



Castor oil-derived benzoxazines: Synthesis, self-metathesis and properties of the resulting thermosets

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ABSTRACT

A series of monofunctional benzoxazine monomers with terminal unsaturated alkyl chains was synthesized from fatty acid-derived renewable compounds: 10-undecenoic acid, 4-pentenoic acid and 10-undecen-1-ol. The monofunctional monomers were dimerized by self-metathesis under mild conditions. Different metathesis catalysts and conditions were tested to obtain the desired dimers in good yields and purity that were characterized by ^1H , ^{13}C NMR and ESI-TOF. The structure, properties affecting processing ability and thermal polymerization behavior of the resulting α,ω -bis-benzoxazines were studied. The properties of the obtained flexible materials were evaluated by DSC, TGA, DMTA and contact angle measurements.

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1. Introduction

Polybenzoxazines are thermosetting phenolic type materials with a number of unique outstanding physical and mechanical properties [1]. Polybenzoxazines are formed by thermally activated ring opening of the corresponding 1,3-benzoxazine monomers without any catalyst and without generating byproducts. Moreover benzoxazine monomers can be prepared from inexpensive and commercially available phenols and amines and formaldehyde. Moreover, the wide benzoxazine molecular design flexibility enables preparing different materials with tailored properties. Industrial and academic interest in this relatively new class of materials has resulted in tremendous advances in the last decades, but in general they are still limited in their practical applications due to three main drawbacks. (i) The high temperatures required in the curing (typically in the range of 200–250 °C), (ii) the excessive brittleness of the resulting materials and (iii) the difficulty in being processed into thin films. The two first shortcomings can be addressed using catalysts, to decrease the curing temperature, or blending with other organic or inorganic materials, to increase toughness. On the contrary, processability is a key issue that remains unsolved until now. Molecular design of benzoxazine monomers is another useful approach for addressing all the above inconvenients [2]. Incorporation of aliphatic soft segments in the benzoxazine monomers has shown to increase its processing and afford inherently tough materials. Thus, different telechelic monomers ended by benzoxazine groups [3–5] or polymers containing benzoxazine groups in the main chain [6–11] have been developed by several authors.

In an effort to spread the use of renewable platform chemicals in polymer chemistry, in a previous work we developed a series of ω -unsaturated alkyl benzoxazines employing fatty acids to introduce the aliphatic moieties. These monofunctional benzoxazines were dimerized by hydrosilylation to afford a series of α,ω -bis-benzoxazine monomers with aliphatic spacers which could be easily processed [12]. After curing, these monomers yielded materials with different degree of toughness and

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flexibility, thus proving the validity of the used synthetic approach. In this work, the study is extended to olefin self-metathesis as a tool to produce α,ω -bis-benzoxazine monomers with the desired aliphatic spacers. After curing, this alternative methodology also allows producing flexible materials with tunable properties in a straight and convenient way.

It must be pointed out that, even fatty acid derivatives have been extensively used in preparing monomers and polymers [13,14], under our best knowledge they have not yet been used in benzoxazine chemistry except by our group [12,15]. The same consideration is applicable to olefin metathesis reactions [15].

2. Experimental

2.1. Materials

Chemicals were obtained from the sources indicated and used as received: Grubbs 1st generation, Grubbs 2nd generation and Hoveyda–Grubbs 2nd generation (Aldrich). All solvents were purified and dried by standard procedures.

2.2. Monomer synthesis

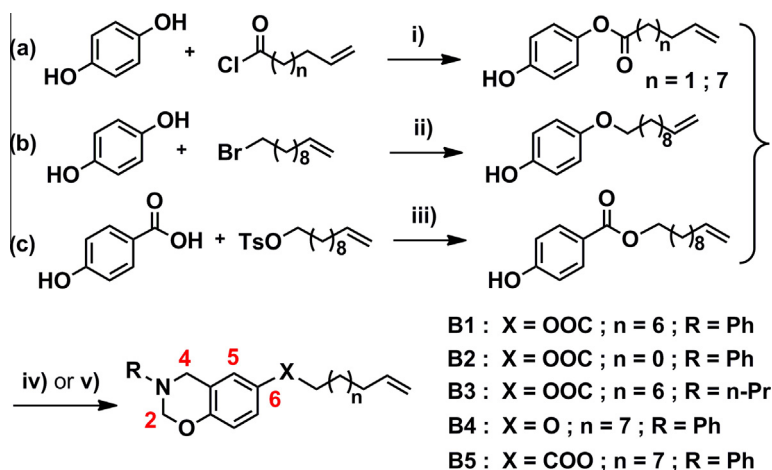
Materials, synthesis and characterization details of phenolic precursors and ω -unsaturated benzoxazine monomers **B1–B5** (Scheme 1) are collected in the supporting information.

2.3. General procedure for olefin self-metathesis dimerization. (Scheme 2)

Metathesis reactions were carried out with 2% or 5% of Grubbs 1st generation catalyst, Grubbs 2nd generation catalyst or Hoveyda–Grubbs 2nd generation catalyst. Reactions were carried out without solvent and under vacuum (2 mmHg) Experiments using p-benzoquinone as additive were also carried out. Under argon about 0.2 g (0.5 mmol) of **B1**, **B2**, **B3**, **B4** or **B5**, the appropriate amount of catalyst and 1 mL of dichloromethane (DCM) were put into a 10 mL Schlenk flask and the mixture was homogenized by stirring at room temperature for 20 min. After evaporating DCM under argon, the temperature was raised up to 40, 60 or 80 °C and maintained with magnetic stirring for 8 or 24 h. The reaction progress was monitored by ¹H NMR spectroscopy. The product was chromatographed using silica gel (hexane/ethylacetate, 10:1) to remove Ru byproducts and finally isolated by solvent evaporation under vacuum. Synthesis of **MB1**, **MB3**, **MB4** and **MB5** bis-benzoxazines was scaled up to 5 mmol scale using 5% Grubbs second generation catalyst at 80 °C for 24 h.

2.3.1. (Z/E)-bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)icos-10-enedioate **MB1**

Pale yellow solid. Yield: 70% mp. 59–62 °C ESI-TOF, exact mass m/z 759.4361 [M + H]⁺. (Theoretical mass: 759.4295). FTIR (ν cm⁻¹): 1749 (C=O), 1250 (C–O–C), 1157 (C–N–C), 1033 (C–O–C), 953 (N–CH₂–Ar Bz ring), 938 (CH=CH). ¹H NMR (CDCl₃, TMS, δ ppm): 7.28–6.75 (m, 16H, Ar–H), 5.39–5.37 (m, 2H, CH=CH), 5.33 (s, 4H, NCH₂O), 4.61 (s, 4H, NCH₂Ar), 2.50 (t, 4H, CH₂CH₂COO), 1.97 (m, 4H, CH₂CH=CH), 1.72 (m, 4H, CH₂CH₂COO), 1.40–1.26 (m, 20H (CH₂)₅). ¹³C NMR (CDCl₃, δ ppm): 172.8 (COO), 152.1 (C–O), 148.4 (C–N), 144.2 (C–OOC), 129.4 (CH=CH), 121.0–118.5 (5 CH 1 C Ar), 117.8 (CH ortho to C–O), 79.7 (NCH₂O), 50.6 (NCH₂Ar), 34.5 (CH₂CH₂COO), 32.7 (CH₂CH=CH), 29.8–29.2 (CH₂)₅, 25.1 (CH₂CH₂COO).



Scheme 1. Structure and synthesis of the ω -unsaturated benzoxazine monomers: (i) THF/Py, 0° to 70 °C; (ii) KOH/EtOH, 80 °C; (iii) (1) K₂CO₃, DMAC, 80 °C, (2) DMSO, 110 °C; (iv) 1,3,5-triphenyltriazine, paraformaldehyde, toluene, 90 °C (**B1**, **B2**, **B4** and **B5**); (v) n-propylamine, paraformaldehyde, bulk, 80 °C (**B3**).

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