Polymer 55 (2014) 3846–3858

Contents lists available at ScienceDirect

Polymer

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

# Evaluation of polyesters from renewable resources as alternatives to the current fossil-based polymers. Phase transitions of poly(butylene 2,5-furan-dicarboxylate)

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ARTICLE INFO

*Article history:*
Received 3 April 2014
Received in revised form
26 May 2014
Accepted 8 June 2014
Available online 13 June 2014

*Keywords:*
Poly(butylene 2,5-furan dicarboxylate)
Polyesters
Crystallization

ABSTRACT

Poly(butylene 2,5-furan dicarboxylate) (PBF) is an alipharomatic polyester that can be prepared using monomers derived from renewable resources such as 2,5-furan dicarboxylic acid and 1,4-butanediol. In the present work the thermal behavior of PBF was studied. Multiple melting was observed during heating traces of samples isothermally crystallized from the melt using differential scanning calorimetry (DSC). The wide angle X-ray diffraction (WAXD) patterns did not reveal the presence of a second crystal population, or a crystal transition upon heating. DSC study showed that the phenomena are closely related to recrystallization. Temperature modulated DSC (TMDSC) tests indeed evidenced enhanced recrystallization. The equilibrium melting point was estimated to be 184.5 °C using the linear Hoffman–Weeks extrapolation. The heat of fusion of the pure crystalline polymer was found equal to 129 J/g or (27.35 kJ/mol), a little lower than that of PBT. The Lauritzen–Hoffman secondary nucleation theory was used and the surface energy values and the work of chain folding were found to be comparable to those of PBT, but quite lower than those of poly(ethylene terephthalate) (PET). The non-isothermal crystallization on cooling and the cold-crystallization of quenched samples were also studied. Condensed spherulites were observed on isothermal crystallization under large supercoolings by using polarized optical microscopy (POM), while the spherulites turned to ring-banded morphology at higher temperatures. In every case the nucleation density was high.



## 1. Introduction

Exploring polymers from renewable resources is of great importance for sustainable chemistry [1]. Chemicals from vegetable feedstocks like sugars, vegetable oils, organic acids, glycerol and others have been proposed as monomers for polymer production. Aliphatic dicarboxylic acids (ADA) like succinic acid, fumaric acid and itaconic acid as well as aliphatic diols including isosorbide, isomannide and isoidide, 1,3-propanediol and 1,4-butanediol can be obtained from carbohydrates by the lignocellulosic feedstock biorefinery [2]. Carbohydrates and lignin are also the major sources for aromatic monomers. 2,5-furandicarboxylic acid (FDCA) and vanillic acid being the most important examples for aromatic monomers from renewable resources [3]. 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 [4]. It is a member of the furan family and has a large potential as monomer to synthesize polyesters, polyurethanes, and polyamides as alternative monomer in order to replace the already used and derived oil sources [5–7].

Benzenearomatic polyesters, such as poly(ethylene terephthalate) (PET), poly(trimethylene terephthalate) (PTT), and poly(butylene terephthalate) (PBT) are excellent thermoplastic polymers and have dominated the market. However, one of their monomers-terephthalic acid is oil-derived [8]. PBT is a high performance semicrystalline engineering thermoplastic [9]. It shows excellent dimensional stability, excellent electrical properties, low moisture absorption and processing advantages [10]. PBT has the

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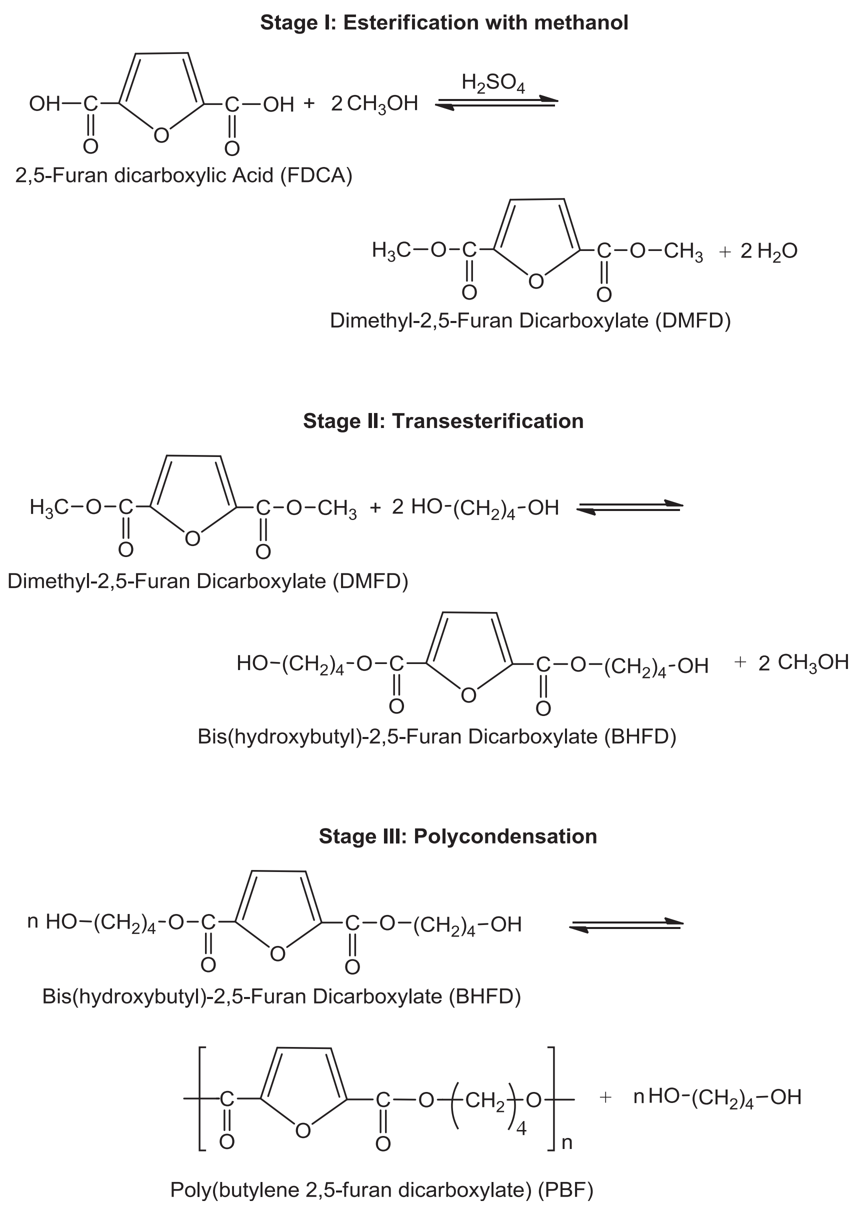
http://dx.doi.org/10.1016/j.polymer.2014.06.025
0032-3861/

ability of facile crystallization and easy dyeability. This enables uses of PBT in durable goods which are formed by injection molding [11].

Polyesters bearing furan moieties like poly(ethylene 2,5-furan dicarboxylate) (PEF) and poly(butylene 2,5-furan dicarboxylate) (PBF) are considered as the biobased alternatives of terephthalates [6,12]. In fact, they have been reported for decades [13–17]. However, in the majority of these attempts, polyesters with low molecular weight and brown to black color have been prepared, due to the decomposition of FDCA. Recently, Gandini et al. reported the synthesis and some properties of polyesters based on FDCA and ethylene glycol or some other diols [5,7]. The structure of FDCA is similar to terephthalic acid, and FDCA has been considered as replacement for terephthalic acid [18–21]. Polymerization of FDCA and 1,4-butanediol (BD) results in poly(butylene 2,5-furandicarboxylate) (PBF), a biobased PBT counterpart [1,22]. Scheme 1 shows the repeating unit of PBF. The chemical structure of PBF is similar to that of PBT, with the furan ring instead of the benzene one. The crystal structure and mechanical properties of PBF were reported in a recent work [20]. The mechanical properties, thermal properties and crystal structures of PBF were similar to PBT. The glass transition temperature was about 32 °C and the melting point was reported to be 169 °C [12]. The unit cell was determined as triclinic with $a = 4.78$ Å, $b = 6.03$ Å, $c = 12.3$ Å, $\alpha = 110.1°$, $\beta = 121.1°$, $\gamma = 100.6°$. In fact two crystalline have been reported. The $\beta$-phase is less stable than the $\alpha$-phase, in analogy with the crystalline structure of PBT [12]. There is a close similarity of the PBF crystal structure to PBT $\alpha$- and $\beta$-forms [20]. For high molecular weight the Young modulus of PBF is above 900 MPa, and the elongation at break exceeds 1000% [20].

In an attempt to reach to fully biobased aliphatic-aromatic copolyesters, Dubois and co-workers synthesized poly(butylene succinate-co-butylene furandicarboxylate) (PBSFs) in full composition range from 2,5-furandicarboxylic acid (FA), succinic acid (SA), and 1,4-butanediol (BDO) via an esterification and polycondensation process [19]. Poly(butylene succinate) (PBSu) is an aliphatic polyester form monomers from renewable resources




**Scheme 1.** Synthetic route for PBF.