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Polymer 47 (2006) 547–552

polymer

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Soluble wholly aromatic polyamides containing unsymmetrical pyridyl ether linkages

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Received 29 September 2005; received in revised form 14 November 2005; accepted 16 November 2005
Available online 15 December 2005

Abstract

Wholly aromatic polyamides were synthesized from the amidation reaction between unsymmetrical diamine containing a pyridyl ether linkage and aromatic dicarboxylic acid chloride. The resulting polyamides containing pyridyl ether linkages showed high thermal stability ($T_{d5}=467$ °C) and enhanced solubility in organic solvents compared with the analogous polyamides having phenyl ether linkages. Substitution of just a single atom in a repeating unit was effective to disrupt the strong inter-chain interaction of parent aramid polymers.

Keywords: High performance polymers; Polyamide; Step-growth polymerization

1. Introduction

Wholly aromatic polyamides (aramids) are high performance polymeric materials with outstanding mechanical properties and excellent thermal and chemical stabilities due to chain stiffness and intermolecular hydrogen bonding of amide groups [1,2]. However, the poor solubility and high softening or melting temperature caused by the high crystallinity of the aramid backbones lead to difficult processing of these materials. For the practical use in various recent applications, new aromatic polyamides possessing both high thermal stability and solubility in common organic solvents have been required. Incorporation of pendent groups [3–6] or molecular asymmetry [7,8] or flexible linkages [9–11] into the backbone is a typical approach to improve solubility and processability while maintaining the high thermal stability of aromatic polyamides. Generally, it is more convenient to synthesize the modified aramids via the structural modification of diamine monomers, followed by the polycondensation reaction with available aromatic dicarboxylic acids or their derivatives. The most popular diamine monomer with a flexible linkage is 4,4′-oxydianiline (ODA) [12–14]. Although the resulting aromatic polyamide, which is produced by the polyamidation reaction with terephthaloyl chloride, has flexible ether linkages along the main chain, it is still insoluble in organic solvents such as NMP or DMSO without lithium chloride.

Recently, we have been interested in the effects of the minimal structural modification on the physical properties of various step-growth polymers. In this study, we incorporate unsymmetrical pyridyl ether linkages instead of phenyl ether linkages into the main chain of ODA-based aramid polymers (Fig. 1). Unsymmetrical pyridyl ether containing aramids are structurally different in the aspect that only single carbon atom of the repeating unit of the corresponding ODA-containing aramid is changed by a nitrogen atom (Fig. 1). This change in a single atom is the least structural modification to the parent ODA based aramid polymers and the modified aramid polymers are isoelectric compared with the parent aramid polymers. It is interesting to investigate how much of the physical and chemical properties are affected with such a minimal structural modification in the repeating unit of polymers. Also, it is well known that aramids containing heterocyclic units in the main chain possess excellent thermal stabilities [15,16]. Therefore, incorporation of pyridyl ether linkages may induce the least detrimental effect on the thermal properties of the polymer.

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doi:10.1016/j.polymer.2005.11.064

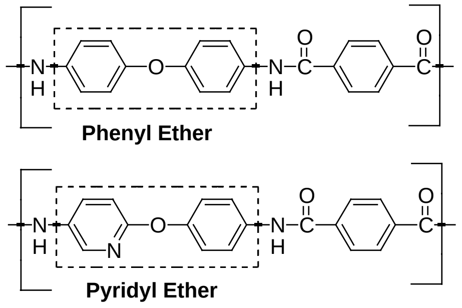

Fig. 1. Structures of aromatic polyamides containing phenyl or pyridyl-ether linkages.

2. Experimental

2.1. Materials

2-Chloro-5-nitropyridine, 4-nitrophenol, benzoyl chloride, palladium (5 wt% on activated carbon), and potassium carbonate (K_2CO_3) were purchased from Aldrich Chemical Company and used as received. Toluene, triethylamine (TEA), *N*-methyl-2-pyrrolidinone (NMP), and *N*,*N*-dimethylacetamide (DMAc) were dried over calcium hydride for 24 h and distilled under reduced pressure. Terephthaloyl chloride (TPC) and isophthaloyl chloride (ITC) (from Aldrich) were purified by recrystallization in hexane.

2.2. Characterization

FT-IR spectra of the compounds were obtained with a Brucker EQUINOX-55 spectrophotometer using KBr pellet. NMR spectra of the synthesized compounds were recorded on Brucker Fourier Transform AVANCE 300 spectrometers. High-resolution mass (HRMS) spectra of the monomers and model compounds were obtained with a Jeol JMS-SX-102 mass spectrometer. Inherent viscosity data were obtained in NMP with a Canon-Ubbelohde type viscometer at a concentration of 0.5 g/dL at 30 °C. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a TA 2200 thermal analyzer system at a heating rate of 10 °C/min in nitrogen. Molecular model was obtained by molecular mechanics (MM+) by means of the Chem 3D Ultra® program (Molecular Modeling System, Version 6.0, 2000; Cambridge Scientific Computing, Inc.).

2.3. Monomer synthesis

2.3.1. 5-Nitro-2-(4-nitrophenoxy)-pyridine (**1**) [17]

2-Chloro-5-nitropyridine (25.40 g, 160.2 mmol), 4-nitrophenol (22.30 g, 160.3 mmol), and K_2CO_3 (22.15 g, 160.3 mmol) were added to a mixture of 210 mL of DMAc and 20 mL of toluene in nitrogen. The solution was heated to 100 °C with the azeotropic distillation of toluene for 14 h. The dark brown solution was cooled and poured into 500 mL of distilled water. The precipitated solid was collected by filtration and dried in vacuo at 60 °C for 12 h. The crude product was used without further purification. Yield: 92%.

FT-IR (KBr): 1606 (C=C and C=N band), 1511, 1354 (NO_2), 1264 cm^{-1} (C–O–C stretching).

^1H NMR (DMSO-d_6, 300 MHz, δ): 9.03 (d, 1H), 8.69 (dd, 1H), 8.33 (d, 2H), 7.52 (d, 2H), 7.42 (d, 1H).

^{13}C NMR (DMSO-d_6, 75.1 MHz, δ): 165.2, 157.8, 144.6, 144.5, 141.1, 136.2, 125.6, 122.5, 112.6.

FAB-MS (*m*/*e*) 261.0388, Calcd 261.0386 for $C_{11}H_7N_3O_5$.

2.3.2. 5-Amino-2-(4-aminophenoxy)-pyridine (**2**) [18]

Dinitro compound **1** (5.00 g, 19.1 mmol) and 5 wt% palladium on activated carbon (0.638 g) were added to 250 mL of anhydrous ethanol. Twenty millilitres of hydrazine monohydrate was added dropwise to this mixture at 50 °C for 1.5 h. After an additional reflux for 1.5 h, the catalyst was removed by hot filtration and the solvent was removed from filtrate by rotary evaporation. The remaining oily mixture was added into 300 mL of distilled water and the resulting solid was collected by filtration. Recrystallization from ethyl acetate gave the desired **2** as white crystalline solid. Yield: 65%. MP: 172 °C.

FT-IR (KBr): 3473, 3384 (N–H), 1617 (N–H out-of-plane bending), 1512 (N–H bending and C–N stretching), 1240 cm^{-1} (C–O–C stretching).

^1H NMR (DMSO-d_6, 300 MHz, δ): 7.49 (d, 1H), 7.03 (dd, 1H), 6.69 (d, 2H), 6.59 (d, 1H), 6.55 (d, 2H), 4.91 (s, NH_2, 2H), 4.80 (s, NH_2, 2H).

^{13}C NMR (DMSO-d_6, 75.1 MHz, δ): 155.4, 145.8, 144.7, 140.8, 132.1, 125.4, 120.7, 114.5, 111.1.

FAB-MS (*m*/*e*) 201.0911, Calcd 201.0902 for $C_{11}H_{11}N_3O$.

2.4. Model reaction

2.4.1. 5-Benzamido-2-(4-benzamidophenoxy)-pyridine (**3**)

Diamine monomer **2** (0.5000 g, 2.485 mmol) and benzoyl chloride (0.6986 g, 4.970 mmol) were dissolved in 11 mL of NMP at 0 °C. After stirring for 3 h, 0.7 mL of triethylamine was added to the solution. The reaction mixture was allowed to warm up to room temperature gradually for 1 h and stirring was continued for 12 h. The reaction mixture was poured into 300 mL of distilled water and the precipitate solid was collected by filtration and dried in vacuo at 80 °C. Yield = 94%.

FT-IR (KBr,): 3294 (N–H), 1647 (C=O), 1543 (N–H bending and C–N stretching), 1237 cm^{-1} (C–O–C stretching).

^1H NMR (DMSO-d_6, 300 MHz, δ): 10.4 (s, –CONH–, 1H), 10.3 (s, –CONH–, 1H), 8,51 (d, 1H), 8.24 (dd, 1H), 7.97 (m, 4H), 7.82 (d, 2H), 7.60 (m, 6H), 7.14 (d, 2H), 7.07 (d, 1H).

^{13}C NMR (DMSO-d_6, 75.1 MHz, δ): 165.6, 165.4, 159.2, 150.1, 139.4, 135.5, 134.9, 134.3, 132.7, 131.8, 131.7, 131.5, 128.5, 128.4, 127.6, 127.5, 121.7, 120.9, 111.1.