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Novel ferrocene modified poly(amide ether amide)s and investigation of physical and thermal properties

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Abstract

A new diamine containing ferrocene group with preformed ether and amide units was prepared via reaction of 1,1′-ferrocenedicarbonyl chloride with two moles of 2,6-bis(5-amino-1-naphthoxy)pyridine. Polycondensation reactions of the prepared diamine with different aromatic and aliphatic diacid chlorides in the presence of trimethylchlorosilane (TMSCl) resulted in preparation of novel ferrocene modified poly(amide ether amide)s. The monomer and polyamides were characterized and the effect of trimethylchlorosilane (TMSCl) as activating agent on the polymerization reaction was studied. The physical and thermal properties of the polyamides including inherent viscosity, solubility, thermal stability and behavior, flame-retardancy and crystallinity of the polymers were studied. The polymers showed good thermal stability and flame-retardancy, and also improved solubility in polar aprotic solvents.

Keywords: Ferrocene; Diamine; Polyamide; Polycondensation; Thermal stability

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1. Introduction

Polymers containing organometallic structure possess interesting chemical and physical properties that attracted considerable interest from both academic and industrial viewpoints [1,2]. They can be used in a variety of applications including resins for ion and electron exchange, radiation-resistant polymers, flame-retardant polymers, catalysts, organic semi-conductors, photoconductors and ferromagnets [3,4]. Ferrocene-containing polymers possess very outstanding properties including air-, heat-, and photo-chemical stability. These interesting features have made them suitable for a wide spectrum of applications including thermal stability lubricants and thermal stability elastomers [5,6].

Aromatic polyamides are heat resistant polymers that generally exhibit outstanding mechanical properties and excellent thermal and oxidative stability. Because of these properties they are of major commercial and industrial importance. They have generally poor processability caused by limited solubility and high melting or softening temperatures. Considerable efforts to modify the structure of polyamides are continuously under way to enhance their

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processability. Structural modifications such as the introduction of bulky pendant substituents [7], the nature of parent chain (types of linkages and aromatic units) [8], non-coplanar biphenylene moieties [9], and flexible spacers [10] have been reported to improve the solubility and to lower the phase transition temperatures. Among these, the incorporation of flexible or angular linkages into the polymer backbone is one of the effective strategies. Introducing flexible units into polyamide chains or substituents in the dicarboxylic acids and diamines leads to low transition temperatures [11,12]. Various rotatable linkages in the main chain, as well as substituent methyl groups, are important variables for controlling the propensity to form ordered morphologies in these polymers.

In our continuous interest to investigate the preparation of new polyamides with flexible linkages through design of novel monomers [13–19], here we wish to describe the preparation of novel ferrocene modified poly(amide ether amide)s through the synthesis of a new ferrocene-containing diamine with built-in ether and amide units. The diamine was prepared through the reaction of 1,1′-ferrocenedicarbonyl chloride with 2,6-bis(5-amino-1-naphthoxy)pyridine. Ferrocene modified poly(amide ether amide)s were prepared by condensation reactions of this diamine with four different diacid chlorides via two different methods: (a) in the presence of TMSCl as an amine activating agent, (b) in the presence of propylene oxide as an acid scavenger.

2. Experimental

2.1. Materials

All chemicals were purchased either from Merck or Aldrich Chemical Co. *N*-Methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF) and toluene were distilled over calcium hydride under reduced pressure. 2,6-Diaminopyridine was recrystallized from benzene. Terephthaloyl chloride (TPC), and isophthaloyl chloride (IPC) were purified by sublimation.

2.2. Instruments

Infrared measurements were performed on a Bruker-IFS 48 FT-IR spectrometer (Ettlingen, Germany). The H NMR spectra were recorded in dimethyl sulfoxide (DMSO-d_6) solution using a Bruker Avance DPX 250 MHz instrument (GmbH, Germany). A CHN-O-Rapid Heraeus elemental analyzer performed elemental analyses (Wellesley, MA). Differential scanning calorimetry (DSC) was recorded on a Stanton Redcraft STA-780 (London, UK). Thermogravimetric analysis (TGA) and Differential thermogravimetric (DTG) trace were recorded on a Polymer Lab TGA-1500 (London, UK). The dynamic mechanical measurements were performed on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (Model MK-II) over a temperature range of 25–250 °C at 1 Hz and a heating rate of 5 °C/min (Surrey, UK). The value of $\tan\delta$ and the storage modulus versus temperature were recorded for each sample. Inherent viscosities were measured by using an Ubbelohde viscometer in a concentration of 0.5 g/dL in DMF at 30 °C. Wide angle X-ray diffraction was performed at room temperature on an X-ray Jeol Jdx-8030 diffractometer (London, UK) using Ni-filtered Cu Kα radiation (40 kV, 25 mA) with scanning rate of 3 °/min. The weight–average molecular weight (M_w) was determined by gel permeation chromatography (GPC). GPC was performed on a Waters 150 C instrument using Styragel columns and a differential refractometer detector. The molecular weight calibration was carried out using polystyrene standards. Calibration and measurements were made at a flow rate of 1 mL/min, and DMF was used as solvent.

2.3. Monomer synthesis

1,1′-Ferrocenedicarboxylic acid was prepared according to the reported procedure [20]. 2,6-Bis(5-amino-1-naphthoxy)pyridine had been prepared in our laboratory previously [21].

1,1′-Ferrocenedicarbonyl chloride was prepared based on the following method:

> A mixture of 3.25 g (0.012 mol) of 1,1′-ferrocenedicarboxylic acid, 50 mL of dry CH_2Cl_2, 5 mL of freshly distilled oxalyl chloride, and 2 drops of pyridine were poured and stirred in a round-bottomed flask at room temperature under N_2 atmosphere in the dark for 14 h and then refluxed at 40 °C for 6 h. The mixture was distilled to dryness under reduced pressure. The residue was extracted repeatedly at 80 °C with dry petroleum ether (b.p. 100–140). Then the solvent was evaporated under reduced pressure and the product was dried under vacuum at 40 °C (yield 76%).