



Synthesis, characterization and properties of an electroactive polymer having oligoaniline and binaphthyl units

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ABSTRACT

A novel polymer containing oligoaniline and binaphthyl units, exhibiting an exciting molecular structure, interesting spectroscopic and electrochemical properties, has been synthesized through oxidative coupling polymerization. The polymerization characteristics and chemical structure of the polymer were systematically studied. The oxidation state and doping level of the polymer were evaluated through X-ray photoelectron spectra. In addition, cyclic voltammetry results suggest that the obtained polymer has an intrinsic electrochemical activity similar to polyaniline. In the case of the optically active polymer, we observed a specific Cotton effect and an ultra high value of the specific rotation of the polymer solution. What is more, the conductivity of the polymer was about $3.26 \times 10^{-6} \text{ S cm}^{-1}$ at room temperature upon preliminarily protonic-doped experiment.

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1. Introduction

Chirality often exists in organic materials and biological molecules, and it plays a dominant role in living systems, such as proteins and DNA, due to the homochirality of the components [1]. Chiral materials are of great interest to both chemists and material scientists because of their potential applications in catalysis, sensors, pharmaceuticals, and enantioselective separation [2,3]. In recent decades, great attention has been focused on the exploration and synthesis of chiral polymers, especially conductive polymers, because these chiral polymers can be applied to chemical and biological sensors, surface-modified electrodes, chiral separation, chiral recognition, etc. [4–6].

Among the conducting polymers, polyaniline has attracted special attention due to its high conductivity, its good environmental stability, its facility of synthesis (chemical or electrochemical oxidation of aniline), the cheapness of its monomer, and its large variety of possible applications, including rechargeable batteries, corrosion inhibition, antistatic coatings, photovoltaic cells, organic field-effect transistors, and electrochromic devices [7–9]. Over the past decade, tremendous efforts have been put forth to prepare chiral polyaniline materials with the aim to synergistically combine the merits of each individual component. Wallace and Wang et al. prepared the chiral polyaniline materials in the presence of (1S)-(+)-10- or (1R)-(–)-10-CSA by using chemical

oxidative polymerization or electropolymerization [10–12]. Kaner reported that the chiral polyaniline materials could be obtained by the acid-doping of an emeraldine base with optical isomers of CSA [13]. Cholli and Wei prepared chiral polyaniline materials with nanostructures by the template method or self-assembly method in the presence of optically active compounds [14,15]. In addition, Goto [16] reported an optically active polyaniline derivative prepared by the interfacial polymerization of a chiral aniline monomer repeat unit in a water/perchloric acid/chloroform system.

On the other hand, chiral binaphthyl compounds play a significant role in the asymmetric synthesis field and chiral molecular recognition. The chirality of binaphthyl compounds is derived from the restricted rotation along the carbon–carbon single bond of the two naphthalene rings, and the C2 asymmetric chiral configuration of binaphthyl is remarkably stable. Recently, we have prepared a series of diameter-controllable chiral rigid macrocyclic molecules containing chiral binaphthyl moieties [17,18]. In the present research, the binaphthyl group was introduced into polymer main chain, and then the optical properties, electrochemical activity and chemical structures of the polymer were investigated in detail.

2. Experimental

2.1. Materials

All reagents were used as received without further purification. The compounds 4,4'-difluorobenzophenone and anhydrous

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potassium carbonate were purchased from Nanjing Chemical Factory. The (*S*)-1,1'-bi-2-naphthol was purchased from Shijiazhuang Chemical Regent Factory, and *p*-hydroxyl-diphenylamine, *p*-phenylenediamine, ammonium persulfate (APS), dichloromethane, acetone, *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), and hydrochloric acid were purchased from Beijing Chemical Factory. Silica gel (GF254) was purchased from Qingdao Haiyang Chemical Co., Ltd.

2.2. Characterization

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 resolution of 4 cm^{-1} in the range of $4000\text{--}400\text{ cm}^{-1}$. The nuclear magnetic resonance spectra (NMR) of both monomers and polymers 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 composition of the monomers was calculated from the results of an elemental analysis. The weight percentages of carbon, hydrogen, nitrogen and oxygen in the samples were measured by a Flash Ea 1112 elemental analysis instrument. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and molecular weight distribution of the polymer 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 the eluent at a flow rate of 1 mL min^{-1} . Calibration was accomplished with monodispersed polystyrene standards. Analysis of the X-ray photoelectron spectra (XPS) was performed using an ESCALAB MKII with Mg as the exciting source. The X-ray powder diffraction (XRD) pattern of the product was recorded on a Siemens D5005 diffractometer using $\text{Cu K}\alpha$ radiation. The cyclic voltammetry (CV) was performed with a CHI 660A Electrochemical Workstation (CH Instruments, USA) in a conventional three-electrode cell, using thin films cast from DMAc solutions onto a g-c electrode. The film was cycled in a $1.0\text{ M H}_2\text{SO}_4$ aqueous solution in the range from -100 mV to $+1000\text{ mV}$. UV-vis spectra were performed on a UV-2501 PC Spectrometer (SHIMADZU). Circular dichroism spectra (CD) were recorded on JOBINYVON-SPEX CD6 using a 1 cm quartz cell. Optical rotation measurements were performed on a Shanghai Precision and Scientific instrument Co. Ltd., WZZ-2S digital automatic polarimeter. A Perkin-Elmer PYRIS 1 TGA was used to investigate the thermal stability of the electroactive polymer in the temperature range from $80\text{ }^\circ\text{C}$ to $810\text{ }^\circ\text{C}$ at a rate of $10.0\text{ }^\circ\text{C min}^{-1}$ under nitrogen protection.

2.3. Synthesis of *S*-BN-DIF

The chiral compound, defined as *S*-BN-DIF, was synthesized by the method reported in the earlier publication of our group [19,20]. The reaction (Scheme 1) was conducted in a 1000 mL three-necked round-bottom flask that was equipped with a mechanical stirrer, a Dean-Stark trap, a nitrogen inlet and a condenser. A mixture of DMF (500 mL), toluene (80 mL), anhydrous potassium carbonate (14.21 g , 0.103 mol), 4,4'-difluorobenzophenone (218 g , 1 mol) were added in the reaction vessel and heated to reflux under pure nitrogen with stirring. Then a DMF solution (200 mL) of (*S*)-1,1'-bi-2-naphthol (28.63 g , 0.1 mol) was added over a period of 1 h . The solution was kept to reflux for another 5 h to ensure the completion of the reaction, and then it was cooled and filtered to remove the salt (KF and K_2CO_3). The solution was poured into 2 L distilled water to precipitate the product. The precipitate was collected by vacuum filtration through a Buchner funnel and washed with

water five times, and then it was washed with ethanol three times, filtered and dried under dynamic vacuum at $40\text{ }^\circ\text{C}$ for 24 h . The product was further purified by chromatography over a silica gel (GF254) column using dichloromethane as the eluent. The white powder was obtained with 81% yield. The characterization of *S*-BN-DIF is as following:

MALDI-TOF-MS: m/z calculated for $\text{C}_{46}\text{H}_{28}\text{F}_2\text{O}_4 = 682.7$; found value = 682.8 .

FTIR (KBr, cm^{-1}): 1660 (m , $\nu_{\text{C=O}}$), 1598 (s , $\nu_{\text{C=C}}$ of benzenoid rings), 1504 (vs $\nu_{\text{C=C}}$ of benzenoid rings), 1247 (s , $\nu_{\text{C-O-C}}$), 929 (m , δ_{CH}), 858 (m , δ_{CH}), 771 (m , δ_{CH}), 601 (m , δ_{CH}).

$^1\text{H NMR}$ (d_6 -DMSO): $\delta = 8.16$ (d , $J = 9.03\text{ Hz}$, 2H , H_{10}), $\delta = 8.07$ (d , $J = 8.19\text{ Hz}$, 2H , H_6), $\delta = 7.67$ (m , 4H , H_2), $\delta = 7.55$ (d , $J = 8.72\text{ Hz}$, 4H , H_3), $\delta = 7.51$ (d , $J = 7.60\text{ Hz}$, 2H , H_8), $\delta = 7.44$ (d , $J = 9.00\text{ Hz}$, 2H , H_7), $\delta = 7.39$ (t , $J = 7.28\text{ Hz}$, 2H , H_9), $\delta = 7.33$ (t , $J = 8.72\text{ Hz}$, 4H , H_1), $\delta = 7.18$ (d , $J = 8.48\text{ Hz}$, 2H , H_5), $\delta = 6.90$ (d , $J = 8.63\text{ Hz}$, 4H , H_4).

A typical elemental analysis for $\text{C}_{46}\text{H}_{28}\text{F}_2\text{O}_4$: Calculated: C 80.93 , H 4.13 , O 9.37 ; Found: C 80.79 , H 4.17 , O 9.46 .

2.4. Synthesis of macromonomer (*S*-BN-MM)

A mixture of DMF (20 mL), toluene (10 mL), anhydrous potassium carbonate (1.087 g), *p*-hydroxyl-diphenylamine (2.778 g , 15 mmol), and *S*-BN-DIF (3.414 g , 5 mmol) were added to a 100 mL three-necked round-bottom flask and heated to reflux under nitrogen with 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 aqueous hydrochloric acid (3% , 1000 mL), which yielded a white precipitate. The precipitate was washed with water and ethanol several times, filtered and dried under dynamic vacuum at $25\text{ }^\circ\text{C}$ for 48 h (yield 88%).

MALDI-TOF-MS: m/z calculated for $\text{C}_{70}\text{H}_{48}\text{N}_2\text{O}_6 = 1013.1$; found value = 1012.8 .

FTIR (KBr, cm^{-1}): 3496 (m , ν_{NH}), 3057 (m , ν_{CH}), 1647 (m , $\nu_{\text{C=O}}$), 1597 (s , $\nu_{\text{C=C}}$ of benzenoid rings), 1496 (vs $\nu_{\text{C=C}}$ of benzenoid rings), 1308 (m , $\nu_{\text{C-N}}$), 1238 (s , $\nu_{\text{C-O-C}}$), 930 (m , δ_{CH}), 841 (m , δ_{CH}), 748 (m , δ_{CH}), 694 (m , δ_{CH}).

$^1\text{H NMR}$ (d_6 -DMSO): $\delta = 8.19$ (s , 2H , H_1), $\delta = 8.15$ (d , $J = 9.05\text{ Hz}$, 2H , H_{16}), $\delta = 8.06$ (d , $J = 8.17\text{ Hz}$, 2H , H_{12}), $\delta = 7.63$ (d , $J = 8.73\text{ Hz}$, 4H , H_8), $\delta = 7.55$ (d , $J = 8.72\text{ Hz}$, 4H , H_9), $\delta = 7.50$ (t , $J = 7.34\text{ Hz}$, 2H , H_{14}), $\delta = 7.43$ (d , $J = 8.99\text{ Hz}$, 2H , H_{13}), $\delta = 7.38$ (t , $J = 7.21\text{ Hz}$, 2H , H_{15}), $\delta = 7.23$ (t , $J = 7.94\text{ Hz}$, 4H , H_3), $\delta = 7.18$ (d , $J = 8.50\text{ Hz}$, 2H , H_{11}), $\delta = 7.15$ (d , $J = 8.85\text{ Hz}$, 4H , H_7), $\delta = 7.07$ (d , $J = 7.76\text{ Hz}$, 4H , H_4), $\delta = 7.05$ (d , $J = 8.87\text{ Hz}$, 4H , H_5), $\delta = 7.00$ (d , $J = 8.74\text{ Hz}$, 4H , H_6), $\delta = 6.91$ (d , $J = 8.72\text{ Hz}$, 4H , H_{10}), $\delta = 6.82$ (t , $J = 7.22\text{ Hz}$, 2H , H_2).

A typical elemental analysis for $\text{C}_{70}\text{H}_{48}\text{N}_2\text{O}_6$: calculated: C 82.98 , H 4.78 , N 2.77 , O 9.48 ; found: C 83.07 , H 4.82 , N 2.58 , O 9.53 .

2.5. Synthesis of chiral polymer

1.216 g (1.2 mmol) of *S*-BN-MM and 0.130 g (1.2 mmol) of *p*-phenylenediamine were dissolved in a 50 mL mixture solution (including 40 mL of DMF, 5 mL of distilled water and 5 mL of concentrated hydrochloric acid). A solution of APS (0.548 g in 10 mL of 1.0 M HCl aqueous solution) was added drop-wise over a period of 30 min to the above solution while stirring at room temperature. After the addition, the resulting solution reacted for another 20 h . Then it was poured into 500 mL of distilled water to precipitate the product. The mixture was filtered and washed with distilled water and acetone several times, followed by drying under dynamic vacuum at $40\text{ }^\circ\text{C}$ for 24 h . M_n : $73,600$, M_w : $267,600$, M_w/M_n : 3.64 .

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