

ARTICLE

Electrochemical Synthesis and Research of Two Polymers Composed of Alternate Carbazole and Thiophene Units

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Two organic conjugated molecules composed of central carbazole and bithiophene groups were prepared via the Stille coupling reaction, conductive polymers were prepared by electrochemical method. Structure and photoelectric research of polymers were investigated. ^1H NMR and ^{13}C NMR of molecules were consistent with the theoretical results, FT-IR showed electrochemical polymeric site were α -position of thiophene units. The smooth morphology and distributed holes were beneficial to improve the electrical conductivity by SEM. When applied voltage was from -0.1 V to 1.2 V, both of the polymer films P1 and P2 showed good electrochromic performances. Compared with P1, P2 had better electrochemical stability and thermal stability due to the better coplanarity by repeated cyclic voltammograms and TGA. The P2 was a promising material in the electrochemical field, meanwhile, it showed that the monomer structure had greatly impact on the performance of polymer.

Key words: Stille reaction, Cyclic voltammetry, Electrochemistry polymerization, Spectroelectrochemistry

I. INTRODUCTION

Conducting polymers have been extensively investigated as electrochemical materials for their low cost, compatibility, easy processing, tunable optoelectronic properties [1, 2], and various applications such as camouflage materials [3], color displays, electrochromic devices [4], and light-emitting diodes [5, 6]. Electrochromic materials can change their optical properties of persistent and reversible response to the alternation of applied voltage pulse conveniently. In the context, we devote to the design and synthesis of two electrochemical conducting polymers composed of carbazole unit and thiophene groups.

Compared with other polymerization methods, electrochemical polymerization is an efficient method for obtaining conducting polymers, the electrochemical process is a noncatalytic reaction, and the polymerization method provides good reproducibility because the polymerization process can be easily controlled by monitoring the current and integrated charge passing through electrochemical cells.

Carbazole and its derivatives have special rigid structure, which is easy to be modified and exhibit many unique properties, conductive polymers composed of carbazole have attract a great attention in various photonic applications, such as electroluminescence, photo-

conductivity and photorefraction [7]. Cabaj *et al.* reported a convenient and higher yielding synthetic route of *N*-alkylcarbazole-bis(thiophene), their electrochemical properties were researched [8], Kawabata *et al.* prepared a series of *N*-alkyl-2,7-di(2-thienyl)-carbazoles via the electrochemical polymerization method, the surface morphology of the polymer films showed nanofiber morphology, which had good and tunable electrochemical properties [9].

High oxidation potential of direct electropolymerization of carbazole causes some degradation of the polymer, which can be overcome by introducing different conjugated units to obtain a low oxidation potential [10, 11]. Electron-rich heteroaromatic thiophene have relatively low oxidation potential [12], which is better for electrochemical polymerization process, meanwhile, which can produce low bandgap polymers.

In this work, we demonstrate electrochemical polymerization of *N*-alkyl-(3,6-),(2,7-)-di(2-thienyl)-carbazole in acetonitrile. The photoelectric performance of different location of thiophene on polymers have been researched, they exhibit different electrochemical and optical features. The target molecules were synthesized and characterized in details, the properties of the conducting polymers, such as electrochemical behavior, structural information, thermal stability, spectroscopic properties were also investigated in detail, and their electrochromic performances were emphasized in particular.

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II. EXPERIMENTS

A. Materials

CDCl_3 and DMSO-d_6 were purchased from Aldrich Chemical. Sodium, benzophenone, 3,6-dibromo-carbazole, 2,7-dibromo-carbazole, 1-bromooctane, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, tributyl(thiophen-2-yl)stannane, DMSO , and other chemicals were all purchased from energy chemical. Toluene was dried over sodium/benzophenone and distilled under argon atmosphere before use. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was dried under vacuum at 60°C for 24 h before use.

B. Characterization

^1H NMR and ^{13}C NMR spectra were collected using a Bruker AM-400WB spectrometer in CDCl_3 and DMSO-d_6 as solvent with tetramethylsilane as the internal standard. Ultraviolet absorption spectra were measured using a Shimadzu UV-1800 UV spectrometer. Cyclic voltammetric measurements were taken on a conventional three-electrode cell using Pt button working electrodes of 2 mm diameter, a platinum wire counter electrode, and a Ag/AgCl reference electrode on a Model 263 A potentiostat-galvanostat (EG&G Princeton Applied research) electrochemical workstation under computer control at room temperature, the polymer films were deposited onto indium/tin oxide (ITO) coated glass slides. Thermal gravimetric analysis (TGA) was performed on an SDT600 thermal analyzer from room temperature to 600°C under a dry nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. Scanning electron microscope (SEM) measurements were made with a cold field emission scanning electron microscope ZEISS SIGMA.

C. Synthesis

1. 2,7-dibromo-9-octyl-9H-carbazole

A mixture of 2,7-dibromo-9H-carbazole (5.00 g, 15.40 mmol) and 1-bromooctane (3.86 g, 20.0 mmol) in DMSO (100 mL) was stirred for 30 min at room temperature, then a sodium hydroxide solution (30 mL, 50vol%) was slowly added and stirred for 24 h. The reaction mixture was poured into water and the precipitate was filtered, repeatedly washed with distilled water and dried under vacuum. The product was obtained as off-white solids without further purification. Yield: 5.32 g, (79%). ^1H NMR (400 MHz, CDCl_3): δ/ppm 7.61 (d, $J=8.4$ Hz, 2H), 7.26 (d, $J=1.2$ Hz, 2H), 7.09–7.07 (m, 2H), 3.90 (d, $J=7.4$ Hz, 2H), 1.60–1.53 (m, 2H), 1.08–1.01 (m, 2H), 0.63 (t, $J=6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ/ppm

141.33, 122.51, 121.36, 119.6, 111.99, 43.32, 31.82, 29.82, 28.97, 27.19, 22.66, 14.13.

2. 9-octyl-2,7-di(thiophen-2-yl)-9H-carbazole (M1)

2,7-Dibromo-9-octyl-9H-carbazole (4.5 g, 10.3 mmol), tributyl(thiophen-2-yl)stannane (11.5 g, 30.9 mmol), and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.55 g, 0.78 mmol) were dissolved in dry toluene (100 mL) and then stirred at 110°C under N_2 for 36 h. After cooling the mixture to the room temperature, the solvent was directly removed. The crude product was purified using column chromatography on a silica gel using petroleum ether as eluent. The product was obtained as white solid. Yield: 3.6 g, (79%). ^1H NMR (400 MHz, CDCl_3): δ/ppm 8.02 (d, 2H), 7.60 (s, 2H), 7.53 (d, 2H), 7.51 (d, $J=3.2$ Hz, 2H), 7.45 (d, $J=4.8$ Hz, 2H), 7.15 (t, $J=6.0$ Hz, 2H), 4.27 (t, $J=7.0$ Hz, 2H), 1.87 (t, $J=7.0$ Hz, 2H), 1.18–1.26 (m, 10H), 0.92 (t, $J=8.7$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ/ppm 145.68, 141.47, 132.19, 128.08, 124.61, 123.07, 122.24, 12.67, 117.99, 105.98, 42.95, 31.89, 29.23, 27.28, 22.70, 14.12.

3. 3,6-dibromo-9-octyl-9H-carbazole

A mixture of 3,6-dibromo-9H-carbazole (5.00 g, 15.40 mmol) and 1-bromooctane (3.58 g, 18.50 mmol) in DMSO (100 mL) was stirred for 30 min at room temperature, then a sodium hydroxide solution (13 mL, 50vol%) was slowly added and stirred for 12 h. The reaction mixture was poured into water and the precipitate was filtered, repeatedly washed with distilled water and dried under vacuum. The product was obtained as off-white solids without further purification. Yield: 4.60 g, (80%). ^1H NMR (400 MHz, CDCl_3): δ/ppm 8.08 (s, 2H), 7.48 (d, $J=8.8$ Hz, 2H), 7.20 (d, $J=7.2$ Hz, 2H), 4.16 (t, $J=6.8$ Hz, 2H), 1.74 (d, $J=6.4$ Hz, 2H), 1.23–1.15 (m, 10H), 0.79 (t, $J=6.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ/ppm 138.00, 127.76, 122.27, 111.03, 109.01, 42.06, 30.69, 28.15, 27.72, 26.11, 21.54, 13.04.

4. 9-octyl-3,6-di(thiophen-2-yl)-9H-carbazole (M2)

3,6-Dibromo-9-octyl-9H-carbazole (3.00 g, 6.80 mmol), tributyl(thiophen-2-yl)stannane (6.42 g, 17.16 mmol), and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.55 g, 0.78 mmol) were dissolved in dry toluene (100 mL) and then stirred at 110°C under N_2 for 36 h. After cooling the mixture to the room temperature, the solvent was directly removed. The crude product was purified using column chromatography on a silica gel using petroleum ether as eluent. The product was obtained as white solid. Yield: 1.34 g, (56%). ^1H NMR (400 MHz, CDCl_3): δ/ppm 8.27 (s, 2H), 7.66 (d, $J=8.0$ Hz, 2H), 7.30 (t, $J=7.4$ Hz,

4H), 7.19 (d, $J=5.2$ Hz, 2H), 7.04 (s, 2H), 4.22 (t, $J=7.0$ Hz, 2H), 1.81 (t, $J=6.6$ Hz, 2H), 1.31–1.15 (m, 10H), 0.80 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ/ppm 144.54, 139.21, 127.06, 124.70, 123.37, 122.52, 122.03, 120.94, 116.90, 108.15, 42.01, 30.72, 28.30, 27.89, 26.96, 21.55, 13.05.

III. RESULTS AND DISCUSSION

A. Cyclic voltammetry

Electrochemical polymerizations were carried out from a 0.1 mol/L acetonitrile (ACN), Bu_4NPF_6 , and 0.01 mol/L monomer solutions at a scan rate of 100 mV/s. The investigation of redox behaviors of the resulting polymers (P1 and P2) was achieved by cyclic voltammetry studies.

The electrochemical growth revealed the electrochemical performance of monomer and the formation of conducting polymer, the first cyclic voltammetry (CV) curve show that the onset oxidation of M1 ($E^{\text{ox}}=1.0$ V) (Fig.1(a)) was observed at higher potentials than that of M2 ($E^{\text{ox}}=0.9$ V), which might be due to strong conjugate between 3,6-thiophene and carbazole unit. In addition, the oxidation and reduction peaks were observed at 1.1 and 0.65 V for P1, 0.75 and 0.58 V for P2, respectively. With the CV scan continuing, the increase of current of redox peaks implies that the amount of the polymer on the electrode is increasing. Both of M1 and M2 have broad redox peaks, which may be due to the wide distribution of the polymer chain length or the conversion of the conductive medium on the polymer main chain from the neutral state to free radical, from free radical to bipolarons and finally from bipolarons to the metallic state [13], these phenomena indicated that conducting films of P1 and P2 were formed on the working electrode.

B. Electrochemistry of polymer films

Figure 2 shows the electrochemical behavior of P1 and P2 in 0.1 mol/L $\text{Bu}_4\text{NPF}_6/\text{ACN}$ at different potential scan rates, CV were carried out to research the electroactivity of the polymer films in the form of a current-potential diagram. The steady CV displayed broad anodic and cathodic peaks, both of them revealed a linear relationship between the currents and the scan rates, which indicated that the redox processes were not controlled by diffusion limits. Furthermore, these polymers could be repeatedly cycled between oxidized and neutral states without significant decomposition, indicating the high redox stability of P1 and P2 films. The P1 film could be oxidized and reduced from 1.0 V to 0.65 V and P2 film from 0.85 V to 0.58 V, respectively.

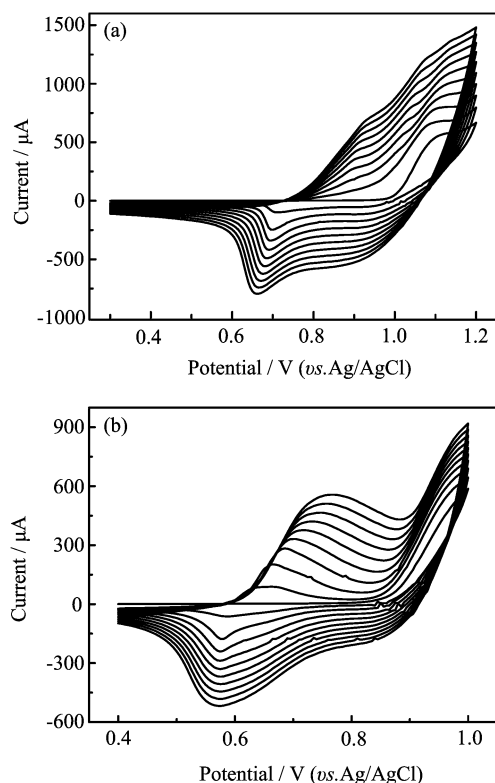


FIG. 1 Electropolymerization of (a) M1 and (b) M2 on ITO in 0.1 mol/L $\text{Bu}_4\text{NPF}_6/\text{ACN}$ at a scan rate of 100 mV/s.

C. Structural characterization of polymers

Figure 3 shows the FT-IR spectra of the monomers and conducting polymers. Compared with the absorption bands of monomers, the spectra of polymers were wide because of chain dispersity of resulting product composed of oligomers/polymers. The peak at 843 cm^{-1} (M1) due to the C–H bending vibration frequency of the thiophene was shifted to 835 cm^{-1} (P1) after electrochemical polymerization, 835 cm^{-1} is characteristic of C–H bending vibration of 2,5-substituted thiophenes [14], the occurrence of a coupling reaction for M1 are at α positions of thiophene units during electrochemical polymerization. Meanwhile, the peak at 845 cm^{-1} (M2) due to the C–H bending vibration frequency of the thiophene was shifted to 840 cm^{-1} (P2) after electrochemical polymerization, which indicated that the occurrence of a coupling reaction for M2 was at α -positions of thiophene units. Furthermore, there were three peaks around 3000 cm^{-1} due to the α , β , and γ -position C–H stretching vibration of thiophene units in the M1 and M2, approximately at the same region, however, compared with that of the M1, The peak at 3005 cm^{-1} (M1) of C–H vibration of the α -position in the thiophene rings disappeared in the electrochemical polymerized sample, it was obvious that the electropolymerization occurred at the α -position of the thiophene units, there were two peaks at 2827 and

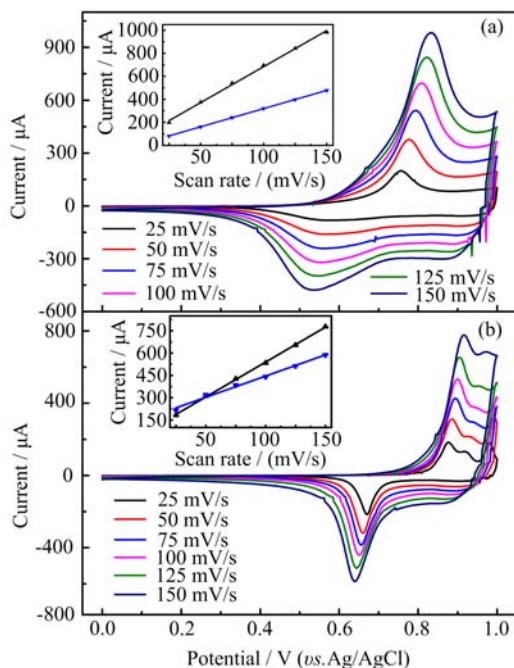


FIG. 2 CV of (a) P1 and (b) P2 in 0.1 mol/L $\text{Bu}_4\text{NPF}_6/\text{ACN}$ at different potential scan rates. Inset: plots of redox peak current *vs.* potential scan rates

2802 cm^{-1} remained after electrochemical polymerization, an absorption of M2 at 3022 cm^{-1} disappeared after polymerization, which confirms that electrochemical polymerization of monomers are between α -position of thiophene units of M1 and M2.

D. Electrochemical stability of polymer films

Cyclic voltammogram of P1 and P2 upon repeated cycling (from 1 cycle to 200 cycles) at the scan rate of 100 mV/s in $\text{ACN-Bu}_4\text{NPF}_6$ (0.1 mol/L) (Fig.4). The long-time cyclic voltammetry method was used to evaluate the electrochemical stability of the polymers, electrochemical activity was equal to ability of cyclic voltammetry of polymers. The scope of scanning potential was from 0 V to 1.0 V for both of them at the scan rate of 100 mV/s . From Fig.4, electrochemical stability of P2 in $0.1\text{ mol/L TBAPF}_6/\text{ACN}$ was better than P1, electrochemical activity of P2 remained 99.0% after 100 cycles, P1 remained 63.9%, after completion of 200 cycles, the electrochemical activity of P1 exhibited a great decrease to 41.5%, while electrochemical activity of P2 still remained 97.2% after 200 cycles, which showed that P2 had a better electrochemical stability among a certain cycles. The coplanarity of thiophenes and carbazole of P2 is better than P1, the internal resistance of molecule is smaller, which can explain that P2 have a better electrochemical stability on the micro-scale.

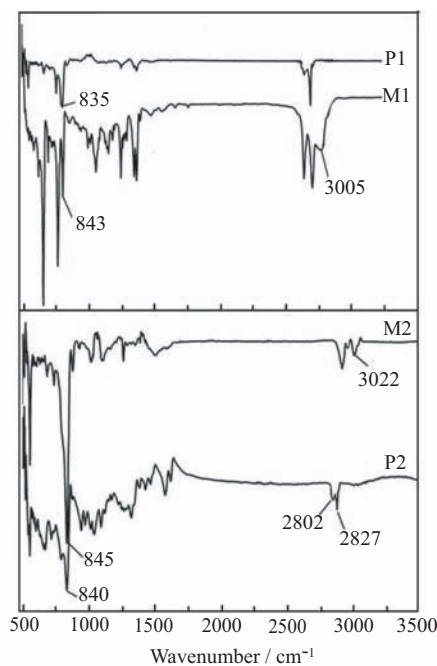


FIG. 3 FT-IR spectra of M1, P1, M2, and P2.

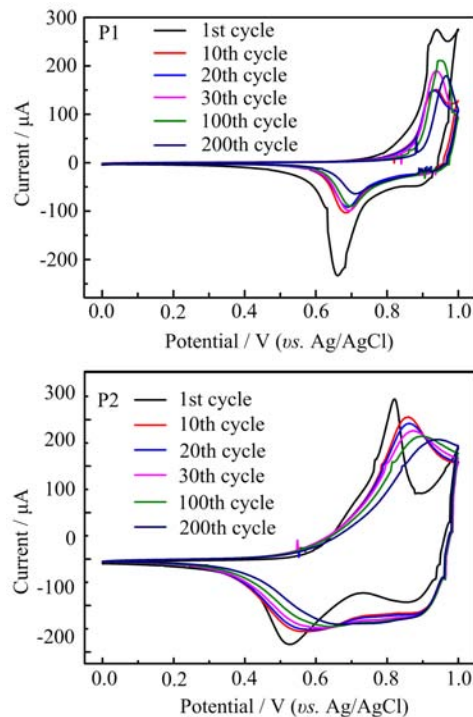


FIG. 4 CV of polymer P1 and P2 upon repeated cycling voltammograms.

E. Thermal stability of polymers

TGA curve of P1 and P2 were investigated under a nitrogen atmosphere at a heating rate of 10 K/min , both P1 and P2 had three-step weight losses as shown in Fig.5, at the first step, weight decrease of P2 was 3.5%

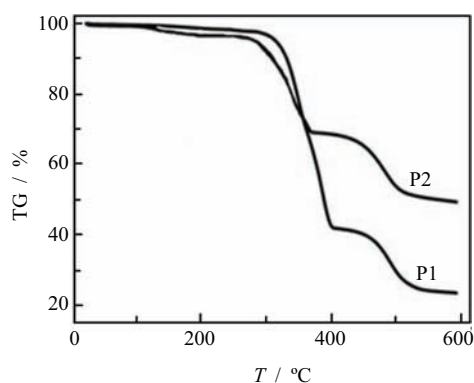


FIG. 5 TGA curves of P1 and P2 under nitrogen atmosphere.

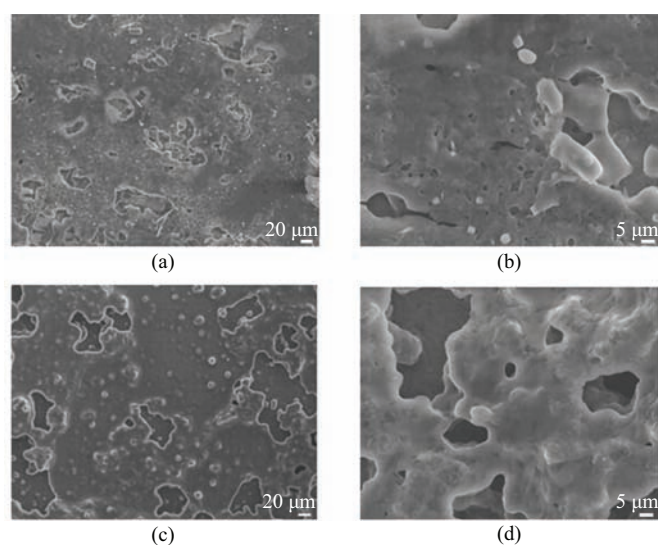


FIG. 6 SEM micrographs of P1 (a and b) and P2 (c and d) films deposited on the ITO glass electrode surface.

from 16.7 °C to 305 °C, weight decrease of P1 was 4.5% from 16.7 °C to 285 °C, which were attributed to moisture and solvent evaporation. With the increasing of the temperature from 306 °C to 401 °C, at the second step, 53% of polymer weight was lost for P1, 25% of polymer weight was lost for P2 from 286 °C to 369 °C, which were essentially due to the thermal decomposition of the backbone chain of polymer. Compared with P1, TGA of P2 showed a better thermal stability because coplanarity of P2 was better than P1 [15, 16], the internal combination of molecule became more firm. Meanwhile, thermal stability of P1 and P2 reached the material requirement.

F. Morphology of polymer films

The surface morphology of P1 and P2 films deposited on the ITO glass electrode surface was investigated by SEM as shown in Fig.6. The films based on P1

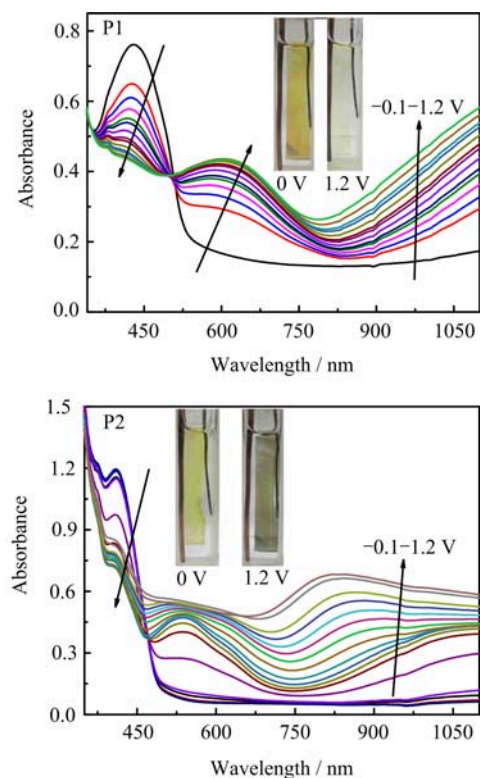


FIG. 7 Spectroelectrochemistry of polymer P1 and P2 in ACN-Bu₄NPF₆ (0.1 mol/L) on ITO between -0.1 and 1.2 V.

and P2 were smooth and homogeneous, accompanied with patches and protruding particles in the surface at 2000 times magnification, when the patches and protruding particles were magnified for 10000 times, there were many scattered holes on the surface at the same time, the surface morphology were helpful for access of doped ions in the process of doping and dedoping conditions, which were extremely beneficial to improve their electrical conductivity and electron transfer capability, meanwhile, they were consistent with polymer properties that both of them had good electrochemical redox feature.

G. Spectroelectrochemical property of polymer films

Spectroelectrochemical curves of electrochemical polymer P1 and P2 are shown in Fig.7 at various applied voltages (from -0.1 to 1.2 V), which were performed to investigate UV-Vis-NIR absorbance curves and the corresponding colors of polymer film correlated to electrode potentials. P1 film has a defined absorption spectrum at 425 nm in the neutral state, upon oxidation, the intensities of 425 nm of π - π^* transition was decreased and 610 nm of π - π^* transition was increased simultaneously with the increasing of potential [17], meanwhile, a new absorption at 900 nm started to intensify due to the formation of charge carrier in P1

film [18]. P2 has an absorption spectrum at 408 nm in the neutral state, compared with absorption spectrum of P1, that of P2 had blue shift (17 nm) due to influence of molecule structure, upon oxidation, the intensities of 408 nm of π - π^* transition was decreased and 537 nm of π - π^* transition was increased simultaneously, meanwhile, a new absorption at 820 nm started to intensify due to the polaron formation [19]. Both P1 and P2 had a color change with the increasing of potential, the corresponding color of P1 film was yellow in the neutral state and transparent white in the doped state (inset in P1), the P2 film exhibited a color change from light yellow in the neutral state to light brown in the doped state (inset in P2), which showed that the P1 and P2 films had good electrochromic phenomena, they might be promising materials in the electrochromic field in the future.

IV. CONCLUSION

Conductive polymers P1 and P2 based on carbazole and thiophene units were synthesized by electrochemical polymerization. FI-IR result shows that electrochemical polymeric site were α -position of thiophene groups. Both P1 and P2 films showed good redox activity and environmental stability in ACN-Bu₄NPF₆ (0.1 mol/L), SEM shows smooth morphology and scattered holes were beneficial to improve the electrical conductivity, meanwhile, the polymers showed good electrochromic performances. Compared with P1 film, P2 film had better performances on the thermal stability and electrochemical stability due to better coplanarity [18, 19]. It was concluded that P2 was a more promising material in the electrochemical field.

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