

# Synthesis of the bio-based polyester poly(propylene 2,5-furan dicarboxylate). Comparison of thermal behavior and solid state structure with its terephthalate and naphthalate homologues



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## ARTICLE INFO

### Article history:

Received 15 August 2014

Received in revised form

2 November 2014

Accepted 31 January 2015

Available online 14 February 2015

### Keywords:

Poly(propylene-2,5-furan dicarboxylate)

Furanoate

Polyesters

## ABSTRACT

Poly(propylene-2,5-furan dicarboxylate) (PPF) is a new aliphatic polyester which can be prepared from monomers derived from renewable resources and efforts are currently being made in order to use PPF as a replacement for its terephthalate (PPT) and naphthalate (PPN) homologues. For this reason, an in-depth comparative study of its thermal behavior and solid state structure was performed in the current manuscript. Conventional and temperature-modulated differential scanning calorimetry were utilized for the evaluation of the different characteristics and behavior of the samples under study. Regarding the structural characteristics, it was found that the different structural rings and the ultimate chain rigidity of the samples play a major role on their final properties. On this basis, the more rigid PPN exhibited higher glass transition temperature and thermal stability than PPF and PPT, as the results suggest. The equilibrium melting point of PPF was found equal to 199 °C, while the heat of fusion of pure crystalline PPF was 141.75 J/g or 27.8 kJ/mol. The spherulitic morphology was also investigated by means of polarized optical microscopy and it was found that PPF forms smaller spherulites than its other two homologues.

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## 1. Introduction

Terephthalates like poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT) or poly(propylene terephthalate) (PPT) are a class of high performance thermoplastic polyesters. As a result of their advantageous properties they are used in a wide range of applications. However, their precursors are fossil based [1]. Naphthalate polyesters show comparable or better properties than terephthalates. For example poly(ethylene-2,6-naphthalate) (PEN) [2–5] shows better characteristics compared to PET, referring to its thermal, electrical and mechanical properties, resistance in chemicals and UV stability and lower gas permeability. The improved properties of PEN are a result of the double naphthalene ring in its structure. However, the cost of PEN is much higher than PET, since the one of its monomers, namely

2,6-naphthalene dicarboxylic acid is more expensive than the terephthalic acid.

Nowadays, there is a growing interest in the preparation of new chemicals and materials based on renewable resources, as biomass-derived fuel and chemicals are a promising alternative to fossil based materials. Chemicals from vegetable feedstocks like sugars, vegetable oils, organic acids, glycerol and others have been proposed as monomers for polymer production [6]. Carbohydrates and lignin are the major sources for aromatic monomers. 2,5-furan dicarboxylic acid (FDCA) and vanillic acid are the most important examples of such aromatic monomers [7].

FDCA has been screened to be one of the most important building blocks or top value-added chemicals derived from biomass by the U.S. Department of Energy [8]. Novel approaches to the preparation of hydroxymethylfurfural lead the way to the large-scale production of FDCA [9]. The latter can be used for the production of polyesters bearing furan moieties like poly(ethylene 2,5-furan dicarboxylate) (PEF) and poly(butylene 2,5-furan dicarboxylate) (PBF) which can be seriously regarded as the bio-based alternatives of terephthalates [10,11].

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Polyesters of 1,3-propanediol were not studied till recently, since the specific diol monomer was not available in quantities and price that might enable production of polymers [12]. However, in recent years more attractive processes have been developed for the production of 1,3-propanediol (1,3-PD) from renewable resources, research on related polymers has attracted interest from both industrial and academic point of view [13,14].

Poly(propylene terephthalate) (PPT), the first and most studied polyester of 1,3-propanediol, is available in the market [15]. The polymer is suitable for industrial fiber production. PPT fibers are characterized by much better resilience and stress/recovery properties than PET and PBT. These properties are due to the crystal structure of PPT. PPT chains are much more angular structured than PET and PBT chains due to the even number of methylene groups of the diol segment. Therefore these chains can be stretched up to 15% with a reversible recovery [16]. PPT is anticipated to gain a significant share in the thermoplastic polyesters market in the next few years. Recently, biodegradable aliphatic polyesters, and especially poly(propylene succinate) (PPSu) and poly(propylene adipate) (PPAd) have received an increasing interest [17,18].

The odd number of methylene units in the diol segment is responsible for the lower melting points, lower degree of crystallinity and higher biodegradation rates of the polymers prepared from 1,3-propanediol, compared with their homologues based on ethylene-glycol or 1,4-butanediol [19].

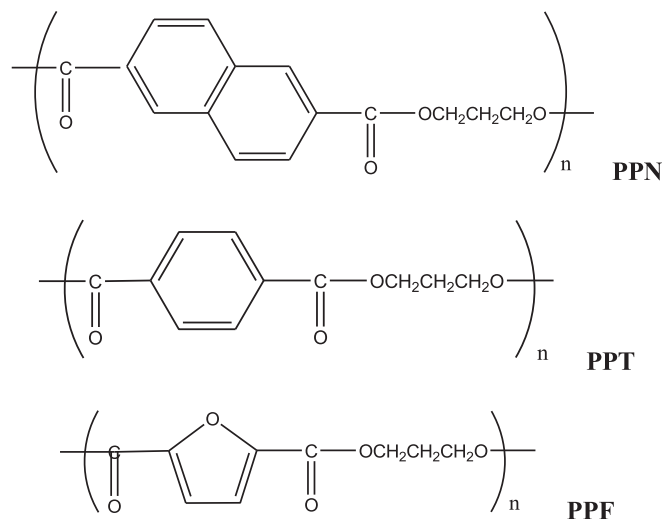
Poly(trimethylene 2,6-naphthalate) (PTN) or poly(propylene 2,6-naphthalate) (PPN) is a semicrystalline polymer whose preparation was first reported in 1969 [20]. The chemical structure of PTN is equivalent to that of poly(trimethylene terephthalate) (PPT) except that a benzene ring in PPT is replaced by a naphthalene ring. Several studies on polymerization kinetics, characterization, rheological and thermal properties as well as crystal structure of PTN have been reported [21–23]. Poly(propylene 2,5-furan dicarboxylate) (PPF) is a thermoplastic polyester the synthesis of which has been reported just recently [24,25]. However, only molecular characterization and transition temperatures have been reported for PPF [25].

The macroscopic properties of semicrystalline polymers are governed by their microscopic morphology, which in turn depends on their crystallization conditions and on their thermal history. Furthermore, the dimensional stability as well as the thermal degradation of polymers are aspects which must be thoroughly assessed prior to the production of those materials in large scale. Thus, the melting behavior and crystallization kinetics are of special interest prior to evaluate the temperature window of a polymeric material for processing and for use and finally its potential of uses in specific applications. In this work, differential scanning calorimetry (DSC), temperature-modulated differential scanning calorimetry (TMDSC), polarized optical microscopy (POM), wide-angle X-ray diffractometry (WAXD) and thermogravimetric analysis (TGA) were used to investigate the thermal behavior, including melting, crystallization and thermal degradation of PPF in comparison to PPT and PPN (Scheme 1).

## 2. Experimental

### 2.1. Materials

2,5-furan dicarboxylic acid (purity 97%), Dimethyl terephthalate (DMT) and tetrabutyl titanate (TBT) catalyst of analytical grade were purchased from Aldrich Co. Dimethyl naphthalate (DMN) was kindly supplied by Amoco Chemicals-Fine Acids (Chicago, IL, USA). 1,3-propanediol (1,3-PDO) was kindly supplied by Du Pont de Nemours Co., Wilmington, DE. All other materials and solvents used were of analytical grade.



Scheme 1. Chemical structure of PPN, PPT and PPF.

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

15.6 g of 2,5-furan dicarboxylic acid, 200 mL of anhydrous methanol and 2 mL of concentrated sulfuric acid was transferred into a round 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<sub>2</sub>CO<sub>3</sub> 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 by the two-stage melt polycondensation method (esterification and polycondensation) in a glass batch reactor [14,18]. For the preparation of the polyesters proper amounts of diester and 1,3-PDO in a molar ratio diester/diol = 1/2.2 were charged into the reaction tube of the polyesterification apparatus. TBT (400 ppm) was added as catalyst and the apparatus with the reagents was evacuated several times and filled with argon in order to remove the whole oxygen amount. The reaction mixture in case of PPF was heated at 160 °C under argon flow (5 mL/min) for 2 h, at 170 °C for additional 2 h and finally at 180 °C for 2 h. For PPT and PPN the reaction mixture was heated at 190 °C for 2 h under argon atmosphere and for additional 2 h at 230 °C. This first step (transesterification) is considered to complete after the collection of almost all the theoretical amount of CH<sub>3</sub>OH, which was removed from the reaction mixture by distillation and collected in a graduate cylinder.

In the second step of polycondensation a vacuum (5.0 Pa) was applied slowly over a period of time of about 30 min to remove the excess of diols and to avoid excessive foaming and furthermore to minimize oligomer sublimation, which is a potential problem during the melt polycondensation. For PPF, the temperature was increased to 220 °C while the stirring speed was increased to 720 rpm. The reaction continued at this temperature for 1 h and after that time the temperature was increased to 235 °C for 2 h and

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