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Synthesis and characterisation of poly(ester-amide)s from aromatic bisoxazoline precursors

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ABSTRACT

A series of novel aliphatic aromatic poly(ester-amide)s (PEA) have been synthesized by condensation reaction of aromatic bisoxazolines with aliphatic dicarboxylic compounds. These polymers have a number average molecular weight of 20,000–25,000. Depending of the aromatic structure of the bisoxazoline precursor, they are either amorphous or semi-crystalline. A good solubility in aprotic solvents was observed for all PEAs.

1. Introduction

Fully aromatic polyamides are well known as high-performance polymer materials with outstanding mechanical properties, good thermal and chemical stabilities [1–3]. However, their applications were restricted in some areas because of their very high melting temperatures, and limited solubility in common organic solvents. On the other hand, aromatic polyesters are recognized as the high performance engineering plastics. However, their thermal–mechanical properties are, in general, not optimal in many end use applications. Another interesting class of polyesters is the aliphatic ones because of their biodegradable character. So combining the key properties of both polyamides, and polyesters appeared as a promising way to access to new polymer materials. In this connection, number research works were focused on the synthesis of various aliphatic poly(ester-amide)s [4–10]. Research works on aromatic poly(ester-amide)s were achieved leading to the development of thermoplastic polymers with high thermal and mechanical properties, and a good solubility in common organic solvents [11–14]. Aromatic aliphatic poly(ester-amide)s were also investigated. For example, Böhme et al. [15] have prepared alternating poly(ester-amide)s by polyaddition reaction of aromatic bisoxazolines with aliphatic dicarboxylic acids.

In addition of thermal and mechanical properties, polymers in many applications must show capacities to fire resistance. Considerable attention has been directed towards this aspect [16,17]. Among the flame-retardant polymers that were developed those containing phosphine oxide moieties were widely investigated [18–21].

Herein, the synthesis and characterisation of a series of new aromatic aliphatic polyesteramides (PEAs) obtained from polymerization of bisoxazoline aromatic compounds with aliphatic linear or cyclic dicarboxylic acid are reported.

2. Experimental

2.1. Materials

Bis(4-carboxyphenyl)phenylphosphine oxide was prepared as describe previously [22].

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Bis(4-carboxyphenyl)ether was washed several times by THF before use. All other reagents were purchased from Aldrich Chemical Co.

The solvents used for polymerization and measurement were used as received.

2.2. Measurements

The ^1H, ^{13}C and ^{31}P NMR spectra were recorded at ambient temperature on a 200 and 400 MHz Bruker AM spectrometers, using deuterated dimethylsulfoxide (DMSO-d_6) as a solvent, with tetramethylsilane (TMS) as internal standard.

A TA instruments apparatus (model 2950) was used for thermogravimetric analysis (TGA) of the polymers. Scans were run from 20 to 700 °C at a heating rate of 10 °C/min in an air atmosphere. The glass transition temperatures (T_g) were obtained by differential scanning calorimetry (DSC) on a Mettler Toledo DSC 822e. Scans were run at 5 °C/min in inert atmosphere. The values were reported from a second scan after heating and rapid cooling.

Molecular weights of the polymers were determined by size exclusion chromatography (SEC) on a system equipped with a Waters 515HPLC pump, a differential refractive index detector (Wyatt optilab-rEX). DMF containing 0.05 M LiBr was used as mobile phase. SEC analyses were performed on two PL gel Mixed D columns at 70 °C. The molecular weights were calculated relative to standard polystyrene samples.

2.3. Precursor synthesis

2.3.1. Bis(4-(2-oxazolylphenyl))phenylphosphine oxide(BOOT2P)

2.3.1.1. Bis(4-chlorocarbonylphenyl)phenylphosphine oxide. 5 g (0.0136 mol) of bis(4-carboxyphenyl)phenylphosphine oxide, 19.45 ml (0.272 mol) of thionyl chloride and 1 ml of *N*,*N*-dimethylformamide were placed in a 100-ml two-necked round bottom flask, equipped with a condenser, a nitrogen inlet, and a magnetic stirrer. The reaction mixture was reached to reflux temperature for 2 h. Then, the excess of thionyl chloride was removed by distillation under vacuum.

The same method was used to obtain the bis(4-chlorocarbonylphenyl)ether from the bis(4-carboxyphenyl)ether.

2.3.1.2. Bis(4-(chloroethylamide)phenyl)phenylphosphine oxide. A solution of 5.5 g (0.0136 mol) of bis(4-chlorocarbonylphenyl)phenylphosphine oxide in 25 ml of chloroform placed in additional funnel was added dropwise to a 100-ml three-necked round bottom flask equipped with a condenser, a nitrogen inlet, and a magnetic stirrer, and containing a mixture of 3.95 g (0.0341 mol) of 2-chloroethylamine hydrochloride, 3.98 g (0.0709 mol) of KOH and 25 ml of water maintained at 0 °C. After complete addition, the reaction mixture was kept at room temperature overnight. By evaporation of the CH_2Cl_2 the product precipitated in presence of water and then was isolated by filtration.

The same operating conditions were used to obtain the bis((4-chloroethylamide)phenyl)ether.

2.3.1.3. Bis(4-oxazolylphenyl)phenylphosphine oxide. 6.65 g (0.0136 mol) of bis(4-(chloroethylamide)phenyl)phenylphosphine oxide, 3.05 g (0.0544 mol) of KOH and 30 ml of methanol placed in a 100-ml two-necked round bottom flask equipped with a condenser, a nitrogen inlet, and a magnetic stirrer were refluxed for 4 h. The methanol was then evaporated and the solid obtained was washed with 300 ml water to eliminate the formed salt. After filtration, the expected product was dried at 80 °C under vacuum for 6 h. The mp of the compound is 253–254 °C.

RMN ^{31}P (ppm, DMSO-d_6): δ 24.64 ppm (P=O). RMN ^1H (ppm, DMSO-d_6): δ 7.5–8.2 (m, 13H, H_{ar}), 3.98 (t, 4H, –CO–HN–**CH**$_2$– oxazoline ring), 4.41 (t, 4H, –**CH**$_2$–O– oxazoline ring).

RMN ^{13}C (ppm, DMSO-d_6) : δ 55 (–CO–HN–**CH**$_2$– oxazoline ring); 68.1 (–**CH**$_2$–O– oxazoline ring); 128.3; 129.3; 131.2; 132.1; 132.4; 132.8; 134.83; 136.8 (C_{ar}); 162.7 (–**CO**–HN– oxazoline ring) .

The bis(4-(2-oxazolylphenyl)ether (BODPE) was synthesized in quite similar conditions. Only the drying step of the isolated product was different: At 50 °C under vacuum overnight. The mp of the compound is 64–65 °C.

RMN ^1H (ppm, DMSO-d_6): δ7.11–7.88 (dd, 8H, H_{ar}), 3.91 (t, 4H, –CO–HN–CH_2– oxazoline ring), 4.39 (t, 4H, –CH_2–O– oxazoline ring).

RMN ^{13}C (ppm, DMSO-d_6): δ 55 (–CO–HN–CH_2– oxazoline ring); 67.9 (–CH_2–O– oxazoline ring); 119.1; 123.9; 131.2; 130.4; 159; 163 (–CO–HN– oxazoline ring).

2.3.2. Synthesis of the polymers 1a–1d

In a 50-ml two-necked cylinder flask equipped with a mechanical stirrer, and a nitrogen inlet were placed 1.6 mmol of bisoxazoline, and 1.6 mmol of dicarboxylic acid. The reaction mixture was heated to 150 °C for 1 h, at 180 °C for 1 h and then at 200 °C for 20 h. After cooling the resulting polymer was dissolved in 1 ml of *N*-methylpyrrolidone (NMP) and poured into methanol. The precipitated polymer was collected by filtration washed several times with methanol and dried at 80 °C under vacuum for 48 h.

2.3.3. Synthesis of the polymers 2a–2d

In a 50-ml two-necked cylinder flask equipped with a mechanical stirrer, and a nitrogen inlet were introduced 0.016 mol of bisoxazoline, and 0.016 mol of dicarboxylic acid along with 18 ml of NMP. The solution was then heated at 150 °C for 1 h, at 180 °C for 1 h and at 200 °C for 5 h. After cooling the reaction mixture was poured into methanol. The precipitated polymer was collected by filtration washed several times with methanol and dried at 80 °C for 48 h.

3. Results and discussion

3.1. Bisoxazoline precursor synthesis

As illustrated in Scheme 1, the synthesis of both BOOT2P and BODPE bisoxazoline compounds involved three distinguished steps: First, the dicarboxylic acid compound was transformed into acid chloride counterpart by