J Mater Sci (2008) 43:1008–1012
DOI 10.1007/s10853-007-2234-1

A free-standing poly(9-(6-(thiophene-3-yl)hexyl)-9H-carbazole) films: electrosyntheses from a novel carbazole monomer bearing thiophene moiety

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Received: 14 August 2007 / Accepted: 4 October 2007 / Published online: 15 November 2007

Abstract The pursuit for the electrosyntheses of high quality polycarbazole (PCz) films is a great challenge for the application of polycabazoles. The incorporation of thiophene unit into carbazole monomer might result in a novel polymer having both the advantages of polythiophene and polycarbazole. As expected in this paper, a novel conducting polymer, free-standing poly(9-(6-(thiophene-3-yl)hexyl)-9H-carbazole) (PTh-H-Cz) films with electrical conductivity of 7.8 S/cm, were synthesized electrochemically by direct anodic oxidation of a novel carbazole monomer, 9-(6-(thiophene-3-yl)hexyl)-9H-carbazole (Th-H-Cz), in boron trifluoride diethyl etherate (BFEE) solution. Incorporation of thiophene unit into carbazole monomer as a pendant led to the electrodeposition of high quality PCz films with metallic shine. Fluorescence spectral study revealed that as-formed polymer film in solid state was a good blue light emitter with strong emission at about 410 nm. This high quality free-standing PTh-H-Cz film will facilitate their potential applications as blue-light-emitting materials in organic light-emitting dioxide.

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Introduction

Polycarbazoles (PCzs) have been attracted increasing interest due to their potential application in hole-transporting and photoluminescence efficiencies units [1–3]. Moreover, PCz has the possibility of substitution at N position. This facile process provides the opportunity to improve both the solubility and functionality of the resulting polymers. At the same time, flexible side chain can cause steric hindrance and thereby provide a means to control the effective conjugation length, thus the color of the emitting light in devices [4–8]. However, the obtained poly(*N*-alkylcarbazole)s obtained by electrochemical deposition usually afford well-soluble polymers in the electrochemical medium, and only poor quality PCz films, usually in the form of powders were obtained [9–12]. Therefore, newly designed carbazole monomers are desired to overcome this limitation. It is well known that the utilization of thiophene monomers are also attracted more attention due to their ease of anodic electrodeposition of free-standing films with high conductivity and good mechanical properties [13]. Therefore, it can be expected that incorporation of thiophene unit into carbazole monomer might result in a novel polymer having both the advantages of polythiophene and polycarbazole.

On the other hand, in the past decade, high quality conducting polymer films have been obtained by choosing boron trifluoride diethyl etherate (BFEE) as solvent and supporting electrolyte [14–16]. The interaction between BFEE and the aromatic monomers can lower the monomer oxidation potentials, and high quality free-standing polymer films can be obtained. Compared to the quality of PCz obtained from acetonitrile (ACN), the quality of PCz obtained from BFEE has been great improved, and the conductivity has been increased from 5.0×10^{-4} S/cm [17] to 7.5×10^{-3} S/cm [18]. However, this improvement cannot satisfy the qualification for application in light-emitting diodes yet. Therefore, the electrochemical syntheses of high quality free-standing PCz films with high conductivity become a significant challenge.

In this paper, 3-(6-bromohexyl)thiophene was synthesized to connect with carbazole at N position. The presence of thiophene unit in the novel monomer, 9-(6-(thiophene-3-yl)hexyl)-9H-carbazole (Th-H-Cz), enabled the electrodeposition of high quality free-standing polymer films with high conductivity in BFEE. Moreover, the electrochemistry and spectroscopic properties of poly(9-(6-(thiophene-3-yl)hexyl)-9H-carbazole) (PTh-H-Cz) were investigated in detail.

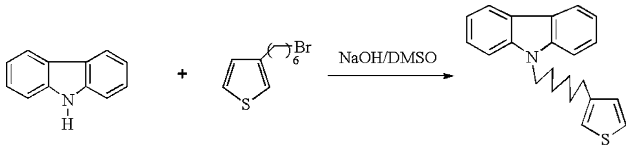
Experiment section

Materials

Carbazole, 1,6-dibromohexane, 3-bromothiophene, and *n*-butyllithium (*n*-BuLi) were purchased from Acros and were used as received. Boron trifluoride diethyl etherate (Beijing Changyang Chemical Plant, China) was distilled and stored at −20 °C before use. Commercial HPLC grade ACN was made by Tianjin Guangfu Fine Chemical Institute (China) and was used directly without further purification. Tetrabutylammonium tetrafluoroborate (TBATFB, Acros Organics, 95%) was dried in vacuum at 60 °C for 24 h before use.

Monomer synthesis

The synthesis of 3-(6-bromohexyl)thiophene was according to previous literatures [19]. Monomer Th-H-Cz was synthesized according to the procedures as following [20]: to a 250 mL three-necked flask containing carbazole (2.0 g, 12 mmol) in DMSO (30 mL) were added 3-(6-bromohexyl)thiophene (3.0 g, 12 mmol) and NaOH (13.75 g, 0.34 mol). The mixture was stirred at room temperature for 4 h, after which, the reaction mixture was poured into water, extracted with $CHCl_3$ (60 mL), washed with H_2O, and dried over $MgSO_4$. After filtration and evaporation of the solvent, the resulting colorless liquid was purified by flash column chromatography using hexane as the eluent. Yield: 2.8 g (70%). IR (KBr): 3051 (m), 2930 (s), 2855 (s), 1923 (w), 1887 (w), 1767 (w), 1627 (m), 1597 (s), 1485 (s), 1453 (s), 1383 (m), 1326 (s), 1231 (s), 1153 (s), 1121 (m), 1079 (m), 1001 (m), 926 (w), 833 (m), 749 (s), 723 (s), 618 (m), 559 (w), 529 (m), 423 (m). ^{1}H-NMR (400 MHz $CDCl_3$): δ 8.00−7.98 (d, 2H), 7.36−7.33 (t, 2H), 7.27−7.25 (d, 2H), 7.14−7.07 (m, 3H), 6.77−6.74 (t, 2H), 4.16−4.12 (t, 2H), 2.47−2.43 (t, 2H), 1.77−1.70 (m, 2H), 1.51−1.41 (m, 2H), 1.25−1.23 (m, 4H) (Scheme 1).



Scheme 1 The synthesis routes of Th-H-Cz

Electrochemical experiments

Electrochemical synthesis and examinations were performed in a one-compartment cell with the use of a Model 263 potentiostat–galvanostat (EG&G Princeton Applied Research). The working and counter electrodes for cyclic voltammetric experiments were platinum wires and stainless steel wires with diameter of 0.5 and 1 mm placed 0.5 cm apart, respectively. For large-scale polymer film production, stainless steel sheets with a surface area of 4 and 5 cm^2, respectively, were employed as working electrode and counter electrode. All potentials were referred to a saturated calomel electrode (SCE). The typical solution was 0.05 M monomer in BFEE solution. The polymer films were deposited on an indium–tin-oxide (ITO) coated glass for optical spectral measurements in solid state. The neutral polymer films were dedoped by applying a constant potential of 0 V until the current passed through the cell became nearly to zero.

Characterizations

UV–visible spectra were taken by using Perkin Elmer Lambda 900 UV–vis–NIR spectrophotometer. Infrared spectra were recorded using Bruker Vertex 70 FT–IR spectrometer with KBr pellets. The ^{1}H-NMR spectrum was recorded on a Bruker AV 400 NMR spectrometer and $CDCl_3$ was used as the solvent. The thermogravimetric (TG) analysis was performed with a thermal analyzer of Netzsch TG 209. The fluorescence properties were determined with Hitachi F-4500 fluorescence spectrophotometer.

Results and discussion

Electrochemical polymerization

The successive cyclic voltammograms (CVs) of Th-H-Cz on a Pt electrode in BFEE solution displayed two oxidation peaks denoted A and B (Fig. 1). According to the previous literatures [13, 18], the initial oxidation potential of carbazole is much lower than that of thiophene. So, peak A can be assigned to the oxidation of the carbazole unit and peak B was the oxidation of thiophene unit. The average

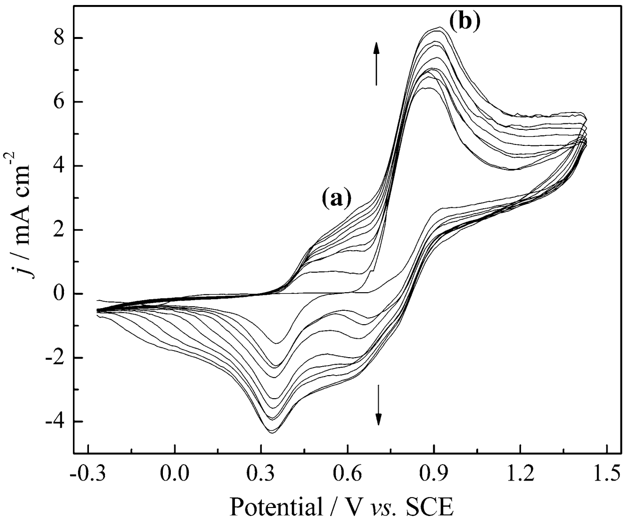


Fig. 1 CVs of 0.05 M Th-H-Cz in BFEE. Potential scan rates: 100 mV s^{-1}

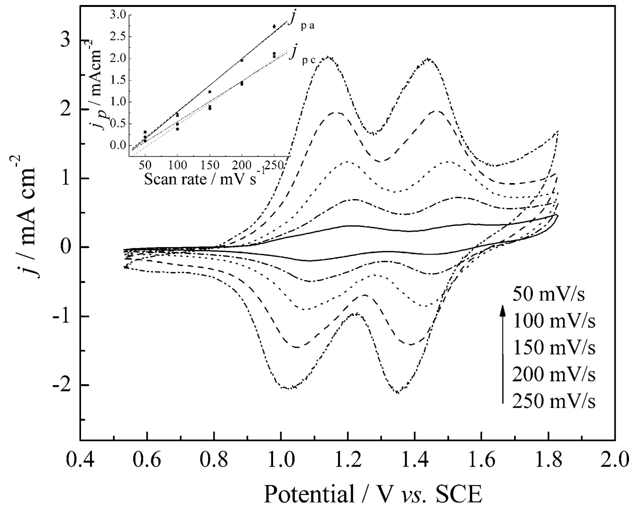
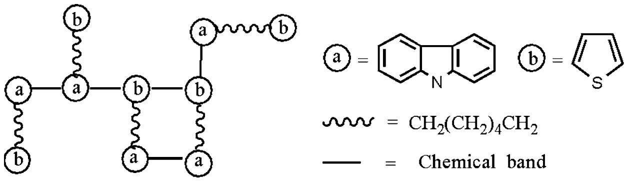


Fig. 2 CVs of PTh-H-Cz films recorded in ACN + 0.1 M TBATFB at the potential scan rates of 250, 200, 150, 100, and 50 mV s^{-1}. The polymer films were synthesized electrochemically from BFEE at a constant applied potential of 1.0 V



Scheme 2 Schematic view of the possibilities for coupling between carbazole unit and thiophene unit

increase of peak A was little higher than that of peak B, indicating more carbazole units than thiophene units were polymerized during the electrochemical polymerization. The reason was due to the anodic oxidation potential onset of carbazole unit was lower than that of thiophene. The increase in the redox wave currents implied that the amount of the polymer on the electrode was 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.

Electrochemistry of polymer films

The electrochemical behavior of this polymer film deposited electrochemically from BFEE solution was also studied in ACN + 0.1 M TBATFB systems as shown in Fig. 2. It was worth noting that there were two reversible oxidation peaks, which can resemble the polymerization process. The first oxidation peak, locating at 1.44 V resulted from the thiophene transition. The second peak, occurring at 1.14 V derived from the carbazole transition. Peak current densities were both proportional to the scan rates (Fig. 2, insert), indicating the good redox behavior of the polymer.

Nature linkages in the polymer

The electrochemical polymerization mechanism of monomer Th-H-Cz was depicted in Scheme 2, which showed three possible polymerization paths for carbazole monomer. The carbazole and thiophene units in monomer were labeled a and b, respectively. Due to the asymmetry of the monomer, the polymer chains can grow through a–a, b–b, or a–b bonds. Because of the great distinction of initial oxidation potential between carbazole and thiophene, it may be very difficult to copolymerize carbazole and thiophene with band a–b. Most of the monomers were cross-linked by bands of a–a modes. And only a small fraction of a–b and b–b bands were also joined the polymerization. However, this small fraction of thiophene units really formed the nature of cross-linkages and leaded the high quality of polymer film due to thiophene monomer can easily polymerize into free-standing film. At the same time, some unpolymerized carbazole and thiophene units were left at the end of polymer chain.

Spectral characterizations

The Infrared spectra of monomer Th-H-Cz and the ded-oped polymer film PTh-H-Cz were shown in Fig. 3A, B, respectively. According to the spectrum of monomer, the band at 3051 cm^{-1} can be ascribed to the C–H stretching

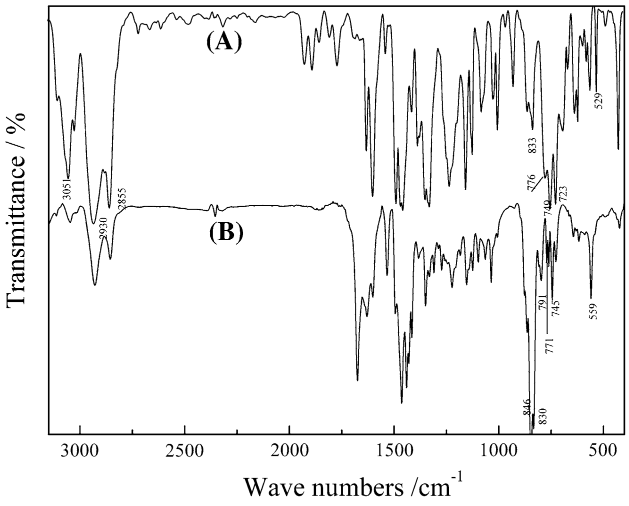


Fig. 3 Infrared spectra of the monomer Th-H-Cz (A) and the dedoped polymer film PTh-H-Cz (B)

vibration of aromatic ring. The bands at 2930 and 2855 cm^{-1} can be ascribed to the aliphatic C–H stretching vibration. Absorption band at 749 cm^{-1} indicated the existence of a 1,2-disubstituted benzene ring. The band at 723 cm^{-1} can be assigned to the out-of-plane vibration of $(CH_2)_4$. The out-of-plane-vibrations of C_α–H and C_β–H in thiophene ring were located at 776 and 833 cm^{-1}, respectively (Fig. 3A). After polymerization, the existence of C–H vibration in alkyl indicated that the hexyl chain was very stable during the polymerization process. At the same time, the polymer exhibited three bands at 846, 797, and 745 cm^{-1}, indicating the emergence of 1,2,4-tri-substituted benzene ring. The intensity of C_α–H out-of-plane deformation vibration reduced and C_β–H vibration remain unchanged, confirming the occurrence of polymerization of thiophene ring at C_α position (Fig. 3B).

The UV–visible and fluorescence spectra of monomer in $CHCl_3$ and polymer film in solid state were illustrated in Fig. 4. In $CHCl_3$ solution, the monomer had an absorption maximum at 246 nm with four significant shoulders at 266, 295, 335, and 348 nm (Fig. 4A-a). At the same time, the UV–visible spectra of the doped and dedoped polymer films on an ITO glass were also showed in Fig. 4A-b,c. the doped state films showed the absorption peaks at 315, 410, and 600–900 nm. The absorptions at 315 and 410 nm might derive from the valence band conduction band (π–π*) transition. The broad band from 600 to 900 nm was the characteristic of conductive species such as the existence of polaron or bipolaron. After being dedoped, the absorptions at 410 and 600–900 nm reduced and the absorption at 315 increased. At the same time, a new shoulder peak appeared at 350 nm.

The fluorescence spectra of monomer in $CHCl_3$ and the doped and dedoped polymer films in solid state were also illustrated in Fig. 4B. The monomer exhibited a strong peak at about 369 nm with a shoulder peak at 354 nm when excited by 280 nm (Fig. 4B-a). Compared to monomer, the fluorescence spectra of the doped and dedoped polymer in solid state had a 40 nm red-shift, with a maximum emission at 410 nm when excited by 300 nm (Fig. 4B-b,c). This indicated that the polymer film in solid state was good blue light emitter.

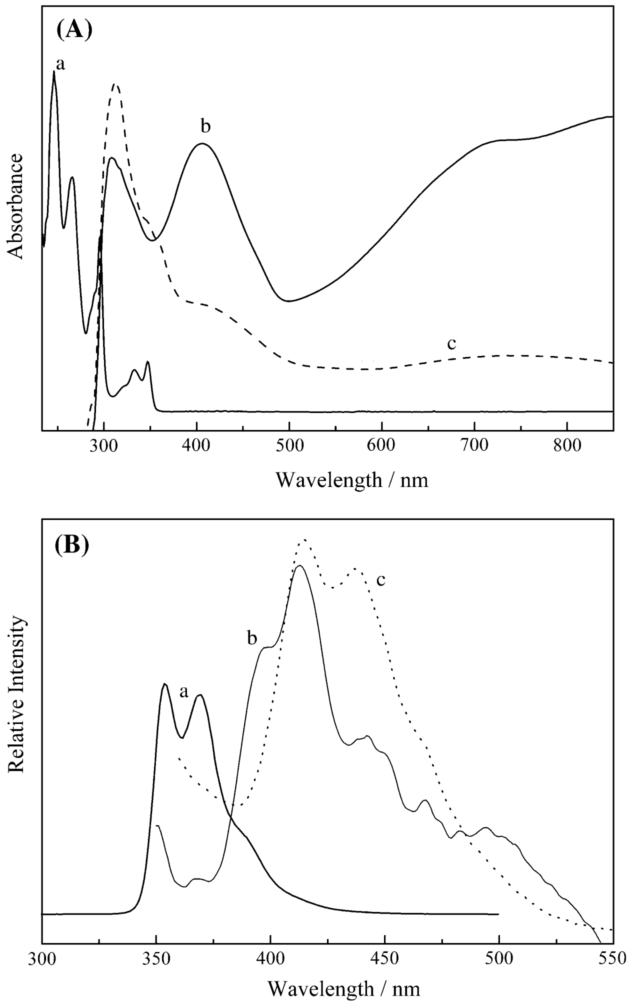


Fig. 4 UV–vis and fluorescence spectra of the monomer Th-H-Cz in $CHCl_3$ (A-a) and the doped and the dedoped polymer PTh-H-Cz on an ITO glass (B-b,c). The polymer films were electrodeposited at a constant applied potential of 1.0 V

Conductivity and morphology

The conductivity of as-formed PTh-H-Cz film was measured to be 7.8 S/cm, which was much higher than that of PCz (7.5×10^{-3} S/cm) obtained from the BFEE + diethyl ether system [14]. The PTh-H-Cz film deposited on the electrode surface was homogeneous and smooth. In addition, the polymer film was flexible and had a fairly good

Fig. 5 A free-standing PTh-H-Cz film peeled off ITO glass and shaped into various shapes with a knife

mechanical strength. It can be peeled off from the electrode surface as a free-standing film and can be cut into various desired structures with a knife as shown in Fig. 5. This property together with its strong fluorescence property will facilitate its application in photoluminescent devices.

Conclusions

In this preliminary study, the electrochemical polymerization of a novel carbazole monomer bearing thiophene unit in BFEE has been performed. The two peaks in the polymerization process were assigned to the oxidation of the carbazole and thiophene units. Incorporation of thiophene unit into carbazole monomer has greatly improved the quality PCz films. A homogeneous and free-standing PTh-H-Cz film with conductivity of 7.8 S/cm was obtained. Fluorescence studies revealed that as-formed polymer films showed strong emission at about 410 nm in solid state, making them good candidates for application in blue light emitters.

Acknowledgements NSFC (50663001, 50503009, and 20564001) and Funds of Ministry of Education of China (2007-20758) are acknowledged for their financial support.

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