

Electrodeposition of high-quality polycarbazole films in composite electrolytes of boron trifluoride diethyl etherate and ethyl ether

GUANGMING NIE¹, JINGKUN XU^{1,2}, SHUSHENG ZHANG^{1,*} and XUEJUN HAN¹

¹College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao, 266042, PR China

²Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang, 330013, PR China

(*author for correspondence, e-mail: shushzhang@126.com)

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Abstract

High-quality polycarbazole (PCZ) films were synthesized electrochemically by direct oxidation of carbazole in boron trifluoride diethyl etherate (BFEE) containing vol. 20% ethyl ether (EE). The oxidation potential of carbazole in this medium was measured to be only 0.90 V vs. SCE, which was lower than that determined in acetonitrile containing 0.1 mol l⁻¹ Bu₄NBF₄ (1.35 V vs. SCE). PCZ films obtained from this medium showed better electrochemical behavior, better thermal stability with conductivity of 7.5 × 10⁻³ S cm⁻¹ being one order of magnitude higher than those reported previously, indicating that BFEE/EE was a better medium than acetonitrile for the electrosyntheses of PCZ films. As-formed PCZ films can be partly dissolved in acetone, acetonitrile and tetrahydrofuran. Spectral analysis provided evidence for the existence of the conjugated structure of the PCZ chain. Fluorescent spectra indicate that electrosynthesized PCZ is an ideal blue light emitter.

1. Introduction

Inherently conducting polymers, such as poly(para-phenylene) [1, 2], polyindole [3, 4], polythiophene [5], polycarbazole (PCZ) [6–8] and polypyrrole [9] are of interest because of their several potential applications. Among them, carbazole and its derivatives are known to exhibit good electro- and photo-active properties [10]. PCZ, with the advantages of good environmental stability and photoconductivity and electrochromic properties, has attracted attention due to its potential industrial applications in electroluminescent applications [6, 11, 12], light-emitting diodes (LEDs) [7, 13, 14], electrochromic displays [15], organic transistors [16] and rechargeable batteries [17]. Another interest of PCZ lies in the fact that carbazole can be viewed as a derivative of pyrrole or indole. Many statements of the structure and polymerization mechanism of PCZ are translated from polypyrrole or polyindole studies. Therefore, extensive work has been devoted to the study of PCZ in the past several years [18–36].

Up to now, the electrodeposition of PCZ films has been mainly carried out in neutral solvents, such as acetonitrile and CH₂Cl₂, using ClO₄⁻ or BF₄⁻ as the supporting electrolyte. It is well known that the properties of the polymers depend strongly on the experi-

mental conditions, such as the solvent and supporting electrolyte. For practical applications, freestanding conducting polymer films are preferable. Recently, freestanding films of polythiophene and its derivatives [37, 38], poly(para-phenylene) [39, 40] and polypyrrole [41] have been produced by direct anodic oxidation of the corresponding monomers in boron trifluoride diethyl etherate (BFEE)-based electrolytes with good mechanical, electrical and thermal properties. The interactions between the Lewis acid BFEE and the aromatic monomers lower their oxidation potentials and the catalytic effect of BFEE facilitates the formation of high-quality freestanding polythiophene and poly(para-phenylene) films. Under these circumstances, BFEE serves not only as the solvent but also as the supporting electrolyte and no other supporting electrolyte is needed. On the other hand, investigations on the electrochemical polymerization of fused ring compounds, such as thianaphthene [42], naphthalene [43], benzofuran [44] and indole [45], have been carried out in BFEE. However, as far as we know there have been no reports on the electrochemical polymerization of carbazole in BFEE.

In this work, high-quality PCZ films were prepared by direct anodic oxidation of carbazole monomer in BFEE containing a certain amount of ethyl ether (EE). The electrochemical properties, morphology and thermal

stability of as-prepared PCZ films were studied. The structures were determined by the FTIR, ^1H NMR and UV-visible spectra. Fluorescent spectra indicate that the polymer is a blue light emitter.

2. Experimental

2.1. Materials

BFEE (Beijing Changyang Chemical Plant) was distilled and stored at $-20\text{ }^\circ\text{C}$ before use. Carbazole (Shanghai Chemical Reagent Plant) was purified by recrystallization from methanol. Tetrabutylammonium tetrafluoroborate (TBATFB, Acros Organics, 95%) was dried in vacuum at $60\text{ }^\circ\text{C}$ for 24 h before use. Commercial HPLC grade acetonitrile (ACN, made by Tianjin Guangfu Fine Chemical Research Institute) was used directly without further purification. Sulfuric acid (98%), ethyl ether and 25% ammonia, made by Ji'nan Chemical Reagent Company, were used as received. Tetrahydrofuran (THF, analytical grade) was made by Shandong Laiyang Fine Chemical Corporation. Deuterium substituted dimethyl sulfoxide (CD_3SOCD_3) was a product of Cambridge Isotope Lab., Inc.

2.2. Electrosyntheses of PCZ films

Electrochemical syntheses and examinations were performed in a one-compartment cell with the use of a Model 263 potentiostat–galvanostat (EG&G Princeton Applied Research) under computer control. The working and counter electrodes for cyclic voltammetry experiments were platinum wires with a diameter of 0.5 mm placed 0.5 cm apart. To obtain a sufficient amount of polymer for characterization, stainless steel sheets with a surface area of 10 and 12 cm^2 each were employed as the working and counter electrodes, respectively. The electrodes were carefully polished with abrasive paper (1500 mesh) and cleaned in water and acetone before each examination. The polymers were deposited on indium–tin-oxide (ITO) coated glass for UV–visible spectral measurements. The electrochemical dedoping of PCZ film was performed at a constant potential of 0 V in a monomer free BFEE/EE solution until the current density was close to zero. The reference electrode was Ag wire coated with AgCl directly immersed in the electrolyte. This reference electrode was very stable and all experimental values were reported relative to the saturated calomel electrode (SCE).

The typical electrolytic solution was BFEE solution containing vol. 20% EE and 0.01 mol l^{-1} carbazole. All solutions were deaerated by a dry argon stream and maintained at a slight argon overpressure during experiments. The amount of polymer deposited on the electrode was controlled by the integrated charge passed through the cell. In order to remove the electrolyte and oligomers/monomer, the electropolymerized films were

rinsed in mixtures of ACN and water containing an increasing amount of water and finally pure water. As-formed PCZ film was in the doped state and was dark green in color. For spectral analysis, the polymer was dedoped with 25% ammonia for 3 days and then washed repeatedly with water. Finally, it was dried under vacuum at $60\text{ }^\circ\text{C}$ for 2 days.

The electrochemical deposition procedures for polyindole, polythiophene and poly(para-phenylene) films were similar to that of PCZ films except that the typical electrolytic solutions were distilled BFEE containing 0.03 mol l^{-1} indole, 0.03 mol l^{-1} thiophene and 2 mol l^{-1} benzene, respectively.

2.3. Characterizations

The current efficiency (η) of polymerization (the charge consumed by the growth of polymer film relative to the total charge passed through the cell) was measured by weighing the polymer (in the dedoped state) deposited on the electrode (W_p) according to Equation (1):

$$\eta = [(nFW_p/M)/Q] \times 100\% \quad (1)$$

where F is Faraday constant (96487 C mol^{-1}), Q is the integrated charge passed through the cell during film growth, n is the number of electrons transferred per monomer attached to the polymer (here n is estimated to be 2), and M is the molar mass of the monomer. The current efficiency of this electrosynthesis was measured to be 75%. The doping levels (f) of as-grown PCZ films were determined electrochemically by using Equation (2) [46]:

$$f = [2Q_o/(\eta Q_d - Q_o)] \times 100\% \quad (2)$$

where Q_d is the total charge used for PCZ deposition and Q_o is the total charge of oxidized species in the PCZ films.

The conductivity of as-formed PCZ film was measured by the conventional four-probe technique. UV–visible spectra were taken by using a Cary 500 UV–Vis–NIR spectrophotometer. Infrared spectra were recorded using a Nicolet 510P FT-IR spectrometer with KBr pellets. The fluorescence spectra were determined with a F-4500 fluorescence spectrophotometer (HITACHI). The ^1H NMR spectrum was recorded on a Bruker AV400 NMR spectrometer and CD_3SOCD_3 was used as the solvent. The thermogravimetric analysis (TGA) was performed with a thermal analyzer of NETZSCH TG209. Scanning electron microscopy (SEM) measurements were taken using a JEOL JSM-6700F instrument.

3. Results and discussion

3.1. Electrochemical syntheses of PCZ films

As mentioned above, high-quality polythiophene [37, 38], poly(para-phenylene) [39, 40] and polyindole [45]

can be electrochemically prepared in pure BFEE. Therefore, pure BFEE was also tested directly as the solvent and electrolyte for the electrochemical polymerization of carbazole. Unfortunately, it was found that the solubility of carbazole in pure BFEE was relatively low. In order to increase the solubility, a small amount of EE was added to BFEE. Experimental results indicated that carbazole was very stable in BFEE solution containing vol. 10–30% EE. Therefore, mixed electrolytes of BFEE containing a certain amount of EE were chosen as the solvent and supporting electrolyte for the electropolymerization of carbazole.

Figure 1 shows the anodic polarization curves of carbazole in the composite electrolytes of BFEE mixed with different volume percentages of EE and in ACN containing 0.1 mol l^{-1} TBATFB (inset) for comparison. It should be noted that BFEE is electrochemically silent in the whole potential range [37]. The oxidation onset of carbazole is initiated at 0.95 V vs. SCE when EE concentration is vol. 10%. The onset of oxidation decreases to 0.90 V vs. SCE when the addition of EE is 20%. However, the introduction of 30% EE in BFEE increases the oxidation potential to 1.05 V vs. SCE . All these values are much lower than that of carbazole in ACN containing 0.1 mol l^{-1} TBATFB (1.35 V vs. SCE), as shown in the inset of Figure 1. Based on this discussion, it is obvious that the oxidation potential is the lowest when the volume percentage of EE is around 20%. Generally, the lower the oxidation potential, the less possible are the side polymerization reactions as well as coupling defects. Therefore, BFEE containing vol. 20% EE is more appropriate for the electrochemical polymerization of carbazole.

The successive cyclic voltammetric growth of PCZ in BFEE containing vol. 20% EE on a platinum wire electrode is shown in Figure 2. The cyclic voltammograms of carbazole in this medium show characteristic

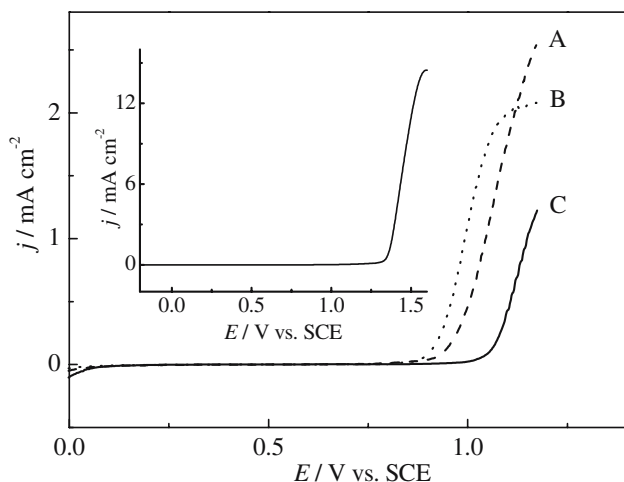


Fig. 1. Anodic polarization curves of 0.01 mol l^{-1} carbazole in the mixed electrolytes of BFEE containing vol. 30% (A), 20% (B), 10% (C) EE and in acetonitrile containing 0.1 mol l^{-1} TBATFB (inset). The working and counter electrodes are platinum wires, respectively. Potential scan rates: 20 mV s^{-1} .

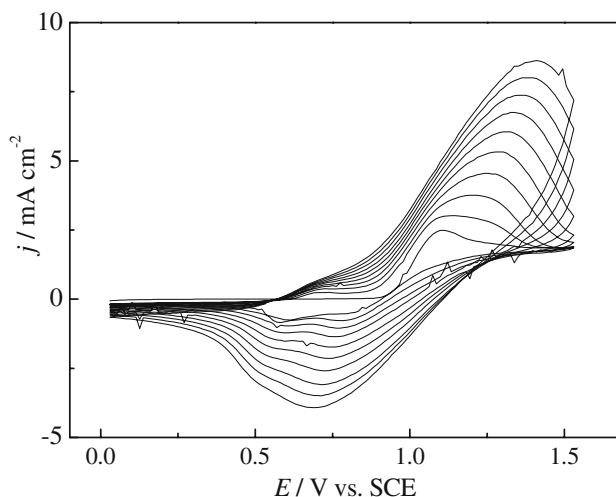


Fig. 2. Cyclic voltammetric growth of PCZ film in BFEE containing vol. 20% EE and 0.01 mol l^{-1} carbazole. The working and counter electrodes are platinum wires, respectively. Potential scan rates: 50 mV s^{-1} .

features similar to other conducting polymers such as polythiophene and polypyrrole during potentiodynamic syntheses. The peak current of the redox system increases regularly during the successive scans, indicating an electroactive polymer film is formed on the working electrode surface. In Figure 2, PCZ can be reduced and oxidized between 0.62 and 0.75 V vs. SCE . The increase in the redox wave currents implies that the amount of polymer on the electrode is increasing. The broad redox waves of as-formed PCZ film may be ascribable to the wide distribution of the polymer chain length [47] or the conversion of conductive species on the polymer main chain from the neutral state to polarons, from polarons to bipolarons and finally from bipolarons to the metallic state [48]. All these phenomena indicate that a high-quality conducting PCZ film is formed on the working electrode.

3.2. Electrochemistry of PCZ films

The electrochemical behavior of PCZ films deposited electrochemically from BFEE containing vol. 20% EE (Figure 3A) and ACN containing 0.1 mol l^{-1} TBATFB (Figure 3B) were studied in concentrated sulfuric acid. Similarly to the results in the literature [49], the steady-state cyclic voltammograms show broad anodic and cathodic peaks. It is noteworthy that PCZ films obtained from BFEE/EE can be cycled repeatedly between the conducting (oxidized) and insulating (neutral) states without significant decomposition of the materials in sulfuric acid (Figure 3A). However, PCZ films prepared from ACN degrade during successive scans in sulfuric acid (Figure 3B). These results indicate that the stability of the polymer obtained from BFEE/EE is higher than that from ACN. In addition, the peak current densities of PCZ films from BFEE/EE are proportional to the scan rate (Figure 3A, inset) while the peak current densities of PCZ films prepared from

ACN are not linear with the scan rate (Figure 3B, inset). According to Figure 3A, the polymer film obtained from BFEE/EE can be oxidized and reduced from 0.64 (Ea) to 0.58 V (Ec). However, much higher potentials, from 1.05 (Ea) to 0.95 V (Ec), are needed to oxidize or reduce the polymer film prepared from ACN containing 0.1 mol l^{-1} TBATFB (Figure 3B). The value of half-wave potential ($E_{1/2} = [E_a + E_c]/2$) is 0.61 V for the PCZ obtained from BFEE/EE while it is 1.0 V for that from ACN. Generally, the negative shift of redox potential of conducting polymers during cyclic voltammograms indicates higher conjugation length [47] on the polymer main chain, i.e., higher quality of as-prepared polymer. Moreover, the difference of ($E_a - E_c$) related to the kinetics of the doping–dedoping reaction [50], is equal to 0.06 V for PCZ prepared from BFEE/EE and 0.10 V for PCZ prepared from ACN. This implies that the redox properties of PCZ films from BFEE/EE are more reversible than those obtained from ACN. It can be reasonably concluded that the redox properties of PCZ

films from BFEE/EE are better than those from ACN, also indicating higher quality of PCZ films prepared from BFEE/EE.

3.3. Structural characterizations

During the potentiostatic process, the color of BFEE containing vol. 20% EE and carbazole darkened with applied potential, which indicated that soluble carbazole oligomers formed during anodic oxidation. With the polymerizing propagation, the part soluble oligomers became insoluble and deposited on the working electrode with extension of the main chain. However, there were still part oligomers diffusing from the electrode into the bulk solution. As a result, the color of the bulk solution became darker. The current efficiency of carbazole polymerization was determined to be only 75%. The PCZ film was transparent and colorless in the dedoped state while it was dark green in the doped form, similarly to the literature [28, 30, 35]. The dedoped PCZ films were only partly soluble even in strong polar solvents such as DMSO, THF and acetone. Thus the UV–visible spectra of the dedoped PCZ were tested on a transparent ITO electrode, as shown in Figure 4. The spectra of PCZ films showed a much broader absorption band from 310 to about 800 nm, which implied the wide molar mass distribution of as-prepared PCZ films during electrosyntheses. The absorption band maximum at 310 nm can be ascribed to the $\pi-\pi^*$ transition of carbazole monomer. The absorption band at 710 nm can be attributed to the radical cation of carbazole units in the doped state [30]. It can further be seen that the intensities of the absorption peaks at 310, 375 and 710 nm enhanced with increase in the deposition charge density, indicating a rise in the concentration of the oxidized species in PCZ film [30]. This optical modification can be clearly observed as the change from colorless to dark green during p-doping (oxidation).

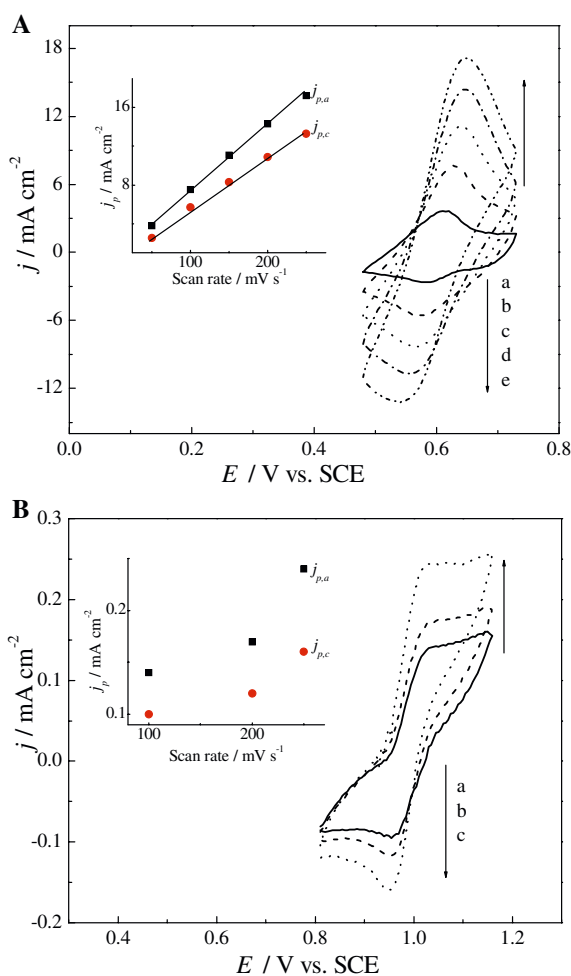


Fig. 3. Cyclic voltammograms of PCZ films in concentrated sulfuric acid at potential scan rates of 50 (a), 100 (b), 150 (c), 200 (d) and 250 mV s^{-1} (e). The films (A) and (B) are synthesized electrochemically in BFEE containing vol. 20% EE and in acetonitrile containing 0.1 mol l^{-1} TBATFB at a constant applied potential of 1.0 V vs. SCE, respectively. The working and counter electrodes are platinum wires, respectively.

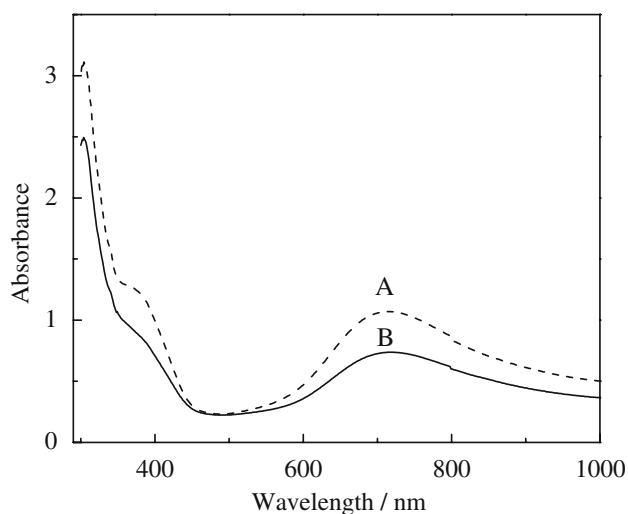


Fig. 4. UV–visible spectra of dedoped PCZ films on ITO coated glass prepared from BFEE containing vol. 20% EE with different deposition charge densities: (A) 8.5 C cm^{-2} , (B) 5.0 C cm^{-2} .

Infrared spectra provide evidence for the existence of the conjugated structure of the PCZ chain, as shown in Figure 5. The typical transmission infrared spectra of the monomer and PCZ obtained from BFEE containing vol. 20% EE are shown in Figure 5A and 5B, respectively. In Figure 5B, the bands are relatively broad mainly because PCZ has a relatively broad chain length distribution. The strong and narrow peak at 3410 cm^{-1} observed in the carbazole spectrum is the characteristic absorption of N–H bond, which is broader and shifts to 3407 cm^{-1} in the spectrum of dedoped PCZ film. The polymer has peaks at 880 and 804 cm^{-1} , evidence for the presence of the trisubstituted benzene ring [24], indicating the occurrence of polymerization on the benzene ring. In addition, the band at 1240 cm^{-1} (Figure 5A) increases and shifts downwards to 1234 cm^{-1} (Figure 5B), which is related to C–C deformation [42]. This indicates that a new C–C bond between two monomers has formed, which also confirms the formation of PCZ. Moreover, the red shift of the C–C bond (from 1240 to 1234 cm^{-1}) implies partial distribution of the C=C bond through the conjugated PCZ main chain. Upon doping, the bands in the region from 1600 to 1100 cm^{-1} (Figure 4B), which mostly consist of the C=C and C–C stretching and shrinking modes, are selectively broadened. This verifies that the main component in PCZ has the characteristics of typical conjugated polymers.

In order to get a deeper insight into the structure of PCZ, the $^1\text{H-NMR}$ spectrum of the dedoped PCZ obtained from BFEE containing vol. 20% EE was recorded, as illustrated in Figure 6. The $^1\text{H-NMR}$ spectrum of carbazole monomer shows five groups of protons: 7.16, 7.36, 7.49, 8.08 and 10.3; this is not included in this paper. As shown in Figure 6, the spectrum of PCZ shows four groups of protons: 7.5, 7.8, 8.3 and 11.2. These proton lines are much broader and have fewer fine structures than the corresponding proton lines of carbazole because of the wide molar

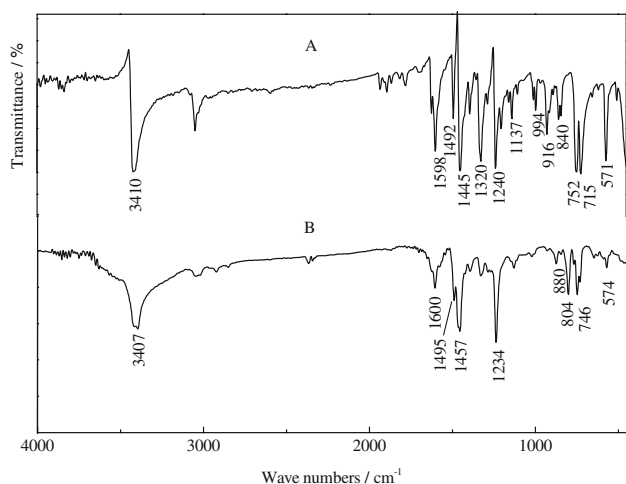


Fig. 5. FTIR spectra of carbazole monomer (A) and PCZ films (B) obtained potentiostatically at 1.0 V vs. SCE from BFEE containing vol. 20% EE on stainless steel sheets after treatment with 25% aqueous ammonia for 3 days.

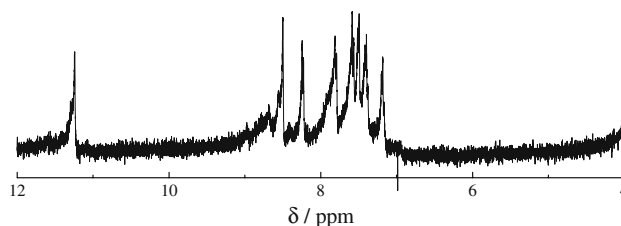


Fig. 6. $^1\text{H-NMR}$ spectra of dedoped PCZ obtained potentiostatically at 1.0 V vs. SCE from BFEE containing vol. 20% EE on stainless steel sheets. Solvent: CD_3SOCD_3 .

mass distribution of PCZ. According to the literature [51], the chemical shift of the N–H bond in the $^1\text{H-NMR}$ spectrum of indole is at 10.1, while that of carbazole is at 10.3. The incorporation of the benzene ring onto the pyrrole ring makes the chemical shift of the N–H bond move to the lower field. Thus the chemical shift of 11.2 is ascribable to the proton of the N–H bond on polymer backbone. This implies that the N–H bond is not the polymerization site and polymerization occurs on the benzene ring. Moreover, the fact that the chemical shift of the proton moves to a much lower field also confirms the formation of a conjugated delocalizing structure [52, 53].

The fluorescence of the dedoped PCZ was examined using THF as the solvent, although PCZ can only be partly dissolved in THF, as shown in Figure 7. The obvious peaks of excitation spectra can be found at 445 nm, while the emission spectra has several peaks mainly at 490 nm. This result is similar to the literature [54]. The wide peak distribution is ascribable to the wide molar mass distribution of PCZ, in accordance with UV–visible spectra. These results indicate the polymer is a good blue light emitter and also mean that this soluble PCZ may have potential applications in various fields, such as the organic laser with blue emitting polymers and the blue–violet polymer LED.

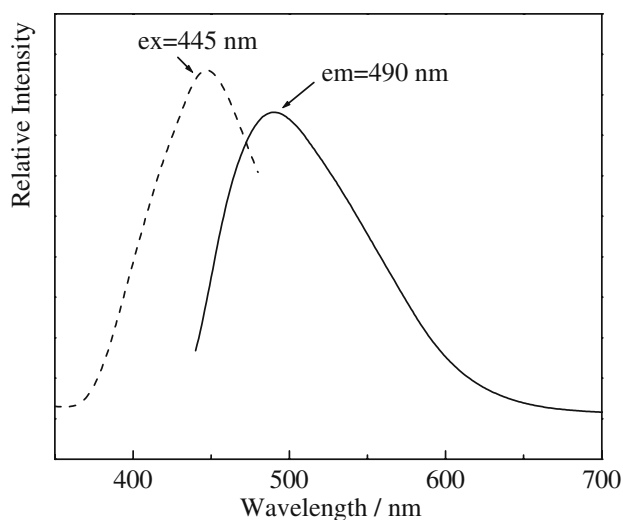


Fig. 7. The emission and excitation spectra of dedoped PCZ prepared from BFEE containing vol. 20% EE on stainless steel sheets. Solvent: THF.

3.4. Thermal analysis

The thermal stability of a conducting polymer is very important for its potential application. Thermogravimetric (TG) and differential thermogravimetric (DTG) analysis are significant and useful dynamic ways to detect the degradation behavior in which the weight loss of a polymer sample is measured continuously while the temperature is changed at a constant rate. In order to investigate the thermal stability of PCZ films prepared from BFEE containing vol. 20% EE, the thermal analysis of PCZ films was tested, as shown in Figure 8A. In comparison, the thermal properties of polyindole (Figure 8B), poly(para-phenylene) (Figure 8C) and

polythiophene film (Figure 8D) were also investigated under the same conditions. All thermal analyses were performed under a nitrogen stream in the temperature range 300–1073 K with a heating rate of 10 K min⁻¹. In Figure 8, curve a represents the TG curve of polymer film, while b denotes the corresponding DTG curve. According to Figure 8A, when the temperature reaches 385 K, the weight loss of the PCZ is about 2.3%. This degradation can be ascribed to the water evaporation or other moisture trapped in the polymer, which is not necessarily associated with a change in polymer structure [14]. However, PCZ films undergo rapid weight loss of 25% from 585 to 753 K. The corresponding maximal decomposition rate is located at 695 K. This decompo-

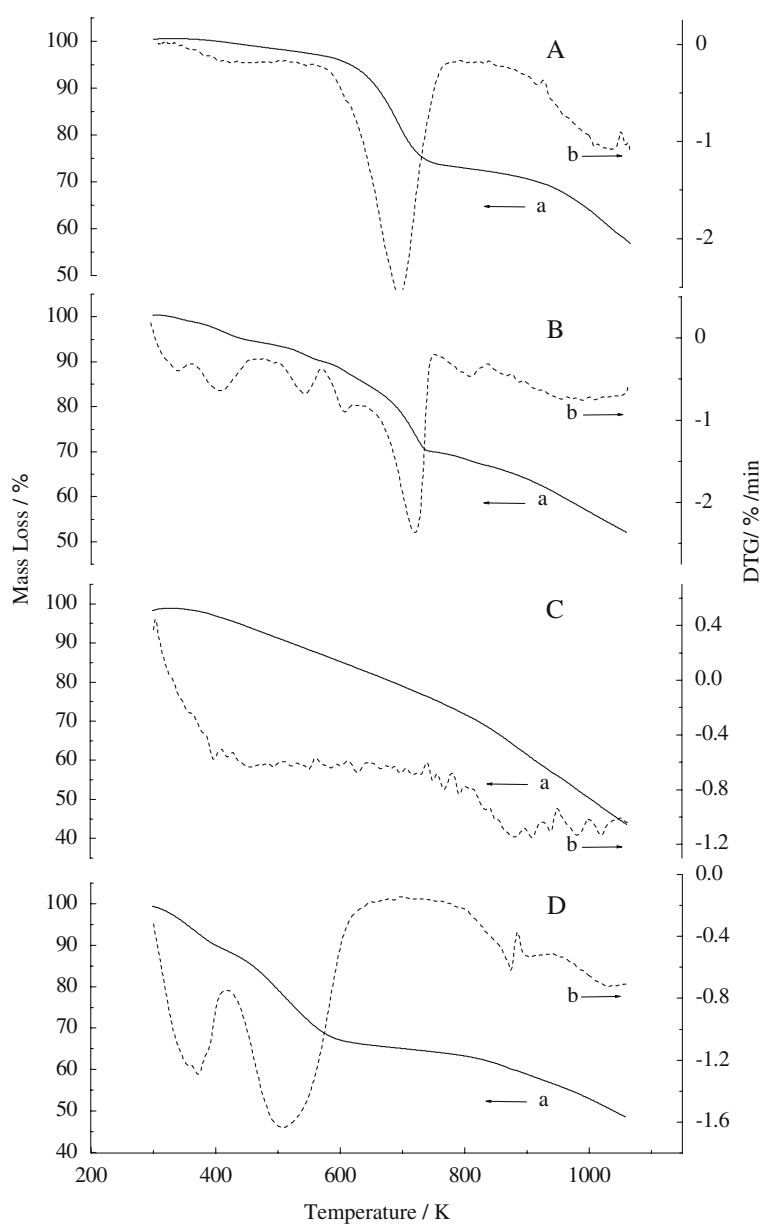


Fig. 8. TG (a) and DTG (b) curves of dedoped PCZ (A), polyindole (B), poly(para-phenylene) (C) and polythiophene films (D), respectively. PCZ film is obtained potentiostatically at 1.0 V vs. SCE from BFEE containing vol. 20% EE. Polyindole film is obtained potentiostatically at 1.2 V vs. SCE from pure BFEE. Poly(para-phenylene) film is deposited potentiostatically at 1.9 V vs. SCE from BFEE. Polythiophene film is prepared potentiostatically at 1.5 V vs. SCE from BFEE. Stainless steel sheets are employed as the working and counter electrodes, respectively.

sition may be caused by the degradation of the skeletal PCZ backbone chain structure. Further weight loss at 950 K indicates that PCZ films have good thermal stability. In comparison, there are more than one evident decomposition processes during thermal degradation of polyindole and polythiophene films, as shown in Figure 8B, D. This indicates that PCZ has better thermal stability than polythiophene and polyindole. According to Figure 8C, poly(para-phenylene) film has a lower decomposition temperature and there is no prominent maximum decomposition rate in the whole process. This may be due to the fact that poly(para-phenylene) films enclose a lot of short-chain oligomers or polymers with different chain lengths (average degree of polymerization was determined to be about 11 [55]). It can be concluded that PCZ films have better thermal stability compared with polyindole, polythiophene and poly(para-phenylene). This better thermal stability is mainly ascribable to the high thermal stability of the incorporation of the benzene ring into the main chain of as-formed PCZ films. This is of special significance for several applications of PCZ, such as coolants for nuclear reactors, where high thermal stability is essential.

3.5. Conductivity and morphology

The conductivity of PCZ film obtained from BFEE containing vol. 20% EE was measured to be $7.5 \times 10^{-3} \text{ S cm}^{-1}$, being one order of magnitude higher than values reported previously ($5.0 \times 10^{-4} \text{ S cm}^{-1}$ [21, 22] and $8.8 \times 10^{-4} \text{ S cm}^{-1}$ [24]). To the best of our knowledge, this is the highest conductivity value of PCZ films that has been reported. Moreover, the doping levels of as-prepared PCZ films were determined to be close to 47% at different deposition charge densities (30–156 mC cm^{-2}). This is much higher than common conducting polymers, such as 28% for poly(3-methylthiophene) [56] and 21% for polythiophene [57].

Various scanning probe techniques, such as scanning electron micrographs (SEM), have revealed a pronounced heterogeneity depending on the substrate, synthesis conditions, compositions of the solution and thickness of polymer films. As-formed PCZ film is flat and compact. A typical scanning electron microscopy image of PCZ film obtained from BFEE containing vol. 20% EE is shown in Figure 9. The film has an ordered cauliflower-like appearance. The coverage efficiency of the film is very high, without pinholes, cracks or evident inhomogeneities [12].

4. Conclusions

High-quality PCZ films with conductivity of $7.5 \times 10^{-3} \text{ S cm}^{-1}$ were electrochemically synthesized in BFEE containing vol. 20% EE and 0.01 mol l^{-1} carbazole. The oxidation potential of carbazole in this medium was determined to be only 0.90 V vs. SCE, which was lower than that in ACN, 1.35 V vs. SCE.

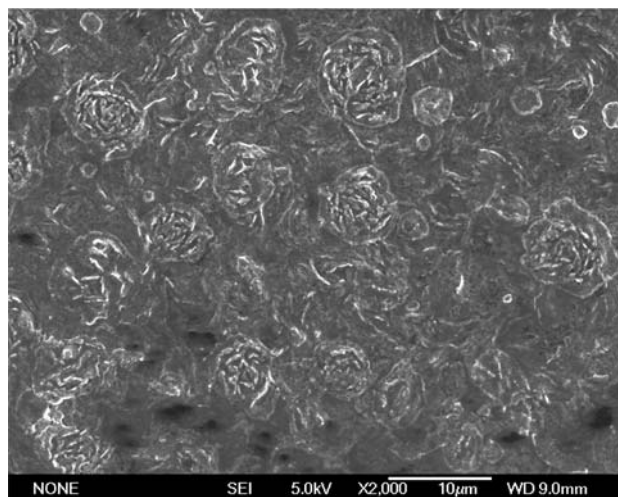


Fig. 9. Scanning electron micrograph of PCZ film deposited on stainless steel electrode surface from BFEE containing vol. 20% EE at a constant applied potential of 1.0 V vs. SCE.

As-formed PCZ films show good redox activity and high stability in concentrated sulfuric acid. Electrochemical, structural and morphology studies indicate that PCZ films with better quality can be obtained from BFEE/EE. TGA results indicate that PCZ films with good thermal stability can be prepared from BFEE/EE. The fluorescence spectra imply that soluble PCZ is a good blue light emitter.

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