



Novel rigid rod polymers from a thermal cyclization reaction



Fabio Borbone^{a,*}, Oreste Tarallo^a, Valentina Roviello^b, Ugo Caruso^a, Beniamino Pirozzi^a, Antonio Roviello^a

^a Department of Chemical Sciences, University of Napoli Federico II, Complesso Monte S. Angelo, Via Cintia snc, 80126 Napoli, Italy

^b Department of Civil, Construction and Environmental Engineering, University of Napoli Federico II, Via Claudio 21, 80125 Napoli, Italy

ARTICLE INFO

Article history:

Received 1 September 2014

Received in revised form 9 December 2014

Accepted 10 December 2014

Available online 18 December 2014

Keywords:

Rigid rod

Cyclization

Liquid crystals

Fiber

Polyamide

ABSTRACT

A new type of rigid rod polymer is reported, easily obtained by thermal cyclization of a soluble/meltable polyamidic precursor. The polyamides are based on a diaminobenzodifurane monomer and are prepared by polycondensation reaction. The polymers are characterized by NMR, FTIR, GPC, TGA, DSC. The cyclization reaction produces insoluble/unmeltable benzodifuroxazinonic based polymers with rigid rod structure. Due to their thermotropic liquid crystalline behavior the polyamides are easily obtained from melt as oriented films under shear and as fibers by extrusion. High degree of orientation and smectic-like arrangement of polyamides are demonstrated by X-ray fiber diffraction. Retention of the orientation upon cyclization is demonstrated by XRFD, optical and electron microscopy.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Polymers with rigid structure have always attracted much interest because they can match high mechanical properties with outstanding temperature resistance [1]. Noteworthy examples are aramidic polymers such as Kevlar [2], whose regular rigid structure and high orientation give rise to high modulus and excellent thermal stability. Another highly performing polymer is Vectra, a copolymer of 4-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid which is also melt-spinnable [3]. In the last decades, besides these aromatic systems rigid rod heterocyclic polymers have had extensive development in the production of fibers [4–8]. Such polymers feature an even higher rigidity of the chains due to the presence of fused heteroaromatic cycles linked by isolated single bonds. In this configuration the degrees of freedom are limited to the sole rotation around single bonds lying along the chain axis leading to rigid rod polymers. The rigid backbone of the

chain often confers lyotropic or thermotropic liquid crystallinity to these polymers, which can be exploited in the production of fibers with high orientation without the need for drawing. However the rigid aromatic structure represents also a drawback for processing, inasmuch the polymers show very low solubility in many solvents (except sulfuric or polyphosphoric acid in some cases) and decompose at high temperatures without melting. The most representative rigid rod polymers known are poly(p-phenylene benzobisoxazole) (PBO) and poly(p-phenylene benzobisthiazole) (PBT) [9–13]. Both are synthesized by condensation reaction between terephthalic acid and respectively 4,6-diamino-1,3-benzenediol dihydrochloride and 2,5-diamino-1,4-benzenedithiol dihydrochloride in polyphosphoric acid. PBO shows a lyotropic liquid-crystalline behavior and can be transformed into fibers (similar to Kevlar) with high decomposition temperature around 620 °C. The presence of electronegative atoms in the skeleton of some of these polymers can also be useful to improve their mechanical properties by exploiting the effect of intermolecular hydrogen bonds, as in the case of polypyridobisimidazoles such as PIPD (poly(2,6-diimi-

* Corresponding author. Tel.: +39 081 674446.

E-mail address: fabio.borbone@unina.it (F. Borbone).

dazo(4,5-b:4'5'-e) pyridinylene-1,4-(2,5-dihydroxy)phenylene) [14]. Due to the great thermal and mechanical characteristics of rigid rod heterocyclic polymers, one topic of interest is the improvement of their processability, for example through the synthesis of meltable/soluble precursor polymers. This goal can be achieved through the introduction of solubilizing groups such as halogens or alkyls. Recently we have demonstrated the formation of compounds containing a five-rings fused heterocycle benzodifuroxazinone prepared through a thermally sustained cyclization reaction [15]. Some derivatives containing fluorinated moieties were synthesized and characterized, featuring an outstanding thermal stability in air, an uncommon enhancement of fluorescent properties in the solid state, an all-planar conformation with π -stacking structure. In the present work we propose the synthesis and characterization of a new type of rigid chain polymers which can be potentially useful for the manufacture of fibers. These polymers are based on a benzodifuroxazinonic repeating unit and can be obtained by thermal cyclization of soluble/meltable diaminobenzodifurane based polyamides, easily synthesized through a polycondensation reaction. The polymers were characterized by NMR, IR, GPC, TGA, DSC, XRD, Optical and Electron Microscopy.

2. Experimental section

All solvents and reagents were purchased from Sigma Aldrich. Optical observations were performed by using a Zeiss Axioscop polarizing microscope equipped with a FP90 Mettler heating stage. Thermal characterization was performed using Perkin Elmer Pyris 1 DSC at a scanning rate of 10 °C/min, under nitrogen flow. Thermogravimetric analysis were performed in air by a TA Instruments SDT 2960 Simultaneous DSC-TGA. Molecular weight characterizations were performed in dimethylsulfoxide with 0.01 M lithium bromide, at 95 °C, on an Agilent PL-GPC 120 instrument and with PMMA calibrants. NMR spectra were recorded on a Varian Spectrometer operating at 200 MHz. UV-Visible and FT-IR (KBr) spectra were recorded with JASCO spectrometers. X-ray diffraction experiments were performed with an automatic Philips diffractometer.

2.1. Synthesis of dioctyl 2,6-diaminobenzo [1,2-b:4,5-b']difuran-3,7-dicarboxylate (BF8)

An amount of 2.00 g of 1,4-benzoquinone (18.5 mmol) was dissolved in 40 mL of absolute ethanol. Octyl cyanoacetate (4.5 mL, 26.5 mmol) and then 7.0 mL of ammonia solution 30 wt%. were added under stirring to the solution at room temperature. The addition of ammonia led to raising of the temperature to about 40 °C and precipitation of a gray solid. After 30 min under stirring the product was filtered under vacuum, washed with small amounts of absolute ethanol and air dried (Yield 35%). ¹H NMR (200 MHz, DMSO-*d*₆, δ): 7.61(s, 4H), 7.29 (s, 2H), 4.19 (t, *J* = 6.6 Hz, 4H), 1.70 (m, 4H), 1.41 (m, 4H), 1.26 (m, 16H), 0.81 (t, *J* = 6.6 Hz, 6H).

2.2. Synthesis of dimethyl 2-chloroterephthalate

The diazonium salt of dimethyl 2-aminoterephthalate was prepared according to a typical method [16]. The salt obtained from 5.23 g of dimethyl 2-aminoterephthalate (25.0 mmol) was poured into a beaker containing 2.97 g (30.0 mmol) of CuCl placed in an ice bath. A green solid precipitated, which was recovered by vacuum filtration and washed with water to neutralize the acidity. The solid was crystallized in boiling heptane (Yield 68%). ¹H NMR (200 MHz, DMSO-*d*₆, δ): 8.1 (s, 1H), 7.9 (d, *J* = 7.8, 1H), 7.8 (d, *J* = 7.8, 1H), 3.9 (s, 6H).

2.3. Synthesis of 2-chloroterephthaloyl chloride

Dimethyl 2-chloroterephthalate was hydrolyzed with KOH in water/ethanol, the acid was precipitated with HCl, filtered and washed with water. The chloride derivative was obtained by refluxing in thionyl chloride and purified by distillation. ¹H NMR (200 MHz, CHCl₃-*d*, δ): 8.2 (s, 1H), 8.06 (d, 1H), 8.07 (d, 1H).

2.4. Polyamides

Triethylamine and N-methylpyrrolidone used in the reaction were subjected to anhydrication. The same synthetic procedure was used for both polymers. By way of example the procedure for PBF1 will be described. An amount of 0.512 g (1.02 mmol) of BF8 and 0.207 g (1.02 mmol) of terephthaloyl chloride was added to 2 mL of hot N-methylpyrrolidone under stirring. The system was placed in a bath at 150 °C under nitrogen flow and 0.292 mL (2.10 mmol) of triethylamine were added. The reaction was kept for 10 min. The orange-colored polymer was precipitated in distilled water, washed with distilled water and air dried. The polymer was purified through Soxhlet extraction in acetone. Yield: 78%.

2.5. Polybenzodifuroxazinones

The cyclized polymers PBFO1 and PBFO2 were obtained by thermal treatment at 300 °C in nitrogen for 4 h.

2.6. Fiber extrusion

About 0.2 g of polymer were put in 1 mL glass syringe. By means of a heat gun the syringe was heated at about 200 °C while the polymer was extruded by pushing the piston. The obtained fiber was subsequently cyclized in an heating stage under nitrogen flow.

3. Results and discussion

The synthesized polyamides are based on dioctyl ester of 2,6-diaminobenzo[1,2-b:4,5-b']difuran-3,7-dicarboxylic acid (BF8), where the octyl chain was chosen to improve solubility. Two acyl chlorides were chosen for the polymerization reaction, terephthaloyl chloride and 2-chloro-terephthaloyl chloride. The terephthaloyl chloride is a classic reagent in the reactions of formation of

Download English Version:

<https://daneshyari.com/en/article/1395427>

Download Persian Version:

<https://daneshyari.com/article/1395427>

[Daneshyari.com](https://daneshyari.com)