



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

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### 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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### 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

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-relief-grating (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  $4\text{ cm}^{-1}$  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 ( $M_n$ ), weight-average molecular weight ( $M_w$ ), 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  $1\text{ mL min}^{-1}$ . 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  $K\alpha$  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  $10.0\text{ }^\circ\text{C min}^{-1}$  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 ( $\lambda_{\text{max}} = 360\text{ nm}$ ). 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,  $\Phi$  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  $H_2SO_4$  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  $C_{31}H_{24}F_2N_4O = 506.5$ . Found 506.6. FTIR (KBr,  $\text{cm}^{-1}$ ): 3369 (s,  $\nu_{\text{NH}}$ ), 3299 (s,  $\nu_{\text{NH}}$ ), 1657 (vs,  $\nu_{\text{C=O}}$ ), 1600 (s,  $\nu_{\text{C=C}}$  of benzenoid rings), 1525 (vs,  $\nu_{\text{C=C}}$  of benzenoid rings), 1303 (s,  $\nu_{\text{C-N}}$ ), 1008 (m,  $\delta_{\text{CF}}$ ), 817 (m,  $\delta_{\text{CH}}$ ), 746 (m,  $\delta_{\text{CH}}$ ), 692 (m,  $\delta_{\text{CH}}$ ).  $^1\text{H NMR}$  ( $d_6$ -DMSO):  $\delta = 10.51$  (s, 1H, due to

$-\text{CONH}-$ ),  $\delta = 7.80$  (s, 1H, due to  $-\text{NH}-$ ),  $\delta = 7.77$  (s, 1H, due to  $-\text{NH}-$ ),  $\delta = 7.65$  (s, 1H, due to  $-\text{NH}-$ ),  $\delta = 7.56$  (t, 1H, due to Ar-H),  $\delta = 7.48$  (d, 2H, due to Ar-H),  $\delta = 7.23$  (t, 2H, due to Ar-H),  $\delta = 7.14$  (t, 2H, due to Ar-H),  $\delta = 6.96$  (m, 12H, due to Ar-H),  $\delta = 6.68$  (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 °C with mechanical stirring for 2 h. The mixture was heated to 195 °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/ $H_2O$  (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,  $\text{cm}^{-1}$ ): 3377 (m,  $\nu_{\text{OH}}$ ), 1589 (vs,  $\nu_{\text{C=C}}$  of benzenoid rings), 1500 (m,  $\nu_{\text{C=C}}$  of benzenoid rings), 1425 (m,  $\nu_{\text{N=N}}$ ), 842 (s,  $\delta_{\text{CH}}$ ), 766 (w,  $\delta_{\text{CH}}$ ), 644 (w,  $\delta_{\text{CH}}$ ).  $^1\text{H NMR}$  ( $d_6$ -DMSO):  $\delta = 10.12$  (s, 2H, due to  $-\text{OH}$ ),  $\delta = 7.71$  (d, 4H, due to Ar-H adjacent to azo group),  $\delta = 6.91$  (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- $\mu\text{m}$  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  $\times$  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 2,6-difluorobenzoyl 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

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