



Ordered structures of poly(butylene 2,5-thiophenedicarboxylate) and their impact on material functional properties

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ABSTRACT

In this contribution, the effect of ordered structures on the functional properties of poly(butylene 2,5-thiophenedicarboxylate) (PBTF) has been studied. By employing a different raw material, i.e. dimethyl-2,5-thiophenedicarboxylate instead of 2,5-thiophenedicarboxylic acid, it has been possible to modulate PBTF mechanical properties and gas permeability, owing to a different degree of crystallinity and amount of mesophase.

Furthermore, PBTF polymorphism is unveiled as three different crystalline structures have been described. The most thermodynamically stable structure has been also identified.

1. Introduction

A recent study estimates that up to 2015 about 6300 Mt of plastic waste had been globally produced, 79% of which accumulated in the environment over the years [1].

Worldwide, 40% of plastic market is dedicated to packaging [2] and, to date, about 99% of polymers used in the packaging industry are derived from fossil resources. Furthermore, they are recalcitrant to biodegradation and can persist undegraded for decades, thus plastic packaging represents an important source of pollution, especially for aquatic ecosystems [3]. This effect is even clearer if we consider that packaging is a short shelf life item and, when contaminated by food contact, its recycling is not a suitable option [4].

In this framework, many research efforts have been focused on finding greener packaging solutions, in particular through the development of biobased and/or biodegradable polymers with suitable characteristics for the above mentioned application. Natural polymers, such as cellulose, chitin and starch have been widely explored since they are abundant and biomass-derived [5]. However, they usually display low water resistance and poor processability [6]. Another very promising polymeric class is represented by polyesters. Their success is mainly due to their cost-effectiveness, easy processability, i.e. they are thermoplastics like polyolefines, and good thermo-mechanical

properties. Moreover, most raw materials can be extracted both from fossil and renewable resources and, with the exception of highly aromatic polyesters, their biodegradability has been extensively proven [7–12]. Among others, the most well-known are poly(lactic acid) [13] poly(butylene adipate-co-terephthalate) [14], poly(butylene succinate) [15] and poly(ethylene furanoate) (PEF) [16]. In particular, PEF has attracted considerable attention in the last years due to its exceptionally low gas permeability with respect to poly(ethylene terephthalate) [17–20].

Recently, poly(butylene 2,5-thiophenedicarboxylate) (PBTF) has been proposed as a possible alternative to PEF, especially for flexible packaging applications [21,22]. Besides the possibility to obtain its raw materials from natural sources [23–25], PBTF display good thermal stability, high melting temperature and stretchability, and very low gas permeability, i.e. better barrier performances than PEF [21]. These peculiar characteristics are due to the presence of a 2D ordered phase, generally denoted as mesophase, which generates high macromolecular packing density. Differently from previous reports [21,22], in this contribution PBTF has been synthesized starting from dimethyl-2,5-thiophenedicarboxylate (DMTFDC) in two different molecular weights and the PBTF polymorphs have been for the first time unveiled. The stability of the various crystalline phases has been deeply investigated and the effect of the ordered structures on mechanical and gas barrier

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behavior has been demonstrated.

2. Experimental

2.1. Materials

2,5-thiophenedicarboxylic acid (TFDCA) (97%) was purchased from TCI (Tokyo, Japan). Hexafluoro-2-propanol (HFP), thionyl chloride, chloroform, methanol, trifluoroacetic acid (TFA), deuterated dimethylsulfoxide (d6-DMSO), deuterated chloroform (CDCl₃), 1,4-butanediol (BD) (99%), and titanium tetrabutoxide (TBT, 97%) were obtained from Sigma Aldrich (Saint Louis, MO, USA). TBT was distilled before use, while other products were used as received.

2.2. Dimethyl-2,5-thiophenedicarboxylate synthesis

5.00 g (29 mmol) of TFDCA and 70 mL (1.74 mol) of anhydrous methanol were placed into a round-bottom flask and the mixture was heated to 70 °C under reflux up to complete dissolution. After cooling to room temperature, 5.1 mL of thionyl chloride were added dropwise. Then, the mixture was heated to 70 °C and let react for 3 h under reflux. During cooling, dimethyl-2,5-thiophenedicarboxylate precipitated as white powder, recovered by filtration and washed several times with methanol. The product was recrystallized by dissolution in methanol at 60 °C and subsequent quenching in ice bath. DMTFDC precipitated in the form of white needles and dried under vacuum. The reaction yield was equal to 92%.

2.3. Polyester synthesis

PBTF was prepared by two-step melt polycondensation by reacting DMTFDC (7.00 g, 35 mmol) with BD (7.88 g, 87.5 mmol) in the presence of 200 ppm/g_{polymer} of TBT.

A 200 mL glass reactor was placed in a silicon oil bath, and the reaction mixture was stirred at 100 rpm by a two-bladed centrifugal stirrer connected to an overhead motor (IKA-Werke GmbH & Co., Staufen, Germany). Nitrogen flow was applied and the temperature was set to 170 °C. When more than 90% of the methanol produced during transesterification was recovered (about 3 h, I step), pressure and temperature were gradually reduced to 0.1 mbar and increased to 230 °C. Polymerization was stopped when constant torque was measured (3 additional hours, II step) to obtain high molecular weight polymer (hereinafter referred to as h₁PBTF). To synthesize low molecular weight PBTF (l₁PBTF), the II step was ended after 1 h.

Lastly, PBTF from TFDCA and BD was prepared according to the procedure previously described [21].

As-synthesized polymers were purified through dissolution in a mixture hexafluoro-2-propanol/chloroform and precipitation in methanol. Purified polymers, in the form of white floccules, were dried at 30 °C under vacuum to constant weight. Thin films of about 150 μm thickness were fabricated by compression molding using a Carver press according to the following procedure: purified powder was placed in between two Teflon plates and heated to 180 °C until complete melting. Then, a pressure of 5 tons m⁻² was applied for 2 min. The film was finally cooled to 23 °C in press by using tap water. Film thickness was determined by a Sample Thickness Tester DM-G (Brugger Feinmechanik GmbH, Munich, Germany). The reported value represents the mean thickness of three experimental tests, each run on 10 different points of the polymer film surface.

2.4. Molecular and thermal characterization

The structure of DMTFDC and PBTF were verified by proton nuclear magnetic resonance (¹H NMR) spectroscopy at room temperature, using a Varian Inova 400-MHz instrument. For DMTFDC d6-DMSO was used as solvent, while for PBTF a CDCl₃/TFA mixture (90:10 v/v) was

employed. Gel-permeation chromatography (GPC) was carried out at 30 °C on a 1100 HPLC system (Agilent Technologies) equipped with PLgel 5-mm MiniMIX-C column. A CHCl₃/HFP mixture (95:5 v/v) as eluent with a 0.3 mL min⁻¹ flow and sample concentrations of about 2 mg mL⁻¹ were adopted. Calibration curve was obtained using polystyrene standards in the range of 800–100,000 g mol⁻¹.

Thermogravimetric analysis (TGA) was carried out under nitrogen atmosphere (40 mL min⁻¹) on a Perkin Elmer TGA7 at 10 °C/min in the range 40–700 °C (sample weight of about 8 mg). For calorimetric measurements, a Perkin Elmer DSC6 was employed. Weighed samples of c.a. 10 mg encapsulated in aluminium pans were heated from –40 °C to 190 °C at 20 °C min⁻¹ (I scan), held for 3 min and then quenched to –40 °C. Lastly, the procedure adopted for I scan was repeated (II scan).

2.5. Structural characterization

The patterns of X-ray diffraction were acquired in reflection mode (step size 0.1°, 250 s/step) by using a PANalytical X'PertPro diffractometer equipped with a copper target, λ = 0.15418 nm, and a fast solid state X'Celerator detector. *In situ* measurements were carried out using an Anton Paar TTK450 device mounted inside the diffractometer. To reduce the residence time of the sample under isothermal conditions, the scans were performed in air at the indicated temperatures by using a short integration time per step (70 s) and a limited angular range (12–35°). Temperature was increased at 20 °C/min from 20 °C to 190 °C to mimic the experimental conditions used in DSC scans. II scan was performed under the same conditions of the I scan after quenching in liquid nitrogen.

2.6. Mechanical characterization

Tensile measurements were carried out on rectangular films (5 mm wide) with a crosshead speed of 10 mm min⁻¹ by using an Instron 4465 tensile testing machine (Norwood, MA, USA), equipped with a rubber grip and a 100 N load cell. A preload of 1 MPa was applied to each specimen prior to testing. At least five replicates were run for each sample and the results are provided as the average ± standard deviation.

2.7. Gas permeability

The permeability determination was performed by a manometric method using a Permeance Testing Device, type GDP-C (Brugger Feinmechanik GmbH), according to ASTM 1434-82, DIN 53 536 in compliance with ISO/DIS 15 105-1 and according to the Gas Permeability Testing Manual of the instrument. Food grade gases (O₂ and CO₂) were employed. All measurements were carried out at 23 °C, by using a gas stream of 100 cm³/min, 0% of gas RH. Permeability measurements were performed at least in triplicate and the mean value ± standard deviation is presented. The gas transmission rate (GTR) was determined.

3. Results and discussion

3.1. Molecular and thermal characterization

The chemical structure of DMTFDC (Fig. 1) and of synthesized PBTFs have been evaluated by ¹H NMR. The spectra did not reveal any impurities and confirmed the expected structure. The molecular weight determination, carried out by GPC, highlighted that the synthetic procedures adopted permitted to obtain polymers of high and comparable molecular weights and narrow polydispersity, both starting from dicarboxylic acid as well as from dimethylester (Table 1). Furthermore, by reducing the reaction time, a 3 × lowering of PBTF molecular weight was obtained (Table 1).

The thermal stability has been investigated by TGA under nitrogen

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