European Polymer Journal 63 (2015) 186–193

Contents lists available at ScienceDirect

European Polymer Journal

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

# Renewable alternating aliphatic-aromatic poly(ester-urethane)s prepared from ferulic acid and bio-based diols

Mouandhoime Zahahe Oulame [a,b,1], Florian Pion [a,b,1], Shaik Allauddin [c], Kothapalli V.S.N. Raju [c], Paul-Henri Ducrot [a,b,*], Florent Allais [a,b,d,*]

[a] *INRA UMR 1318 Institut Jean-Pierre Bourgin, F-78026 Versailles, France*
[b] *AgroParisTech UMR 1318 Institut Jean-Pierre Bourgin, F-78026 Versailles, France*
[c] *Polymers & Functional Materials Division, Indian Institute of Chemical Technology, Hyderabad 500 607, India*
[d] *AgroParisTech, Chaire Agro-Biotechnologies Industrielles (ABI), F-51100 Reims, France*

ARTICLE INFO

*Article history:*
Received 19 August 2014
Received in revised form 20 November 2014
Accepted 22 November 2014
Available online 19 December 2014

*Keywords:*
Aromatic poly(ester-urethane)
Bisphenol
Biomass
Lignocellulose
Ferulic acid
Biobased polyols

ABSTRACT

A new class of eight partially renewable alternating aliphatic-aromatic poly(ester-urethane)s (PEUs) is obtained through the polyaddition of four renewable bisphenols derived from ferulic acid and bio-based diols on two commercially available diisocyanates. The structures and molecular weights of these PEUs are characterized by $^1$H and $^{13s}$C NMR, Fourier transform infrared spectroscopy (FT-IR), and size exclusion chromatography (SEC). The PEUS are further studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). All these thermoplastic PEUs are transparent and rigid at room temperature, with $M_n$ ranging from 4 to 10 kDa, and relatively narrow dispersities (1.7–3.5), prove to be stable up to more than 180 °C ($T_d$ 5%), with $T_g$ varying from 28 to 128 °C depending on their structure.

## 1. Introduction

Polyurethanes (PUs), having an history of more than 70 years, became one of the most dynamic groups of polymers, exhibiting versatile properties suitable for use in practically all fields of polymer applications such as foams, elastomers, thermoplastics, thermosets, adhesives, coatings, sealants, fibers) [1] and additionally, they are used in some specialty applications such as biomedical surgery. Presently, in the industry, PUs are generally obtained by the reaction of a diol or an oligomeric polyol with isocyanates.

In recent years, increased interest appears in bio-based monomers and polymers. However, to be competitive, bio-based products must exhibit functionalities at least equivalent to those of the petroleum-based products. Thus, research should not be limited to pure and simple substitution of existing products, but they must also propose innovative molecules and materials with new value-added features.

Many research programs on new bio-based monomers/additives and polymers are already ongoing in large public and private research institutions [2]. The synthesis of monomers as well as polymers from plant fats, oils and sugars has already found some industrial applications, and recent developments in this field offer promising new opportunities [3]. More recently, scientists got interested in the use of a new bio-based compounds issued from [4]. However, all these resources mainly lead to aliphatic compounds, whereas many key commercial chemicals involve aromatic structures [5]. Therefore, most recently, much focus has been placed on bio-based

---

* Corresponding authors at: INRA UMR 1318 Institut Jean-Pierre Bourgin, Route de Saint-Cyr, F-78026 Versailles, France.

*E-mail addresses:* ducrot@versailles.inra.fr (P.-H. Ducrot), florent.allais@agroparistech.fr (F. Allais).

[1] These authors contributed equally to this work.

http://dx.doi.org/10.1016/j.eurpolymj.2014.11.031
0014-3057/© 2014 Elsevier Ltd. All rights reserved.

aromatic compounds able to replace phenol, bisphenol A, styrene, phenol resins, aromatic polyesters and their biocomposites in industrial applications [6]. A promising approach consists in the preparation of new bio-based materials using monomeric phenolics originating from lignocellulosic biomass [7]. Out of them, ferulic acid has been identified as a promising bio-based platform molecule. Many research groups have indeed recently demonstrated the great potential of ferulic acid through the development of new homopolyesters exhibiting appealing thermal properties [8–10]. Homo- and copolyesters of *p*-hydroxycinnamic acids showing remarkable liquid–crystal [11], biodegradability [12] or biocompatibility [11b] properties were also reported. However, they are often hard to process because of their too high melting temperature ($T_m$). To lower the $T_m$, *p*-hydroxycinnamic acids were copolymerized with aliphatic monomers to increase the structural flexibility of the resulting polymers [13]. Another approach based on the synthesis of bisphenols from vanillin [14], for the preparation of alternating copolymers with aliphatic moieties was described. Following this approach, and having developed expertise in the chemistry of lignin related phenolic compounds [15], we recently focused on the synthesis of a new class of bio-based molecules derived from ferulic acid. We indeed designed a new methodology for the production of bisphenols incorporating ferulic acid and bio-based diols through a chemo-enzymatic process involving *Candida antarctica* lipase B (aka CAL-B, Novozyme®435) [16]. These bisphenolic compounds were efficiently condensed with renewable activated diacid chlorides providing alternating aliphatic-aromatic copolyesters whose thermal properties could be finely tuned by playing with the chemical structure of both diacid and bisphenol, giving access to copolyesters exhibiting $T_g$'s ranging from 0 to 80 °C [17].

Herein we want to report the preparation, characterization and thermal properties of new alternating aliphatic-aromatic PEUs obtained through the polyaddition of these new bio-based bisphenols with two of the most widely used isocyanates for PUs production on an industrial scale. Indeed, PEUs with aromatic urethane bonding structures have shown good thermal degradation and mechanical properties. Based on overall properties analysis, such polymers are expected to be good candidates as protective coatings [18].

## 2. Experimental

### 2.1. Materials and methods

All reagents, including *C. antarctica* lipase B supported on acrylic resin were purchased from Aldrich Chemical Co. FT-IR spectra were recorded on a Thermo Nicolet Nexus 470. $^1H$ and $^{13}C$ NMR spectra were recorded in $CDCl_3$ on a Bruker Ascend 400 at 400 MHz and 100.6 MHz respectively, reference in $CDCl_3$: 7.26 ppm for $^1H$ and 77.16 ppm in $^{13}C$; in $(CD_3)_2SO$: 2.50 ppm in $^1H$ and 39.52 in $^{13}C$; $\delta$ are given in ppm and $J$ in Hz. Size exclusion chromatography (SEC) was performed in chloroform ($CHCl_3$) with a Gilson 305 pump, an UltiMate 3000 Autosampler from Dionex, a Mixed-B column (600 mm × 7.5 mm, 10 mm) from PL calibrated with polystyrene standards at 25 °C, using UV detection at 254 nm with an Ultimate 3000 PDA from Dionex. Results were calculated with Cirrus GPC 3.0. Samples were dried in a vacuum-oven at 50 °C for 18 h prior to analysis. Thermo-Gravimetric Analysis (TGA) was recorded using a Q-500 from TA. About 5–10 mg of each sample were heated from 25 to 600 °C at 10 °C/min under inert atmosphere. Differential Scanning Calorimetry (DSC) was recorded under inert atmosphere on a DSC 6000 from Perkin Elmer. About 5–10 mg of each sample were weighted in an open pan that went to heat/cool/heat cycle at 10 °C/min. Data are given from the second heating scan.

### 2.2. Bisphenols preparation [16]

Available in ESI.

### 2.3. General procedures for polyurethanes preparation

#### 2.3.1. Bulk polymerizations

In a round-bottom flask under argon were successively added bisphenol (**EDF**, **PDF**, **BDF** or **IDF**) (1 eq) and diisocyanate (HDI or TDI) (1 eq). The reaction mixture was magnetically stirred under argon and heated (100–140 °C) for the given time. The resulting polymer was dissolved in chloroform, precipitated in cold methanol and recovered by filtration.

#### 2.3.2. In-solvent polymerizations

In a round-bottom flask under argon were successively added bisphenol (**EDF**, **PDF**, **BDF** or **IDF**) (1 eq), solvent ($CHCl_3$, MEK, MIBK or 1,4-dioxane) and diisocyanate (HDI or TDI) (1 eq). The reaction mixture was magnetically stirred under argon and heated (100–140 °C) for the given time. The resulting polymer was precipitated in cold methanol and recovered by filtration.

#### 2.3.3. Poly[1,6-hexamethylene diisocyanate-alt-(bis-O-dihydroferuloyl ethylene glycol)] (PHDI-EDF)

(Yields: 88% in MEK and 99% in bulk.)

NMR: $\delta_H$ 400 MHz; $CDCl_3$ 6.98 (2 H, m, $H_{7,7'}$), 6.66–6.78 (4 H, m, $H_{8,8',10,10'}$), 5.22 (bs, Ar-OH), 5.17 (bs, OCONH), 4.26 (4 H, s, $H_{16,16'}$), 3.81 (6 H, s, $H_{12,12'}$), 3.23 (4 H, m, $H_3$), 2.85–2.93 (4 H, m, $H_{13,13'}$), 2.59–2.65 (4 H, m, $H_{14,14'}$), 1.56 (4 H, m, $H_2$), 1.38 (4 H, m, $H_1$). $\delta_C$ 100.6 MHz; $CDCl_3$ 172.9 (s, $C_{15'}$), 172.7 (s, $C_{15}$), 154.7 (s, $C_5$), 151.6 (s, $C_{11}$), 146.6 (s, $C_{6'}$), 144.2 (s, $C_{11'}$), 138.9 (s, $C_9$), 138.6 (s, $C_6$), 132.4 (s, $C_{9'}$), 123.4 (d, $C_7$), 120.9 (d, $C_{8'}$), 120.4 (d, $C_8$), 114.5 (d, $C_{7'}$), 112.7 (d, $C_{10}$), 111.1 (d, $C_{10'}$), 62.3 (t, $C_{16}$), 62.2 (t, $C_{16'}$), 56.0 (q, $C_{12,12'}$), 41.3 (t, $C_3$), 36.1 (t, $C_{14'}$), 35.7 (t, $C_{14}$), 30.8 (t, $C_{13}$), 30.6 (t, $C_{13'}$), 29.8 (t, $C_2$), 26.4 (t, $C_1$); FT-IR: $\nu_{max}/cm^{-1}$ 3360 (NH), 1732 (C=O), 1506 (C=C); UV: $\lambda_{max}$(THF)/nm 242 and 278.

#### 2.3.4. Poly[1,4-toluene diisocyanate-alt-(bis-O-dihydroferuloyl ethylene glycol)] (PTDI-EDF)

(Yields: 85% in MEK and 99% in bulk.)

NMR: $\delta_H$ (400 MHz; $(CD_3)_2SO$) 10.62 (bs, $H_2$), 9.36 (1 H, m, $H_{10}$) 7.61–6.59 (9 H, m, $H_{4,6,7,13,14,18,13',14',18'}$), 5.52 (bs, Ar-OH), 5.29 (bs, OCONH), 4.25 (4 H, s, $H_{22,22'}$), 3.76 (6 H,