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Synthesis and electrochemical properties of electroactive hyperbranched poly(aryl ether ketone) bearing oligoaniline segments

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ABSTRACT

A novel electroactive hyperbranched poly(aryl ether ketone) (EHPAEK) with oligoaniline segments has been prepared by K_2CO_3-mediated nucleophilic aromatic polycondensation. The structure of EHPAEK was confirmed by Fourier-transform infrared spectra (FTIR), nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC). Its thermal stability and spectroscopic properties were also studied using thermogravimetric analysis (TGA) and UV–vis spectroscopy. Due to the oligoaniline segment, EHPAEK was found to be electroactive, which was explored by cyclic voltammetry in 0.5 M H_2SO_4. The electrochromism of EHPAEK thin film was examined using EHPAEK/ITO as the working electrode coupled with UV–vis spectroscopy, which exhibited good electrochromic properties with high contrast value, moderate switching times, acceptable coloration efficiency. Furthermore, the Tafel plots analysis and electrochemical impedance spectroscopy was applied to study the anticorrosion of the EHPAEK coatings on the cold rolled steel (CRS) in 3.5 wt% NaCl electrolyte solution. The enhanced corrosion protection ability of the EHPAEK coatings was ascribed to the redox catalytic capabilities of the oligoaniline segment.

1. Introduction

Conducting polymers such as polyaniline (PANI), polypyrrole, and polythiophene have attracted great attention as advanced materials [1,2]. Among these conducting polymers, PANI is considered one of the most frequently investigated conducting polymers potential for advanced applications such as electromagnetic interference shielding, anticorrosion coatings, rechargeable batteries, biosensor, chemical sensor and electrochromic display [3–13] because of its high conductivity, good environmental stability, easy synthesis and unique redox reversibility [14,15]. However, the poor solubility and processability of PANI in common organic solvents is an obstacle to practical application. More recently, a new kind of polyaniline derivative containing oligoaniline units have been designed and synthesized, and exhibit improved solubility and processability [16–18]. Taking the advantage of the molecular diversity and tailoring, some functional units such as fluorescene, dyestuff and chirality have been introduced into the polymer structure. As a result, electrochromic device, electrochemically responsive diffraction gratings, fluorescent sensors for the redox material, anticorrosion coatings, and ammonia sensors based on the resulting multifunctional polymers have been fabricated and investigated [19–24].

Since hyperbranched polymers have been defined by Kim and Webster, a wide variety of hyperbranched polymers have been designed and presented in the literatures, due to the relatively simple methods and unique properties. Usually, the hyperbranched polymers possess excellent solubility, low solution viscocity, no tangle and low crystallization, and exhibit potential for applications such as surface modification, additives, coatings, medicine and non-linear optics [25–27]. Recently, several of functional hyperbranched polymers emerged and revealed attractive application prospect.

We recently reported several electroactive polymers bearing oligoaniline segments, which were designed and synthesized with different topological structures, such as graft, alternating, hyperbranched and block-lick polymers [18,19,28,29]. Herein, we describe the synthesis of a novel electroactive hyperbranched poly(aryl ether ketone) with oligoaniline units. The properties of the EHPAEK, such as organic solubility, thermal stability, electroactivity, electrochromism and anticorrosion are also described in detail.

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2. Experimental

2.1. Materials

N-phenyl-*p*-phenylenediamine, 2,6-difluorobenzoyl chloride, *p*-dihydroxybenzene were purchased from Aldrich. Ferric chloride, ammonium persulfate (APS), potassium carbonate, sodium chloride, hydrochloric acid (37%) and ammonia water (25%) were obtained from Tianjin Chemical Factory. *N,N′*-Dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethyl sulphoxide (DMSO), *N*-methyl-2-pyrrolidinone (NMP), toluene, dichloromethane, acetone, diethyl ether and ethanol were purchased from commercial sources and used as received without further purification. 1,3,5-Tris(4-fluorobenzoyl) benzene (TFBB) was synthesized in our lab and recrystallized from ethanol before use. Electroactive 2,6-difluorobenzoyl aniline tetramer (DFAT) was synthesized from 2,6-difluorobenzoyl chloride and parent aniline tetramer in dry dichloromethane and dried under the vacuum before use [30].

Optically transparent Indium-Tin Oxide (ITO) glass substrates were obtained from Reintech Electronic Technologies Co., Ltd. (Beijing) and used as working electrode substrate in the electrochemical experiments. The composition of cold rolled steel (CRS), used in the anticorrosion tests, is as following (wt%): C 0.07%, Mn 0.3%, P 0.022%, S 0.01%, Si 0.01%, Al 0.03% and Fe bal.

2.2. Synthesis of EHPAEK

1,3,5-Tris(4-fluorobenzoyl) benzene (TFBB) and 2,6-difluorobenzoyl aniline tetramer (DFAT) were used as the starting monomers for nucleophilic polycondensation reaction, which were prepared in our lab by established synthetic route. The ^{1}H NMR data of the two monomers are given as following. ^{1}H NMR data for TFBB (d_6-DMSO): δ = 8.24 (s, 1H, due to Ar—H of three substituted benzene), δ = 7.96 (m, 2H, due to Ar—H), δ = 7.46 (t, 2H, due to Ar—H next to the fluorine group). ^{1}H NMR data for DFAT (d_6-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).

EHPAEK was synthesized by potassium carbonate mediated nucleophilic polycondensation reaction as depicted in Fig. 1. First, DFAT (2 mmol), TFBB (2 mmol), *p*-dihydroxybenzene (4.9 mmol), potassium carbonate (5.5 mmol), NMP (15 mL) and toluene (10 mL) were added into a 50 mL three-necked round flask equipped with a stirrer, a nitrogen inlet and a Dean-Stark trap. The mixture was heated to reflux for 3 h to remove the water by azeotropic distillation with toluene, and then the toluene was removed. The mixture was heated to flux at about 200 °C for 8 h to get a viscous solution. When cooled to the room temperature, the solution was poured into the distilled water with yielding a gray precipitate. The precipitate was washed with distilled water and ethanol for three times, filtered and dried under dynamic vacuum at 50 °C for 20 h. (Yield 91%)

FTIR (KBr, cm^{-1}): 3408 (υ_{N-H}), 3022 (υ_{C-H}), 1643 ($\upsilon_{C=O}$), 1595 ($\upsilon_{C=C}$ of benzenoid rings), 1511 ($\upsilon_{C=C}$ of benzenoid rings), 1309 (υ_{C-N}), 1244 (υ_{C-O-C}), 833 (δ_{C-H}), 746 (δ_{C-H}), 657 (δ_{C-H}). ^{1}H NMR (d_6-DMSO): δ = 10.24 (s, —CO—NH—), δ = 8.16 (m, Ar—H), δ = 7.84 (m, —NH—), δ = 7.34–6.59 (m, Ar—H). GPC results: Mn: 37,460, Mw: 75,110, PDI: 2.01.

2.3. Characterization and measurements

2.3.1. Sturcture analysis of EHPAEK

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 cm^{-1}. The NMR spectra of EHPAEK in deuterated dimethyl sulfoxide were run on a Bruker-500 spectrometer. Number-average molecular weight (Mn), weight-average molecular weight (Mw), and molecular weight distribution ($Đ$) of EHPAEK was measured on Shimadzu Gel permeation chromatography (GPC) unit equipped with a Shimadzu GPC-802D gel column and SPD-M10AVP detector, calibrated by polystyrene standards. *N,N′*-Dimethylformamide was used as the eluent at a flow rate of 1 mL/min.

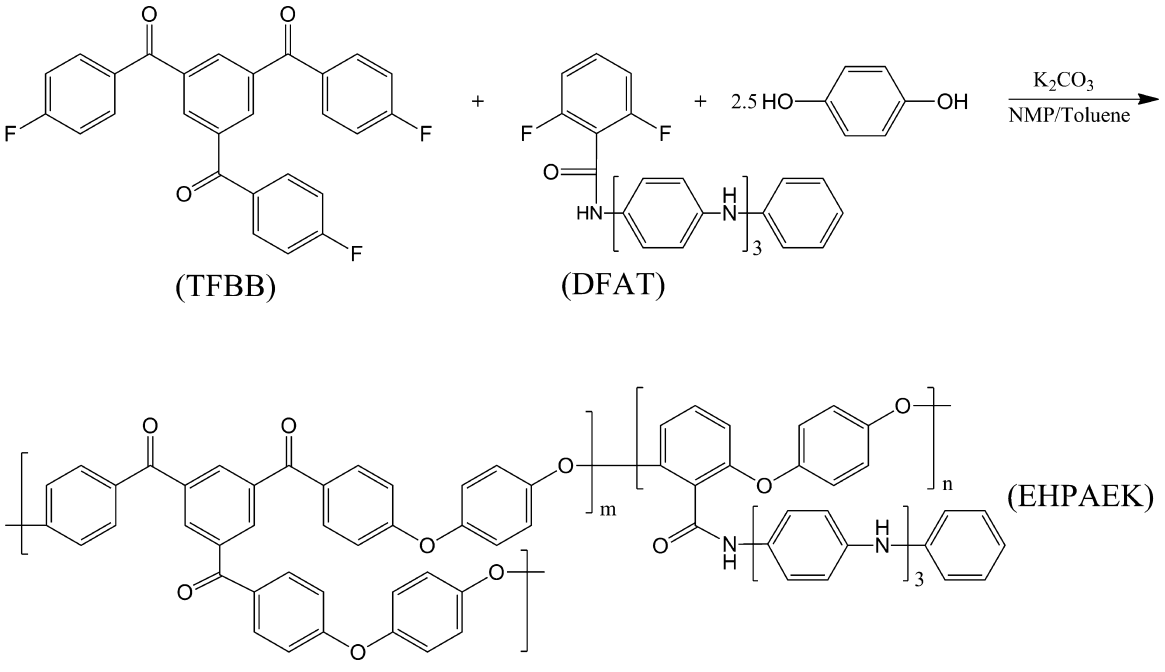

Fig. 1. Synthetic route of EHPAEK.