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A novel poly(aryl ether) containing azobenzene chromophore and pendant oligoaniline: Synthesis and electrochromic properties

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1. Introduction

Electrochromic devices exhibit reversible and visible changes in their transmission and reflection due to variations in the redox states [1-3], and can be used as large area displays, smart mirrors and windows [4]. Many electrochromic devices have been previously investigated based on a variety of organic [5] and inorganic materials [1] and conducting polymers [6,7]. The high contrast value in the optical absorption spectrum of conducting polymers makes these materials prime candidates for electrochromic devices [8]. Among conducting polymers, polyaniline (PANI) has been extensively studied for electrochromic application due to its unique optical properties, excellent switching speed, and high environmental stability. Many PANI-based electrochromic devices have recently been reported. Hu et al. studied the electrochromic properties of PANI-poly(2-acrylamido-2-methyl-1-propanosulfonic acid) composite thin films, which exhibited a lower optical switching voltage and higher contrast value [9,10]. Some other PANI/polyacid composites used as electrochromic devices have also been investigated and reported [11,12]. The method of layer-by-layer assembly was been applied to prepare electrochromic devices and

ABSTRACT

A novel poly(aryl ether), containing pendant oligoaniline and azobenzene moieties (Azo-PAE-p-OA), was synthesized by nucleophilic polycondensation. The structures were confirmed spectroscopically via nuclear magnetic resonance (NMR) and Fourier-transform infrared spectra (FTIR), morphological data was ascertained via X-ray diffraction (XRD), and the thermal stability was probed via thermogravimetric analysis (TGA). Due to the coexistence of oligoaniline and azobenzene groups, Azo-PAE-p-OA shows reversible electroactivity and expectable photoresponse to light irradiation, chemical redox and electrochemical modulation. The electrochromic performance of a Azo-PAE-p-OA film on indium tin oxide (ITO) was investigated by spectrochronoamperometry, and exhibited electrochromic properties with high contrast value, good coloration efficiency, moderate switching times, and acceptable stability.

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improvement in electrochromic contrast were reported [13,14]. Tu et al. prepared electrochromic devices by PANI derivatives (poly(o-anisidine) and poly(o-anisidine-co-o-nitroaniline)) and compared them electrochromic performance [15]. Sonavane et al. and Zhou et al. studied multicolor electrochromic devices based on PANI that exhibited high electrochromic contrast and coloration efficiency [16,17].

Although PANI/polyacid composites, PANI derivatives and PANI blends have been widely used for electrochromic devices, its full utilization is dependent on advancements to improve its inherent shortcomings in solubility and processability. So it can be envisioned that electroactive polymers bearing oligoaniline groups with excellent film forming ability and solubility should be a highly competitive candidate for an electrochromic device. Recently, considerable effort has been devoted toward synthesizing electroactive polymers containing oligoaniline groups, such as graft [18–20], alternating [21–23], block-like [24,25], star-like [26] and network [27] polymers. To the best of our knowledge, only a few electrochromic devices prepared from these electroactive polymers have been presented [20,21,28].

Recently azobenzene-containing polymers have attracted considerable attention because of their variety of photoreponsive properties, such as photoinduced birefringence and dichroism [29,30], optical switching [31], and photoinduced surface-reliefgrating (SRG) formations [32,33]. Due to its properties as a dye, azobenzene group has been usually introduced to construct multicolor electrochromic device [34–36], which generally have a great

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contrast value. Here, we reported the synthesis of a novel poly(aryl ether) containing pendant oligoaniline and azobenzene moieties (Azo-PAE-p-OA) by nucleophilic polycondensation and its performance in an electrochromic device.

2. Experimental

2.1. Materials

N-phenyl-*p*-phenylenediamine, 2,6-difluorobenzoyl chloride and 4-nitrophenol were purchased from Aldrich. 4,4'-Dichlorodiphenylsulfone and potassium hydroxide were purchased from Shanghai Chemical Factory. K_2CO_3 was dried at 110 °C for 24 h before used. All other reagents were obtained from commercial sources and used as received without further purification. Distilled and deionized water was used.

2.2. Measurement

Mass spectroscopy (MS) was performed on an AXIMA-CFR laser desorption ionization flying time spectrometer (COMPACT). Fourier-transform infrared spectra (FTIR) measurements were recorded on a BRUKER VECTOR 22 Spectrometer by averaging 128 scans at a solution of 4 cm^{-1} in the range of $4000-400 \text{ cm}^{-1}$. The nuclear magnetic resonance spectra (NMR) of 2,6-difluorobenzoyl aniline tetramer, 4,4'-dihydroxyazobenzene and Azo-PAE-p-OA in deuterated dimethyl sulfoxide (DMSO) were run on a BRUKER-500 spectrometer to determine the chemical structure and tetramethylsilane was used as the internal standard. The number-average molecular weight (*Mn*), weight-average molecular weight (*Mw*), and molecular weight distribution of Azo-PAE-p-OA were measured with a gel permeation chromatography (GPC) instrument equipped with a Shimadzu GPC-802D gel column and SPD-M10AVP detector with N,N'-dimethylformamide as an eluent at a flow rate of 1 mL min⁻¹. Calibration was accomplished with monodispersed polystyrene (PS) standards. X-ray powder diffraction (XRD) patterns of Azo-PAE-p-OA were recorded on a Siemens D5005 diffractometer using Cu Ka radiation. Perkin-Elmer PYRIS 1 TGA was used to investigate the thermal stability of Azo-PAE-p-OA in the temperature range from 100°C to 700°C at a rate of 10.0 °C min⁻¹ under nitrogen protection. Photoisomerization of Azo-PAE-p-OA in a DMAc solution and/or spin-coated thin film were conducted using high pressure mercury lamp in conjunction with band-pass UV filter (λ_{max} = 360 nm). UV-vis spectra were performed on UV-2501 PC Spectrometer (SHIMADZU) in dilute DMAc solution. The CV was investigated on a CHI 660A Electrochemical Workstation (CH Instruments, USA) with a conventional three-electrode cell, using a Ag/AgCl as the reference electrode, a platinum wire electrode as the counter electrode, and a glassy carbon electrode (GCE, ϕ 3.0 mm) as the working electrode. Spectroelectrochemical measurements were carried out in a cell built from a 1 cm commercial cuvette using a UV-2501 PC Spectrometer (SHIMADZU). The ITO-coated glass was used as the working electrode, a Pt wire as the counter electrode, an Ag/AgCl cell as the reference electrode and 0.5 mol/L H₂SO₄ was used as the electrolyte.

2.3. Synthesis of 2,6-difluorobenzoyl aniline tetramer

The synthesis of 2,6-difluorobenzoyl aniline tetramer was conducted according to the literature [20].

MALDI-TOF-MS: *m/z* calculated for C₃₁H₂₄F₂N₄O = 506.5. Found 506.6. FTIR (KBr, cm⁻¹): 3369 (s, υ_{NH}), 3299 (s, υ_{NH}), 1657 (vs, $\upsilon_{C=O}$), 1600 (s, $\upsilon_{C=C}$ of benzenoid rings), 1525 (vs, $\upsilon_{C=C}$ of benzenoid rings), 1303 (s, υ_{C-N}), 1008(m, δ_{CF}), 817 (m, δ_{CH}), 746 (m, δ_{CH}), 692 (m, δ_{CH}). ¹H NMR (d₆-DMSO): δ = 10.51 (s, 1H, due to

-CONH-), δ = 7.80 (s, 1H, due to -NH-), δ = 7.77 (s, 1H, due to -NH-), δ = 7.65 (s, 1H, due to -NH-), δ = 7.56 (t, 1H, due to Ar-H), δ = 7.48 (d, 2H, due to Ar-H), δ = 7.23 (t, 2H, due to Ar-H), δ = 7.14 (t, 2H, due to Ar-H), δ = 6.96 (m, 12H, due to Ar-H), δ = 6.68 (t, 1H, due to Ar-H).

2.4. Synthesis of 4,4'-dihydroxyazobenzene

Potassium hydroxide (100 g), 4-nitrophenol (20 g) and water (20 mL) was added into a 500 mL three-necked round-bottom flask and heated to $150 \,^{\circ}$ C with mechanical stirring for 2 h. The mixture was heated to $195 \,^{\circ}$ C with blowing off bubble. After the completion of the reaction, the obtained mixture was cooled to room temperature and dissolved in the 200 mL water. Adjusted the pH of the solution by adding of dilute hydrochloric acid and yielding an orange precipitate which was recrystallized twice from ethanol/H₂O (1:1) to give a product of red crystals, followed by drying under dynamic vacuum at room temperature for 24 h (30% yield).

MALDI-TOF-MS: *m/z* calculated for $C_{12}H_{10}N_2O_2 = 214.2$. Found 215.1. FTIR (KBr, cm⁻¹): 3377 (m, υ_{OH}), 1589 (vs, $\upsilon_{C=C}$ of benzenoid rings), 1500 (m, $\upsilon_{C=C}$ of benzenoid rings), 1425 (m, $\upsilon_{N=N}$), 842 (s, δ_{CH}), 766 (w, δ_{CH}), 644 (w, δ_{CH}). ¹H NMR (d₆-DMSO): δ = 10.12 (s, 2H, due to –OH), δ = 7.71 (d, 4H, due to Ar–H adjacent to azo group), δ = 6.91 (d, 4H, due to Ar–H adjacent to hydroxy group).

2.5. Synthesis of Azo-PAE-p-OA

A typical polymer synthesis procedure is as follows. A mixture of NMP (30 mL), toluene (10 mL), anhydrous potassium carbonate (1.451 g), 2,6-difluorobenzoyl aniline tetramer (1.013 g, 2 mmol), 4,4'-dichlorodiphenylsulfone (2.297 g, 8 mmol), and 4,4'dihydroxyazobenzene (2.142 g, 10 mmol) were added to a 100 mL three-necked round-bottom flask and heated to reflux under nitrogen with magnetic stirring for 2 h to remove the water by azeotropic distillation with toluene, and then the toluene was removed. The mixture was heated to reflux for 8 h to ensure the completion of the reaction. The solution was cooled to room temperature and poured into 200 mL water, which yielded a yellow precipitate. The precipitate was washed with water and ethanol several times, filtered and dried under dynamic vacuum at 40 °C for 24 h (93% yield).

2.6. Fabrication of electrochromic electrode

The ITO substrates were washed ultrasonically in ethanol for 5 min and then in the deionized water for another 5 min, followed by drying in the air before use. Azo-PAE-p-OA (0.03 g) was dissolved in 1 mL DMAc to form a dark brown solution, and filtered through 0.2- μ m poly(tetrafluoroethylene)syringe filter. Then, Azo-PAE-p-OA films were spin-coated onto the ITO substrates using the DMAc solution of Azo-PAE-p-OA. The spin-coating process started at 500 rpm for 5 s and then 1000 rpm for 30 s. A copper tape (1.0 cm × 0.5 cm) was applied to the top edge of ITO substrates, before electrochromic measurements, as the bus bar.

3. Results and discussion

3.1. Synthesis and characterization of Azo-PAE-p-OA

The synthetic procedure for Azo-PAE-p-OA is depicted in Scheme 1. The polymerization proceeded by K_2CO_3 mediated nucleophilic aromatic polycondensation using 4,4'-dihydroxyazobenzene as bisphenol monomer. The ratio of 2,6difluorobenzoyl aniline tetramer to 4,4'-dichlorodiphenylsulfone is about 0.2:0.8. The reaction temperature was held at 140 °C to remove the water by azeotropic distillation with toluene, and then increased to 200 °C to facilitate the polymerization. The chemical



Scheme 1. Synthesis of electroactive Azo-PAE-p-OA

structure of Azo-PAE-p-OA was confirmed by FTIR, ¹H NMR spectroscopy, GPC and XRD. FTIR spectra of Azo-PAE-p-OA showed the characteristic absorption bonds around 3386 cm⁻¹ corresponding to N-H stretching vibration, around 3062 cm⁻¹ based on C-H stretching vibration of aryl groups and around 1670 cm⁻¹ due to C=O stretching vibration of arvl carbonyl groups. The vibration at around 1583 cm⁻¹ and 1489 cm⁻¹ is attributed to the stretching vibration of C=C of the benzene rings, and the peak at 1240 cm^{-1} can be assigned to the stretching vibration of C-O-C of the aryl ether linkages. The bands at 1296 cm⁻¹ (v_{C-N}), 835 cm⁻¹ (δ_{CH}), and $692 \,\mathrm{cm}^{-1}$ (δ_{CH}), based on the structure of oligoaniline, were also found. And the bands at 1147 cm⁻¹ ($v_{0=S=0}$), 1103 cm⁻¹ (δ_{CH}), and 550 cm⁻¹ (δ_{CH}) were attributed to the vibrations of diphenylsufone segment. In the ¹H NMR spectra of Azo-PAE-p-OA, the signals at δ = 10.25 ppm are attributed to the amino protons and the signals around δ = 7.98 ppm are ascribed to the aryl protons adjacent to the diphenylsufone groups, the integral area ratio of the two peaks is near 1:16, which indicates that the Azo-PAE-p-OA has been synthesized according to expectation. Furthermore, other aromatic protons appeared at δ = 7.37–6.59. All of the ¹H NMR signals support the proposed molecular structure of Azo-PAE-p-OA. The number average molecular weight (Mn) and the polydispersity index of Azo-PAE-p-OA, obtained by GPC, are 51,400 and 1.66, respectively. Moreover, Azo-PAE-p-OA exhibited outstanding solubility in polar solvents such as THF, DMF, DMAc, DMSO and NMP, due in part to the bulky pendant groups, which can impede the interchain entanglement to some extent.

The wide-angle XRD patterns of Azo-PAE-p-OA (Fig. 1) show a broad peak from 10° to 30° , which is characteristic of the diffraction by an amorphous polymer. It is mainly due to the fact that the

bulky pendant oligoaniline groups decrease the interchain hydrogen bonding and π - π interactions and disturb the close packing and regularity of the polymer chains. The amorphous structure is a basic requirement for polymers used in optoelectronic devices, because aggregation and microcrystallization will greatly affect stability and uniformity of the device.

The thermal properties of Azo-PAE-p-OA were evaluated by TGA (Fig. 2). A single stage mass loss beginning at 310 °C is observed corresponding to the decomposition of main chain. Weight loss temperatures of the obtained polymer for a loss of 5% and 10% are 350 °C and 381 °C, respectively. This indicates that the obtained polymer has good thermal stability and higher degradation temperature than the usual polyaniline materials [37].

3.2. Spectroscopic properties of Azo-PAE-p-OA by chemical oxidation

The optical properties of the Azo-PAE-p-OA were investigated by UV-vis spectroscopy. A small amount of Azo-PAE-p-OA was dissolved in DMAc solution followed by the addition of trace amount of $(NH_4)_2S_2O_8$. This oxidation process was monitored by UV-vis spectra with time intervals at about 4 min; the obtained UV-vis spectra are presented in Fig. 3. First, the absorption peaks at 347 nm were observed, which are associated with π - π * transitions in the benzoid rings and trans-azobenzene groups [38–40]. When slow oxidation took place, the absorption peak at 347 nm started to undergo a red shift (from 347 nm to 353 nm) while decreasing in intensity. Then the UV-vis spectra showed a new absorption peak at about 590 nm. This has been assigned to the exciton-type



Fig. 1. The wide-angle XRD patterns of Azo-PAE-p-OA.



Fig. 2. TGA thermograms of Azo-PAE-p-OA in N₂.



Fig. 3. UV-vis spectra monitoring the chemical oxidation of Azo-PAE-p-OA. (a) From the leucoemeraldine base to the emeraldine base and (b) from the emeraldine base to the pernigraniline base.

transition between the HOMO orbital of the benzoid ring and the LUMO orbital of the quinoid ring [41] and continually increased in intensity. When its intensity reached the maximum, the Azo-PAE-p-OA was in the emeraldine oxidation state with the parent aniline tetramer segment containing one quinoid ring. With further oxidization of Azo-PAE-p-OA, all the absorption peaks decreased and finally absorption in the 400 nm and 800 nm range disappeared, which showed that the Azo-PAE-p-OA has reached in the pernigraniline oxidation state with parent aniline tetramer segment containing two quinoid rings. The chemical oxidation process of Azo-PAE-p-OA is similar to that of polyaniline and its derivatives [22,23].

3.3. Photoisomerization of Azo-PAE-p-OA

Trans-cis isomerization of Azo-PAE-p-OA in leucoemeraldine oxidation state was investigated by irradiating the DMAc solution and spin-coated thin film, respectively. The UV–vis spectra changes were monitored during the ultraviolet and visible irradiation. As shown in Fig. 4(a), the intensity of the absorption of Azo-PAE-p-OA

DMAc solution at about 347 nm, associated with the π - π * transition of the trans-azobenzene groups and benzoid rings, gradually decreased as irradiation time increased. This occurred concurrently with a blue shift, due to the trans-to-cis photoisomerization process of the azobenzene chromophore. The blue shift of the absorption was attributed to the overlap of the π - π ^{*} transition of the trans-azobenzene groups and benzoid rings [35,40]. UV-vis spectra changes were obtained with time intervals about 2 min and the trans-cis isomerization reached to a steady state 10 min later, then the above solution was transferred to visible radiation. As shown in Fig. 4(b), the intensity of the absorption, associated with π - π * transition of the trans-azobenzene group, gradually increased with the anticipated red shift. The absorption at about 347 nm nearly reached the intensity of original values after 18 min. Photoisomerization of Azo-PAE-p-OA thin film were given in Fig. 4(c) and (d), which also presented a similar reversibility to those in solution. However, the absorption peak associated with $\pi - \pi^*$ transition for the thin film red-shifted to 350 nm, due to the solvachromic effect of azobenzene group. In addition, the time for the film to reach a photostationary state was little shorter than in solution, because



Fig. 4. UV-vis spectra changes of Azo-PAE-p-OA with the different irradiation time: (a and b) in DMAc solution and (c and d) as spin-coated film.



Fig. 5. Cyclic voltammograms of Azo-PAE-p-OA electrode in $1 \text{ mol/L H}_2\text{SO}_4$ at different potential scan rates: $10-100 \text{ mV s}^{-1}$. Inset shows the relationships between the oxidation peaks and reduction current vs. potential scan rate.

of the relative lower concentration of Azo-PAE-p-OA. Those results confirm that Azo-PAE-p-OA retained the photoisomerization characteristics of azobenzene.

3.4. Electrochemical activity

Fig. 5 shows the cyclic voltammetry of Azo-PAE-p-OA using Ag/Ag⁺ as the reference electrode in 1.0 M H₂SO₄ at different potential scan rates (10–100 mV s⁻¹). The DMAc solution of Azo-PAE-p-OA was cast on the g-c working electrode and was evaporated to form a thin solid film. Under these conditions, the cyclic voltammetry of Azo-PAE-p-OA showed two redox processes with the oxidation peaks at 350 and 500 mV, which were respectively assigned to the transition of leucoemeraldine base (LEB)/emeraldine base (EB), and emeraldine base/pernigraniline base (PNB). A linear dependence of the peak currents, as a function of scan rates in the region of $10-100 \text{ mV s}^{-1}$ (inset of Fig. 5), confirmed both a surface controlled process [42] and that the electroactive polymer film was well-adhered. The good adherence of the Azo-PAE-p-OA, attribute to its poly(aryl ether) main chain structure, makes it a good electrode material. The Azo-PAE-p-OA film was found to be very stable, without change in CV diagram after 30 repeated cyclic scans between 0 and 900 mV.

3.5. Spectroelectrochemistry and electrochromic performances

Spectroelectrochemical studies were performed on the film of Azo-PAE-p-OA spin-coated on the ITO glass slide in 0.5 mol/L



Fig. 6. The spectral changes of Azo-PAE-p-OA/ITO electrode $(0.6 \text{ cm} \times 3 \text{ cm})$ in 0.5 mol/L H₂SO₄ at different potentials. Inset shows photographs of the Azo-PAE-p-OA/ITO electrode at different potentials.

H₂SO₄ coupled with applied potentials of -0.2, 0, 0.2, 0.4, 0.6, 0.8 and 1.0 V (vs. Ag/AgCl). It is clear from Fig. 6, the Azo-PAEp-OA film shows different UV-vis absorption spectra at various applied potentials. The optical constrast value ($\%\Delta T$) was found to be 25% at 700 nm measured between its coloring and bleaching states. The color of the Azo-PAE-p-OA thin films changed drastically from a transmissive yellow (at -0.2 V), to green (at 0.4 V), and finally to an absorptive brown blue (at 0.8 V) (inset of Fig. 6). In conclusion, as a multicolor electrochromic material with color changing from yellow to blue, Azo-PAE-p-OA would have a wider application in an electrochromic device compared with polyaniline materials.

Besides the optical constrast value ($\%\Delta T$), the switching time and the electrochromic efficiency are usually used to evaluate the electrochromic devices. The electrochromic performances of Azo-PAE-p-OA were recorded by spectrochronoamperometry in the optical contrast at 700 nm during repeated potential stepping between reductive (-0.2 V) and oxidative state at 0.8 V with a residence time of 30 s. Fig. 7 presents the results for the first 5 cycles. The switching time is the time required to bring Azo-PAEp-OA to its reduced state from its oxidized state or vice versa. Here, it is defined as the time required for reaching 95% of the full change in coloring/bleaching process. The Azo-PAE-p-OA film required a switching time of 3.3 s at 0.8 V for the coloring process at 700 nm and 1.4 s at -0.2 V for bleaching. The coloration efficiency CE ($\eta = \Delta OD/Q$) is a practical tool for measuring the power requirements of an electrochromic material. The electrochromic behavior of Azo-PAE-p-OA exhibited CE up to $107.4 \text{ cm}^2/\text{C}$ (at 700 nm) at the oxidation stage. Usually, electrochromic devices stability was damaged drastically under the acid conditions, because the ITO substrate would like to lose its conductivity in the acid. In our test, to investigate the stability of the electrochromic device, the



Fig. 7. (a) Current consumption and (b) absorbance changes monitored at 700 nm of Azo-PAE-p-OA/ITO electrode in 0.5 mol/L H₂SO₄ for the first 5 and 101st-105th cycles when the anodic potential was switched between -0.2 V and 0.8 V with a residence time of 30 s.

electrochromic performance was collected after 100 cycles of potential switching. The switching time increased to 4.2 s at 0.8 V for the coloring process and 2.0 s at -0.2 V for bleaching, and the coloration efficiency decreased to 91.2 cm²/C. The optical contrast value also partially decreased after 100 cycles.

While the optical contrast value and the switching time of Azo-PAE-p-OA film were not good enough to achieve the demand of the electrochromic devices, due to the low content percent of the oligoaniline in Azo-PAE-p-OA. It makes a highly competitive candidate for an electrochromic material, however, because the parameters including the optical contrast value, the switching time and the coloration efficiency could be modulated easily by using different concentrations of the two chromophores in the polymer architecture. Further research on the multicolor electrochromic materials with the satisfactory parameter is currently underway.

4. Conclusion

We described the synthesis of a novel poly(aryl ether) containing oligoaniline and azobenzene groups by a nucleophilic polymercondensation reaction. The obtained polymer Azo-PAE-p-OA exhibits good solubility in the organic solvents and excellent thermal stability. Based on the coexistence of oligoaniline and azobenzene groups, Azo-PAE-p-OA possesses reversible electroactivity and expectable photoresponse to light irradiation, chemical redox and electrochemical modulation. Moreover, the electrochromic performance of Azo-PAE-p-OA is of interest as it shows three accessible color states by the color mixing of the two different chromophores. The multicolor Azo-PAE-p-OA film exhibits good electrochromic properties with high contrast value, moderate coloration efficiency, acceptable switching times and stability. Taking into account molecular diversity and tailoring, a multicolor polymer with oligoanilines and other chromophores would be a highly competitive candidate for electrochromic devices.

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