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Effect of photoisomerization on the electroactivity and electrochromic behavior of aniline pentamer-based polymers with azo chromophore as reversibly switchable pendant group

Hsiu-Ying Huang, Jhong-Wei Jian, Yu-Ting Lee, Yi-Ting Li, Tsao-Cheng Huang, Jung-Hsiang Chang, Lu-Chen Yeh, Jui-Ming Yeh*

Department of Chemistry, Center for Nanotechnology at CYCU, Chung Yuan Christian University, Chung Li 32023, Taiwan, ROC

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ABSTRACT

By an oxidative coupling polymerization approach, we have synthesized an electroactive polymer with good solubility containing alternating phenyl-capped aniline pentamer in the main chain and azo chromophores in the side chain. In this study, we present reversible example of photochemically induced switching of electroactivity by performing electrochemical CV in two ways: (i) in that the photochemical reaction switch can be photochemically reverted by reirradiation at a different wavelength (ii) in that a photoreaction is used that is thermally reversible. At the same time, electrochemical investigations of electrochromic properties of an aniline-pentamer-based electroactive poly(azine-azo) (EPAA) coating prepared by oxidative coupling polymerization are presented. The *in-situ* chemical oxidation of the reduced form of soluble, electroactive poly(azine-azo) (EPAA) in N-methyl-2-pyrrolidone (NMP) was monitored by UV–Visible absorption spectra. Moreover, the electrochromic performance of EPAA was investigated by measuring electrochromic photographs and UV absorption spectra.

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1. Introduction

Among photoresponse materials azobenzene and related compounds represent one of the most widely studied systems, due to their ease of synthesis and facile detection of photoisomerization [1,2]. The isomerization, which has first been described by Krollpfeiffer et al. [3], occurs at the N=N double bond yielding two different states, viz. the trans- and the cis-isomer. The two isomers exhibit different chemical and physical properties and can be interconverted reversibly by irradiation with light [4]. Interconversion between trans and higher energy cis isomeric states can be effected both photochemically (trans \Leftrightarrow cis) and thermally (cis \Leftrightarrow trans) with a high degree of efficiency and an absence of competing side reactions [5,6]. That one configurational isomer is furnished photochemically while the other is favored thermally makes it possible to effectively drive or switch azobenzene modified species into a desired geometry and polarity. As the trans-form is thermodynamically more stable, the cis-form can also react to the trans-form thermally in the dark [5]. Polymers containing azobenzene moieties often display remarkable photo- and thermo-regulated behaviour when subjected to changes

E-mail address: juiming@cycu.edu.tw (J.-M. Yeh).

in incident light or heat [6–8]. Materials of this kind are of considerable theoretical and experimental interest and are well suited for a variety of smart applications [9,10].

Electroactive polymers have been classified as a new class of materials in the past decades and have attracted extensive research activity as a result of their broad spectrum of potential commercial applications in electronic [11], optical [12] and biological [13] research fields. Among these conducting polymers, polyaniline occupies special place among the electroactive polyconjugated polymers due to its stability to the action of the environmental conditions, and because of the easy and cheap method of its synthesis and the unique properties [14,15]. It has a broad spectrum of probable use as the anticorrosion covering [16,17], in the accumulator batteries [18–20], for the separation of gases and hardly separable liquids [21–23], as bio and chemosensor [24–26], etc. Research activities have been focused particularly on the synthesis of aniline oligomers with well-defined structures and end-groups because of their good solubility and ability to undergo further polymerization. The synthesis of a number of aniline oligomers has been reported [27,28]. Recently, electroactive aniline-oligomerderivative polymers have evoked great research attention [29-35]. For example, the preparation and electrochemical behaviour of electroactive polymer have been reported by Wang et al. [29,31] and Wei et al. [30,32], they developed oxidative coupling

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^{*} Corresponding author.

polymerization to couple oligoaniline and 1,4-phenylenediamine [32–34]. The resulting polymers contain well-defined conjugated segments and provide an opportunity for developing a better understanding of the structure–property relationships and the conduction mechanism of conjugated polymers; this understanding has been limited by the complex molecular structures of these polymers and their poor solubility in organic solvents.

In the series of polyconjugated electroactive polymers the substances containing aromatic azo-groups in the main chain and in the side groups [36,37] are studied rather scarcely. Recently, Wang et al. prepared electroactive polymers containing azo-groups in the main chain and side chain, which exhibited electrochemical properties, high dielectric constants, and electrochromic behavior [38,39]. Synthesis of electroactive polymer containing the amino and the azogroups in the main polymer chain is actuality because the polymers obtained combine specific features of polyaniline and polyazo-arylenes and may exhibit new valuable properties. With the purpose of obtaining such polymers we for the first time studied oxidative coupling polymerization of Azine-Azo with phenyl-capped aniline pentamer under the ammonium persulfate.

In this work, we have synthesized a novel electroactive polymer with good solubility containing alternating phenyl-capped aniline pentamer in the main chain and azo chromophores in the side chain by oxidative coupling polymerization. UV–Vis spectra were used to monitor the photoisomerization mainly owing to the photoisomerization derived from azo chromophores in the side chain. Moreover, we present reversible example of photochemically induced switching of electroactivity by performing electrochemical CV in two ways: (i) in that the photochemical reaction switch can be photochemically reverted by reirradiation at a different wavelength (ii) in that a photoreaction is used that is thermally reversible. The electrochromic performance of EPAA was investigated by measuring electrochromic photographs and UV absorption spectra.

2. Experimental

2.1. Materials and instrumentation

Aniline (Sigma-Aldrich) was doubly distilled prior to use. 2-Chloro-4,6-diamino-1,3,5-triazine (Aldrich), 4-phenyl-p-phenylenediamine (98%, Aldrich), sodium nitrite (NaNO₂, Sigma–Aldrich), N,N'-diphenyl-1,4-phenylenediamine (Aldrich), ammonium persulfate (APS, 98%, Merck), N-methyl-2-pyrrolidone (NMP, 99%, Merck), hydrochloric acid (37%, Riedel-deHaën), ammonium hydroxide (30%, Riedel-deHaën), and acetone (99%, Acros) were used as received without further purification. All of the chemicals were of reagent grade unless otherwise stated. Fourier transform infrared spectra were collected using an FTIR spectrometer (JASCO FT/IR-4100) at room temperature. The chemical structure of the oligoaniline and the electroactive poly(azine-azo) (EPAA) were determined by ¹H NMR spectroscopy on a Bruker 400 spectrometer, using deuterated dimethyl sulfoxide (DMSO) as the solvent. Molecular weight of EPAA was determined by gel permeation chromatography (GPC), Waters-150CV using N-methyl-2-pyrrolidone (NMP) as eluant. Calibration was accomplished with monodispersed polystyrene (PS) standards. UV-Visible absorption spectra were collected using a UV-Visible spectrometer (JASCO V-650). Electrochromic characterization of EPAA was carried out using an AutoLab (PGSTAT302N) electrochemical workstation in an aqueous 1.0 M H₂SO₄ solution.

2.2. Synthesis of 4-aminoazobenzene

Aniline (0.92 g, 10 mmol) was added dropwise to a solution of concentrated HCl (37%, 3 mL) in deionized water (30 mL). The mixture was stirred in an ice bath to keep the reaction temperature

at 0-5 °C. Then a water solution (5 mL) of sodium nitrite (0.70 g, 10.1 mmol) was added slowly for 10 min. The mixture was stirred at 0-5 °C for further 60 min. A yellow transparent diazonium salt solution was obtained. A coupling solution was prepared as follows: aniline (0.93 g, 10.1 mmol) and HCl (1 N, 10 mL) was dissolved in 30 mL of water under vigorous stirring at 0-5 °C. Then the diazonium salt solution was added dropwise to the coupling solution with the temperature of 0-5 °C. The system was kept being stirred at 5 °C for 3 h. Then the final solution was added slowly to 30 mL of NH₃ (1 N) and a yellow-orange precipitate of the azo-compound formed. The precipitate was filtered and washed with water containing a little amount of sodium hydrogen carbonate (pH = 8). The precipitate was collected by filtration, washed with deionized water three times, and dried under vacuum. Compound was obtained as yellow-orange crystal (1.32 g, yield: 71.3%). The characteristic analytical data involved are as follows: LC-MS ($M_w = 197$) m/z 195.9 [M]⁻. ¹H NMR (400 MHz, DMSO- d_6): $\delta = 6.10$ (s, 1H, -NH₂), 6.66–6.69 (d, 2H, ArH), 7.41–7.53 (m, 3H, ArH), 7.65–7.75 (d, 4H, ArH). Elemental analysis: Calculated (%): C 73.09, H 5.58, N 21.31; Found (%): C 72.91, H 5.98, N 20.93.

2.3. Synthesis of phenyl-capped aniline pentamer (AP)

AP could be easily synthesized by oxidative coupling of N,N'diphenyl-1,4-phenylenediamine (1.20 g) and 4-phenyl-p-phenylenediamine (2.21 g) with ammonium persulfate (1.05 g) as oxidant as shown in Scheme 1(a). Then, the AP product (1.21 g, 35% yield) was dispersed into a stirring mixture solution (12 mL hydrazine hydrate in 120 mL of 1.0 M ammonium hydroxide) and stirred for 24 h. The AP was reduced to the leucoemeraldine state. Finally, it was filtered using a Buchner funnel and water aspirator, and the filter was washed with distilled water several times, followed by drying under dynamic vacuum at 40 °C for 24 h. The detailed characterizations for the AP were listed as follows: LC-MS $(M_{\rm w} = 440.2) m/z 441.2 [M]^+$. FTIR (KBr, cm⁻¹): 3388 (s, $v_{\rm NH}$), 1595 (s, $v_C =_C$ of quinoid rings), 1516 (vs, $v_C =_C$ of benzenoid rings), 1308 (s, $v_C = N$), 817 (m, para-substitution of benzene ring). ¹H NMR (400 MHz, DMSO- d_6): $\delta = 6.6-7.1$ (m, 22 H, ArH), 7.9 (s, 2H, -NH). Elemental analysis: Calculated (%): C 81.79, H 5.49, N 12.72; Found (%): C 81.38, H 4.98, N 12.39. The MS, FTIR and ¹H NMR spectrum of AP were shown in Figs. 1–3 respectively.

2.4. Synthesis of Azine-Azo [40]

2-Chloro-4,6-diamino-1,3,5-triazine (0.7 g) was dissolved in 35 mL of NMP and 1 mL of 1 M HCl was added. The mixture was stirred at 40 °C for 30 min, 4-aminoazobenzene (1.0 g) was then added, and the mixture was heated at 100 °C for 5 h, after which it was cooled to room temperature as shown in Scheme 1(b). It was neutralized with a solution of 1 M NaOH. A yellow solid was filtered off and dried under vacuum (1.5 g, 84% yield). LC-MS ($M_w = 306.1$) m/z 307.0 [M]⁺. FTIR (KBr, cm⁻¹): 3395 (m, v_{NH2}), 1496 (vs, $v_{C=C}$ of benzenoid rings), 1406 (m, $v_{N=N}$), 1308 (s, $v_{C=N}$), 812 (m, para-substitution of benzene ring). ¹H NMR (400 MHz, DMSO- d_6): δ 6.47 (s, 4H, $-NH_2$), 7.50–7.58 (m, 3H, ArH), 7.79–7.84 (d, 4H, ArH), 8.04–8.07 (d, 2H, ArH), 9.38 (s, 1H, -NH). Elemental analysis: Calculated (%): C 58.81, H 4.61, N 36.58; Found (%): C 58.71, H 4.74, N 36.12. The MS, FTIR and ¹H NMR spectrum of Azine-Azo were shown in Figs. 1–3 respectively.

2.5. Preparation of electroactive poly(azine-azo) (EPAA)

EPAA was prepared by simultaneously dissolving 1.0 g (2.2 mmol) of AP and 0.7 g (2.2 mmol) of Azine-Azo that contained 30 mL of NMP and 1 mL of 1 M HCl was added. Subsequently, a solution containing 0.52 g of APS and 1 mL of 1.0 M aqueous HCl



Scheme 1. Synthesis route of the (a) AP (b) Azine-Azo and (c) EPAA.

was added dropwise while stirring at 60 °C for 12 h. A black product was then precipitated by pouring the obtained solution into 200 mL of distilled water with continuous stirring for 0.5 h. The mixture was filtered and washed with distilled water and acetone several times. The as-obtained product was then dried under dynamic vacuum at 30 °C for 24 h as shown in Scheme 1(c). The typical yield of as-prepared EPAA powder was ca. 81%. The EPAA characterization is given as follows: GPC: The number-average molecular weight (M_n) is 1.1×10^4 , weight-average molecular weight (M_w) is 2.8×10^4 , and molecular weight distribution of the polymer is 2.53. FTIR (KBr, cm⁻¹): 3336 (m, v_{NH}), 1600 (s, $v_C = c$ of quinoid rings), 1534, 1498 (vs, $v_C =_C$ of benzenoid rings), 1415 (m, $v_N =_N$), 1303 (s, $v_{C=N}$), 812 (m, para-substitution of benzene ring). ¹H NMR (400 MHz, DMSO- d_6): δ 6.42 (s, -NH), δ = 6.78–7.32 (m, ArH), 7.45-8.09 (m, ArH), 7.73-7.86 (s, -NH), 9.36 (s, -NH). The FTIR and ¹H NMR spectrum of EPAA were shown in Figs. 2 and 2 respectively.

2.6. Reduction of electroactive poly(azine-azo) (EPAA)

The obtained EPAA (0.4 g) was dispersed into a solution of 4 mL hydrazine hydrate in 40 mL 1.0 M ammonium hydroxide and stirred for 24 h. The reaction mixture was then filtered, washed with distilled water several times, and dried under dynamic vacuum at 30 °C for 24 h. Finally, the EPAA was reduced to the leucoemeraldine oxidation state (0.37 g, 92%).

2.7. Electrochemical cyclic voltammetry (CV) and photoresponsive electrochemical measurements [41,42]

(1) In films

To study the redox behavior of EPAA, sample was examined systematically by electrochemical cyclic voltammetry (CV) in 100 mL of 1.0 M H_2SO_4 in the 0.0–1.0 V range at a scan rate of

50 mV s⁻¹. The viscous NMP solution containing EPAA was subsequently cast onto a working electrode of a platinum foil (surface area = 1 cm²), and the organic solvent was evaporated to produce a dense thin solid film with a thickness of $30 \pm 2 \mu$ m. All electrochemical cyclic voltammetric measurements were performed in a double-wall jacketed cell. The electrochemical CV measurement was repeated at least three times to ensure repeatability and reproducibility.

(2) In solutions

Photoresponsive electrochemical experiments were conducted in a single-compartment, three electrode cell, which has a small quartz window for introducing the irradiation light. The glassy carbon electrode was used as a working electrode. An Ag/AgCl, saturated KCl and a Pt wire were employed as the reference and auxiliary electrodes, respectively. All the CVs were carried out at a scan rate of 50 mV/s, in 0.1 M aqueous sodium perchlorate solution, buffered to pH 5.0 with Britton–Robinson buffer, was employed as the electrolyte. All cyclic voltammograms (CV) were taken using a VoltaLab 40 (PGZ 301) potentiostat.

2.8. Electrochromic performance

Electrochromic characterization of the EPAA film was carried out using an AutoLab (PGSTAT302N) Electrochemical Workstation in an aqueous 1.0 M H_2SO_4 solution. A compact, three-electrode electrochemical cell using Ag/AgCl as the reference electrode connected to an AutoLab system that fits in a quartz cell (including indium tin oxide (ITO) as the working electrode and Pt wire as an auxiliary electrode) was placed in the UV–Visible sample holder. The absorption of the resulting thin films was monitored at different oxidation states (for different voltages) by setting the UV– Vis detector wavelength to detect across 250–900 nm.



Fig. 1. Mass spectra of (a) AP and (b) Azine-Azo.



Fig. 2. FTIR spectra of (a) AP and (b) Azine-Azo (c) EPAA.



Fig. 3. ¹H NMR spectra of (a) AP and (b) Azine-Azo (c) EPAA.

3. Results and discussion

3.1. Polymer synthesis and characterization

The synthetic routes for the preparation of oligoaniline, Azine-Azo, EPAA are shown in Scheme 1. Fig. 2(c) shows the FTIR spectra of the obtained EPAA materials. For example, in both of the FTIR spectra, the characteristic peak found at 3336 cm⁻¹ was attributed to the N–H stretching modes. Moreover, characteristic peaks at 1600 cm⁻¹ and 1534 cm⁻¹ were designated as the stretching modes of N=Q=N and N–B–N respectively. (Q represents the quinoid ring, and B represents the benzene ring structure.) The characteristic peak at 1303 cm⁻¹ was assigned to C=N stretching. The absorption band found at 812 cm⁻¹ corresponded to the out-of-plane C–H deformation mode. The azo group in both the EPAA polymer and the Azine-Azo monomer manifested itself by the peak at 1405–1435 cm⁻¹ which corresponded to the stretching vibration mode of such a group [43,44]. These changes in the characteristic peaks of EPAA indicated that EPAA was successful synthesized.

3.2. Chemical oxidation of EPAA

In order to study sequential oxidation process of the conjugated aniline pentamer components, the polymer was reduced to the leucoemeraldine oxidation state in NMP solution by UV–Visible absorption spectroscopy as shown in Fig. 4(a). Subsequently, trace amounts of the oxidant, $(NH_4)_2S_2O_8$, was introduced into the EPAA solution. It should be noted that upon oxidation, the color of the EPAA solution varied from dark blue to purple. Initially, one absorption band was visible at 305 nm, which was associated with the π – π * transition of the conjugated ring system [45], second absorption band was at 570 nm, which attributed to the transition π_b – π_q from benzene ring to quinoid ring.

Upon the addition of trace amounts of the oxidant, slow oxidation of the aniline pentamer segments in EPAA was observed. Further oxidation caused hypsochromic shifts of all peaks presented in the spectrum. The 302 nm absorption band detected by UV–Visible spectroscopy underwent a blue shift from 302 to 291 nm, accompanied with a decreasing in intensity. At the same time, the 570 nm peak intensity increased after its intensity reached a maximum, λ_{max} of a second absorption began to undergo hypsochromic shifted from 570 to 550 nm with the oxidation process.

One possible interpretation of this result is presented as follows. During the continuous oxidation of EPAA in the emeraldine oxidation state with each aniline pentamer segment contained only one quinoid ring, which showed a second absorption at a longer wavelength. Subsequently, it was oxidized to the second emeraldine oxidation state with each aniline pentamer segment



Fig. 4. (a) UV–Vis spectra monitoring the chemical oxidation of the EPAA in the leucoemeraldine oxidation state and (b) a schematic presentation of the oxidation state change of aniline-pentamer-based EPAA.

containing two quinoid rings, which corresponded with the increase in intensity of the second absorption. After the second absorption peak reached maximum intensity, it exhibited a blue shift. This blue shift is indicative of the conversion past the emeraldine base state to the pernigraniline oxidation state, which is in agreement with the two pairs of redox peaks in the cyclic voltammogram as shown in Fig. 5. The chemical oxidation process of EPAA was similar to that of oligoaniline [46].

3.3. Electroactivity of EPAA coatings

Electrochemical cyclic voltammetric (CV) studies have been widely used to characterize the redox properties of electroactive polymers. In this study, the polymers were characterized by cyclic voltammetry using a typical three-electrode electrochemical cell. As shown in Fig. 5, the cyclic voltammetry curve of EPAA shows a two-pair redox peak (470 and 680 mV) [47]. It should be noted that three different oxidation states of EPAA can be found: emeraldine base I (one quinoid ring in oligoaniline segment, EBI),



Fig. 5. Cyclic voltammetry measurements of electroactive EPAA thin film on ITO-coated glass electrodes in aqueous H_2SO_4 (1.0 M) at a scan rate of 50 mV s⁻¹.

emeraldine base II (two quinoid rings in oligoaniline segment, EBII), and pernigraniline base (PNB), as shown in Fig. 4(b).

For the cyclic voltammetry curve of EPAA, the first oxidation peak (470 mV) corresponded to the transition from EBI to EBII, the second peak (680 mV) corresponded to the transition from EBII to PNB. On the other hand, in the case of EPAA, a typical two-pair redox peak was found, which corresponded to the transition between three different oxidation states. This included the emeraldine base I, emeraldine base II and pernigraniline forms of the aniline pentamer in EPAA.

3.4. Electrochromic characteristics

Electrochromism has been broadly defined as a reversible optical change in a material induced by an external voltage. Among the various electrochromic polymers, PANI has multiple colored forms depending on the oxidation states, including LB, emeraldine base, and pernigraniline base [48,49]. In previous literature, the PANI film switched from a pale yellowish neutral state to the green/ bluish green and then blue oxidized states [15]. The electrochromism of the EPAA thin film was examined by means of ITOcoated glass oxidized at different potentials coupled with UV-Vis spectroscopy, as shown in Fig. 6. For in-situ UV-Vis spectra measurements, the electrode bearing the EPAA thin film was held in a 1.0 M H₂SO₄ aqueous solution in a quartz cuvette, with Ag/AgCl as the reference electrode and a Pt wire as an auxiliary electrode. Fig. 7 shows the 3-D spectra for the absorbance-wavelengthapplied potential correlations of EPAA. From Figs. 6 and 7, one can see that the peak for the characteristic absorbance at 620 nm gradually increased with an increasing in the applied potential from 0.00 to 0.8 V. This strong absorbance resulted from the delocalization of the radical cation (polaron) along the doped electroactive structure [47]. While being oxidized at 1.00 V, EPAA showed a much lower intensity and a blue shift of the polaron band because the benzoid ring was gradually replaced with the quinoid ring [47,50]. These electrochromic properties conformed to the cyclic voltammetry data (Fig. 5). During a complete redox cycle, we also observed a continuous color change (inset of Fig. 6). The color of the EPAA thin film changed from green (at 0 mV), to Cyan (at ca. 470 mV), to indigo (at ca. 680 mV). In conclusion, as a multicolor electrochromic material with color changing from green to indigo, EPAA would have a wider application in an electrochromic device similar to polyaniline materials [15].



Fig. 6. The electrochromic behavior of the EPAA thin film on ITO-coated glass electrodes at different oxidation potentials in a 1.0 M H₂SO₄ solution.

3.5. Photochemical behavior of the Azine-Azo monomer and electroactive poly(azine-azo) (EPAA) polymer

While the spectrum of the trans-isomer of azo-compound shows an intense $\pi - \pi^*$ transition band around $\lambda = 360$ nm and a weaker (forbidden) $n-\pi^*$ band around $\lambda = 440$ nm, the spectrum of the cis-isomer is characterized by a more intense $n-\pi^*$ transition band around $\lambda = 440$ nm [4]. Irradiation of the trans form with UV light of a suitable wavelength induces a trans \rightarrow cis photoisomerization reaching a photostationary state. The back $cis \rightarrow trans$ isomerization can occur either via a thermal reaction, because the trans-form is thermodynamically more stable, or via a photoinduced isomerization by irradiation into the $n-\pi^*$ band of the cis form. We present reversible example of photochemically induced switching in two ways: (i) in that the photochemical reaction switch can be photochemically reverted by reirradiation at a different wavelength (ii) in that a photoreaction is used that is thermally reversible. The result of the isomerization processes was monitored by UV-Vis spectroscopy.

Fig. 8 showed that the Azine-Azo monomer displayed photoisomerization behavior in NMP solution in a sealed quartz cuvette under alternate exposed to UV lamp (365 nm) for 1 min and visible lamp (420 nm) for 1 min. The spectra were typical of azobenzene



Fig. 7. 3-D spectroelectrochemical behavior of the EPAA thin film on an ITO-coated glass electrode between 0.00 and 1.00 V (vs Ag/AgCl).

chromophore. The maximum absorption peak centered at 359 nm is attributed to the $\pi - \pi^*$ transition. (see curve A of Fig. 8(a)). Irradiation with UV light for 1 min caused the absorption peak at 359 nm obviously decreased (λ_{max} changes from 359 to 348 nm), while a broad absorption at around 440 nm ($n-\pi^*$, curve B of Fig. 8(a)) with an isosbestic point at 422 nm was developed, indicating the occurrence of trans to cis photoisomerization. And from Fig. 8(a) curve (C) we can see that the cis isomer reconverted to the trans isomer again under visible illumination for 1 min, which resulted in a recovery of the spectral features of trans isomer. It is seen that the recovered absorbance of trans-azobenzene is slightly lower than that before irradiation. However, in Fig. 8(b), spectra have taken before and after irradiation as well as during the thermal back reaction were shown. Under these conditions (in the dark room temperature), the back reaction took about 30 min for completion. It is obvious that $cis \rightarrow trans$ isomerization thermally reversible is more easily reduced than photochemically reverted. These results demonstrate that Azine-Azo monomer is thermodynamically compound. From the result described above, the obtained monomer retained the photoisomerization characteristics of azobenzene [51].

In order to study its trans \Leftrightarrow cis isomerization, the polymer in the emeraldine oxidation state without processing was dissolved in NMP solution and UV–Vis spectra changes were monitored during the ultraviolet irradiation. This photoinduced trans⇔cis isomerization was analyzed in the EPAA as presenting in Fig. 9. The polymer absorption band at 387 nm due to azopolymer decreased gradually, while the absorption band at 580 nm due to aniline pentamer remained unchanged. Under this aniline pentamer band was hidden the smaller band at 440 nm due to the cis form of azopolymer. As same as monomer, Fig. 9(a) was photochemically reverted and Fig. 9(b) was thermally reversible results. That cis→trans isomerization thermally reversible is more easily reduced than photochemically reverted. These results demonstrate that EPAA is thermodynamically compound, too. These characteristics are due to the presence of a trans \Leftrightarrow cis azo isomer of EPAA. Moreover, this trans⇔cis behavior of EPAA can also be further identified by electrochemical cyclic voltammetry (CV) approach, as shown in Fig. 10.

3.6. Photoresponsive electrochemical behavior of EPAA solutions

Azobenzene molecules in organic solution undergo reversible trans⇔cis isomerization under light illuminations [52,53].



Fig. 8. UV-Vis spectra of Azine-Azo in NMP solution (a) as a function of different UV irradiation and (b) as a function of time in dark, at room temperature.

However, such a photochromic property is often restricted in films because the closely packed film structure cannot provide enough free volume to allow the trans to cis photoisomerization which is accompanied by a volume-increased structural change [53,54]. This makes it difficult to conduct the electrochemistry studies of cisazobenzene in such molecular assemblies. Scheme 2 illustrates this concept schematically. As the configuration of azobenzene changes from trans to cis, θ moves to the high angle region with a most probable angle of ca. 10° close to planar. The result causes the π - π * interaction increased between the benzene ring C and D for EPAA as shown in Scheme 2. This concept is based on the fact that the cross-sectional area of cis-azobenzene is larger than that of trans-azobenzene. This means that trans-to-cis isomerization gives rise to an increasing in the cross-sectional area of azobenzene. Free volume means not only that there are actual voids, but also that additional space can be created easily by changing the tilt angle of the molecules. When there is enough free volume, photoisomerization will proceed as shown in the left part. On the other hand, if the molecules are closely packed in the film, the molecules will not photoisomerize [55]. To understand the electrochemical behavior of trans⇔cis isomerization EPAA was used as solution which could be researched in aqueous solutions.

Previous studies demonstrated that the azobenzene moiety was also electrochemical activity [56,57]. Thus, in order to investigate the influence of photochromic in azobenzene groups on electrochemical behavior of the EPAA, it is necessary to avoid the reduction of azobenzene groups. Fujishima et al. showed that the reduction potential of azobenzene to hydroazobenzene was lower than -0.6 V (vs SCE) [56,57]. Thus, when the scanning potential was

much higher than the reduction potential of azobenzene, the electrochemical reduction of azobenzenes to hydroazobenzene could be eliminated, just as shown in other literature [58-61]. Therefore, the scanning potential is confined from 0 to +1.0 V in the CV experiment, which is much higher than -0.6 V. In this study, we present reversible result of photochemically induced switching of electroactivity by performing electrochemical CV in two ways: (i) in that the photochemical reaction switch can be photochemically reverted by reirradiation at a different wavelength (ii) in that a photoreaction is used that is thermally reversible. Fig. 10(a) showed the cyclic voltammetric (CV) of EPAA in aqueous solutions under photochemical reaction switched by reirradiation at a different wavelength. Two pairs of waves from the redox of EPAA were observed from each curve. Curve A was the before irradiation case, corresponding to the voltammetric behavior of trans-EPAA. When exposing the sample to UV light, a clear cut Faradaic response was observed curve B. This was attributed to the electrochemical reduction-oxidation of UV-created cis-EPAA isomers. The photochromic property of EPAA molecules provided an alternative approach for corroborating the above reactions. In curve C of Fig. 10(a), the EPAA was exposed to visible illumination after being irradiated with UV light. Since the UV-generated cis-EPAA isomers were mostly reconverted into trans-EPAA by the visible illumination, the Faradaic response was greatly decreased, in nice agreement with our prediction. By repeating the UV and visible irradiations, the increasing and decreasing of electrochemical response was also changed reversibly, indicative of the reversible trans-cis photoisomerization of EPAA molecules. A preliminary explanation of those changes was given below: the trans-cis



Fig. 9. UV-Vis spectra of EPAA in NMP solution (a) as a function of different UV irradiation and (b) as a function of time in dark, at room temperature.



Fig. 10. Cyclic voltammetry measurements of electroactive EPAA in 0.1 M aqueous sodium perchlorate solution, buffered to pH 5.0 with Britton–Robinson buffer (a) as a function of different UV irradiation and (b) as a function of time in dark, at room temperature.



Scheme 2. Schematic illustration of the concept of free volume.

isomerization of azo chromophores could change the side chains from rodlike to globularity, which might influence the shapes of polymer chains, accompanied by the changes of the current of the polymer chains. The above observations indicate that the EPAA has enough free space to undergo the reversible trans \Leftrightarrow cis photoisomerization and then the electrochemical reduction oxidation of cis isomers. Fig. 10(b) shows that thermally driven cis \rightarrow trans in the dark the Faradaic response was also greatly decreased. From the result described above, we could conclude that photoisomerization of the azobenzene in the side chain could directly affect the redox activity phenyl-capped aniline pentamer in the main chain of EPAA.

4. Conclusions

In this work, a novel functional alternating polymer with oligoaniline in the main chain and azo group in the side chain has been prepared by an oxidative coupling polymerization approach. Based on the coexistence of oligoaniline and azobenzene groups, reversible switching of EPAA was possible without changing temperature or composition. Moreover, the electrochromic performance of EPAA was investigated by measuring electrochromic photographs and UV absorption spectra. The color of the EPAA thin films changed from green (at 0.0 V), to Cyan (at ca. 0.4 V), to indigo (at ca. 0.8 V). The electroactive poly(azine-azo) showed photoactive and electroactive properties, suggesting that it has great potential for many applications, such as for use as photo materials and in electrochromic devices.

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