



Furan-based poly(esteramide)s by bulk copolycondensation

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ABSTRACT

Polyesteramides based on diethyl 5,5'-(propane-2,2-diyl)-bis(furan-2-carboxylate), a bio-based diester, are synthesized by high temperature bulk polycondensation with mixtures of hexane-1,6-diamine and ethane-1,2-diol. The ester/amide ratio in final copolymers is governed by the initial diester/diamine ratio, any diol excess being eliminated during the synthesis via a series of interchange reactions. The copolyesteramides are thermally stable, amorphous compounds. Their structural characterization shows the existence of minor side reactions: diol etherification, and two reactions, specific to furan-2-carboxylate structure, the formation of nonreactive 2-furyl end groups and chain branching resulting from amidine formation by amide-amine condensation.

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1. Introduction

Polyesteramides are an attractive class of polymers, since they can combine the excellent mechanical properties of polyamides and the biodegradability of polyesters and lead to a number of potential applications, such as disposable bags, agricultural films, drug carriers or matrix resins for biomedical materials [1]. The synthesis of these materials has attracted a substantial amount of attention in the past few decades and various copolymers have been prepared by one of four main methods, namely (i) polycondensation of dicarboxylic acids or derivatives with diols and diamines, amino-alcohols and/or lactams [2–6], (ii) polyesterification or polyamidation of monomers containing amide or ester groups, respectively [7–11], (iii) high temperature interchange reactions between polyesters and polyamides [12–15] and (iv) reactions of polyesters

and polyamides bearing reactive end groups with efficient coupling agents such as bisoxazolines [16,17]. Only a few studies, however, have been carried out on biobased polyesteramides, an example being the synthesis of polyesteramides from saccharide-based renewable resources by the solution polycondensation of bis(p-nitrophenyl) aliphatic dicarboxylates with p-toluenesulfonate salts of isosorbide or isomannide diesters of natural aminoacids [18,19].

During the past decade, the synthesis as well as the polymerization of different furanic monomers derived from furfural, which can be easily obtained by simple chemical treatment of vegetal biomass, have been investigated [20–22]. In this context, the synthesis of several polymers of 5,5'-(propane-2,2-diyl)-bis(furan-2-carboxylic acid) (BFA) were investigated: Polyesters by interfacial, solution or bulk polyesterifications [23,24], copolymers by ester interchange reactions between homopolymers [25] and polyamides by interfacial or solution polymerization [26–28]. However, the synthesis and properties of furanic polyesteramides have not yet been investigated.

The present work is devoted to the synthesis of a series of polyesteramides based on BFA diester, hexamethylene diamine and ethane-1,2-diol and to the characterization

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of the resulting materials by NMR and MALDI TOF MS, in order to study their microstructure, to detect possible structural defects and to gain more insight into the interchange reactions that can take place during the polycondensation.

2. Experimental part

2.1. Materials

Ethyl furan-2-carboxylate (99%, Aldrich), hexane-1,6-diamine (HMD, 99 + % Fluka), ethane-1,2-diol (ED, 99 + % Fluka), dodecan-1-amine (DA, 99 + %, Aldrich) and zinc acetate ($\text{Zn}(\text{AcO})_2$, 99.99% Aldrich) were used as received.

2.2. Synthesis

Diethyl 5,5'-(propane-2,2-diyl)-bis(furan-2-carboxylate) (DEF) was synthesized, as already reported [29], by the condensation of ethyl furan-2-carboxylate with acetone in an acidic medium. DEF was purified by double distillation under reduced pressure followed by recrystallization from ether petroleum and was finally vacuum dried at room temperature.

2.3. Polymer syntheses

Polyesteramides PEA1-6 were prepared according to the general procedure described below for PEA3: 3.05 g of DEF (9.52 mmol), 2.36 g of ED (38.06 mmol) and 0.44 g of HMD (3.79 mmol) were introduced in a 50 mL glass kettle equipped with a central mechanical stirrer, a nitrogen inlet, a distillation head connected to a condenser and a receiver flask. The kettle was placed in a salt bath at 150 °C. After 5 min heating, the reaction medium was homogeneous and 60 μL of a 5 wt% solution of $\text{Zn}(\text{AcO})_2$ in DMSO was introduced in the mixture using a hypodermic syringe. Bath temperature was raised gradually to 220 °C and ethanol distilled off. After 6 h heating, pressure was slowly reduced to 0.07 mbar and reaction continued for 7 h. PEA3 was analyzed after cooling, without further purification.

Hydroxy-terminated poly[ethylene 5,5'-(propane-2,2-diyl)-bis(furan-2-carboxylate)] (PEF) was prepared by the melt polycondensation of 2.00 g DEF (6.24 mmol) with excess ED (1.16 g, 18.72 mmol) in the presence of catalyst (0.1 wt% of $\text{Zn}(\text{AcO})_2$), using the same procedure as above.

PEA7 was prepared by the melt polycondensation of PEF (2.00 g) and HMD (0.45 g, 3.88 mmol) with the same procedure as above, except no catalyst was used and the vacuum step was carried out for 3 h.

Amino-terminated poly(hexane-1,6-diyl 5,5'-(propane-2,2-diyl)-bis(furan-2-carboxamide)] (PAF) was prepared by the melt polycondensation of 20.00 g DEF (62.4 mmol) with 8.72 g of HMD (75 mmol) without added catalyst, using the same procedure as above.

2.4. Analytical techniques

The NMR spectra were recorded on a Bruker Avance 500 spectrometer at 500 MHz (^1H NMR) and 125 MHz (^{13}C NMR)

using a 5 mm inverse probe. 2D ^{13}C - ^1H correlation spectra were recorded through a phase sensitive gradient enhanced 2D HSQC using echo-antiecho experiment (HSQCETGP sequence). 2D ^{13}C - ^1H long-distance correlation HMBC spectra were recorded via heteronuclear zero and double quantum coherence experiment (HMBCGPLNDQF sequence). The samples were dissolved in DMSO- d_6 or in 4/1 v/v CDCl_3 /trifluoroacetic anhydride (CDCl_3 /TFAh) solvent mixture.

The MALDI-TOF MS analyses were performed on a Bruker Autoflex III smartbeam time-of-flight mass spectrometer equipped with a nitrogen laser ($\lambda = 337 \text{ nm}$). Spectra were recorded in reflector delayed extraction mode at an acceleration voltage of 20 kV. 5 μL of a PEA solution (1 mg in 1 mL dichloromethane/trifluoroacetic acid (1/1 v/v)) was mixed with 20 μL of matrix solution (20 g/L of 2,5-dihydroxybenzoic acid in methanol/dichloromethane (1/1 v/v)) and 5 μL of NaI solution (10 g/L in methanol/dichloromethane (1/1 v/v)). 0.3 μL of this solution was deposited onto the stainless steel sample slide and dried. The spectra represent averages of 5000 consecutive laser shots. The spectrometer was calibrated with a monomethyl ether poly(ethylene glycol) standard ($M_n = 1000 \text{ g/mol}$).

DSC analyses were carried out on a 2920-Modulated TA Instruments apparatus equipped with a liquid nitrogen cooling accessory, at cooling and heating rate of 10 °C/min. Glass transition temperatures (T_g) were measured on the second heating curves and taken at the inflection point. Thermogravimetric analyses (TGA) were carried out on a Q50 TA-instruments thermogravimetric analyzer system at a heating rate of 10 °C/min under nitrogen atmosphere.

3. Results and discussion

The furanic-aliphatic polyesteramides PEA1-6 were prepared as shown in Scheme 1 by copolycondensation of diethyl 5,5'-(propane-2,2-diyl)-bis(furan-2-carboxylate) (DEF), hexane-1,6-diamine (HMD) and an excess of ethane-1,2-diol (ED), in the presence of $\text{Zn}(\text{OAc})_2$, a catalyst widely used in polyester synthesis [24]. The reaction was first carried out under atmospheric pressure, leading to oligoesteramide formation with ethanol elimination, then under vacuum with ED elimination to obtain the final high-molar-mass polyesteramide.

We first concentrated on a specific monomer composition, DEF/HMD/ED (1/0.4/4), leading to PEA3, and then extended the study to other compositions to obtain a series of furanic-aliphatic PEAs with various ester/amide ratios (Table 1).

The 6–7.5 ppm region of the ^1H NMR spectrum of trifluoroacetylated PEA3 shows two series of peaks, corresponding to the H^4 and H^5 protons of furan moieties (Fig. 1 and Table 2). Each series is splitted into four doublets, reflecting the presence of EFE, EFA, AFA triads, where F represents furanic moieties and A and E, amide and ester groups, respectively. These resonances are noted H^{4a} (AFA), H^{4ae} and H^{4ea} (EFA), and H^{4e} (EFE) and were assigned by comparison with the spectra of pure polyester, pure polyamide and copolyesteramides with various compositions. The same triads are observed on protons H^5 , showing that a

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