European Polymer Journal 68 (2015) 115–127

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

On the bio-based furanic polyesters: Synthesis and thermal behavior study of poly(octylene furanoate) using fast and temperature modulated scanning calorimetry

George Z. Papageorgiou [a,*], Nathanael Guigo [b], Vasilios Tsanaktsis [c], Dimitrios G. Papageorgiou [d], Stylianos Exarhopoulos [a,e], Nicolas Sbirrazzuoli [b], Dimitrios N. Bikiaris [c,*]

[a] Chemistry Department, University of Ioannina, P.O. Box 1186, 45110 Ioannina, Greece
[b] Université Nice Sophia Antipolis, CNRS, Laboratoire de Physique de la Matière Condensée LPMC – UMR 7336, Parc Valrose, 06100 Nice, France
[c] Laboratory of Polymer Chemistry and Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-541 24 Thessaloniki, Macedonia, Greece
[d] School of Materials, University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom
[e] Department of Food Technology, Technological Educational Institute of Thessaloniki, PO Box 141, GR-57400 Thessaloniki, Greece

ARTICLE INFO

Article history:
Received 23 February 2015
Received in revised form 9 April 2015
Accepted 10 April 2015
Available online 23 April 2015

Keywords:
Poly(octylene 2,5-furan dicarboxylate)
Biobased polyesters
Crystallization
Melting behavior
Fast scanning calorimetry

ABSTRACT

Nowadays, there is a constantly growing interest on furanoate-based polyesters in an attempt to substitute the terephthalate-based ones, which are petrochemical-derived. In the present work, the melt polycondensation method has been applied for the preparation of a bio-based furanic polyester, poly(octylene furanoate) (POF). Modern calorimetric approaches such as temperature modulation (TMDSC) and Fast Scanning Calorimetry (FSC) have been employed for the thorough study of the thermal characteristics of the specific polymer, which are described for the first time in literature. The glass transition temperature was found equal to −5 °C, while the equilibrium melting temperature was 157 °C. Additionally, a crystallization regime I to regime II transition was observed at 128 °C as a breakpoint in the Lauritzen–Hoffman plot. The extensive recrystallization was realized by both TMDSC and FSC, since even rates equal to 1000 °C/s could not prevent the phenomenon from occurring. Finally, from the polarized optical microscopy images it was found out that the size of POF spherulites was less than 10 μm.

1. Introduction

Nowadays, there is a growing demand for new polymers prepared from monomers derived from renewable resources, especially for plastics having enhanced properties [1]. 2,5-Furandicarboxylic acid (FDCA) and vanillic acid are two of the most important examples of aromatic monomers from renewable resources and they can be formed starting from carbohydrates or lignin [2]. Furfural and hydroxymethylfurfural (HMF), which are available from saccharide sources, can be used for synthesis of FDCA and other monomers [3,4]. Following the biorefinery concept, novel approaches to the preparation of hydroxymethylfurfural can lead the way to the large-scale production of FDCA which is used for the synthesis of poly(ethylene-2,5-furandicarboxylate) (PEF), among others [5,6]. As a matter of fact, polyesters of FDCA like PEF and poly(butylene 2,5-furan dicarboxylate) (PBF) are currently considered as the biobased alternatives of terephthalates [3,7]. The structure of FDCA is similar to terephthalic acid

---

[*] Corresponding authors.

E-mail addresses: gzpap@cc.uoi.gr (G.Z. Papageorgiou), dbic@chem.auth.gr (D.N. Bikiaris).

http://dx.doi.org/10.1016/j.eurpolymj.2015.04.011
0014-3057/

(TPA), so FDCA has been considered as viable replacement for TPA [8–13]. According to the U.S. Department of Energy, FDCA is one of the most important building blocks or top value-added chemicals derived from biomass [14]. It is a member of the furan family and has a large potential as alternative monomer in order to replace the already used form oil sources in synthesis of polyesters, polyurethanes, and polyamides [15,16].

Although furanoates have been reported for decades [17–19], in the early attempts polyesters with low molecular weight and brown to black color were only obtained [20]. The main reason for these problems was the decomposition of FDCA during the polymerization process. Recently, Gandini et al. reported the synthesis and some properties of polyesters based on FDCA and ethylene glycol or some other diols [21]. The synthesis and characterization of bio-based furanic polyesters or copolyesters with ethylene glycol or other diols has been also reported in a few recent works [8,10,16,22–24]. Such polyesters can be used for films, fibers, bottles, thermoforming articles, etc., and are proposed as alternative materials for the already used alipharomatic polyesters (PET, PBT, etc.), due to their favorable properties.

The aim of the present work is to synthesize another new polyester of the furanoate series like poly(octylene furanoate) (POF) and its thermal behavior to be extensively studied. The polyester was initially characterized by intrinsic viscosity measurement and gel permeation chromatography for molecular weight determination and by proton magnetic resonance (^{1}H NMR) to identify the chemical structure. The solid state structure was characterized by Wide Angle X-ray Diffractometry (WAXD) and standard Differential Scanning Calorimetry (DSC). The thermal behavior of the polyester however, was thoroughly investigated by using Temperature Modulated DSC (TMDSC) and Fast Scanning Calorimetry (FSC). The latter is a powerful and not widely available tool in polymer characterization since heating or cooling scans allow calorimetric measurements up to thousands of degrees per seconds can be performed and this enables investigation of nucleation and crystallization on dynamic conditions or study of complex phenomena like multiple melting and re-crystallization on heating.

2. Experimental

2.1. Materials

2,5-Furan dicarboxylic acid (purum 97%), 1,8-octanediol (98%, m.p. = 57–61 °C and b.p. = 172 °C/20 mmHg) and tetrabutyl titanate (TBT) catalyst of analytical grade were purchased from Aldrich Co. All other materials and solvents used were of analytical grade.

2.2. Synthesis of 2,5-dimethylfuran-dicarboxylate (DMFD)

15.6 g of 2,5-furandicarboxylic acid, 200 mL of anhydrous methanol and 2 mL of concentrated sulfuric acid was transferred into a random flask (500 ml) and the mixture was refluxed for 5 h. The excess of the methanol was distilled and the solution was filtered through a disposable Teflon membrane filter. During filtration dimethylester was precipitated as white powder and after cooling 100 mL of distilled water was added. The dispersion was partially neutralized by adding Na_2CO_3 5% w/v during stirring while pH was measured continuously. The white powder was filtered and the solid was washed several times with distilled water and dried. The isolated white methylester was recrystallized with a mixture of 50/50 v/v methanol/water. After cooling 2,5-dimethylfuran-dicarboxylate (DMFD) was precipitated in the form of white needles. The reaction yield was calculated at 83%.

2.3. Polyester synthesis

The polyester was prepared using a variation of the two-stage melt polycondensation method (esterification and polycondensation) in a glass batch reactor. DMFD and 1,8-octamethylenediol at a molar ratio of diester/diol = 1/2 were charged into the reaction tube of the polyesterification apparatus. The reaction mixture was heated at 150 °C under argon atmosphere for 2 h, at 160 °C for additional 2 h and finally at 110 °C for 1 h. This first step (transesterification) is considered to complete after the collection of almost all the theoretical amount of CH_3OH, which was removed from the reaction mixture by distillation and collected in a graduate cylinder. After this stage the corresponding bishydroxyoctamethylene-2,5-furan carboxylate (BHOFD) has been formed. In the second stage BHOFD has been reacted with DMFD in a molar ratio 1/1.05 at 150 °C under argon atmosphere for 2 h, at 160 °C for additional 2 h and finally at 170 °C for 1 h. During this stage methanol was also removed as byproduct. After that time in the third step of polycondensation a vacuum (5.0 Pa) was applied slowly over a period of time of about 30 min. The temperature was increased to 210 °C and the polymerization was continued for 1 h at this temperature, at 220 °C for 1 h and at 230 °C for 1 h using a stirring speed 720 rpm. After the polycondensation reaction was completed, the polyester was easily removed, milled and washed with methanol.

2.4. Polyester characterization

2.4.1. Intrinsic viscosity and molecular weight measurement

Intrinsic viscosity [η] measurements were performed using an Ubbelohde viscometer at 30 °C in a mixture of phenol/1,1,2,2-tetrachloroethane (60/40, w/w). Number-average molecular weight (M_w) was measured by Gel permeation chromatography (GPC) using a Waters 150 °C apparatus equipped with differential refractometer as detector and three ultrastyragel (103, 104, 105 Å) columns in series. Tetrahydrofuran was used as mobile phase at a flow rate 0.5 mL/min at 40 °C. Calibration was performed using polystyrene standards with a narrow molecular weight distribution.

2.4.2. Nuclear magnetic resonance (^{1}H NMR)

^{1}H NMR spectra of polyesters were obtained with a Bruker spectrometer operating at a frequency of 400 MHz for protons. Deuterated trifluoroacetic acid (dTFA) was