



Original article

Synthesis of renewable isosorbide-based monomer and preparation of the corresponding thermosets



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ABSTRACT

Two kinds of difunctionalized isosorbide derivatives containing norbornene groups were designed and synthesized by a facile one-step reaction under mild conditions. ¹H NMR spectroscopy confirmed the chemical composition and differential scanning calorimetry (DSC) revealed the distinct curing behaviors between conventional petroleum-based dicyclopentadiene (DCPD) and synthesized renewable isosorbide-based monomer (ISN). In contrast to DCPD, ISN was low viscous liquid at room temperature and had even higher reactivity to perform ring-opening metathesis polymerization (ROMP) in the presence of Grubbs' catalyst. Due to the presence of flexible and elastic Si–C long chains, the cured poly(ISN) thermosets not only had good mechanical properties but also exhibited much higher storage modulus at the rubbery state in comparison with traditional poly(DCPD).

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1. Introduction

In the past decades, there have been increasing concerns about the fast consumption of fossil resources and growing environmental problems caused by petroleum-based materials [1,2]. Utilization of abundant and renewable resources such as starch, cellulose and lignin as a platform to develop new chemicals and polymeric materials appears to be of importance both from an ecological and economical point of view [3–6]. Among the studied bio-based chemicals, isosorbide is a valuable V-shaped diol consisting of two *cis*-fused tetrahydrofuran rings with 120° angle and can be produced in large scale from starch through three main chemical reactions (shown in Fig. 1). First, starch is hydrolyzed to glucose and then hydrogenated to sorbitol. At last sorbitol is dehydrated to isosorbide. Due to the distinctive properties of isosorbide such as attractive price, molecular rigidity, high thermal stability, biodegradability, renewability, and non-toxicity, a lot of research have focused on exploring new isosorbide-based derivatives (monomers) to prepare high-performance materials for a wide range of applications [7–11].

Smart materials, which could respond to environmental change in automatic ways, have attracted much attention and represent a new paradigm in materials design. Self-healing polymers are one of

most interesting smart materials [12,13]. In these materials, damage can trigger autonomic healing response. Norbornene-based derivative, such as dicyclopentadiene (DCPD), was widely studied as potential self-healing agent because it could easily performed ring-opening metathesis polymerization (ROMP) and form valuable materials in the presence of Grubbs' catalyst [14,15]. Recently, our research group reported the synthesis of a new norbornenyl-functionalized vegetable oil and prepared two kinds of ROMP-based thermosets with good thermal and mechanical properties [16].

In this paper, continuing to develop novel bio-based reactive systems and monomers suitable for high performance materials, we took advantage of isosorbide as a platform and incorporated high reactive norbornene functional group into isosorbide backbone to synthesize one novel bio-based norbornenyl-functionalized isosorbide (ISN). The ROMP curing behaviors of ISN were evaluated in comparison with conventional petroleum-based DCPD and the dynamic mechanical properties and tensile strength of cured poly(ISN) thermosets were also investigated and compared with cured poly(DCPD).

2. Experimental

High purity isosorbide (99.5%, **1**), 5-norbornen-2-yl(ethyl)-chlorodimethylsilane (**2**), anhydrous triethylamine (TEA), 4-dimethylaminopyridine (DMAP) and 2nd generation Grubbs' catalyst [1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]-dichloro(phenylmethylene)-(tricyclohexylphosphine) ruthenium

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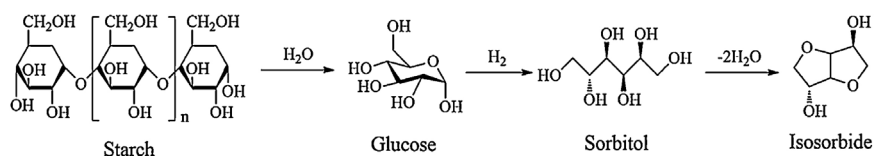


Fig. 1. Scheme of the conversion of starch to isosorbide.

were purchased from Sigma-Aldrich (Milwaukee, WI). 5-Norbornene-2,3-dicarboxylic anhydride (**3**), sodium bicarbonate, anhydrous magnesium sulfate, ammonium chloride and dichloromethane (CH_2Cl_2) were supplied by Fisher Scientific (Fair Lawn, NJ). Dicyclopentadiene (*endo*-DCPD) was obtained from Acros Organics (Belgium). CH_2Cl_2 was refluxed with sodium hydride under nitrogen flow and distilled immediately prior to use. All other reagents were used as received without further purification.

The norbornenyl-functionalized isosorbide monomers were synthesized by following procedures. For ISN, in a three-neck flask equipped with a nitrogen inlet and magnetic stirrer, **1** (10 mmol), TEA (33 mmol), DMAP (1.5 mmol) and CH_2Cl_2 (100 mL) were charged and mixed with vigorous stirring. Under ice bath, **2** (21 mmol) dissolved in 10 mL CH_2Cl_2 was dropwise added into the solution of **1** in 1 h. Then the reaction mixture was kept stirring at room temperature for 12 h, followed by adding saturated NH_4Cl solution. The organic layer was subsequently separated and evaporated under reduced pressure to obtain the desired product ISN with a high yield of 96%.

The corresponding thermosets were prepared via ring-opening metathesis polymerization (ROMP) in the presence of Grubbs's catalyst. First, 2nd generation Grubbs's catalyst was freeze-dried prior to dissolution in monomer. In a typical procedure, catalyst (100 mg) was dissolved in benzene (2 mL) in a small vial and then flash-frozen in a liquid nitrogen bath. The frozen solution was placed in an ice bath under vacuum for 5 h to remove the benzene. Freeze-dried 2nd generation Grubbs's catalyst (0.05 wt%) was added to ISN resin cooled in an ice bath, which was vigorously stirred to dissolve catalyst completely. Then the resin mixture was placed in Teflon molds and cured according to the following schedule: isothermal cure at 50 °C for 1 h and 110 °C for 2 h, followed by post-cure at 130 °C for 12 h. After curing the resulting thermosets were removed from oven and cool down in the air.

^1H NMR spectra were recorded on a Bruker AC 400 nuclear magnetic resonance instrument with CDCl_3 as solvent and tetramethylsilane as internal standard. Differential scanning calorimetry (DSC, TA instruments) was used to evaluate the curing behaviors of ISN monomer. The thermal stabilities of cured materials were studied using a thermogravimetric analyzer (Discovery TGA, TA Instruments). The dynamic mechanical properties of poly(ISN) thermosets were investigated using a strain-controlled rheometer (ARES G2, TA Instruments) in DMA mode with the torsion geometry. The specimens were tested in a temperature range from -50 °C to 220 °C at a heating rate of 3 °C/min, a strain of 0.065%, and an oscillation frequency of 1 Hz. Tensile properties were tested at room temperature by an Instron 4505 universal testing apparatus under a constant crosshead rate of 5 mm/min. Each batch included five specimens to yield an average value.

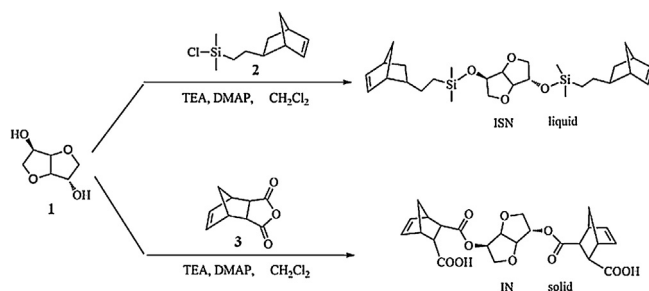
3. Results and discussion

As shown in Scheme 1, two different chemicals 5-norbornen-2-yl(ethyl)chlorodimethylsilane (**2**) and 5-norbornene-2,3-dicarboxylic anhydride (**3**) were selected as modification reagents to functionalize isosorbide (**1**). Through a facile one-step reaction at

room temperature the corresponding two norbornenyl-functionalized isosorbide derivatives ISN and IN were synthesized, respectively. In contrast to solid IN ($T_m = 47$ °C), ISN has low melting point (-15 °C) and is low viscous liquid at room temperature, which means that ISN is more likely to wet the crack surface through capillary effects and perform ROMP to repair the potential microcracks in the materials for the future self-healing application. In addition, non-isothermal differential scanning calorimetry (DSC) indicated that IN could not conduct ROMP in the presence of Grubbs' catalyst because no obvious exothermic peaks were observed during the whole curing process. This could be explained by the difference of molecular structures between ISN and IN. Compared to ISN, the two rigid reactive norbornene end groups in IN were too close to the center rigid two-fused tetrahydrofuran rings, which made the molecular structure of IN even more crowded and then inhibited the formation of macromolecules. Meanwhile, the presence of carboxylic acid groups attached to norbornene groups also could form intramolecular hydrogen bonds in IN and further increased the molecular rigidity. Additionally, Lambeth *et al.* ever reported that the existence of carboxylic acid group was likely to react and form coordinated complex with transition metals of Grubbs' catalyst, which dramatically decreased the catalyst efficiency [17].

The chemical compositions of ISN were characterized and verified by ^1H NMR spectroscopy (shown in Fig. 2). The resonances centered at 6.11–6.09 and 5.90–5.87 ppm were assigned to the two different protons of $-\text{CH}=\text{CH}-$ of norbornene moiety, while the peaks located in the area ranging from 4.45 ppm to 3.44 ppm was corresponded to the eight protons of two-fused rings of isosorbide segment. The signals at 2.78–2.73 and 1.92–1.78 ppm were caused by the end-protons (CH) and middle-protons (CH_2) of bridged $-\text{CH}-\text{CH}_2-\text{CH}-$ of norbornene moiety. In addition, multiplets corresponding to the protons of $-\text{CH}_2-\text{CH}_2-\text{Si}(\text{CH}_3)_2-$ chain-linker appeared around 1.11–1.01, 0.67–0.50 and 0.15–0.05 ppm, respectively.

The curing behaviors of ISN in the presence of Grubbs' catalyst was investigated by non-isothermal DSC at heating rate of 5 °C/min and compared with the conventional petroleum-based DCPD. As presented in Fig. 3, pure ISN only exhibited one exothermic peak, while there were two different exothermic peaks appeared in the DCPD curing spectrum. As we know, the cyclic carbon double bonds could easily be triggered by the Grubbs' catalysts to conduct ring-opening metathesis polymerization (ROMP) and form macromolecules. As a difunctional monomer, ISN is comprised of two



Scheme 1. Synthetic route of norbornenyl-functionalized isosorbide ISN and IN.

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