Electrosyntheses of Freestanding and Conducting Poly[poly(*N*-vinyl-carbazole)] Films in Tetrahydrofuran Containing Additional Boron Trifluoride Diethyl Etherate

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ABSTRACT: Freestanding and conducting poly[poly(*N*-vinyl-carbazole)] (PPVK) films with good fluorescence property were synthesized electrochemically by direct anodic oxidation of poly(*N*-vinyl-carbazole) (PVK) in tetrahydrofuran containing boron trifluoride diethyl etherate (BFEE) (12%, by volume) and Bu₄NBF₄ (0.05 M). The oxidation onset potential of PVK in this medium was measured to be 1.07 V vs. SCE. PPVK films obtained from this medium showed good electrochemical behavior and good thermal stability with conductivity of 10⁻² S cm⁻¹. PPVK films were black in doped state and transparent white in dedoped state. Structural studies showed that the secondary polymerization of PVK occurred at benzene ring. These polymer films had good mechanical properties, which can be easily cut into a variety of structures with a knife or a pair of scissors. [DOI 10.1295/polymj.38.369]

KEY WORDS Electrochemical Polymerization / Conducting Polymers / Poly[poly(*N*-vinyl-carbazole)] / Boron Trifluoride Diethyl Etherate / Freestanding Film /

Conjugated polymers have been considered as a very important class of electroactive and photoactive materials by both academic and industrial laboratories.^{1–3} Among the conducting polymers (CPs) electrosynthesized during the past quarter century, polycarbazole had attracted significant attention as a material with possible applications in sensors, rechargeable batteries, photocorrosion inhibition, electrocatalysis, electrochromic displays and electronic devices.^{4–11} Recently, extensive research work has been devoted to the investigation of carbazole-based polymers due to polycarbazole with optical properties and good hole-transporting ability in light-emitting devices.^{12–16} In the previous studies, the polycarbazole-based electrochemical transistor was superior to other conducting polymer transistors.¹⁷ Although there had been several reports on the electrochemical polymerization of carbazole,^{18–20} it is very difficult to prepare freestanding and conducting polycarbazole films by direct anodic oxidation of carbazole. Therefore, the preparation of freestanding and conducting polycarbazole film became a great challenge.

Previous studies had indicated that the incorporation of traditional polymer backbone, such as polyethylene main chain, can be helpful for high quality film formation.^{21,22} Under this circumstance, the poly-

ethylene main chain plays the main role for the mechanical property improvement of the corresponding conducting polymers. Based on this consideration, the electrochemical polymerization of poly(*N*-vinyl-carbazole) (PVK) may be a better choice for the preparation of high quality polycarbazole films.

On the other hand, PVK has also attracted attention in applications related to organic light-emitting diodes.^{23–25} Devices in which the emitting layer was formed by PVK blended with other polymeric systems have shown remarkable increase in luminance efficiency, in comparison with those in which PVK was not incorporated. PVK was non-conjugated vinyl polymer with pendant carbazole unit.^{26–28} Many of its applications were limited due to PVK polymerized through the vinyl group was only in neutral forms. At present, Baba *et al.*²⁹ have reported this “precursor polymer” route by depositing and patterning films using electrochemical methods. A polymer precursor is first synthesized chemically and containing pendant electroactive monomer units. The precursor is then electropolymerized on the conducting substrate to form an insoluble cross-linked network of conjugated polymers (oligomers). So PVK possibly has the advantage, that is, it has a polyvinyl polymer backbone and a capacity for secondary polymerization through

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the carbazole units.

The electrodeposition of conducting polymer films has mainly been performed in neutral solvents, such as acetonitrile and CH_2Cl_2 , using ClO_4^- or BF_4^- as the supporting electrolyte. Commonly, the oxidation potentials of the polymer precursors in neutral solvents were very high. The qualities of the polymer films obtained from these media were very poor. It is well known that the catalytic effect of BFEE facilitates the formation of high quality freestanding polymer films.^{30–34} In our previous studies polycarbazole films can be prepared from pure BFEE by direct anodic oxidation of carbazole.³⁵ However, the mechanical property of polycarbazole films still needs to be improved. As far as we know, there have been no reports on the secondary electrodeposition of high-quality freestanding poly[poly(*N*-vinyl-carbazole)] (PPVK) films through the carbazole units from BFEE based mixed electrolyte.

The goal of the present work was the secondary electrodeposition of PVK precursor. High quality freestanding PPVK films can be easily prepared by anodic oxidation of PVK precursor directly in THF containing BFEE and Bu_4NBF_4 (0.05 M). The electrochemical properties, morphology, thermal stability, spectroscopic properties, of as-prepared PPVK films were studied in detail.

EXPERIMENTAL

Materials

BFEE (Beijing Changyang Chemical Plant) was distilled and stored at -20°C before use. Poly(*N*-vinyl-carbazole) (PVK, Acros Organics, $M_w = 90,000$), Sulfuric acid (98%) and 25% ammonia (made by Jinan Chemical Reagent Company), were used as received without further purification. Tetrabutylammonium tetrafluoroborate, (Bu_4NBF_4 , Acros Organics, 95%), was dried in vacuum at 60°C for 24 h before use. Tetrahydrofuran (THF, analytical grade) was made by Beijing Chemical Plant.

Electrosyntheses of PPVK Films

Electrochemical syntheses and examinations were performed in a one-compartment cell with the use of Model 263 Potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control. For electrochemical examinations, 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, and the two electrodes were placed 5 mm apart. To obtain a sufficient amount of polymer for characterization, stainless steel sheets with a surface area of 10 and 12cm^2 each were employed as the working and counter electrodes, respectively. Elec-

trodes mentioned above were carefully polished with abrasive paper (1500 mesh), and cleaned by water and acetone successively before each examination. All potentials were referred to a saturated calomel electrode (SCE).

The typical electrolytic solution was THF containing BFEE (12%, by volume) and PVK (0.03 M) and Bu_4NBF_4 (0.05 M). 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, oligomers and monomer, the electropolymerized films were rinsed by diethyl ether. As-formed PPVK film was in doped state and metallic dark 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°C for 24 h.

Characterizations

The experimental result proved the current efficiency (η) close to 100%. The doping levels (f) of the as-formed PPVK films were determined electrochemically by using eq 1:³⁶

$$f = [2Q_0/(Q_d - Q_0)] \times 100\% \quad (1)$$

where Q_d is the total charge used for PPVK deposition and Q_0 is the total charge of oxidized species in the PPVK films measured by reducing the films at 0 V.

The conductivity of as-formed PPVK film was measured by conventional four-probe technique. UV-vis 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 thermogravimetric analysis (TGA) was performed with a thermal analyzer of NETZSCH TG209. Scanning electron microscopy (SEM) measurements were taken by using a JEOL JSM-6700F scanning electron microscope.

RESULTS AND DISCUSSION

Electrochemical Syntheses of PPVK Films

Generally, high quality conducting polymer films can be electrodeposited from pure BFEE. However, PVK precursor was only soluble in THF. It was found that very stable and high quality polymer films can be electrodeposited in THF containing small amount of BFEE. Therefore, THF containing certain amount of BFEE was chosen as the media for the electrochemical polymerization of PVK precursor.

Figure 1 showed the anodic polymerization curves of PVK in THF containing different amount of BFEE and Bu_4NBF_4 (0.05 M). Bu_4NBF_4 was introduced in

Figure 1. Anodic polarization curves of PVK (0.03 M) in THF containing 0% (A), 6% (B), 8% (C), 10% (D), 12% (E) BFEE (by volume) and Bu_4NBF_4 (0.05 M). Potential scan rates: 20 mV s^{-1} .

Figure 2. Cyclic voltammograms of PVK (0.03 M) in THF containing Bu_4NBF_4 (0.05 M) (A), or in THF containing BFEE [6% (B), 10% (C), 12% (D), by volume] and Bu_4NBF_4 (0.05 M). Potential scan rates: 50 mV s^{-1} .

Scheme 1. Mechanism of the complexation of THF with BFEE.

order to improve the ionic conductivity of the mixed electrolyte. The oxidation onset of PVK was initiated at 1.58 V vs. SCE in THF containing Bu_4NBF_4 (0.05 M) (Figure 1A). The addition of 6, 8, 10, 12% BFEE into THF decreased the oxidation potential of the PVK precursor significantly to about 1.18, 1.11, 1.10, 1.07 V (Figures 1B–1E), respectively. As a Lewis acid, BF_3 can interact with a Lewis base, such as thiophene, benzene, fused ring compound, etc.^{37,38} This interaction can decrease the resonance energy of these aromatic compound, thus leading the lose of an electron from these compounds much easier and making high quality conducting polymer films formation possible. On the other hand, this interaction leads to the significant decrease of oxidation onset potential of monomer. From this point of view, BFEE is helpful for the electropolymerization of PVK because generally the lowering of the oxidation onset potential of the PVK precursor can avoid side reactions and lead to higher quality of polymer films. However, the addition polymerization occurred immediately and non-conjugated polymer was precipitated when the volume amount of BFEE exceeded 12%. Therefore, THF containing BFEE (12%, by volume) and Bu_4NBF_4 (0.05 M) was the best choice for the electro-syntheses of conducting PPVK films.

The successive cyclic voltammograms (CVs) of

PVK (0.03 M) in THF containing different amount of BFEE and Bu_4NBF_4 (0.05 M) on a Pt electrode were shown in Figure 2. In THF containing Bu_4NBF_4 (0.05 M) (Figure 2A), the CVs of PVK were not very good and no anodic peaks of the polymer were found. This implied the electrochemical polymerization of PVK in THF containing Bu_4NBF_4 (0.05 M) was not successful. The main reason for this phenomenon can be ascribed to the strong nucleophilicity of THF. The donor number of THF was about 20.³⁹ It is well known that the electrochemical polymerization mechanism for the formation of the conducting polymer film is through radical cations.⁴⁰ During the polymerization, THF as a strong nucleophilic agent can attack the intermediate radical cations. Therefore, the electropolymerization was interrupted by THF and PVK oligomers may be formed. On the other hand, THF can form very stable complex with BF_3 . In comparison with BFEE, the complex of THF with BF_3 is more stable⁴¹ (Scheme 1). The interaction between THF and BF_3 was stronger than hydrogen bond but inferior to covalent bond. Therefore, BF_3 can exchange from one THF molecule to another because of dynamic balance. Therefore, it can be reasonably expected that the nucleophilicity can be greatly decreased by the introduction of small amount of BFEE into THF solution.

In sharp contrast, in the medium of THF containing BFEE and Bu_4NBF_4 (0.05 M), the CVs of PVK showed a good pair of reduction and oxidation waves in the potential range of 0–1.8 V during potentiodynamic syntheses (Figures 2B–2D). This may be ascribed to the introduction of BFEE not only interact with the PVK precursor, which led to the decreases of the PVK precursor oxidation potentials, but also interact with the solvent THF, which decreased the nucleophilicity during the polymerization.

As the CV scans continued in Figures 2B–2D, a thin and uniform polymer film was formed on the Pt electrode surface (green to black as the deposit thickened). The increases of the redox wave currents implied that the amount of the polymer on the electrode increased. The potential shift of the wave current maximum provides information about the increase of the electrical resistance in the polymer film and the over-potential needed to overcome the resistance.⁴² It can also be seen from Figure 2 that the redox wave current densities per cycle increased with the content of BFEE in the mixed electrolytes increasing. The increases of the redox wave current densities per cycle was the highest in THF containing 12% BFEE (Figure 2D). This may be ascribed to the fact that the oxidation potential of monomer was decreasing when further increasing BFEE concentration (Figures 1B–1E). According to the electrochemical kinetics, at a given applied potential (E), the polymerization rate is exponential to the potential difference ($E - E^0$) of E and the oxidation potential of the monomer (E^0). The addition of BFEE decreased E^0 of the monomer. Thus the polymerization rates increased at give applied potentials when increasing BFEE content. This resulted in the phenomena shown in Figures 2B–2D.

Electrochemistry of PPVK Films

The electrochemical behavior of the PPVK films deposited electrochemically from THF containing BFEE (12%, by volume) and Bu_4NBF_4 (0.05 M) was studied in pure BFEE (Figure 3A) and in concentrated sulfuric acid (Figure 3B), respectively. Similar to the results in the literature,⁴³ the steady-state cyclic voltammograms represented broad anodic and cathodic peaks. The peak current densities were proportional to the scan rates (insert of Figures 3A, 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 high stability of the polymer. The polymer film can be oxidized and reduced from 1.17 (E_a) to 0.51 V (E_c) in pure BFEE (Figure 3A), and from 1.10 (E_a) to 0.69 V (E_c) in concentrated sulfuric acid (Figure 3B), respectively.

Figure 3. Cyclic voltammograms of a PPVK film in BFEE (A) and in concentrated sulfuric acid (B) at potential scan rates of 50, 100, 150, 200, 250 mV s^{-1} , respectively. The PPVK film was synthesized electrochemically in THF containing BFEE (12%, by volume) and Bu_4NBF_4 (0.05 M) at a constant applied potential of 1.33 V vs. SCE.

Structural Characterizations

During potentiostatic deposition of PPVK in THF containing BFEE (12%, by volume) and Bu_4NBF_4 (0.05 M), freestanding PPVK films can be well formed on stainless steel sheet. As-prepared PPVK films from this medium were in doped state and dark in color. When dedoped by chemical or electrochemical method, their color turned transparent white. Both the doped and dedoped PPVK films were insoluble in general solvent.

The UV-vis spectra of PVK precursor (a), dedoped (b) and doped (c) PPVK films deposited on ITO surface were examined, as shown in the insert of Figure 4. In the insert of Figure 4, the spectra of polymer showed a broader absorption band than that of PVK precursor with several fine structures at 240, 260, 294 and 342 nm. The longer wavelength in the spectra

Figure 4. Fluorescence spectra of PVK precursor (A) using an excitation wavelength of 355 nm, doped (B) and dedoped (C) PPVK films in solid state using an excitation wavelength of 350 nm. Insert: UV-vis spectra of PVK precursor (a), dedoped (b) and doped (c) PPVK films in solid state.

usually indicates a longer polymer sequence.⁴⁴ Therefore, these spectral results confirmed a conjugated polymer formation with a broad molar mass distribution. Doped PPVK showed an absorption peak at 420 nm, which disappeared for the dedoped PPVK. On the other hand, a broad absorption band from 750 to 1000 nm in the spectrum of the doped PPVK was the characteristic of the existence of conductive species polaron (or bipolarons) on the polymer main chain.⁴⁵ In the course of the doping process, the originally filled valence band of PPVK became partially empty. The Fermi level lowers the valence band, which ensures a metallic behavior to the PPVK. It could be expected that at higher doping level of PPVK, the more empty the valence band would become. As a consequence, the polaron (or bipolaron) concentration would increase, and the conductivity of the PPVK would also increase.

The fluorescence spectra of PVK precursor (A), doped (B) and dedoped (C) PPVK films in solid state were also examined, as shown in Figure 4. The emission spectrum of PVK precursor was at 372 nm, while the emission spectra of doped and dedoped PPVK films have two peaks at 374, 412 nm and one peak at 404 nm, respectively. The red-shift of emission wavelength indicated that the conjugated extent of polymers was increased. These results demonstrated that PPVK film was a good blue light emitter.

Figure 5 displayed the transmittance FT-IR spectra of monomer (A) and dedoped PPVK (B) films obtained from THF containing BFEE (12%, by volume) and Bu₄NBF₄ (0.05 M). In Figure 5A, the bands at 3043, 2928 cm⁻¹ can be assigned to the stretching of aroma or aliphatic C–H bonds. In Figure 5B, the band at 3049 cm⁻¹ was the stretching of aroma C–H bonds, while the strong bands at 2941, 2856, 2796 cm⁻¹ and at 1113 cm⁻¹ were ascribed to the deformation vibration of CH₂ and C–O–C of THF, respective-

Figure 5. FT-IR spectra of PVK precursor (A) and dedoped PPVK films (B) obtained potentiostatically at 1.33 V vs. SCE from THF containing BFEE (12%, by volume) and Bu₄NBF₄ (0.05 M) after a treatment with 25% aqueous ammonia for 3 days.

ly. This indicated that THF had been co-deposited into PPVK. The peak at 1314 cm⁻¹ was the deformation vibration of C–N on the PVK. In contrast, the stretching vibration of the C–N shifted to higher wave number (1368, 1332 cm⁻¹) in the spectrum of PPVK. The peaks located at 878, 794 cm⁻¹ were ascribed to the out-of-plane deformation vibration of 1,2,4-trisubstituted benzene ring,⁴⁶ which indicated the polymerization on the benzene ring. The peaks at 745, 721 cm⁻¹ implied that small amount of independent carbazole units still existed in the polymer. The bands in the region from 1640 to 1100 cm⁻¹ were assigned to the stretching and shrinking modes of the C=C and C–C, which were selectively broadened for PPVK. This verified that the main component in PPVK had the characteristics of typical conjugated polymers.

Thermal Analysis

The thermal stability of conducting polymers is very important for their application. TGA is a significant dynamic way to detect the degradation behaviors. The weight loss of a polymer sample is measured continuously, whereas the temperature is changed at a constant rate. Figure 6 showed the TG curves of doped (A) and dedoped (B) PPVK. As seen from Figure 6A, there was weight loss from 469 to 564 K, up to 21.8%, mainly due to the degradation of low molecular components such as doping-anion and other moisture trapped in the polymer. The decomposition up to 21% occurred between 564 and 686 K, possibly due to the overflow of some oligomers decomposed from the PPVK. The decomposition of polymer was taken place after the temperature above 686 K and weight loss up to 28.8%. In Figure 6B, the decomposition of polymer occurred between 715 and 783 K. On the other hand, Figure 6 showed that no evident thermal degradation occurred in the measured temperature from 783 to 1156 K, which indicated that the residue was thermally stable.

Figure 6. TGA curves of doped (A) and dedoped (B) PPVK films obtained potentiostatically at 1.33 V vs. SCE from THF containing BFEE (12%, by volume) and Bu_4NBF_4 (0.05 M) after a treatment with 25% aqueous ammonia for 3 d.

Figure 7. Photograph of a freestanding conducting PPVK film prepared from THF containing BFEE (12%, by volume) and Bu_4NBF_4 (0.05 M) at a constant applied potential of 1.33 V vs. SCE.

Morphology and Conductivity

As-formed PPVK films prepared in THF containing BFEE (12%, by volume) and Bu_4NBF_4 (0.05 M) can be peeled off from the electrode into free-standing state. This polymer film has good flexibility and can be cut like a metal sheet with a knife or a pair of scissors into a variety of structures (Figure 7). The SEM images of a PPVK film were shown in Figure 8. It was clear that as-formed PPVK films on stainless steel electrodes were macroscopically uniform (Figure 8A). Microscopically, there were some aggregates adjacent to each other (Figure 8B). This structure facilitated the good electrochemical properties of as-formed PPVK films, in well accordance with the results in Figure 3.

The conductivity of the PPVK film obtained from THF containing BFEE (12%, by volume) and Bu_4NBF_4 (0.05 M) was measured to be $10^{-2} \text{ S cm}^{-1}$. This value was much higher than that of PVK precursor

(A)

(B)

Figure 8. SEM micrographs of a PPVK film deposited on the electrode surface from THF containing BFEE (12%, by volume) and Bu_4NBF_4 (0.05 M) at a constant applied potential of 1.33 V vs. SCE.

($4 \times 10^{-6} \text{ S cm}^{-1}$).⁴⁷ Moreover, the doping level of as-formed PPVK films were determined to be close to 21%. These semiconducting properties will be greatly helpful for the applications of PPVK films.

CONCLUSIONS

Freestanding and conducting PPVK films with conductivity of $10^{-2} \text{ S cm}^{-1}$ and good fluorescence property were electrochemically synthesized in THF containing BFEE (12%, by volume) and Bu_4NBF_4 (0.05 M). As-formed PPVK films showed good redox activity and high electrochemical stability in pure BFEE and in concentrated sulfuric acid. According to IR spectra, the coupling between the PVK precursor units occurred at benzene ring. TGA results indicated good thermal stability of PPVK films. PPVK films

prepared from these media were black in doped state and transparent white in dedoped state. As-formed freestanding PPVK films could be cut into a variety of structures with mechanical properties. These properties of PPVK may facilitate its further application such as in optoelectronics.

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