



Efficient and quantitative chemical transformation of vegetable oils to polyols through a thiol-ene reaction for thermoplastic polyurethanes



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ABSTRACT

Vegetable oils (VOs) such as castor oil and soybean oil were quantitatively transformed to polyols to afford industrially important thermoplastic polyurethanes (TPUs). Photoinduced thiol-ene click chemistry was investigated for the efficient preparation of VO based polyols with primary hydroxyl groups. To improve the reaction efficiency, experimental parameters, such as the concentration of the thiol compounds and reaction temperature, were carefully adjusted. For the first time, nearly complete and quantitative transformation of the carbon-carbon double bonds of the VOs to hydroxyl groups was achieved. The quantitative transformation of the carbon-carbon double bonds to hydroxyl groups allowed for the preparation of polyols with predetermined hydroxyl functionalities. The polyols were successfully incorporated into TPUs, affording elastomers with hyperbranched chain architectures. The TPUs exhibited high toughness along with excellent transparency and improved hysteresis behaviors under high deformation conditions. The study demonstrated efficient synthetic procedures for transforming sustainable plant resources to TPUs to modulate their mechanical and optical properties.

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1. Introduction

Interest in the development of an eco-friendly process to prepare industrially valuable materials from renewable resources is continuing to increase. Several bio-renewable resources, such as cellulose, starch, protein, natural oils and sugar, have gained considerable attention as potential feedstocks (Gandini, 2008; Tanaka et al., 2008; Zhang et al., 2014a). Vegetable oils (VOs) are one of the most important eco-friendly plant resources and have received significant attention due to their unique combination of characteristics such as universal availability, renewability, non-toxic nature, competitive cost, biodegradability and potential for chemical transformation (Miao et al., 2014; Pfister et al., 2011; Seniha Güner et al., 2006). The annual world VO production has increased in the past few decades due to the increasing adaptability in various industries (e.g., agrochemical, coatings, inks, lubricants, plasticizer and polymers) (Miao et al., 2014; Pfister et al., 2011).

VOs typically contain a significant amount of palmitic, steric, oleic, linoleic and linolenic acids. More importantly, the double bonds and ester groups in their structures allow for incorporation of foreign functional groups into the VO molecules to provide

novel raw materials with pre-determined functionalities (Alagi et al., 2016; Alagi and Hong, 2015; Desroches et al., 2012). Several methodologies have been proposed for the functionalization of VOs including epoxidation (Gobin et al., 2015; Zhang et al., 2015; Zlatanić et al., 2002), ozonolysis (Kong and Narine, 2007; Petrović et al., 2005), hydroformylation (Guo et al., 2002; Petrović et al., 2008), amidation (Chaudhari et al., 2014; Chaudhari et al., 2013), transesterification (Mohammed et al., 2013; Petrović et al., 2010) and thiol-ene reaction (Alagi et al., 2016; Caillol et al., 2013; Desroches et al., 2011).

The thiol-ene click reaction can be achieved through a radical or nucleophile mechanism to provide new perspectives for synthesis and modification of chemicals with targeted functionalities (Dondoni, 2008; Kolb et al., 2001; Lowe, 2010). The radical process is typically induced photochemically or thermally by following typical chain reaction processes involving initiation, propagation and termination (Scheme S1, Supporting information). Initially, radicals are generated by a photoinitiator, followed by subsequent reaction of the radicals with a thiol molecules and the formation of thiyl radicals. These thiyl radicals combine with the carbon-carbon double bond in the propagation step. These propagating species abstract hydrogen from another thiol molecule and form a thiol-ene product (Derboven et al., 2013). This reaction is an economically desirable one-step process, with additional benefits of high reaction speed,

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negligible by-products, solventless reaction and tolerance to impurities such as water and oxygen (Dondoni, 2008).

Polyol, a raw material essential for producing industrially important polymers, has been primarily obtained from petrochemical resources. Polyurethane (PU) is an industrially important and representative example of polymers from polyols (Choi et al., 2015; Li et al., 2014). In general, PU is extensively used in automotive, coating, construction and medical applications (Hojabri et al., 2009; Hu et al., 2014; Maisonneuve et al., 2013). Thermoplastic PU (TPU) is one class of the PUs that is thermally processable via extrusion, injection molding and thermoforming, which results in recyclability (Maisonneuve et al., 2013). TPUs are produced over 400 thousand metric tons in 2010 and widely used in various applications due to their superior flexibility, elasticity, strength, transparency, and abrasion resistance (Tang et al., 2014; Yilgör et al., 2015). VO-based polyols have often been used to prepare rigid PU foam (Pillai et al., 2016; Zieleniewska et al., 2015). However, only a limited number of studies have demonstrated the synthesis of TPU from VO-based polyols (Datta and Głowińska, 2014; Hablot et al., 2008; Meier et al., 2007).

Chemical transformations of the unsaturated carbon–carbon double bonds of VOs into hydroxyl functionalities create VO-based polyols. Thiol-ene route is one of the most attractive approaches for incorporating hydroxyl groups into VOs, especially primary hydroxyl groups. The design and development of bio-based polyols that are prepared from VOs using the thiol-ene reaction have been the focus of several researchers (Caillol et al., 2013; Desroches et al., 2011; Türünç and Meier, 2010). Auvergne et al. prepared polyols from rapeseed oil using the thiol-ene reaction under ultraviolet (UV) irradiation (Desroches et al., 2011). However, the transformation of the carbon–carbon double bond to a hydroxyl group was only ~65% with an average number of hydroxyl groups per triglyceride molecule of 3.6. In addition, no detailed properties of the resulting PUs have been reported. Caillol et al. also reported similar results for the preparation of soybean oil-based polyols via the thiol-ene reaction, demonstrating only partial (~65%) transformation of the carbon–carbon double bond to hydroxyl groups at 80 °C (Caillol et al., 2013). Currently available bio-based polyols from soybean oil, such as Agrol® polyol from BioBased Technologies, also has a hydroxyl value of only <200 mg KOH/g. To the best of our knowledge, no study has successfully demonstrated the complete and quantitative transformation of carbon–carbon double bonds of VOs to primary hydroxyl groups to prepare VO-based polyols. The controlled architectures and functionalities of the polyols, which can be achieved by the quantitative control over the transformation of the carbon–carbon double bonds in the VOs to hydroxyl groups, are a crucial prerequisite for facilitating control over the properties and performances of the resulting PUs.

In this study, VO-based polyols were prepared from castor and soybean oils using a thiol-ene click reaction under controlled reaction conditions to achieve complete transformation of the carbon–carbon double bonds to primary hydroxyl groups. 2-Mercaptoethanol (ME) was adopted as a model thiol compound. Polyols with a hydroxyl value of over 200 mg KOH/g were targeted. The polyols were incorporated into TPUs and the characteristics of the materials were investigated.

2. Experimental

2.1. Materials

Castor oil (hydroxyl value of 160 mg KOH/g, Aldrich, St. Louis, MO, USA) and soybean oil (Aldrich, St. Louis, MO, USA) were used as supplied. The representative chemical structures of castor oil and soybean oil are shown in Scheme 1. 2,2-Dimethoxy-2-

phenylacetophenone (DMPA, 99%, Aldrich, St. Louis, MO, USA), ME (>99%, Aldrich, St. Louis, MO, USA), poly(tetrahydrofuran) diol (PTMEG, Aldrich, St. Louis, MO, USA, Mn ~2000 g/mol), 4,4'-methylenebis(cyclohexyl isocyanate) (MHI, 90%, Aldrich, St. Louis, MO, USA), dibutyltin dilaurate (DBTDL, 95%, Aldrich, St. Louis, MO, USA) and 1,4-butanediol (BD, 99%, Aldrich, St. Louis, MO, USA) were also used as received. Tetrahydrofuran (THF, >99%, Daejung Chemicals, Seoul, Korea), *N,N*-dimethylformamide (DMF, 99%, Samchun Chemicals, Seoul, Korea), ethyl acetate (EA, 99%, Samchun Chemicals, Seoul, Korea), methanol (99.5%, Samchun Chemicals, Seoul, Korea) and *n*-hexane (95%, Samchun Chemicals, Seoul, Korea) were used without purification.

2.2. Preparation of castor oil-based polyols (MCO) with primary hydroxyl groups

The photoinduced thiol-ene reaction was carried out in a 100 mL Schlenk flask equipped with a magnetic stirrer. A representative reaction procedure is as follows: Castor oil (10 g, 0.0107 mol), ME (7.52 g, 0.0963 mol), DMPA (0.17 g, 1.0% by weight) and THF (10 mL) were added to a Schlenk flask. The reaction was carried out at –10 °C for 12 h under UV irradiation (254 nm) in a nitrogen atmosphere. During the reaction, the conversion of the carbon–carbon double bonds was monitored by proton nuclear magnetic resonance spectroscopy (¹H NMR) at timed intervals (every 2 h). After the completion of the reaction, the viscous liquid was dissolved in EA (50 mL) followed by extraction with saturated aqueous NaCl (50 mL). The extraction procedure was repeated three times. The organic layer was dried over anhydrous magnesium sulfate and filtered. The resultant was further washed with hexane to remove unreacted castor oil. The viscous liquid was recovered by drying under vacuum at 50 °C for 24 h.

2.3. Preparation of soybean oil-based polyols (MSO)

Similar to the preparation of MCO, the photoinduced thiol-ene reaction of soybean oil was carried out in a 100 mL Schlenk flask equipped with a magnetic stirrer. A representative reaction procedure is as follows: Soybean oil (10 g, 0.0108 mol), ME (16.87 g, 0.216 mol), DMPA (0.37 g, 1.0% by weight) and THF (10 mL) were added to the Schlenk flask. The reaction was carried out in a UV chamber (254 nm) at –20 °C for 24 h. After completion of the reaction, the final product was purified and dried following the same procedure as that employed for the preparation of castor oil-based polyols.

2.4. Preparation of TPU from MCO and MSO

VO-based TPU was synthesized in a three-neck flask equipped with a mechanical stirrer, condenser, nitrogen inlet and thermometer. The reaction was carried out in two steps. In the first step, a NCO-terminated prepolymer was prepared by reacting PTMEG, MCO or MSO and an excess amount of MHI in DMF at 80 °C for 2 h. After preparation of the prepolymer, the reaction mixture was cooled to room temperature. Certain amount of BD and DBTDL (0.01% by weight) was added to the reaction mixture as a chain extender and catalyst, respectively. The reaction mixture was further heated to 80 °C for 4 h. After a sufficient increase in the viscosity, the reaction was quenched by the addition of methanol. This reaction mixture was precipitated in 10-fold excess of methanol and dried under vacuum at 40 °C for 24 h. PU prepared with commercially available PTMEG diol was also synthesized as a reference according to the same procedure. The TPUs exhibited complete solubility in solvents such as THF, chloroform and DMF.

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