European Polymer Journal 58 (2014) 207–217

Contents lists available at ScienceDirect

European Polymer Journal

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

Modulation of furanic-sulfonated isophthalic copolyesters properties through diols units control

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ARTICLE INFO

Article history:
Received 13 May 2014
Received in revised form 21 June 2014
Accepted 24 June 2014
Available online 1 July 2014

Keywords:
Polycondensation
Sulfonated polyester
Furanic acid
Bio-based polymer

ABSTRACT

A series of furanic sulfonated copolyesters containing 20 mol.% of sodium sulfoisophthalate units were synthesized via a two-step melt polycondensation process from (5,5′-isopropylidene-bis(ethyl 2-furoate)) and (dimethyl 5-sodiosulfoisophthalate) with different diols: alkyl (1,2-ethanediol, 1,4-butanediol, 1,6-hexanediol) or ether (diethylene glycol and triethylene glycol). Structural characterization of copolyesters was deeply investigated by ^{1}H and ^{13}C (1D and 2D) NMR spectroscopy and by SEC. The results showed that the final structures not only depend on the initial monomers composition but also on the process which can induce at high temperature etherification and decarboxylation side reactions. For the alkyldiols series low molecular weights were obtained when side reactions occurred and when the monomer excess was difficult to remove from the reaction medium. Finally, it has been displayed that the modulation of diols composition allows for tuning copolyesters properties. Thus the copolyesters are amorphous with T_g ranging from 19 to 66 °C whereas their liquid water sorption and hydrolytic degradation resistance are in relation with the flexibility of the chain and their water accessibility to the ester linkages.

1. Introduction

Nowadays, replace petroleum raw materials by renewable bio-based resources is a major concern in terms of both economic and environmental viewpoints [1–7]. Some bio-based polymers, including polylactide, poly(butylene succinate) and poly(trimethylene carbonate) have been highly studied because of their biodegradability [8–10]. These polymers can be ultimately biodegraded into CO_2 and water even when discarded as waste in the environment. As novel monomers, furan-based diols, diacids, and diamines were prepared from two basic structures, namely furfural and 5-hydroxymethyl furfural readily accessible from pentose and hexose. Various furan-based polymers (polyesters, polyamides, polyurethanes, polyazomethines, poly(ester amide)s...) have thus been reported [11–15]. Furanic polyesters were shown to undergo hydrolysis at moderate temperature (50 °C) in neutral conditions and to be slowly degraded in environmental conditions where actinomycetes appear to be involved [16]. In a previous work, we described the synthesis of furanic–terephthalic copolyesters by a two-step melt polycondensation between 5,5′-isopropylidene-bis(ethyl 2-furoate), dimethyl terephthalate and 1,2-ethanediol. The resulting polymers were amorphous (T_g = 70–80 °C) with high thermal stability ($T_{d5\%}$ > 380 °C) indicating that the insertion of furanic monomer in PET backbone led to potentially degradable polyesters exhibiting high T_g [12]. Recently, we have studied the polycondensation of difuranic monomer with the dimethyl 5-sodiosulfoisophthalate and ethanediol to obtain the poly(ethylene furylate-co-sulfoisophthalate) PEFSI [17].

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http://dx.doi.org/10.1016/j.eurpolymj.2014.06.018
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The monitoring of the polymerization by ^{1}H NMR highlighted that we have succeeded in suppressing largely the formation of dioxyethylene units DEG by the control of the etherification side reactions. By limiting and keeping constant the content of DEG units a series of copolyesters PEFSI with high number average molecular weights (Mn > 19,000 g mol^{-1}) were obtained and the actual effect of sulfonated units content on the increase of the T_g was evidenced. Indeed that monomer unit rigidifies the copolyester backbone giving rise to higher T_g and thermal stability than nonsulfonated homopolymer PEF. This study also clearly showed the major role of the sodium sulfoisophthalate units on the vapor water sorption and the hydrolytic degradation behavior. As a continuation of our previous study, we have herein investigated the synthesis of new furanic copolyesters having constant sodium sulfoisophthalate units content (at 20 mol.% of diester units) with various diol units: 1,2-ethanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol or triethylene glycol. Finally further investigations of the thermal behavior, the water liquid sorption and the hydrolytic degradation were achieved aiming to the modulation of the properties of these bio-based sulfonated copolyesters according to their composition.

2. Experimental

2.1. Materials

Dimethyl 5-sodiosulfoisophthalate (Na-DMSI) (98.00%), 2-ethyl furoate (99.00%), 1,2-ethanediol (ED) (99.80 + %), diethylene glycol (DEG) (99%), triethylene glycol (TEG), 1,4-butanediol (BD) (99 %), 1,6-hexanediol (HD), tetrabutoxytitanium ($Ti(OBu)_4$) (97.00%) and zinc acetate ($Zn(OAc)_2$) (99.99%) were all purchased from Sigma–Aldrich and used as received .

2.2. Synthesis

5,5′-Isopropylidene-bis(ethyl 2-furoate) (DEF).

DEF was prepared by the condensation of ethyl furoate with acetone following the procedure described previously [11].

2.3. Copolymerization

In this section, we report the synthesis by melt copolymerization of seven new furanic copolyesters containing sodium sulfoisophthalate units based on ED, DEG, TEG, BD and HD.

As an example, the preparation of **PEFSI** is described.

PEFSI Poly(ethylene furoate-co-ethylene sodium sulfoisophthalate). First, 3 g (9.37 mmol) of DEF and 0.69 g (2.34 mmol) of Na-DMSI were reacted with 2.9 g (46.80 mmol) of ED and of 0.1 wt.% zinc acetate, for 3 h in a nitrogen atmosphere at 200 °C. Then 0.1 wt.% $Ti(OBu)_4$ was added to the resulting reaction medium and it was the heated at high temperature 240 °C during 6 h under vacuum to remove the remaining diol as efficiently as possible [17].

The same procedure was used for the preparation of the others copolyesters but with the corresponding changes in the nature of diols. In the case of diethylene glycol (DEG) monomer the polycondensation was achieved either with ethylene glycol or without.

PDEFSI Poly(diethylenefuroate-co-diethylene sodium sulfoisophthalate). First, 3 g (9.37 mmol) of DEF and 0.69 g (2.34 mmol) of Na-DMSI were reacted with 4.97 g (46.84 mmol) of DEG.

PEDEFSI Poly[(ethylene-co-diethylene furoate)-co-(ethylene-co-diethylene sodium sulfoisophthalate)]. First, 3 g (9.37 mmol) of DEF and 0.69 g (2.34 mmol) of Na-DMSI were reacted with the mixture of 2.32 g (37.47 mmol) ED and 0.99 g (9.37 mmol) of DEG.

PETEFSI Poly[(ethylene-co-triethylene furoate)-co-(ethylene-co-triethylene sodium sulfoisophthalate)]. First, 3 g (9.37 mmol) of DEF and 0.69 g (2.34 mmol) of Na-DMSI were reacted with the mixture of 2.32 g (37.47 mmol) ED and 1.40 g (9.37 mmol) of TEG.

PBFSI Poly(butylene furoate-co-butylene sodium sulfoisophthalate). First, 3 g (9.37 mmol) of DEF and 0.69 g (2.34 mmol) of Na-DMSI were reacted with 4.21 g (46.80 mmol) of BD.

PHFSI Poly(hexamethylenefuroate-co-hexamethylene sodium sulfoisophthalate). First, 3 g (9.37 mmol) of DEF and 0.69 g (2.34 mmol) of Na-DMSI were reacted with 5.52 g (46.80 mmol) of HD.

The resulting copolymers were used for characterization without further purification.

2.4. Films preparation

Films were prepared using two different methods: solvent casting process and melting process.

2.4.1. Solvent casting process

Films referenced as (**PEFSIcp, PEDEFSIcp, PETEFSIcp, PBFSIcp** and **PHFSIcp**) were prepared by casting 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 vacuo at 50 °C to constant weight. The thickness of the obtained films was measured with a digital linear gauge (Ono Sokki EG-100); the values were **about** 180 μm.

2.4.2. Melting process

Films referenced as (**PEFSImp, PEDEFSImp, PETEFSImp, PBFSImp** and **PHFSImp**) were prepared by pressing the sample in its molten state between two plates heated at 120 °C. The thickness of the films also measured with a digital linear gauge was about 75 μm.

2.5. Analytical techniques

1D and 2DNMR spectra were recorded on a BrukerAvance III spectrometer (400 MHz for ^{1}H and 100.6 MHz for ^{13}C) equipped with a 5 mm multinuclear broad band probe (BBFO+) with a z-gradient coil. 2D ^{1}H–^{1}H and ^{13}C-^{1}H correlation spectra were recorded through gradient enhanced H-HCOSY, HSQC and HMBC experiments. Samples were dissolved in DMSO-d6 and analyzed at 90 °C.