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Synthesis, characterization and thermal, hydrolytic and oxidative degradation study of biobased (BisFuranic-Pyridinic) copolyesters

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ABSTRACT

Polymers from renewable resources are of high interest since it could be possible to valorize the biomass and in parallel to tune their macromolecular structures in relation with their properties. Here novel bisfuranic-pyridinic copolyesters, namely poly (ethylene furoate-co-ethylene pyridinate) (**PEBF-co-PEPy**) were prepared by applying a two-stage melt polycondensation method at high temperature, in a presence of titanium derivatives as catalyst. Molecular weights of resulting copolyesters are in the range 24000–45200 g mol^{-1} and their chemical microstructures statistical as shown by NMR. These furano-pyridinic copolyesters are amorphous with Tg ranging from 62 to 67 °C and their thermal and hydrolysis stabilities are influenced by presence of the pyridinic dyads Py-ED-Py. Finally the oxidative degradation in $H_2O_2/CoCl_2$ cannot be effective because of the chelating properties of pyridinic moieties.

1. Introduction

In recent years much has been written about renewable resources and their use in polymer science [1,2]. The molecular framework of furan has been a source of inspiration to chemists as supported by the rich literature dealing with a large variety of structures and properties [3]. Furan-based compounds have also been explored as monomeric units for synthesis of several polymers by various groups [4–6]. A number of studies have described the synthesis of various difuranic monomers from ethyl-2-furoate or furfurylamine through a simple coupling procedure. They were used, in conjunction with other monomers such as diols, diamines, dianhydrides and diisocyanates, to prepare several polyesters [7–11], polyamides [12–14], polyhydrazides [15,16], polyimides [17] and polyureas [18]. All these polymers exhibited a regular structure, high molecular weight and physical properties which made them attractive for applications as engineering polymers. More recently our team has described furan-based poly(esteramide)s [19] and copolyesters with terephthalic [20] and/or sodium sulfoisophthalic [21,22] moieties allowing to cover a wide range of physicochemical properties and proving the interest of adding new functionality. To continue our investigation in such direction, we herein explore the interest of the pyridinic functions which can impart chelating properties due to their ability to form extremely stable complexes with metal ions [23]. Moreover the presence of such functions will open the scope of applications toward biology. Indeed the pyridine dicarboxylate was reported to be a competitive inhibitor of bovine liver glutamate dehydrogenase [24,25]. Surprisingly, only few examples of polymers having pyridinic moieties inside the backbone or in a side position were already published. One concerned the development of copoly(amide-ester)s as a promising alternative for optoelectronic applications [26] and the others concerned the modification of chitosan which thus has been applied to a wide range of potential applications: metal recovery according to the enhancement of the chelating properties due to the pyridinic functions [27,28], antimicrobial activity [29,30], gene delivery [31], sensor application [32] and biomedical application [33,34].

In this work we present a straight forward methodology to precisely design a new family of furanic copolyesters enclosing pyridinic moieties and obtained by the melt polycondensation between 5,5′-isopropylidene-bis(ethyl 2-furoate) (DEBF), Dimethyl 2,6-pyridinedicarboxylate (DMPy) and Ethanediol (ED). These copolyesters have potential interesting attributes: their bio-sourced origin, their relatively high thermal stability due to the semi-aromatic character of the furoate units, their sensibility

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toward hydrolysis and compatibility with biological media. Therefore, we deeply studied their thermal and hydrolytic properties as well as their *in vitro* behavior in oxidative environment which indirectly allows estimating their stability within biological media [35].

2. Experimental

2.1. Materials

Dimethyl 2,6-pyridinedicarboxylate (DMPy), 2-ethyl furoate, 1,2-ethanediol (ED), tetrabutoxytitanium ($Ti(OBu)_4$) and zinc acetate ($Zn(OAc)_2$) were all purchased from Sigma-Aldrich and were used without further purification.

2.2. Synthesis of 5,5′-isopropylidene-bis(ethyl 2-furoate) (DEBF)

DEBF was prepared by the condensation of ethyl furoate with acetone following the procedure described previously [7]. Its structure and purity were confirmed by spectroscopic techniques.

2.3. Synthesis of copolyesters

The poly(ethylene furoate-co-ethylene pyridinate) **PEBF-co-PEPy** was produced by the melt copolymerization according to three Processes:

2.3.1. Process *(a)*

(**DEBF**, **DMPy**), (0.8/0.2: mol/mol) were reacted with (**ED**, 4 mol) in the presence of zinc acetate **$Zn(OAc)_2$** (10^{-3} of total mass) for 3 h in a nitrogen atmosphere at 200 °C. The resulting reaction was carried out at high temperature 240 °C in the presence of 0.1 wt-% **$Ti(OBu)_4$** under 0, 01 mmHg vacuum to remove the diol as efficiently as possible.

2.3.2. Process *(b)*

Transesterification reactions were carried out at 200 °C under a nitrogen flow in the presence of 0.1 wt-% **$Ti(OBu)_4$**, the polycondensation reactions were performed at 240 °C under 0, 01 mmHg vacuum.

2.3.3. Process *(c)*

The same procedure as in the process (b), with the corresponding changes in the concentration of the catalyst of the transesterification steps 0.2 wt % **$Ti(OBu)_4$**.

The resulting copolymer (Process **(a)**, **(b)** and **(c)**) was used for characterization without further purification.

2.4. Films preparation

Films referenced as **FilmPEBF-co-PEPy$_4$**, were prepared by casting a sample of **PEBF-co-PEPy$_4$** copolyester at room temperature from a 10% (w/v) solution in $CHCl_3$/MeOH (8/1 v/v) on silanized Petri dish. The films were cut and dried in vacuum at 50 °C to constant weight. The thickness of the obtained films was 200 ± 10 μm.

2.5. Degradation procedures

The hydrolytic degradation trials were performed with **FilmPEBF-co-PEPy$_4$.** Samples were immersed in purified water under acidic aqueous conditions ($pH = 4.35$), neutral conditions ($pH = 7.4$) and basic conditions ($pH = 9.5$ and 11.5) at 37 °C. After immersion for fixed periods of time, each sample was rinsed thoroughly in water and dried to constant weight. Sample weighting, was used to follow the evolution of the hydrolytic degradation.

The oxidative degradation was also performed with **FilmPEBF-co-PEPy$_4$** in solution composed of 30 vol% H_2O_2 and in solution composed of 20 vol% H_2O_2 in combination with 0.1 M $CoCl_2$ for 15 days at 37 °C [36]. Sample weighting and NMR spectroscopy were used to follow the rate of the oxidative degradation.

2.6. Analytical methods

^{1}H spectra were recorded on a BruckerAvance III 400 spectrometer at 90 °C. Samples were dissolved in DMSO. Chemical shifts were referenced to the peak of TMS at 0.0 ppm. The degree of randomness (B) and the number-average sequence length of BisFuranic ($\bar{L}_{n,BF}$) and Pyridinic units ($\bar{L}_{n,Py}$) are given by:

$$B = P_{PyBF} + P_{BFPy} = \frac{F_{BF-ED-Py}}{2F_{Py}} + \frac{F_{BF-ED-Py}}{2F_{BF}} \tag{1}$$

$$\bar{L}_{n,BF} = \frac{1}{P_{BFPy}} = \frac{2F_{BF}}{F_{BF-ED-Py}} \tag{2}$$

$$\bar{L}_{n,Py} = \frac{1}{P_{PyBF}} = \frac{2F_{Py}}{F_{BF-ED-Py}} \tag{3}$$

(P_{PyBF}) The probability of finding a BisFuranic unit next to an Pyridinic unit.(P_{BFPy}) The probability of finding a Pyridinic unit next to an BisFuranic unit.

Size exclusion chromatography (SEC) analysis was performed with Viscotek machine using a system of three columns in series (Styragel HR 4E DMF) in dimethyl formamide (DMF) mixture to (LiBr 0.05 M) at 70 °C. Inherent viscosities were determined at 25 °C from DMSO solutions with a polymer concentration of 0.15 g dL^{-1} using an Ubbelhode AVS-400 microviscosimeter.

The differential scanning calorimetry experiments (DSC) were performed with TA-instruments Q 23 to study the thermal properties and crystallization behavior. The samples were cut and placed in closed capsules. The samples were tested under dry nitrogen flow, a heating rate at 10 °C/min, covering the range of 30–230 °C, a cooling rate at 10 °C/min, covering the range of 230–30 °C. Glass transition temperatures (Tg) were measured on the second heating curves. It was taken at the inflection point.

Thermogravimetric analysis (TGA) was performed with a (TA-instruments Q500). Data were collected on samples of 10–20 mg during a ramp of temperature from 30 to 550 °C at 10 °C/min under a dry nitrogen atmosphere.

3. Results and discussion

3.1. Synthesis of poly (ethylene bisfuroate-co-ethylene pyridinate) *PEBF-co-PEPy*

The synthesis of poly(ethylene bisfuroate-co-ethylene pyridinate) **PEBF-co-PEPy** was performed according to a process inspired from that previously described by El Gharbi et al. [7] and comprising a two-step melt polycondensation reactions (Scheme 1) between 5,5′-isopropylidene-bis(ethyl 2-furoate) (DEBF), dimethyl 2,6-pyridinedicarboxylate (DMPy) and 1,2-ethanediol (ED). The first step was carried out for 3 h under a nitrogen atmosphere in the presence of zinc acetate as transesterification catalyst. The temperature was gradually raised from 180 to 200 °C during this step in order to avoid sublimation of reagent and side reactions [21]. The second step was completed at higher temperature (240 °C) under vacuum in order to release the excess of diol and to shift the