

Synthesis of Poly(aryl ether ketone)s from New Bisphenol Monomers

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Abstract: New bisphenol monomers, (4-fluoro)phenylhydroquinone and (3,4-bifluoro) phenylhydroquinone, were prepared in a two-step synthesis. Poly(aryl ether ketone)s were derived from these bisphenols via a nucleophilic aromatic substitution polycondensation with 4,4'-Difluorobenzophenone. The polycondensation proceeded quantitatively in N,N-dimethyl acetamide (DMAc) in the presence of anhydrous potassium carbonate and afforded the polymers with inherent viscosities of 0.50 and 0.92 dL/g. The glass transition temperatures were 151°C and 159°C respectively. The polymers also had high thermal decomposition temperatures and the temperatures of 5% weight loss were all above 527°C and the 10% weight loss were above 587°C in nitrogen atmosphere. There were no melting endotherms that were observed on DSC traces, which indicated that the copolymers were amorphous and the amorphous structures were further confirmed by wide-angle X-ray diffraction. The polymers' solubility was improved by the introduction of bulky pendant groups and all of them exhibited good solubility in some common solvents such as NMP, DMF, DMSO, CH₂Cl₂, THF, CHCl₃ etc. Transparent, strong and flexible films were formed by the DMAc solutions of the polymers with tensile strengths of 98.3 MPa, 95.2 MPa, Young's moduli of 2.74 GPa, 3.06GPa and elongation at break of 27% and 32%. The dielectric constants at 1 MHz of the polymers were 2.82 and 2.75.

Keywords: Poly(aryl ether sulfone), fluoro-substituted phenyl, solubility, mechanical property, dielectric property.

1. Introduction

Poly(aryl ether ketone)s (PAEKs) are currently receiving considerable commercial interest as high performance engineering thermoplastics. Excellent combination of chemical, physical and mechanical properties make them a class of important advanced materials used in aerospace, automobile, electronics, and other high technology fields [1-4]. Conventional PAEKs show high crystalline properties, resulting in very high melting temperature and poor solubility towards common organic solvents, which restrict their application in thin films and coating materials. Lots of researches have focused on improving the solubility, processability and other desired properties through structure modification such as varying the para/meta connectivity [5], changing the ether-to-ether ratio [6], and introduction of pendant groups onto the molecular chain [7-10]. The incorporation of fluorine atoms (or groups containing fluorine atoms) into polymer chains has been developed as an effective method to increase the solubility, glass transition temperature and thermal stability and also decrease the dielectric constants, moisture absorption and refractive index [11-17].

In this paper, we report the successful preparation of two new bisphenol monomers, (4-fluoro)

phenylhydroquinone and (3,4-bifluoro) phenylhydroquinone. The nucleophilic aromatic substitution polymerization of these bisphenol monomers with 4,4'-difluorodiphenylketone affords the formation of new PAEKs with many interesting properties.

2. Experiment

2.1 Materials

4-fluoroaniline (Alfa), 3,4-difluoroaniline (Alfa), 1,4-benzoquinone (Shanghai Medicine Group Chemical Reagent Co.), zinc powder (Shanghai Medicine Group Chemical Reagent Co.), hydrochloric acid (Shanghai Medicine Group Chemical Reagent Co.), sodium nitrite (Shanghai Medicine Group Chemical Reagent Co.), sodium bicarbonate (Shanghai Medicine Group Chemical Reagent Co.), toluene (Shanghai Medicine Group Chemical Reagent Co.), potassium carbonate (Shanghai Medicine Group Chemical Reagent Co.), 2-Phenylhydroquinone (Alfa), 4,4'-Difluorobenzophenone (Alfa) and N,N-dimethyl acetamide (Shanghai Medicine Group Chemical Reagent Co.) were used as received. The syntheses of the new biphenol monomers and polymers are illustrated in Schemes 1 and 2 respectively.

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2.2 Measurements

FTIR spectra were recorded on a Nicolet Magna 470 spectrometer. ^1H (400 MHz) and ^{19}F (376.5 MHz) NMR spectra were recorded on a Bruker AV 400 MHz instrument with tetramethyl silane (^1H) or CFCl_3 (^{19}F NMR) as a reference. Differential scanning calorimetry (DSC) analysis was performed on a TA 2900 M DSC instrument at a heating rate of $20^\circ\text{C}/\text{min}$ in nitrogen atmosphere. Glass transition temperatures (T_g) were read at the middle of the transition in the heat capacity from the second heating scan after quick cooling from 220°C at a cooling rate of $20^\circ\text{C}/\text{min}$. Thermogravimetric analysis (TGA) of the samples were measured on a DuPont 2000 SDT-2960 instrument at a heating rate of $20^\circ\text{C}/\text{min}$ in nitrogen atmosphere, and Td_5 and Td_{10} were reported as the temperatures where 5 and 10% weight loss were observed, respectively. Inherent viscosities ($\eta_{inh} = \ln \eta_r/c$) were measured at a concentration of 0.5 g/dL in DMAc at 25°C with an Ubbelohde viscometer. Wide-angle X-ray diffraction (WAXD) patterns were obtained at room temperature on a Rigaku D/MAX 2500 powder diffractometer with a scanning speed of $4^\circ/\text{min}$, and the patterns were recorded in the 2θ range of 5 – 40° . The solubility of the copolymers was determined with 10 mg of a polymer in 1 mL of a solvent. The polymer thin films for stress–strain tests were cast from DMAc solutions onto glass plates and this was followed by evaporation of the solvent and drying at 100°C for 1 h, 150°C for 1 h and at 200°C in vacuum for 2 hrs. The tensile properties were measured on an Instron 3365 Tensile Apparatus. The dielectric constant was determined on an Agilent 4291B instrument at a frequency of 1 MHz to 1.1 GHz at 25°C .

2.3 Monomer synthesis

2.3.1 Synthesis of (4-fluoro)benzoquinone (4F-BQ) and (3,4-fluoro)benzoquinone (3,4F-BQ)

4F-BQ: Into a 500-mL beaker equipped with a mechanical stirrer a dropping funnel and a thermometer were placed in hydrochloric acid (11.8 M, 48 mL) and ice water (48 mL). 4-fluoroaniline (13.32 g, 0.12 mol) was added dropwise into the stirred mixture through the dropping funnel and then a concentrated water solution of sodium nitrite (8.28 g, 0.12 mol) was added dropwise. The mixture was stirred for 2 h at 0 – 5°C and yielded a clear solution. The resulting solution was filtered and added dropwise to a mixture of 1,4-benzoquinone (11.66 g, 0.11 mol),

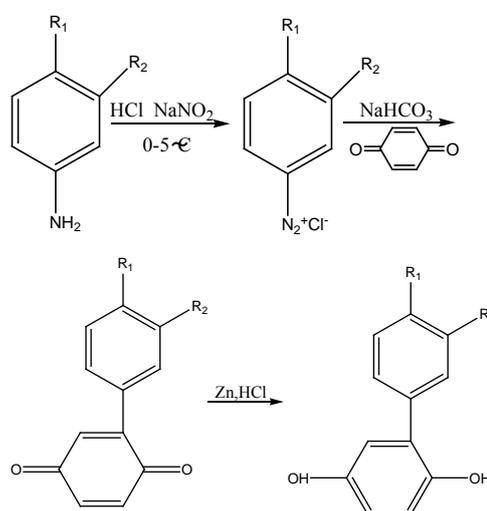
sodium bicarbonate (20.41 g, 0.24 mol) and water (700 mL). The reaction mixture was stirred at 8 – 12°C for about 2 hrs and then at room temperature for 2 hrs. The precipitate was collected by filtration, washed thoroughly with water and dried at 60°C in a vacuum oven. The product was recrystallized from *n*-butanol and gave yellow crystals. Yield: 80%.

3,4F-BQ: The procedure was similar to the synthesis of 4F-BQ, except that 3,4-difluoroaniline was used as the starting material. Yield: 90%.

2.3.2 Synthesis of (4-fluoro)

phenylhydroquinone(4F-PH) and (3,4-fluoro) phenylhydroquinone(3,4F-PH)

4F-PH: 4F-BQ (10.74 g, 0.05 mol), Zn powder (10.35 g, 0.15 mol), and 100 mL of deionized water were placed into a 500-mL, three-necked flask equipped with a mechanical stirrer, a condenser and a dropping funnel. The mixture was heated to 95°C with stirring which was followed by the addition of 35 mL of HCl (11.8 M) dropwise at a rate of 0.5 drops per second. After complete addition the reaction mixture was allowed to reflux for 3 h. Then the hot mixture was filtered. The filtrate was cooled to room temperature and poured into a large amount of deionized water. The white solid was collected. Yield: 65%.



Scheme 1. Synthesis of bisphenol monomers.
 (4-fluoro)phenylhydroquinone: $R_1:\text{F}$, $R_2:\text{H}$;
 (3,4-bifluoro) phenylhydroquinone: $R_1:\text{F}$, $R_2:\text{F}$