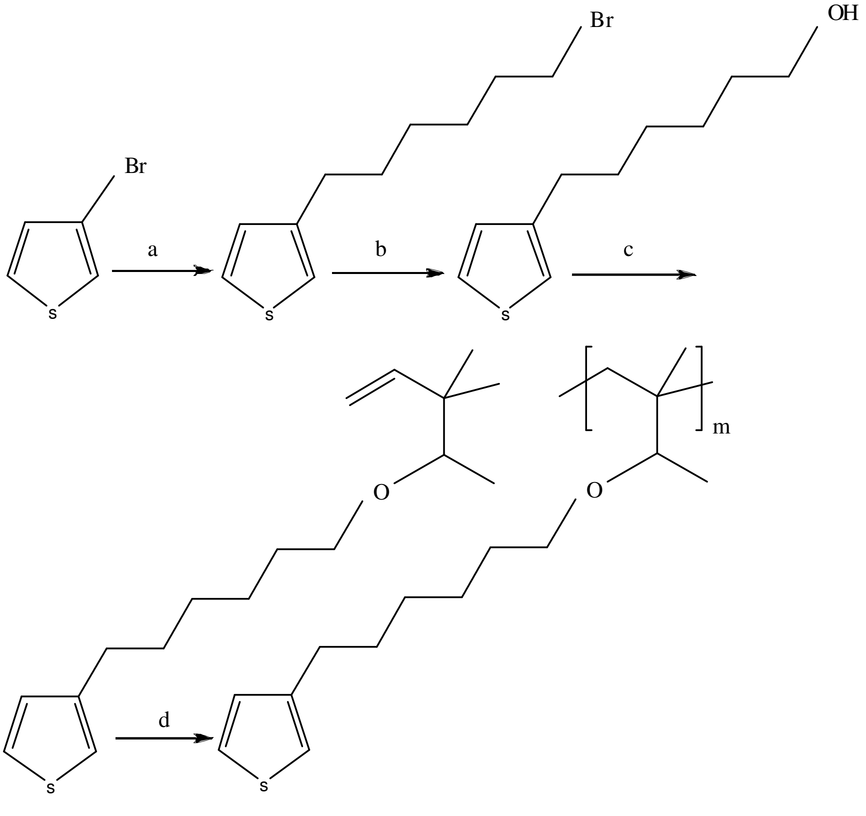
Preparation of MT: The polymethacrylate-substituted conjugated polymer was prepared by **Scheme-II**. ^1H NMR ($CDCl_3$), δ (ppm): 7.23 (t, 1H), 6.91 (t, 2H), 6.12 (t, 1H), 5.53 (t, 1H), 4.12 (d, 2H), 2.64 (t, 2H), 1.98 (m, 3H), 1.65(m, 4H), 1.39 (m, 4H).

Chemical ploymerization: PMT *via* AIBN 5 mol % to chemical ring opening. After 48 h, sodium chloride to demulsification. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated.

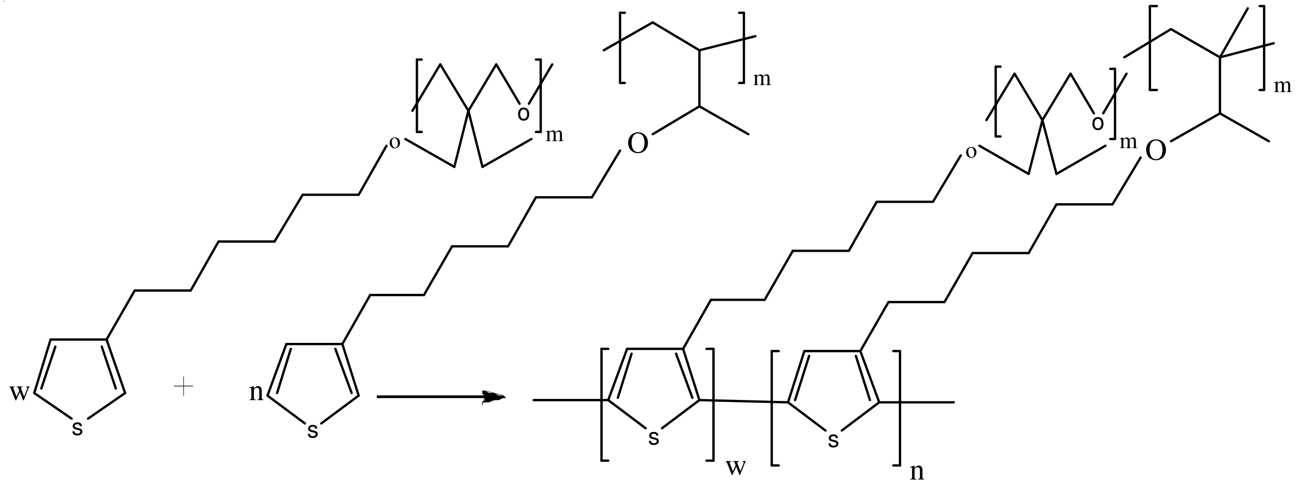
Copolymerization: High quality freestanding PPOMT network films were synthesized successfully in CH_2Cl_2 containing additional 25 % (by volume) BFEE by direct anodic oxidation **Scheme-III**.

RESULTS AND DISCUSSION

Electrochemistry copolymerization: It is clearly shown that on the first cyclovoltammetry 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 cyclovoltammetry

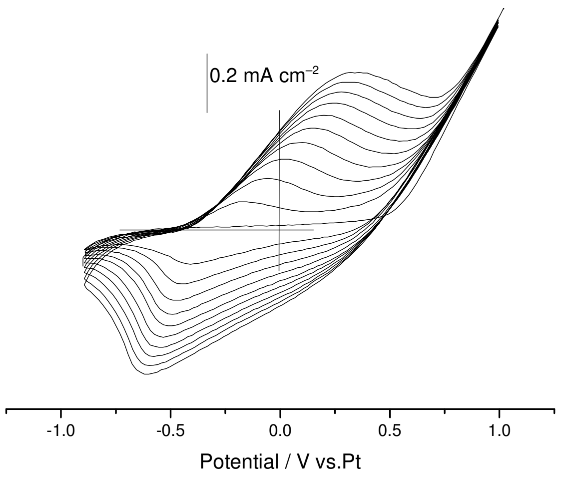


Scheme-II: (a) *n*-BuLi, -40 ºC, then 1,6-dibromohexane, -10 ºC; (b) anhydrous sodium acetate, DMF, 90 ºC, then hydrolysis; (c) methacryloyl chloride, -10 ºC; (d) AIBN, THF, reflux for 2 days

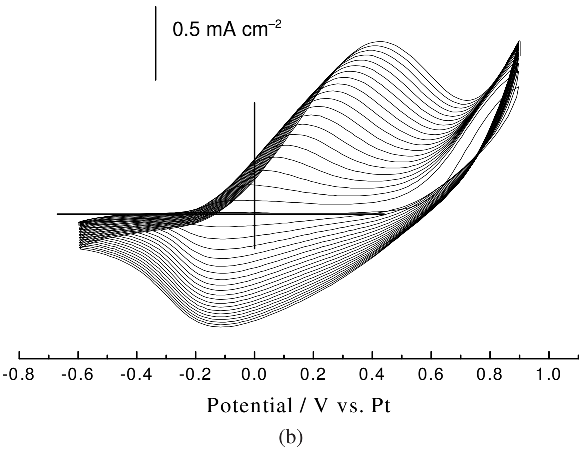


Scheme-III: Copolymerization

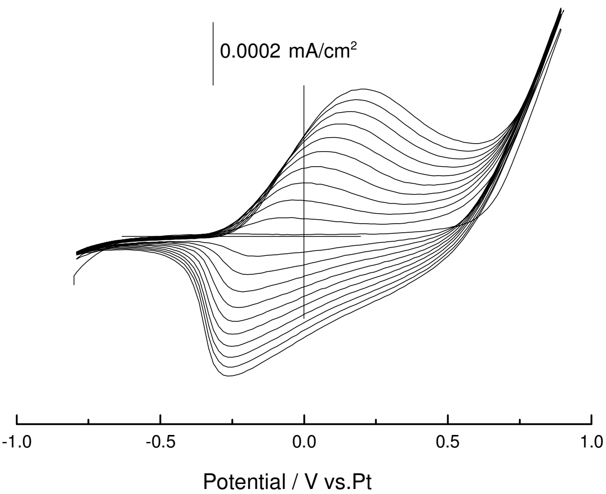
cycle. At the same time, with the potential scans continues, a polymer film was formed on the electrode surface. The increases of the redox wave currents implied that the amount of the polymer on the electrode surface has increasing. The potential shift of this maximum provided information about the increase of the electrical resistance in the polymer film and the over-potential was needed to overcome the resistance (Fig. 1). All these phenomena indicated that high-quality PPOMT films were formed on the anode surface.



(a)



(b)



(c)

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

UV-VIS and fluorescence spectra: The UV-VIS spectra of PTO, PMT prepared from CH_2Cl_2, PPOMT prepared from CH_2Cl_2 containing 25 % BFEE (by volume) are shown in Fig. 2. The UV spectrum of the monomer PTO shows peaks at 236 nm. PMT shows peaks at 248 nm. On the contrary, the spectra of the copolymer have a much broader absorption at 422 nm. The longer wavelength in the spectra indicated a longer polymer sequence. These spectral results also confirmed a conjugated copolymer formation with a broad molar mass distribution.

The fluorescence spectra of the PTO, PMT, PPOMT as shown in Fig. 3. As shown in the figure, an obvious emission peak was found at 314 and 315 nm for PTO and PMT, respectively while the emission peak of the PPOMT films was found at 497 nm. The red shift of emission peak indicated that longer conjugation PPOMT was formed. These results imply that PPOMT may be used in yellow light-emitting material.

Thermal analysis: The polymer films prepared electrochemically by using CH_2Cl_2 containing 25 % BFEE (by volume) thermal analysis of PPOMT was shown in Fig. 4. The thermal analysis of PPOMT was tested under a nitrogen

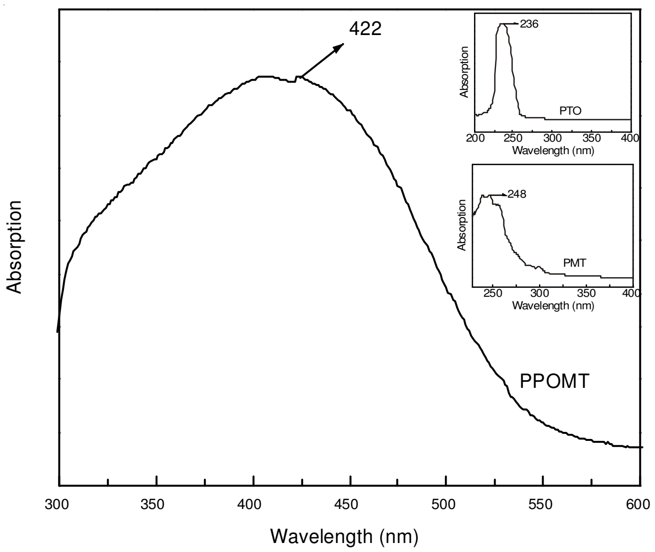


Fig. 2. UV-visible spectra of PTO, PMT, PPOMT

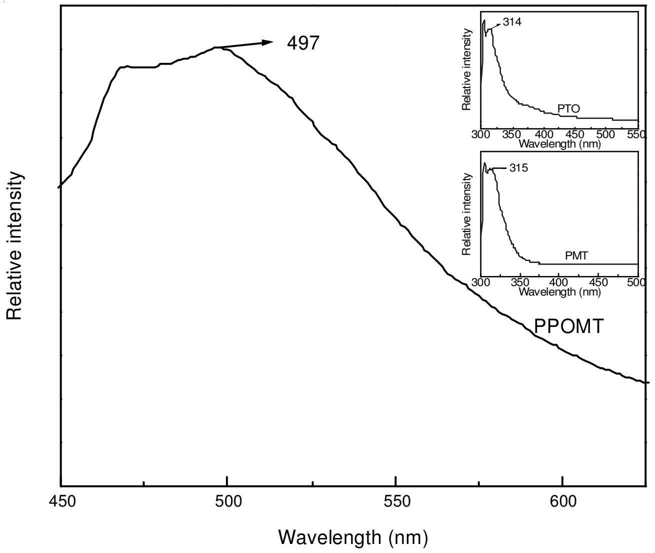


Fig 3. Fluorescence spectra of PTO, PMT in CH_2Cl_2 and the PPOMT films coated on an optically transparent ITO electrode

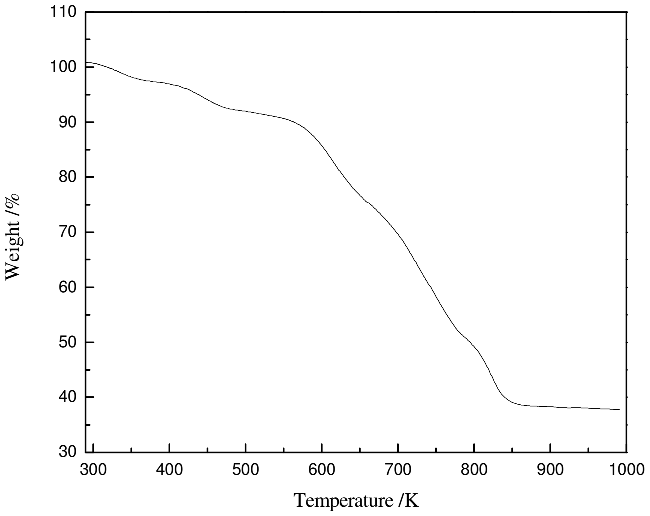


Fig. 4. TGA curves of PPOMT films obtained potentiostatically at 1 V *versus* Pt from CH_2Cl_2 containing 25 % BFEE (by volume)

stream from 290-1000 K with a heating rate of 10 K/min. There are two steps in weight loss. The first one is from 300-500 K, up to 8 %, which can be ascribed to water evaporation or other moisture trapped in the polymer. The second occurred from 500-650 K with a weight loss 25 %. 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 650-780 K, up to 25 %, which was attributed to the degradation radiation of the PPOMT. The main weight loss of PPOMT was found from 780-1000 K with a weight loss of 10 %, which results from the degradation of the PPOMT main backbone. All these results indicate that PPOMT has a good thermal stability.

Conclusion

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

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