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Novel thermally stable polyimides based on flexible diamine: synthesis, characterization, and properties

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Abstract

A novel diamine with built-in sulfone, ether, and amide structure was prepared via three-step reactions. Nucleophilic reaction of 4-aminophenol with 4-nitrobenzoyl chloride in the presence of propylene oxide led to preparation of *N*-(4-hydroxy phenyl)-4-nitrobenzamide (HPNB). The nitro group of this compound was reduced with hydrazine and Pd/C to afford 4-amino-*N*-(4-hydroxy phenyl)benzamide (AHPB). Two moles of AHPB were reacted with bis-(4-chloro phenyl)sulfone to provide a novel sulfone ether amide diamine (SEAD). All the prepared compounds were characterized by common spectroscopic methods. The prepared diamine (SEAD) used to prepare related polyimides by reaction with different aromatic dianhydrides. The obtained poly(sulfone ether amide imide)s were characterized and their properties were studied.

Keywords: Diamine; Polyimide; Thermally stable; Synthesis; Polycondensation

1. Introduction

Wholly aromatic polyimides are well accepted as high performance polymers and they are well as high temperature resistant material [1]. They exhibit favorable balance of physical and chemical properties and show excellent thermal, mechanical and electrical properties and they are widely used in microelectronic and aerospace engineering [2,3]. However, the technological and industrial application of rigid polyimides are limited by processing difficulties due to their high melting or glass transition temperatures and lack of solubility in most organic solvents [4]. Strong interaction between polyimide chains and their rigid structure are the main reasons for these behaviors.

To overcome such a drawback, different methods have been introduced based on the modification of polymer structure. Much effort has been achieved in designing and synthesizing new dianhydrides [5–8] and diamines [9–15], and therefore producing a great variety of soluble and processable polyimides for various purposes and applications. Incorporation of flexible units such as –NHCO–, –O–, and $–SO_2–$ is one of the most important approaches to overcome these processing problems [14,16].

Poly(amide-imide)s have deserved particular attention, as they are probably the class of copolyimides that most closely resemble the thermal properties of aromatic polyimides. Furthermore the inclusion of an amide group into the polyimide backbone increases its processability, solubility, and moldability [17]. Poly(amide-imide)s are an important group of high performance polymers having excellent resistance to high temperatures and

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favorable balance of other physical and chemical properties [18].

This article presents synthesis of a novel diamine with preformed sulfone, ether, and amide groups and also polycondensation reactions of the diamine with different aromatic dianhydrides to prepare new soluble, thermally stable poly(sulfone ether amide imide)s.

2. Experimental

2.1. Materials

All chemicals were purchased either from Merck or Aldrich chemical Co. 4-Aminophenol and bis-(4-chlorophenyl)sulfone were recrystallized from ethanol. Dianhydrides were dried in a vacuum oven at 110 °C for 5 h. *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF) and toluene were distilled over calcium hydride under reduced pressure.

2.2. Instruments

Infrared measurements were performed on a Bruker-IFS 48 FTIR spectrometer (Ettlingen, Germany). The H-NMR spectra were recorded in DMSO-d_6 solution using a Bruker Avance DPX 250 MHz (GmbH, Germany). Elemental analyses were performed by a CHN-O-Rapid Heraeus elemental analyzer (Wellesley, MA). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Stanton Redcraft STA-780 (London, UK). The dynamic mechanical measurements were recorded on a Polymer Laboratories. Dynamic Mechanical Thermal Analyzer (DMTA) in the bending mode at 1 Hz and a heating rate of 5 °C/min (Surrey, UK). Inherent viscosities were measured by suing an Ubbelohde viscometer.

2.3. Monomer synthesis

2.3.1. Synthesis of N-(4-hydroxy phenyl)-4-nitrobenzamide (HPNB)

A 100-ml, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube, and calcium chloride drying tube was charged with 5 mmol of the 4-aminophenol and 15 ml of dry NMP. The mixture was stirred at 0 °C for 0.5 h. Then about 3 ml of propylene oxide was added, and after a few minutes 5 mmol of 4-nitrobenzoyl chloride was added and the mixture was stirred at 0 °C for 0.5 h. The temperature was raised to room temperature and the solution was stirred for 6 h. HPNB was precipitated by pouring the flask content into water. Then it was filtered, washed with hot water and dried overnight under vacuum at 70 °C. (Yields 89%.)

2.3.2. Synthesis of 4-amino-N-(4-hydroxy phenyl)benzamide (AHPB)

2.3 g of the HPNB, 0.1 g of 10% Pd–C, and 130 ml of ethanol were introduced in to the three-neck flask to which 10 ml of hydrazine monohydrate was added dropwise over a period of 1 h at 85 °C. After the complete addition, the reaction was continued at reflex temperature for another 4 h. To the suspension, 20 ml of tetrahydrofuran was added to redissolve the precipitated product, and refluxing was continued for 1 h. The mixture was filtered to remove the Pd–C and the filtrate was poured in to water. The product was filtered off, washed with hot water and dried. (Yield 86%.)

2.3.3. Synthesis of sulfone ether amide diamine (SEAD)

Into a 100-ml, three-necked, round-bottomed flask equipped with a Dean-Stark trap, a condenser, a nitrogen inlet tube, a thermometer, an oil bath, and a magnetic stirrer was placed 0.01 mol of 2,6-dichloropyridine, 25 ml of dry NMP, and 15 ml of dry toluene and 0.021 mol of HNAB. Then 0.0315 mol of K_2CO_3 was added to the mixture and the reaction mixture was heated to 140 °C for 6 h with continuous stirring. The generated water was removed from the reaction mixture by azeotropic distillation. The reaction temperature was raised to 165 °C by removing more toluene, and kept at the same temperature for 18 h. During this time, progress of the reaction was monitored by thin-layer chromatography (TLC). The resulting reaction mixture was cooled and poured into water. Then 100 ml of 3% NaOH was added to the mixture and the mixture was washed repeatedly with a 3% NaOH solution and water. The obtained diamine was dried in a vacuum oven at 60 °C. (Yield 78%.)

2.4. Polyimide synthesis

The synthesis of polyimide typically was carried out as follows: A 100-ml, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube, and calcium chloride drying tube was charged with 2 mmol of the diamine (SEAD) and 15 ml of dry NMP. The mixture was stirred at 0 °C for 0.5 h. Then 2 mmol of dianhydride was added and the mixture was stirred at 0 °C for 1 h. The temperature was raised to room temperature and the solution was stirred for 24 h. Poly(amic acid) was precipitated by pouring the flask content into 200 ml of a 3:1 volume mixture of water and methanol. Then it was filtered, washed with hot water and dried overnight under vacuum at 40 °C. (Yields over 88%.) Chemical cyclization was applied for conversion of poly(amic acid) to polyimide: Into a 100-ml, two-necked, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube, and a reflux condenser was placed 1.0 g of poly(amic acid) and 5 ml of dry DMAc. The mixture was stirred and then 5 ml of acetic