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Polymer 46 (2005) 2825–2829

polymer

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Synthesis of a new electroactive poly(aryl ether ketone)

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Received 13 November 2004; received in revised form 9 January 2005; accepted 10 January 2005

Abstract

In this communication, we report for the first time the synthesis of a new electroactive poly(aryl ether ketone) derived from the phenyl-capped aniline tetramer. The general properties are studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The polymer has high serving temperature and good thermal stability. And its chemical oxidation process was studied by UV–Vis spectra. It was found the polymer was oxidized to its EB form and then to the pernigraniline oxidation state, which is same as the PANI.

Keywords: Electroactivity; Poly(aryl ether ketone); UV–Vis spectra

1. Introduction

After the first oxidation of aniline [1], the electrical conductivity of polyaniline (PANI) was recognized [2]. Among conductive polymers, PANI is remarkable for its excellent environmental stability [3], and unique in the ease with which its properties may be tuned by changes in oxidation state [4] or in degree of protonation [5]. Advances in the electropolymerization of aniline [6], and in solution-processing of the chemically synthesized polymer [7], have allowed the study of PANI in numerous practical applications, including rechargeable organic batteries [8], electrochromic displays [9], electromechanical actuators [10], anticorrosion coatings for steel [11], and electromagnetic interference shielding [12]. In addition, many efforts have been devoted to investigate the PANI structure synthesized by chemical and electrochemical means, and the data reveal that most PANI exhibits an ill-defined structure and has limited solubility in a handful of organic solvents [13]. It is therefore a very important challenge to design the PANI and its derivatives in a form that is easily processible and applicable, and at the same time gives the final product a well-defined structure. One approach is the incorporation of a well-define oligoaniline into the copolymer backbone structure. Such a synthetic strategy leads to polymers not only with better solubility and a non-defective conjugated structure but also with good mechanical properties and electroactivity [14]. Poly(aryl ether ketone) high performance engineering plastics and matrix resins have attracted considerable interest because of their high yield stress, ductile behavior, other mechanical properties, and stability at high temperature [15]. The availability of oligoanilines and their derivatives allowed us to make the incorporation of a well-define oligoaniline into the backbone structure of poly(aryl ether ketone) to exploit a new electroactive poly(aryl ether ketone). And the new electroactive poly(aryl ether ketone) has not only the electroactivity of PANI but also the mechanical properties and stability at high temperature of poly(aryl ether ketone).

In this communication, we report for the first time the synthesis of a new electroactive poly(aryl ether ketone) which has alternating conjugated (phenyl-capped aniline tetramer) and non-conjugated segment in the main chain. The general properties of the polymer were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The chemical oxidation process of the polymer was studied by UV–Vis spectra, and the electrochemical analysis was studied by CV.

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doi:10.1016/j.polymer.2005.01.070

2. Experimental part

2.1. Materials

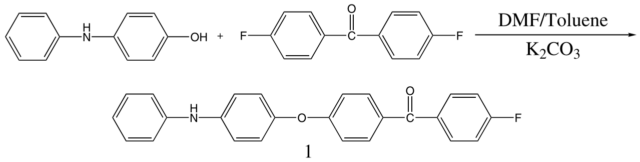
All chemicals were used as received. Ammonium persulfate (98%, Shenyang Chemical Factory), hydrochloric acid (37%, Changchun Chemical Factory), ammonium hydroxide (30%, Changchun Chemical Factory), phenylhydrazine (99%, Beijing Chemical Factory), dimethylformamide (DMF, 99%, Beijing Chemical Factory), *N*-methyl-keto-pyrrolidine (99% Beijing Chemical Factory.), anhydrous potassium carbonate (99%, Shenyang Chemical Factory), *p*-phenylenediamine (99%, Beijing chemical factory), diethyl ether (99%, Tianjin Chemical Factory), 4,4′-difluorobenzphenone (99%, Nanjing Chemical Factory), *p*-hydroxyl-diphenylamine (99% Beijing Chemical Factory).

2.2. Instruments

IR Spectra of KBr powder-pressed pellets were recorded on a BRUKER VECTOR 22 Spectrometer. Elemental analysis results were obtained on a Flash Ea 1112 elemental analysis instrument. ^{1}H NMR spectra were run on a BRUKER-500 spectrometer, referenced to internal tetramethylsilane, DMSO as solvent. UV–Vis spectra were performed on UV-2501 PC Spectrometer (SHIMADZU). Mass spectra were performed on a AXIMA-CFR laser desorption ionization flying time spectrometer (COMPACT). The cyclic voltammetry was recorded on a Bas 100B electrochemical analyzer by using thin film cast onto g-c electrode from NMP solution, with a Pt pellet as counter electrode and SCE as reference electrode. The film was cycled at 1 M H_2SO_4 aqueous solution in the range -0.2 V to $+0.8$ V. METTLER TOLEDO DSC821 instrument was used for the differential scanning calorimetry (DSC) analysis with a heating rate of 10 °C/min under nitrogen protection.

2.3. Synthesis of compound (1)

The reaction (Scheme 1) was conducted in a 1 l three-necked round-bottom flask which was equipped with a Dean-Stark trap, a nitrogen inlet and condenser. A mixture of DMF (500 mL), toluene (25 mL), anhydrous potassium carbonate (15.7 g), *p*-hydroxyl-diphenylamine (18.4 g), and 4, 4′-difluorobenzphenone (109.2 g) were added in the reaction vessel and heated to reflux under pure nitrogen with stirring. The solution was kept to reflux for 4 h to ensure completion of the reaction, and then it was cooled and filtered to remove the salt (KF and K_2CO_3). The solution was concentrated to 200 mL, and then it was poured into 2400 mL 3% HCl to precipitate the product. The precipitate was collected by vacuum filtration through a Buchner funnel and washed with water, then it was recrystallized from ether and dried in a vacuum oven at 50 °C for 24 h. Yellow powder was got in 65% yield.



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Scheme 1. Synthesis of compound (**1**).

2.3.1. Characterization of 1:

MALDI-TOF-MS: *m/z* calculated for $C_{25}H_{18}FNO_2$ = 383.4. Found 383.8 (M^+).

IR (cm^{-1}): 3364, 3031, 2921, 1645, 1600, 1525, 1503, 1406, 1312, 1272, 1235, 1197, 1172, 1151, 1113, 966, 930, 872, 857, 845, 768, 742, 693, 679, 597, 571, 508.

^{1}H NMR (*d_6*-DMSO): 6.82 (t, 1H), 7.05 (broad, 6H), 7.15 (d,2H), 7.24 (t, 2H), 7.39 (t, 2H), 7.75–7.81 (broad, 4H), 8.2 (s,1H).

A typical elemental analysis for $C_{25}H_{18}FNO_2$: Calcd. C 78.31, H 4.73, N 3.65, O 8.35; Found C 78.15, H 4.88, N 3.43, O 8.15.

2.4. Synthesis of monomer (**2**)

3.83 g (0.01 mol) Compound 1 and *p*-phenylenediamine 0.54 g (0.005 mol) were dissolved in 60 mL mixture solution (including 45 mL DMF, 7.5 mL distilled water and 7.5 mL concentrated hydrochloride). The solution of ammonium persulphate ($(NH_4)_2S_2O_8$ 2.28 g in 50 mL 1 M HCl) was added to above solution dropwise via an addition funnel at room temperature with stirring. After the addition, the resulted solution reacted for another 1 h. Then it was poured into 300 mL distilled water to precipitate the product. The precipitate was collected by vacuum filtration through a Buchner funnel and washed by 1 M HCl for three times, then dedoped by 1 M ammonium hydroxide. After drying at 40 °C under vacuum, it was reduced to the leucoemeraldine oxidation state by phenyl-hydrazine and recrystallized from ethanol (78%) (Scheme 2).

2.4.1. Characterization of 2:

MALDI-TOF-MS: *m/z* calculated for $C_{56}H_{40}F_2N_4O_4$ = 870.3. Found 870.1 (M^+).

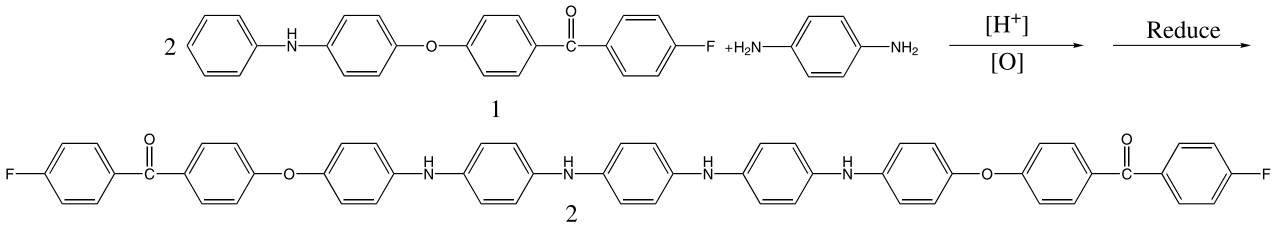
IR (cm^{-1}): 3366, 3033, 2920, 1647, 1602, 1528, 1501, 1403, 1310, 1271, 1234, 1199, 1174, 1153, 1110, 968, 931, 874, 859, 843, 768, 741, 694, 677, 595, 571, 506.

^{1}H NMR (*d_6*-DMSO): 7.87 (s, 4H), 7.80 (t, 4H), 7.75 (t, 4H), 7.64 (s, 4H), 7.38 (t, 4H), 6.93–7.04 (broad, 20H).

A typical elemental analysis for $C_{56}H_{40}F_2N_4O_4$: Calcd. C 77.23, H 4.63, N 6.43, O 7.35; Found C 76.98, H 4.49, N 6.58, O 7.06.

2.5. Synthesis of the polymer (**3**)

The reaction (Scheme 3) was conducted in a 250 mL three-necked round-bottom flask which was equipped with a



Scheme 2. Synthesis of monomer (**2**).

Dean-Stark trap, a nitrogen inlet and condenser. A mixture of DMF (150 mL), toluene (20 mL), anhydrous potassium carbonate (13.8 g), monomer 2 (8.71 g), and bisphenol A (2.28 g) were added in the reaction vessel and heated to reflux under pure nitrogen with stirring. The solution was kept to reflux for 4 h to ensure completion of the reaction, and then it was cooled and filtered to remove salt (KF and K_2CO_3). The solution was concentrated to 100 mL, and then it was poured into 800 mL 3% HCL to precipitate the product. The precipitate was collected by vacuum filtration through a Buchner funnel and washed with water, after washing with tetrahydrofuran it was dried in a vacuum oven at 50 °C for 24 h. Black-brown powder was got in 73% yield. M_n: 32910, M_w: 36860, M_w/M_n: 1.12.

IR (cm^{-1}): 3361, 3029, 2965, 1882, 1646, 1598, 1509, 1446, 1362, 1297, 1238, 1177, 1113, 1083, 1014, 931, 828, 758, 722, 553, 532, 521.

^1H NMR (d_6-DMSO): 7.92 (broad, –NH–), 7.74 (broad, Ar-H), 7.64 (broad, Ar-H), 7.37–7.49 (broad, Ar-H), 7.18–7.30 (broad, Ar-H), 6.68–7.05 (broad, Ar-H), 1.60–1.77 (broad, –CH3).

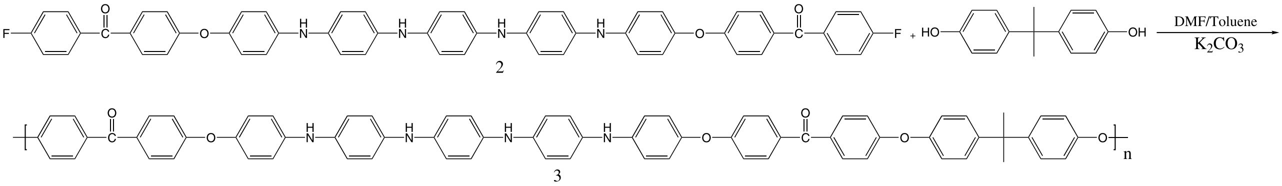
3. Results and discussion

In this synthetic approach, we first used *p*-hydroxyldiphenylamine and 4, 4′-difluorobenzphenone to synthesize compound (**1**). And the monomer (**2**) was synthesized by oxidative coupling reaction of *p*-phenylene-diamine and compound (**1**). This synthetic approach protected the hydroxyl terminal group from oxidation. The compound (**1**) and the monomer (**2**) were characterized by IR, elemental analysis, MALDI-TOF-MS, and ^1H NMR. The electroactive polymer was synthesized by means of polycondensation from the monomer (2) and bisphenol A. The general properties of the polymer were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The chemical oxidation process of the polymer was monitored by UV–Vis spectra, and the electroactivity of the polymer was studied by CV.

The TGA curve of the pure polymer was represented in Fig. 1. The initial weight loss of the polymer starts at around 296 °C, which is associated with the loss of hydrogen of the oligoaniline chain [16]. The polymer has a quite excellent thermal stability, and the decomposition temperature reaches 567 °C, under nitrogen atmosphere.

The polymer was first heated to 290 °C and held at this temperature for 1 min and then quenched in ice water to ensure that the polymer component was amorphous. DSC analysis of the amorphous polymer was recorded on METTLER TOLEDO DSC821 instrument with a heating rate of 10 °C/min under nitrogen protection. From DSC result, the polymer showed single glass transition. The T_g value of the polymer is 181 °C which is much higher than that of pure PEEK. The relative higher T_g value indicating that the molecular segments of the polymer present much higher rigidity than that of pure PEEK, and the reason can be attribute to the introduction of the aniline oligomers segment which will present high rotation energies as compared with the correspondent ether–ether motivies. The rigidity of the oligomer segment originated from the strong bondage of the π–π conjugate system, in addition, the wide-range existed hydrogen bond also give a rise in difficulties of free-rotation to the molecular chains.

The polymer in the leucoemeraldine oxidation state was dissolved in NMP solution. Trace amount of $(NH_4)_2S_2O_8$ was added to it. The solution gradually turned to dark blue and finally purple upon being oxidized. This process was monitored by UV–Vis spectra continuously, UV–Vis spectra obtained is shown in Fig. 2. First only one absorption (band a, at lower wavelength) at 335 nm was observed which is associated with a π–π* transition of the conjugated ring system [17,18]. When it is slowly oxidation, the absorption started to undergo a blue shift, with the intensity decreasing, and the UV–Vis spectra show a new absorption (band b, at longer wavelength) at 588 nm which is assigned to the



Scheme 3. Synthesis of the polymer (**3**).

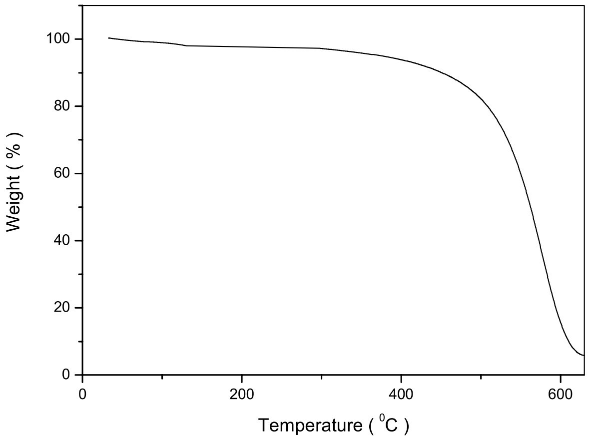


Fig. 1. TGA thermograms of the polymer.

benzenoid to quiniod excitonic transition [19] and continually increases in intensity. After band ***b*** in intensity reaching the maximum, it exhibited a blue shift. This showed that the emeraldine oxidation state has been reached and just exceeded to form a pernigraniline oxidation state. The chemical oxidation process is the same as PANI.

We have chosen to examine the electrochemical behavior of the polymer in 1 M H_2SO_4. The NMP solution of the polymer was cast on the g-c working electrode and was evaporated to form thin solid film. Under these conditions, the cyclic voltammogram (Fig. 3) of the polymer showed one oxidation-reduction peak (the oxidative peak's position is at 428 mv), different from PANI which has two oxidationreduction peaks in the cyclic voltammogram. A possible explanation of this phenomenon is as following: Because the oxidation-reduction peak current of the polymer depends on the aniline unit content [20]. The aniline unit content of the polymer is low, so the second oxidation–reduction peak current of the polymer is so weak that it did not show in the cyclic voltammogram. Therefore, there is only one oxidation–reduction peak in the cyclic voltammogram. With increasing number cycles, the peak in potential did not show any shift, but the peak in current decreased gradually. And the peak in current kept invariably, after the six cycles. This indicates that the polymer has some degree of eletroactivity.

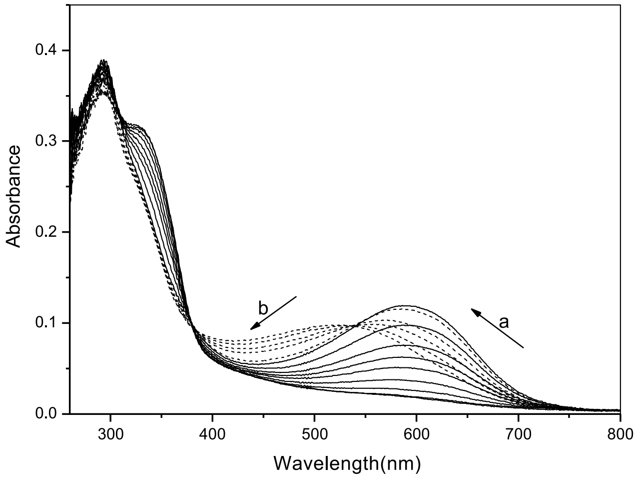


Fig. 2. UV–Vis spectra monitoring chemical oxidation of the polymer in the leucoemeraldine oxidation state (a): the intensity of absorbance increased while being oxidized. (b): the intensity of absorbance decreased after reaching the maximum.

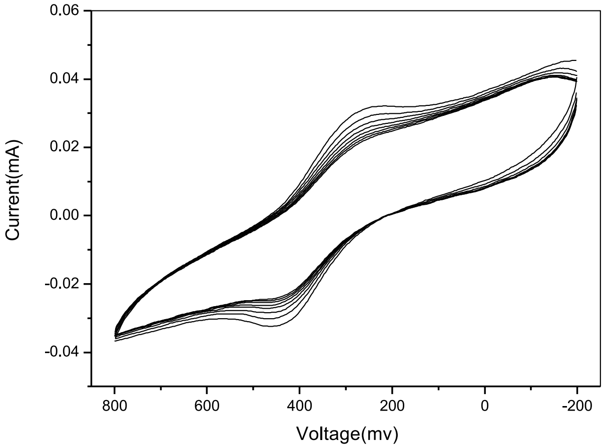


Fig. 3. Cyclic voltammetry of the polymer.

4. Conclusions

A new electroactive poly(aryl ether ketone) was synthesized derived from the phenyl-capped aniline tetramer. The general properties are studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), the polymer has high serving temperature and good thermal stability. The chemical oxidation process of the polymer was studied by UV–Vis spectra. It was found the polymer was oxidized to its EB form and then to the pernigraniline oxidation state, which is same as the PANI. Further investigation on the mechanical and thermal properties of the poly(aryl ether ketone) is ongoing.

Acknowledgements

The financial support from the National Natural Science Foundation of China (NNSFC-50473007), the Major International Collaborative Project of National Natural Science Foundation of China (Grant 20320120169) and the National Major Project for Fundamental Research of China (National 973 Program No 001CB610505 and No G2003CB615604) is greatly appreciated.

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