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Reactive & Functional Polymers 66 (2006) 924–930

REACTIVE & FUNCTIONAL POLYMERS

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Selective reactivity of aromatic amines toward 5-maleimidoisophthalic acid for preparation of polyamides bearing *N*-phenylmaleimide moieties

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Received 17 October 2005; received in revised form 15 December 2005; accepted 20 December 2005
Available online 24 January 2006

Abstract

Both of the maleimide and carboxylic acid groups in 5-maleimidoisophthalic acid (MIPA) are reactive toward an amine group. The selective reaction between carboxylic acid and amine groups was successfully established and applied in preparation of polyamides (PA-MI) and copolyamides possessing maleimide pendants. The chemical structures of the polymers obtained were characterized with FTIR, ^{1}H NMR, and elemental analysis. Some polyamides showed good solubility in organic solvents and are for further chemical modifications. Success of phosphorylation on PA-MI polymers demonstrated this kind of polyamide could be used as reactive polymers for further modification and functionalization.

Keywords: Polyamide; Maleimide; Reactive polymers, Polymer modification

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1. Introduction

Polyamide is one of the most important classes of polymers. Continuous attempts are reported on preparation of new and functional polyamides in recent years. One of the popular targets is to improve the solubility of polyamides without sacrificing their attractive properties [1–3]. Biodegradable and biocompatible polyamides from nature resources have received considerable attentions of studies [4–6]. Searches of new approaches of polyamidation and polyamide synthesis are also attractive [7]. On the other hand, functionalization on polyamides might bring more chemical versatility to the polymers and extend their fields of applications. Choi and Jung [8] interrupted the hydrogen-bonding between amide groups by incorporation of benzodiimide units to polyamide mainchains so as to decrease the chain interactions between polyamides. Gandini et al. [9,10] prepared series of polyamides containing furan moieties in the mainchains. Such polyamides had potential in further functionalization by means of Diels–Alder reaction. Liou et al. [11] prepared polyamides having pendent diphenylamino and carbazolyl groups for using as hole-transporting layer materials in polymeric light

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doi:10.1016/j.reactfunctpolym.2005.12.005

emission diode (PLED). Other examples are polyamides possessing crown ether moieties in the polymer mainchains [12] and in the pendants [13]. These polyamides were cation-binding materials for use in gas separation processes.

Maleimide groups can undergo dimerization and Michael addition reactions under certain reaction conditions. Therefore, aromatic *N*-phenylmaleimide compounds have been used for polymer synthesis. Incorporation of maleimide groups to polymers exhibited effectiveness on increase of crosslinking density, enhancement of thermal stability, and improvement of flame retardancy [14–16]. Therefore, incorporation of maleimide groups to polyamide polymers is attractive. About 20 years ago, De Abajo and coworkers reported their attempts of preparation of such maleimide-containing polyamides (PA-MI) [17,18]. In these work De Abajo et al first converted 5-maleimidoisophthalic acid (MIPA) to its acid chloride analogue by thionyl chloride. The acid chloride compound was then polymerized with aromatic diamines to result in polyamides. The chlorination reaction of MIPA and utilization of acid chloride in a polymerization system made the synthesis route more moisture-sensitive and complicated. In this work, the selective reactivity of aromatic amine toward carboxylic acids, rather than toward maleimide groups, under the polyamidation reaction condition was demonstrated. Basing on the reaction selectivity, PA-MI polyamides were consequently prepared from direct polymerization of MIPA with aromatic diamines. In addition, as prior reports only studied the curing behavior of maleimide groups in PA-MI polymers, we further examined the chemical modification and functionalization of PA-MI polyamide, which would significantly tailor the properties and extend the application fields of polyamides.

2. Experimental

2.1. Materials

5-Maleimidoisophthalic acid (MIPA) was prepared from 5-aminophthalic acid and maleic anhydride according to the reported method [16]. 4,4′-Diaminodiphenylmethane (DDM), 4,4′-oxydianiline (ODA), 4″,4‴-(hexafluoroisopropylidene)-bis-4-phenoxyaniline (6FPPA), and 4,4′-(hexafluoroisopropylidene)dianiline (6FDA) were purchased from Aldrich Chemical company and used as received. 1,3-Bis(4-aminophenoxy)benzene (APB), 4,4′-dicarboxydiphenylether (DCDPE), and 9,10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) were received from TCI company (Tokyo, Japan). 2DOPO-A was prepared in the laboratory by the reported method [19].

2.2. Characterization

FTIR spectra were measured with a Perkin Elmer Spectrum One FTIR. ^{1}H and ^{31}P NMR NMR spectra were recorded with a Brüker MSL-300 (300 MHz) NMR spectrometer. Thermogravimetric analysis (TGA) was performed by a Thermal Analysis TGA-2050 at a heating rate of 10 °C/min under nitrogen or air atmosphere. The gas flow rate was 100 ml/min. Elemental analysis was measured with a Heraeus CHN-O rapid elementary analyzer with benzoic acid as a standard. Inherent viscosity was measured with a polymer solution of 0.5 g/dl in NMP at 25 °C.

2.3. Preparation of polyamides

All polyamides were obtained through the same manners. The preparation of PA-1 was shown below as an example. DDM (1.98 g, 10 mmol) and MIPA (2.62 g, 10 mol) were dissolved in 30 ml of *N*-methyl-2-pyrrolidone (NMP). The solution was charged into a 250 ml round-bottom flask. After addition of triphenylphosphite (TPP, 32 ml), pyridine (32 ml), and calcium chloride (0.8 g), the solution was stirred at 100 °C for 3 h. After cooling to room temperature, the reaction mixture was poured into a large excess of methanol. The precipitate was filtered, washed with methanol and hot water. The obtained polymer was continuously extracted with hot methanol for 4 h. After being dried under vacuum at 150 °C for 24 h, polyamide (PA-1) was obtained with a yield of 89%. Elemental analysis, Calculated: C, 70.92%, H, 4.02%, N, 9.93%. Found: C, 70.12%, H, 3.88%, N, 9.25%.

2.4. Phosphorylation on polyamide

PA-4 (0.5 g) and excess amount of DOPO were charged into a 50 ml round-bottom flask. The mixture was heated to 130 °C, and PA-4 was observe to dissolve in the molten DOPO. The solution was reacted at 130 °C for 6 h, and then poured into excess methanol. The precipitate was filtered, washed with toluene and methanol, and then dried