

ELECTROCHEMICAL POLYMERIZATION OF 5-CYANOINDOLE IN MIXED ELECTROLYTES OF BORON TRIFLUORIDE DIETHYL ETHERATE AND DIETHYL ETHER*

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Abstract High quality poly(5-cyanoindole) (P5CI) films were electrosynthesized by direct anodic oxidation of 5-cyanoindole on stainless steel sheet in the mixed electrolytes of boron trifluoride diethyl etherate (BFEE) and diethyl ether (EE) (by volume 1:1) + 0.05 mol L⁻¹ Bu₄NBF₄. The film formed can be peeled off the electrode into freestanding films. The addition of EE into BFEE can improve the solubility of monomer. P5CI films obtained from this medium showed excellent electrochemical behavior with conductivity of 10⁻² S cm⁻¹. Structural studies showed that the polymerization of 5-cyanoindole occurred at the 2,3 position. As-formed P5CI films were thoroughly soluble in strong polar organic solvent dimethyl sulfoxide (DMSO) while partly soluble in tetrahydrofuran (THF) or acetone. Fluorescence spectral studies indicated that P5CI was a good blue-light emitter.

Keywords: Electrochemical polymerization; Conducting polymers; Polyindole; Poly(5-cyanoindole); Boron trifluoride diethyl etherate.

INTRODUCTION

Among the inherently conducting polymers, polyindole and its derivatives have attracted significant attention due to their fairly good thermal stability, high redox activity and stability^[1-4], a slow degradation rate in comparison with those of polyaniline and polypyrrole^[3] and air-stable electrical conductivity in doped state^[5]. Polyindole may be a good candidate for applications in various domains like electronics, electrocatalysis, anode materials in battery, anticorrosion coatings and pharmacology.

Polyindole films were mainly synthesized through electrochemical oxidation except several works^[1-6] concerning direct chemical oxidation of indole by FeCl₃. Electrochemical polymerization has been proven to be one of the most useful approaches for preparing conducting polymer. Electrochemical studies can give fast information on the characteristics and properties of electropolymerized materials with good accuracy and precision^[7]. In previous studies, polyindole and its derivatives were mainly synthesized in neutral solvents^[2, 6, 8, 9]. Polyindoles prepared from these media were usually in the form of powder and thus their application was greatly limited due to the poor processability. In our previous studies, it was found that high quality freestanding polyindole films can be easily prepared in boron trifluoride diethyl etherate (BFEE)^[10], similar to high quality

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conducting polymer films formation such as polythiophenes^[11], polypyrrole^[12, 13, 14], polyfuran^[15, 16], poly(*para*-phenylene)^[17]. As one of the most important indole derivatives, there were several reports on the electrochemical polymerization of 5-cyanoindole in neutral solvent such as acetonitrile (ACN)^[9]. The interest for cyano-substituted indole is that its electron-withdrawing CN group can affect the properties of corresponding polymers which can be further modified by functional molecules, which a popular method used in the syntheses of functional conducting polymers. The first step for this purpose is to prepare high quality poly(5-cyanoindole) (P5CI). The properties of polyindoles were affected greatly due to the effect of electron-withdrawing cyano substituent. Generally, P5CI film prepared from ACN was not very good, especially in its mechanical properties^[18–23]. As far as we know, there have been no reports on the electrochemical polymerization of 5-cyanoindole in BFEE.

In this paper, high-quality freestanding P5CI films can be easily electrodeposited from the mixed electrolyte of BFEE + 50% diethyl ether + 0.05 mol L⁻¹ Bu₄NBF₄. As-formed P5CI films were soluble in strong polar solvent such as DMSO with relatively strong fluorescence.

EXPERIMENTAL

5-Cyanoindole (Shandong Pingyuan Hengyuan Chemical Plant, analytical grade) was used directly. Boron trifluoride diethyl etherate (Beijing Changyang Chemical Plant) was distilled and stored at -20°C before use. Diethyl ether (EE) was purified according the method described in organic synthesis^[24]. Acetonitrile (G.R. grade, Tianjin Guangfu Fine Chemical Research Institute) was used directly without further purification. Tetrabutylammonium tetrafluoroborate, (Bu)₄NBF₄ (TBATFB, Acros Organics, 95%), was dried in vacuum at 60°C for 24 h before use.

The electrodeposition of P5CI was carried out in a one-compartment cell using CHI 660 potentiostat-galvanostat (Shanghai Chenhua Instrumental Cooperation Ltd., China) under computer control. The working and counter electrodes were Pt wire with a diameter of 0.5 mm and stainless steel wire with diameter of 1 mm, respectively. They were placed 5 mm apart during examinations. To obtain a sufficient amount of polymer for characterization, stainless steel sheets with a surface area of 10 cm² and 12 cm² each were employed as the working and counter electrodes, respectively. All potentials were referred to a saturated calomel electrode (SCE). The solutions were deaerated by a dry nitrogen stream and maintained a slight nitrogen overpressure during experiments. The electrolytic solution was BFEE/EE (by volume 1:1) and 0.05 mol L⁻¹ TBATFB and 0.05 mol L⁻¹ 5-cyanoindole. For spectral analysis, the polymer was dedoped with 25% ammonia for 3 days and dried in vacuum at 60°C for 24 h.

The conductivity of as-formed P5CI film was measured by conventional four-probe technique. UV-Vis spectra were taken by using a Perkin Elmer Lambda 900 UV-Vis-NIR spectrophotometer. The fluorescence spectra were determined with a F-4500 fluorescence spectrophotometer (Hitachi). The ¹H-NMR spectra were recorded on a Bruker AV400 NMR spectrometer and CD₃SOCD₃ was used as the solvent.

RESULTS AND DISCUSSION

Electrochemical Syntheses of P5CI Films

The successive cyclic voltammograms (CVs) of 0.05 mol L⁻¹ 5-cyanoindole in mixed electrolyte of BFEE + 50% EE + 0.05 mol L⁻¹ TBATFB on a Pt electrode are shown in Fig. 1. The CVs of 5-cyanoindole in this medium show characteristic features like other conducting polymers during potentiodynamic syntheses, such as polypyrrole and polythiophene. As the CV scans continued, a polymer film was formed on the Pt electrode surface. The increase of the redox wave currents implies that the amount of the polymer on the electrode is increasing per cycle. The broad redox waves of as-formed P5CI film may be ascribable to the wide distribution the polymer chain length^[25] or the conversion of conductive species on polymer main chain from the neutral state to polarons, then to bipolarons and finally the metallic state^[26]. All these phenomena indicate that a conducting P5CI film is formed on the working electrode.

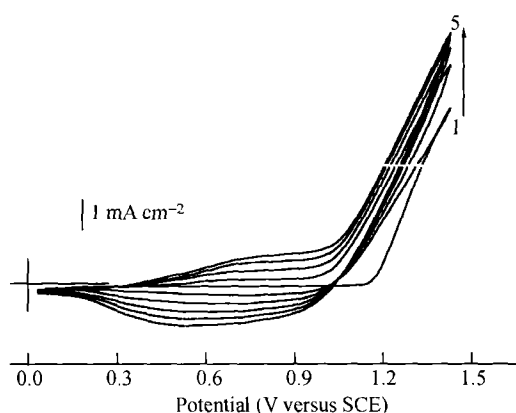


Fig. 1 Cyclic voltammograms of 0.05 mol L^{-1} 5-cyanoindole in BFEE + 50% EE + 0.05 mol L^{-1} TBATFB
Potential scan rates: 100 mV s^{-1}

Electrochemistry of P5CI Films

The electrochemical behavior of the P5CI films deposited electrochemically from this medium was studied in monomer-free BFEE + 50% EE + 0.05 mol L^{-1} TBATFB (Fig. 2a) and in monomer-free ACN + 0.1 mol L^{-1} TBATFB (Fig. 2b), respectively. Similar to the results reported in the literature^[2], the steady-state cyclic voltammograms represent broad anodic and cathodic peaks. The peak current densities are proportional to the scan rates (Figs. 2a & b), indicating the reversible redox behavior of the polymer. Furthermore, these films could be cycled repeatedly between the conducting (oxidized) and insulating (neutral) states without significant decomposition of the materials, indicating the high stability of the polymer. The polymer film obtained from this medium could be oxidized and reduced from 1.20 (E_a) to 0.88 V (E_c) in monomer-free BFEE/50% EE + 0.05 mol L^{-1} TBATFB (Fig. 2a) and from 1.26 (E_a) to 1.09 V (E_c) in monomer-free ACN (Fig. 2b). All these results indicate that as-formed P5CI films have good electrochemical and redox properties.

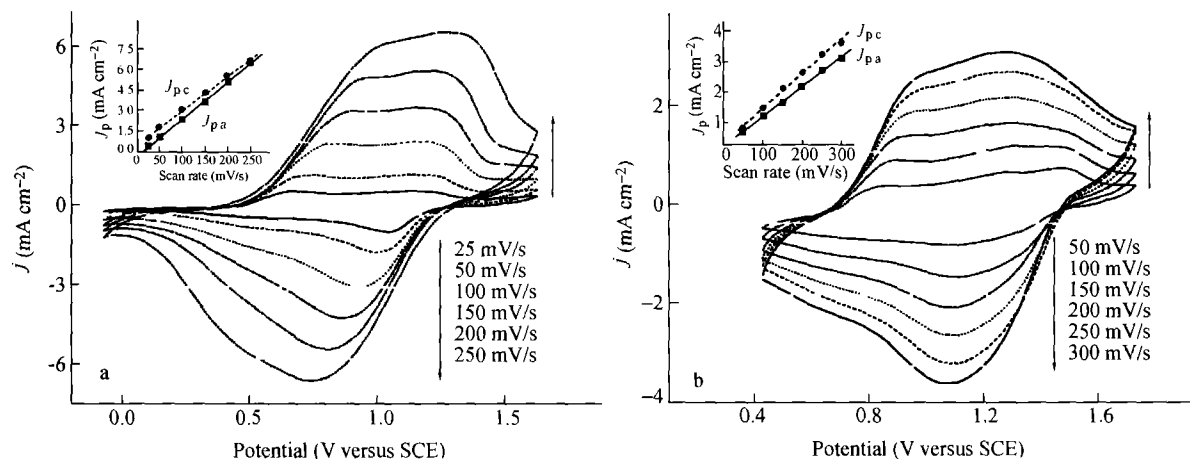


Fig. 2 Cyclic voltammograms of a P5CI film in monomer-free BFEE + 50% EE + 0.05 mol L^{-1} TBATFB (a) and in monomer-free ACN + 0.1 mol L^{-1} TBATFB (b) at different potential scan rates
The P5CI film was synthesized electrochemically in BFEE + 50% EE + 0.05 mol L^{-1} TBATFB at a constant applied potential of 1.23 V versus SCE.

Structural Characterizations

P5CI films electrodeposited on large-area stainless steel sheet were homogeneous and could be peeled from the electrode into freestanding films. For comparison, the electrochemical polymerization of 5CI in ACN + 0.1 mol L^{-1}

TBATFB was also studied and the P5CI films formed dropped easily from the electrode during the polymerization. When taking the anode out of the ACN, only small amount of P5CI films can be found on the electrode surface. These phenomena implied that the properties of P5CI films thus prepared from ACN were rather poor, especially their mechanical properties, further implying that BFEE was a better medium for the electrochemical polymerization of 5CI.

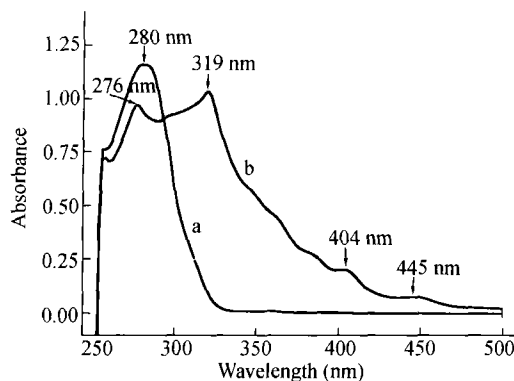


Fig. 3 UV-Visible spectra of 5-cyanoindole (a) and dedoped P5CI (b)
Solvent: DMSO; The P5CI film was synthesized electrochemically in BFEE + 50% EE + 0.05 mol L^{-1} TBATFB at a constant applied potential of 1.23 V versus SCE.

As-prepared P5CI films from the mixed electrolytes were in doped state and metallic dark in color. When dedoped by 25% ammonia, their color changed slightly and was thoroughly soluble in strong polar solvent DMSO but partly soluble in THF or acetone. The UV-Vis spectra of 5-cyanoindole (a) and dedoped P5CI (b) dissolved in DMSO are shown in Fig. 3. The 5-cyanoindole monomer shows characteristic absorption at 280 nm, while the spectra of the dedoped P5CI films shows a much broader absorption with several fine structures at 276, 319, 404 and 445 nm. Generally, absorption at longer wavelength in the spectra usually indicates higher conjugation length. This implies that P5CI has a longer polymer chain length^[27]. These spectral results confirmed a conjugated polymer formation with a broad molar mass distribution.

In order to get a deep insight of the structure of as-formed P5CI film, the $^1\text{H-NMR}$ spectra of 5-cyanoindole (a) and dedoped P5CI (b) were recorded, as illustrated in Fig. 4. The proton lines of dedoped P5CI are much broader than the corresponding proton lines of 5-cyanoindole because of the wide molar mass distribution of P5CI or the complex structure of P5CI, which leads to slightly different environment of the atoms. According to the literature^[28], the chemical shift of N—H bond in $^1\text{H-NMR}$ spectrum of indole is at δ 10.1, while that of pyrrole is at around δ 8.0. The incorporation of benzene ring onto pyrrole ring makes the chemical shift of N—H bond move to lower field. Therefore, it could be reasonably deduced that, through the incorporation of a higher conjugation length onto the P5CI main chain, the chemical shift of N—H bond could move to lower field further. On the basis of these considerations, the chemical shift of δ 12.57, δ 12.08 and δ 12.01 in Fig. 4 can be assigned to the N—H bond in P5CI. This means that the N—H bond was still present on the main chain of the polymer. The presence of N—H bond in $^1\text{H-NMR}$ spectrum of as-formed P5CI films proves that the electropolymerization of 5-cyanoindole occurs at the 2,3 position, in well accordance with the literatures^[9]. The three peaks between δ 9.0 and δ 9.4 arise from the proton in the 4-position of the benzene ring on one of the indole units. The group peaks at lower chemical shifts, around δ 7.9, arise from the protons in the 6- and 7-positions of the benzene rings^[29]. Confirmation of these assignments is found by integrating the peaks, which shows that the peaks around δ 12, δ 9 and δ 8 arise from nearly one, one and two protons, respectively.

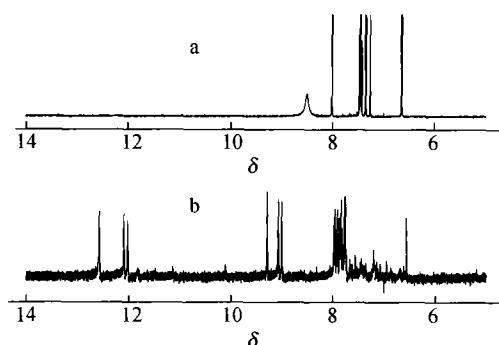


Fig. 4 ^1H -NMR spectra of 5-cyanoindole (a) and dedoped P5CI (b)
Solvent: CD_3SOCD_3 ; The P5CI film was synthesized electrochemically in BFEE + 50% EE + 0.05 mol L^{-1} TBATFB at a constant applied potential of 1.23 V versus SCE.

The fluorescence spectrum of dedoped P5CI was examined using DMSO as the solvent through the wavelength scans of excitation-emission, as shown in Fig. 5. The obvious peaks of excitation spectra can be found at 277, 320 nm, while the emission spectra have several peaks mainly at 425, 440, 450 nm. The wide peak distribution can be ascribed to the wide molar mass distribution of P5CI, in well agreement with UV-Vis spectra and ^1H -NMR results. These results demonstrated that P5CI is a good blue light emitter.

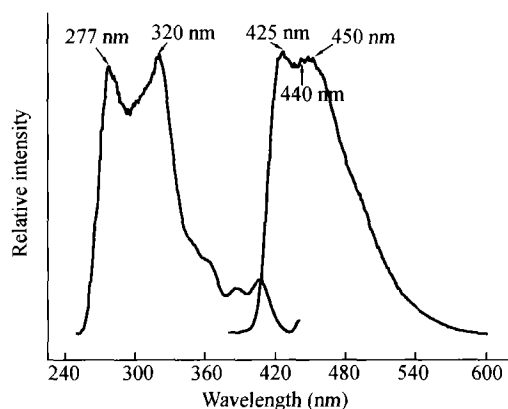


Fig. 5 The fluorescence spectra of dedoped P5CI
Emission spectra were acquired using an excitation wavelength of 320 nm; Excitation spectra were acquired using an emission wavelength of 440 nm; Solvent: DMSO;
The P5CI film was synthesized electrochemically in BFEE + 50% EE + 0.05 mol L^{-1} TBATFB at a constant applied potential of 1.23 V versus SCE.

Conductivity

The conductivity of the P5CI film obtained from BFEE/50% EE + 0.05 mol L^{-1} TBATFB was measured to be $10^{-2} \text{ S cm}^{-1}$. This semiconductivity can facilitate the application of P5CI in various domains.

CONCLUSIONS

P5CI films with conductivity of $10^{-2} \text{ S cm}^{-1}$ were electrochemically synthesized in BFEE + 50% EE + 0.05 mol L^{-1} TBATFB by direct anodic oxidation of 5-cyanoindole. As-formed P5CI films showed good redox activity and high stability in both BFEE and ACN. They were thoroughly soluble in strong polar solvent DMSO and partly soluble in tetrahydrofuran and acetone. According to ^1H -NMR spectra, the existence of N—H bond implies the coupling between the monomer units occur at 2,3 position. The fluorescence spectra suggest that soluble P5CI is a good blue light emitter. The introduction of cyano group on the conducting polymer main backbone will

provide a novel approach for the functionalization of inherently conducting polymers such as reducing cyano group into amido group. Further work is in progress.

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