European Polymer Journal 67 (2015) 383–396

Contents lists available at ScienceDirect

European Polymer Journal

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

Furan-based polyesters from renewable resources: Crystallization and thermal degradation behavior of poly(hexamethylene 2,5-furan-dicarboxylate)

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ARTICLE INFO

Article history:
Received 9 July 2014
Received in revised form 14 August 2014
Accepted 31 August 2014
Available online 28 September 2014

Keywords:
Poly(hexamethylene 2,5-furan dicarboxylate)
Renewable resources
Crystallization
Thermal decomposition

ABSTRACT

In the present study poly(hexamethylene 2,5-furan dicarboxylate) (PHF), a polyester prepared from monomers derived from renewable resources, was synthesized by applying the melt polycondensation method. The polymer exhibited a melting temperature of about 145 °C while the glass transition temperature was 7 °C. After isothermal crystallization, PHF showed multiple melting behavior which was attributed to partial melting–recrystallization and final melting. The equilibrium melting temperature of the polymer was found to be 157 °C, while the heat of fusion of the purely crystalline material was found to be 34 kJ/mol (143 J/g). A crystallization regime I to regime II transition was observed at 134 °C as a breakpoint in the Lauritzen–Hoffman plot. The K_{gI} and K_{gII} values were calculated 0.9×10^5 and 1.76×10^5 respectively. Polarized optical microscopy was also employed for the study of the isothermal crystallization of PHF. PHF can be regarded thermally stable since its decomposition starts above 350 °C. Thermal degradation kinetics were investigated by means of thermogravimetric analysis.

1. Introduction

Polyesters of 2,5-furan dicarboxylic acid (FDCA), like poly(ethylene 2,5-furan dicarboxylate) (PEF) and poly(butylene 2,5-furan dicarboxylate) (PBF) can be seriously regarded as the biobased alternatives to the polyesters of terephthalic acid, like poly(ethylene terephthalate) (PET) and poly(butylene terephthalate((PBT), which are produced and used in a vast amount of commercial applications [1,2]. Polyesters based on FDCA have been reported for decades [3–5]. However, in most of these attempts, polymers with low molecular weight and brown to black color were prepared, due to the thermal decomposition of FDCA. Recently, Gandini et al. reported the successful synthesis of high molecular weight polyesters based on FDCA and various diols [6,7]. The structure of FDCA, which can be synthesized from renewable resources, is quite similar to the one of terephthalic acid, and FDCA has been considered as replacement for the fossil based terephthalic acid [8–11]. For the above reasons, 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 [12]. It has a large potential as a bio-based monomer for synthesis of polyesters, polyurethanes, and polyamides [2,7].

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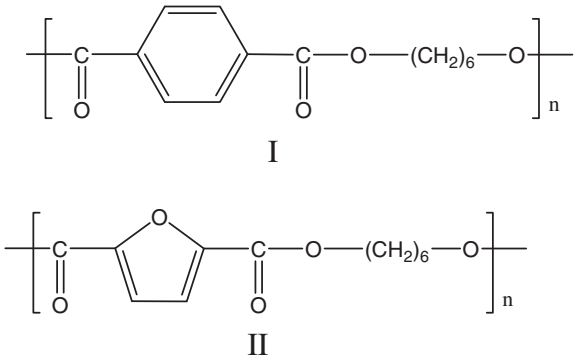
http://dx.doi.org/10.1016/j.eurpolymj.2014.08.031
0014-3057/

Poly(hexamethylene terephthalate) (PHT) is a non-commercial aromatic polyester of both academic and applied interest [13–15]. Similar to many semicrystalline aromatic polyesters, PHT (I) (Scheme 1) exhibits fair mechanical properties and an excellent chemical resistance [16]. Due to the presence of the flexible hexamethylene segment in the polyester chain, PHT has a relatively low melting temperature (T_m = 140 °C), which could be regarded advantageous for more economical and easier processing procedures [17]. Poly(hexamethylene 2,5-furan dicarboxylate) (PHF) (II) (Scheme 1) is a furan based polyester with similar structure with PHT. Synthesis of PHF was first reported in 1978 by Moore and Kelly [18] while synthesis and characterization of some poly(alkylene 2,5-furan dicarboxylate)s including PHF was reported recently by Jiang et al. [19].

PHF is a polyester which is synthesized from monomers produced from renewable resources. Its characteristics can be considered quite satisfactory [19]. Therefore, it can be used in some applications, where up to this time point, fossil based polyesters like terephthalates are most commonly used.

Poly(butylene terephthalate) (PBT) is an important terephthalate polyester, currently produced in industry in large amounts, because of its numerous applications [1,2,9]. In fact, recent work in our lab showed that poly(butylene 2,5-furan dicarboxylate) (PBF), the furanoate homolog of PBT, shows slow crystallization rates on cooling and can be hardly used as a PBT alternative in the production of cast polymeric parts. Furan based polyesters like PBF and PHF have much lower environmental impact than PBT [10]. In contrast to PBF, poly(hexamethylene terephthalate) shows a beneficial fast crystallization and it could be potentially used as a new polyester, derived from renewable resources, for the replacement of PBT in many of its applications involving injection molding in the processing [19]. PHF also exhibits comparable or higher thermal properties, but also higher mechanical properties, compared to several other aliphatic polyesters, such as poly(L-lactic acid) (PLLA) or poly(butylene succinate) (PBS) [19].

The crystallization phenomenon and crystallization kinetics are very important for polymeric materials, since they determine the final degree of crystallinity and the morphology of the final product after processing [20]. In turn, the morphology and the degree of crystallinity determine several parameters of the final polymer products that are crucial for their potential applications, such as mechanical properties, ultimate use temperature as well as dimensional stability, gas permeability and others. Despite the fact that thermodynamics govern crystallization and thus decide whether, under given conditions, crystals can exist or not in a polymeric material, the kinetics of the process determine whether crystallization takes place, and its speed [21]. Crystallization studies are in most cases limited to ideal and constant external conditions, since these are prerequisite for an easy theoretical analysis [22]. However, polymer processing and therefore crystallization, proceeds under non-isothermal conditions, meaning that the external conditions change continuously. Thus, non-isothermal crystallization of polymers is of special importance [23–28]. The temperature window of a polymer is determined by its transition temperatures and its thermal stability.



Scheme 1. Chemical structure of PHT (I) and PHF (II).

To avoid a gradual deterioration of the physical properties of the product, thermal degradation reactions must be inhibited or retarded. In turn, successful stabilization must be based on an understanding of the precise mechanism by which each type of degradation occurs. Thus, much research has been conducted by the polyester producers and by textile research institutes towards this direction, as well as by academia. Thermogravimetry (TG) is widely used to investigate the thermal decomposition of polymers and to assess their relative thermal stabilities. Also, considerable attention has been directed towards the exploitation of thermogravimetric data at different heating rates for the determination of kinetic parameters such as activation energy, pre-exponential factor and reaction mechanisms [29].

In this work, Poly(hexamethylene 2,5-furan-dicarboxylate) (PHF), was synthesized and thoroughly characterized with a variety of techniques. A detailed investigation of the crystallization, melting and thermal degradation of PHF was performed by using differential scanning calorimetry (DSC), temperature modulated DSC (TMDSC), wide-angle X-ray diffractometry (WAXD), polarized optical microscopy (POM) and thermogravimetric analysis (TGA). Important parameters such as the equilibrium melting temperature, the heat of fusion and the activation energy of the pure crystalline polymer were also determined. Finally, a thorough analysis of the kinetics of crystallization as well as of thermal degradation was performed and it is presented for first time in literature.

2. Experimental

2.1. Materials

2,5-Furan dicarboxylic acid (purum 97%), 1,6-hexanediol (99%, HD) 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