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Decomposition mechanism of polyesters based on 2,5-furandicarboxylic acid and aliphatic diols with medium and long chain methylene groups

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ABSTRACT

Three different polyesters have been synthesized using 2,5-dimethylfuran dicarboxylate (DMFD) and diols with 5, 6 and 9 methylene groups, namely poly(pentylene 2,5-furanoate) (PPeF), poly(hexylene 2,5-furanoate) (PHF) and poly(nonylene 2,5-furanoate) (PNF), respectively. These polyesters that can be prepared from monomers derived from renewable resources were synthesized by melt polycondensation technique. Their structure was confirmed by ^{1}H NMR spectroscopy. Thermal stability of polyesters was investigated using thermogravimetric analysis (TGA) and their decomposition mechanism was evaluated with Pyrolysis-Gas chromatography/Mass spectroscopy (Py–GC/MS). It was found that all polyesters decompose with a similar way and decomposition takes place mainly via β-hydrogen bond scission and less extensive with homolytic scission.

1. Introduction

The worldwide concern on the shortage of non-renewable petroleum resources over the last decades, has lead the interest of the academic and industrial community towards the development of novel chemicals and materials based on renewable resources [1–4]. Biomass contains a large amount of organic molecules which provide a satisfactory carbon balance for chemical and fuel production.

Among these efforts, polymers based on furan monomers, constitute a unique family of polymers prepared from vegetable renewable resources. 5-hydroxymethylfurfural (HMF) is already widely available today and it is synthesized from sugars and polysaccharides like cellulose. In its turn, HMF can be used to synthesize 2,5-furandicarboxylic acid (FCDA), which is one of the most important biomass-derived products [5,6] and is considered one of the most promising monomers for the synthesis of polyesters, polyamides, polyurethanes and thermosettings [7]. The key structural feature associated with FCDA is the close resemblance to its aromatic counterparts, which enables it to synthesize polymers via step-growth mechanisms [8]. FCDA has structure similar to that of terephthalic acid (TA) and in the near future, it is expected to replace the petrochemical-based TA on several occasions [9]. Besides, their similar structure, some differences in their furan ring size and their polarity can attribute to different characteristics and enhanced mechanical and gas barrier properties of FCDA, compared to TA-based polyesters [10]. Thus, furanoate-based polyesters have been studied intensively receently, as possible replacement for the conventional petrochemical-derived polyesters like poly(ethylene terephthalate) (PET) and other aliphar-omatic polyesters.

The increased interest for furanoate polyesters has led to the synthesis of many types of polyesters from 2,5-FDCA and almost the whole series of aliphatic diols using melt polycondensation procedure [11–18] or biocatalytic approach [19]. Some of the most serious problems to overcome in these efforts were the synthesis of polyesters with diols having high number of methylene groups like 8–12. Despite their higher boiling point and the problems caused in the synthesizing procedure, in our previous work it became possible to synthesize such biobased furanoate polyesters with

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long chain diols using a new strategy of polymerization [18]. The main problems that our group had to overcome were the difficulty to remove the used nonvolatile diols and also the thermal instability of the used 2,5-FDCA monomer, both leading to yellow-brown polyesters. This is due to the decomposition of furanoate polyesters at elevated temperatures.

The thermal stability of a polymer constitutes a very important property which determines firstly the synthetic procedure and the appearance of polyester and afterward its applications. For this reason in our previous publications we studied the thermal degradation and decomposition mechanisms of furanoate polyesters prepared from 2,5-FDCA and low methylene group number diols, i.e. poly(ethylene furanoate) (PEF), poly(propylene furanoate) (PPF) and poly(butylene furanoate) (PBF) [20], as well as with high methylene groups number, namely poly(octamethylene furanoate) (POF), poly(decamethylene furanoate) (PDeF) and poly(dodecamethylene furanoate) (PDoF) [21]. However, there are not any published works dealing with the thermal degradation of furanoate polyesters of 1,5-pentanediol, 1,6-hexanediol and 1,9-nonenodiol.

In the current manuscript, our group almost completes thermal decomposition studies on 2,5-FDCA polyesters by preparing a set of furan based polyesters like poly(pentylene furanoate) (PPeF), poly(hexylene furanoate) (PHF) and poly(nonenylene furanoate) (PNF) using 2,5-DMFD and aliphatic diols with medium (5 and 6) and high (9) methylene groups. Especially synthesis and study of polyesters based on diols with odd number of methylene groups is always a challenge. Pyrolysis-gas chromatography/mass spectroscopy (Py-GC/MS) was employed on these polyesters in order to identify the individual fragments from each sample and obtain structural information concerning their decomposition mechanism.

Table 1
Intrinsic viscosity and carboxyl end groups content of PPeF, PHF and PNF.

Sample	IV (dL/mg)	−COOH end groups (eq/10^6 g)
PPeF	0.53	52 ± 8
PHF	0.48	65 ± 11
PNF	0.50	48 ± 6

2. Experimental

2.1. Materials

2,5-furan dicarboxylic acid (purum 97%), 1,5-pentanediol (97%, b.p. = 206 °C), 1,6-hexanediol (99%, m.p. = 38–42 °C and b.p. = 250 °C), 1,9-nonenodiol (99%, m.p. = 45–47 °C and b.p. = 177 °C/15 mmHg) and tetrabutyl titanate (TBT) catalyst of analytical grade were purchased from Aldrich Co. All other materials and solvents used were of analytical grade.

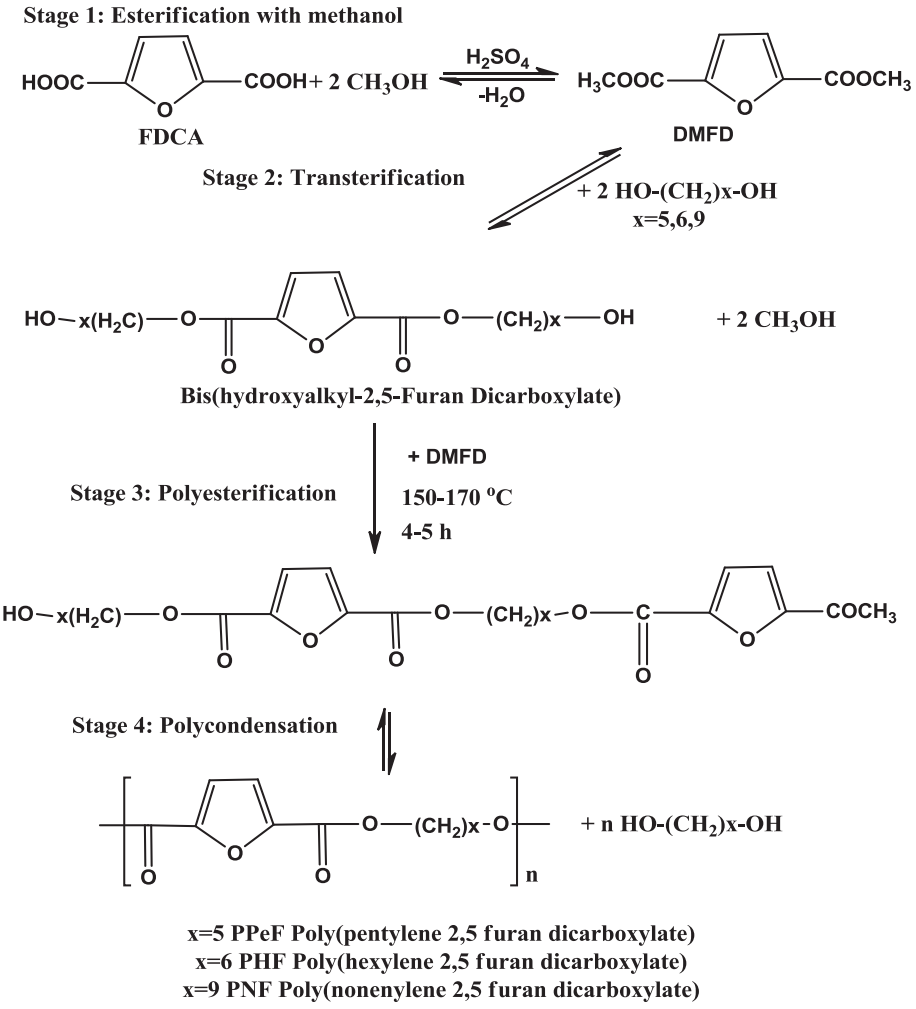

Fig. 1. Synthetic route for 2,5-furandicarboxylate polyesters.