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Synthesis and characterization of novel optically active poly(amide–imide)s via direct amidation

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Abstract

N,*N*′-Pyromelliticdiimido-di-L-methionine (**3**) was prepared from the reaction of pyromellitic dianhydride (**1**) with L-methionine (**2**) in glacial acetic acid and pyridine solution at refluxing temperature. The direct polycondensation reaction of the monomer diimide–diacid (**3**) with 1,3-phenylenediamine (**4a**), 1,4-phenylenediamine (**4b**), 2,6-diaminopyridine (**4c**), 3,5-diaminopyridine (**4d**), 4,4′-diaminodiphenylether (**4e**) and 4,4′-diaminodiphenylsulfone (**4f**) was carried out in a medium consisting of triphenyl phosphate, *N*-methyl-2-pyrolidone, pyridine and calcium chloride. The resulting poly(amide–imide)s having inherent viscosities 0.45–0.53 dl g^{-1} were obtained in high yields and are optically active and thermally stable. All of the above compounds were fully characterized by IR spectroscopy, elemental analyses and specific rotation. Some structural characterization and physical properties of these new optically active poly(amide–imide)s are reported.

Keywords: *N*,*N*′-Pyromelliticdiimido-di-L-methionine; Poly(amide–imide)s; Direct polycondensation; Optically active and thermally stable polymers

1. Introduction

Thermally stable polymers have received much interest over the past decade, due to increasing demands for high-performance polymers as a replacement for ceramics or metals in the microelectronic, aerospace and automotive industries. Polyimides and their copolymers are certainly one of the most useful classes of high-performance polymers, which have found many applications in those industries [1,2]. Aromatic polyimides are well known as polymer materials of high performance for their excellent thermal stabilities and balanced mechanical and electrical properties [3]. Poor thermoplastic fluidity and solubility are the major problems for wide application of polyimides. However polyamide–imide (**PAI**) is the most successful material, which combines the advantages of high-temperature stability and processability [4]. A notable example is Torlon (Amoco Co.), a commercial PAI obtained from trimellitic anhydride chloride and 4,4′-diaminodiphenylmethane [5]. The synthesis and application of optically active polymers are the newly considerable topics which have been paid more

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attention recently [6a,6b]. Most of the natural polymers are optically active and have special chemical activities, such as catalytic properties that exist in genes, proteins and enzymes. Some other applications are: (1) constructing chiral media for asymmetric synthesis, (2) chiral stationary phases for resolution of racemic mixtures by chromatographic techniques, (3) chiral liquid crystals in ferroelectrics and nonlinear optical devices [7–10]. These applications have caused more considerations to improve different synthetic procedures of optically active polymers. Recently, we have synthesized optically active polymers by different methods [11–13]. The triphenyl phosphate activated polycondensation (phosphorylation reaction) technique for the synthesis of polyamides has been reported by Yamazaki et al. [14]. In this article, we report the synthesis and characterization of new optically active **PAI**s from aromatic diamines and *N*,*N*′-Pyromelliticdiimido-di-L-methionine, a monomer perfor-med imide groups, by the direct polycondensation method.

2. Experimental

2.1. Materials

All chemicals were purchased from Fluka Chemical Co. and Aldrich Chemical Co. Pyromellitic dianhydride was purified by recrystallization from acetic anhydride and 4,4′-diaminodiphenylsulfone (4f) from water/ethanol. 1,3-phenylenediamine (4a), 1,4-phenylenediamine (4b), 2,6-diaminopyridine (4c), 3,5-diaminopyridine (4d) and 4,4′-diaminodiphenylether (4e) were purified by sublimation.

2.2. Techniques

IR spectra were recorded on a FT/IR-680 plus. Band intensities are assigned as weak (w), medium (m), strong (s) and band shapes as shoulder (sh), sharp (s) and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon Fensk routine viscometer. Specific rotations were measured by a JASCO P-1030 Polarimeter. Thermal gravimetric analysis (TGA) data for polymers were obtained by a Mettler TGA-50 in air atmosphere at a rate of 10 °C/min. Differential scanning calorimetry (DSC) data for polymer (**5e**) was obtained by a Mettler DSC-30 under nitrogen atmosphere. Elemental analyses were performed by the Research Institute of Petroleum Industry, Tehran, Iran.

3. Monomer synthesis

Into a 25 ml round-bottomed flask 1.716 g (7.83×10^{-3} mol) of pyromellitic dianhydride (**1**), 2.345 g (1.57×10^{-2} mol) of L-methionine (**2**), 10 ml of mixture of acetic acid and pyridine (3:2) and a stirring bar were placed. The mixture was stirred at r.t. for 2 h and then refluxed for 7 h. The solvents were removed under reduced pressure and 5 ml of cold concentrated HCl was added. A white precipitate was formed, filtered off, washed with hot water and dried to give 3.735 g (99.4%) of compound (**3**). m.p. > 300 °C, $[\alpha]_D^{25} = -80°$ (0.050 g in 10 ml DMF); IR (KBr): 3500–2400 (m, br.), 2910 (m, s), 1700 (s, br), 1380 (s, s), 1249 (w, s), 1106 (m, s), 735 (m, s) cm^{-1}.

Elemental analysis: calculated for $C_{20}H_{20}N_2O_8S_2$, C (50.0%), H (4.2%), N (5.8%); Found, C (50.2%), H (4.3%), N (5.7%).

4. Model compound

The model compound was prepared by a direct amidation method, into a 10 ml round-bottomed flask fitted with a water cooled condenser and a magnetic stirrer, was placed 0.155 g (3.27×10^{-4} mol) of diimide–diacid (**3**), 0.1 g of calcium chloride, 0.327 ml (1.24×10^{-3} mol) of triphenyl phosphate (TPP), 0.29 ml of pyridine, 0.061 g (6.54×10^{-4} mol) of aniline and 0.8 ml of NMP. The mixture was stirred and heated under nitrogen atmosphere in an oil bath at 60 °C for 1 h, then at 90 °C for 0.5 h and finally at 100 °C for 3 h. The reaction mixture was poured into 50 ml of H_2O and precipitated was dissolved in 30 ml of CH_2Cl_2, washed with water (3×15 ml), HCl (5%) (2×15) and $NaHCO_3$ (5%) (2×15) and finally was purified by a short column chromatography (60:40, cyclohexane:acetic acid) to yield 0.197 g (96%, 3.13×10^{-4} mol) of white solid, mp > 300 °C; IR (KBr): 3383 (m, br), 2916 (w, s), 1762 (w, s), 1715 (s, br), 1510 (s, s), 1382 (s, s), 1351 (s, s), 725 (w, s) cm^{-1}.

Elemental analysis: calculated for $C_{32}H_{30}N_4O_6S_2$, C (60.9%), H (4.8%), N (8.9%); Found, C (61.0%), H (4.9%), N (8.5%).

5. Polymerization: synthesis of polymer (5a)

The **PAI**s were prepared by direct polycondensation using the following general procedure: General procedure for polymerization of **5a**: into a 10 ml round-bottomed flask fitted with a water cooled condenser and a magnetic stirrer, was placed 0.155 g (3.27×10^{-4} mol) of diimide–diacid (**3**), 0.1 g of calcium chloride, 0.327 ml (1.24×10^{-3} mol) of triphenyl phosphate, 0.29 ml of pyridine, 0.035 g (3.27×10^{-4} mol) of diamine (**4a**) and 0.8 ml of NMP. The mixture was stirred and heated under nitrogen atmosphere in an oil bath at 60 °C for 1 h, then at 90 °C for 0.5 h and finally at