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Renewable polymers derived from ferulic acid and biobased diols via ADMET

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ABSTRACT

Renewable α,ω-diene monomers have been prepared from ferulic acid, biosourced diols (isosorbide and butanediol) and bromo-alkenes using a chemo-enzymatic synthetic pathway then studied as monomers in ADMET polymerization. All monomers and polymers have been thoroughly characterized using NMR, GPC, DSC and TGA. ADMET polymerization was optimized with regard to catalyst loading (Hoveyda–Grubbs II), reaction medium (in mass vs. in solvent), and temperature, which led to polymers with molecular weight up to 25 kDa. Thermal analysis of these new poly(ester-alkenamer)s showed excellent thermal stabilities (283–370 °C) and tunable T_g depending on the nature of the biobased diol and the chain length of the alkene in the α,ω-diene monomer.

1. Introduction

The collapse of fossil resources and rising prices may have been the first trigger for a biobased economy. Nevertheless, today, industries, customers and regulators (e.g., REACH) are increasingly demanding eco-friendly and bio-based chemicals as well as sustainable industrial processes. In this context, the production of new platform chemicals from biomass through green processes is an alluring strategy for a sustainable development. Indeed, biomass offers a wide range of molecules that can be used to access valuable synthons such as polyols, furans, fatty acids, aliphatic alkanes/alkenes or aromatics/phenolics to name a few [1]. Ferulic acid (**1**), one of the three *p*-hydroxycinnamic acids found in lignocellulosic biomass is one of these sustainable and valuable chemical feedstocks. Present in relatively large quantities in wheat and rice brans as well as in sugarbeet pulp or sugarcane bagasse, its production at industrial scale from these biorefineries and food industries byproducts is been investigated, particularly in our team. According to the best estimates, prices could be as low as $1–3 per kg, reasonable target price for a commercial monomer. Ferulic acid can also be readily synthesized from vanillin, a phenolic compound industrially produced from lignins (sale price ca. $6–15 per kg); however this synthetic pathway requires extra synthetic/purifications step leading to higher production cost.

The α,β-unsaturated carboxylic acid and phenol functional groups present in ferulic acid offer a wide range of possibilities in terms of (bio)chemical transformations which enables the synthesis of value-added molecules such as drugs, functional additives (e.g., antioxidants), monomers and polymers. Many research groups have

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recently demonstrated the great potential of ferulic acid-derived AB-type monomers through the development of new homopolyesters exhibiting appealing thermal properties through either metal-catalyzed polycondensation [2], oxalyl- [3] or thionyl- chloride- [4] activated polycondensations. Other homo- and copolyesters of natural *p*-hydroxycinnamic acids showing remarkable liquid–crystal [5], biodegradability [6] or biocompatibility [5b] properties have also been reported.

Having developed expertise in the chemistry of lignin related phenolics [7], we recently contributed to this research topic through the synthesis of a new class of bio-based polyfunctional molecules derived from ferulic acid. We 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) [8]. This strategy allowed the incorporation of aromatic and aliphatic segments into renewable A_2-type bisphenolic structures under mild conditions in bulk as well as in solvent. These bisphenolic structures were efficiently condensed with renewable activated diacid chlorides (i.e., succinoyl and azelaoyl acid chlorides) and two isocyanates thereby providing renewable alternating aliphatic–aromatic copolyesters [9] and poly(ester-urethane)s [10], respectively. The thermal properties of these novel biobased copolymers can be finely tuned by designing the chemical structure of both the diacid, or diisocyanate, and the bisphenol.

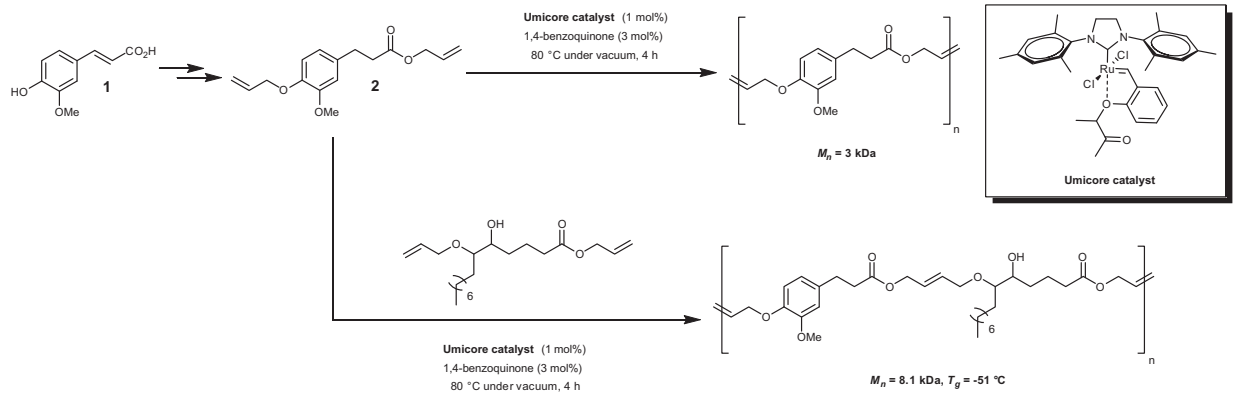
Thanks to the ease of handling and high functional group tolerance of the Ru-based catalysts used in acyclic diene metathesis (ADMET), this method is a very useful approach for the construction of defined polymer architectures [11] and allowed the synthesis of renewable polymers, such as polyesters, polyethers, polyamides and many others, very promising for commercial applications [12]. In spite of extensive research to develop commercial ferulic acid derived renewable polymers [2,8–10], to the best of our knowledge, there is only one example of ADMET polymerization involving ferulic acid derivatives as diene substrates. Indeed, Meier and co-workers reported the use of a bisallylated ferulic acid derivative (**2**) as α,ω-diene monomer for the synthesis of renewable poly(ester-alkenamer)s (Scheme 1) [12a]. In their study, homopolymerization and copolymerization of **2** with oleic and erucic acid-derived α,ω-dienes resulted in polymers with molecular weights of 2–3 kDa and 9 kDa, respectively. Though these polymers were obtained in relatively low molecular weights, this study demonstrated the potential of ferulic acid-derived monomers in ADMET chemistry.

In this work, the ferulic acid-based bisphenols, obtained through lipase-mediated chemo-enzymatic synthesis were used as precursors for the synthesis of novel α,ω-dienes monomers incorporating dihydroferulate ester moieties. These monomers were then submitted to ADMET polymerization to determine their suitability to such method and compare their reactivity to previously reported ferulic-acid derived α,ω-diene monomer **2**. The structure and thermal properties of the novel poly(ester-alkenamer)s were then studied in order to evaluate their potential in industrial applications.

2. Experimental

2.1. Materials and methods

All reagents were purchased from Sigma–Aldrich and used as received. Solvents were purchased from Thermo Fisher Scientific, DMF was dried on a mBraun SPS 800 system. Deuterated chloroform ($CDCl_3$) was purchased from Euriso-top. Evaporations were conducted under reduced pressure at temperature below 40 °C. Column chromatography was carried out with an automated flash chromatography (PuriFlash 4100, Interchim) and pre-packed INTERCHIM PF-30SI-HP (30 μm silica gel) columns. FT-IR and UV analyses were performed respectively on Cary 630 FTIR and Cary 60 UV–Vis from Agilent technologies. NMR analyses were recorded on a Bruker Fourier 300. ^{1}H NMR spectra of samples were recorded in $CDCl_3$ at 300 MHz, chemicals shifts were reported in parts per million relative to the internal standard tetramethylsilane (TMS, $\delta = 0.00$ ppm). ^{13}C NMR spectra of samples were recorded at 75 MHz ($CDCl_3$ residual signal at $\delta = 77.16$ ppm). Thermo-gravimetric analyses (TGA) were recorded on a Q500, from TA. Around 5 mg of each sample was heated at 10 °C min^{-1} from 25 to 500 °C under nitrogen flow (60 mL min^{-1}). Differential scanning calorimetry (DSC)



Scheme 1. Synthesis of the first ferulic acid-derived ADMET polymers by Meier and co-workers [12a].