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High performance thiol-ene thermosets based on fully bio-based poly(limonene carbonate)s

Chunliang Li[a], Mats Johansson[b], Rafaël J. Sablong[a,c,*], Cor E. Koning[a,d]

[a] Laboratory of Physical Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
[b] Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden
[c] Polymer Technology Group Eindhoven B.V. (PTG/e), P.O. Box 6284, 5600 HG Eindhoven, The Netherlands
[d] DSM Coating Resins, Ceintuurbaan 5, 8022 AW Zwolle, The Netherlands

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ABSTRACT

High glass transition temperature (T_g) thiol-ene networks (TENs) based on poly(limonene carbonate)s (PLCs), derived from orange oils and of potential degradability are described here. PLCs with moderate molecular weight were prepared by copolymerization of limonene oxide with CO_2 and subsequent breakdown reactions. These PLCs were cured with multifunctional thiol monomers in the presence of thermal initiators via thiol-ene chemistry to generate poly(thioether-co-carbonate) networks. The thermal curing experiments were optimized by a kinetic study using real-time ATR-FTIR, in which a delayed gelation was observed. For the first time, an interesting "cage" effect was observed during the network formation initiated by DCP, in which the addition reactions of pendant isopropenyls on high molecular weight PLC chains were significantly enhanced by thiol-ene crosslinking at 160 °C. The resulting homogeneous TENs with high T_gs (> 100 °C) and a wide range of thermomechanical properties, including rubbery moduli from 2.9 to 28.2 MPa, were obtained. The TENs also showed promising properties such as high transparency, good acetone resistance and high hardness, suggesting their potential application in coatings.

1. Introduction

Aliphatic polycarbonates (APC)s have attracted growing attention because of their unique properties, for example, biodegradability and biocompatibility [1–3]. The use of CO_2 as the building block of APCs is attractive because CO_2 is a nontoxic, nonflammable and naturally abundant C1 feedstock. Moreover, epoxides of different varieties can be used in the copolymerization with CO_2 and give APCs with various structures and properties. APCs are generally amorphous and their low absorption in the UV region makes them suitable for outdoor use. However, the lack of functionalities for subsequent modification, a way to reach desired properties limits their applications [4–6].

(*R*)-Limonene, existing as the major essential oil component of citrus peels, is mainly used as a valuable solvent, cleaning or dispersing agent and for fragrance [7,8]. Recently, there has been an increasing interest in using (*R*)-limonene as a mono/bifunctional monomer/precursor for polymer synthesis via thiol-ene chemistry [9–11]. The traditional binary thiol-ene systems, employing non-homopolymerizable ene monomers, exhibit features like rapid polymerization, little oxygen inhibition and homogeneous network formation, which is advantageous for applications like tissue engineering and optical elements [12]. Meier and coworkers reported the addition of thiols to limonene to obtain series of alcohol- and/or ester-functionalized monomers as renewable building blocks in

* Corresponding author at: Polymer Technology Group Eindhoven B.V. (PTG/e), P.O. Box 6284, 5600 HG Eindhoven, The Netherlands.
E-mail address: rafael.sablong@ptgeindhoven.nl (R.J. Sablong).

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polycondensation reactions [10]. Johansson et al. studied the free-radical thiol-ene reaction dynamics between (*R*)-limonene and isotridecyl 3-mercaptopropionate, which revealed a much higher reactivity of the external isopropenyl group than the trisubstituted 1-methyl-cyclohexene unsaturation. This allowed the preparation of limonene-terminated resins as multifunctional precursors for the synthesis of thiol-ene thermosets and polymeric networks [9,13]. Comparable poly(limonene thioether)s also showed promising properties like long-term in vivo 3D structural support and elastomeric mechanical behavior after being fabricated into tissue engineering scaffolds [11]. However, the addition of thiols to double bonds led to flexible thioether linkages, which limits the glass transition temperatures (T_gs) of the resulting polymeric networks. Therefore, such low T_g thiol-ene networks (TENs) are not suitable for applications requiring high modulus and high T_gs such as automotive and aerospace resins [14–16]. An effective way to improve the mechanical and physical properties of the TEN materials is to crosslink linear, high T_g polymers carrying pendant double bonds [6,17,18].

Limonene 1,2-monoepoxide, known as limonene oxide (LO), has been investigated recently for its abundant availability from renewable resources like orange oil, turpentine oils and waste tire pyrolysis, and also for its unique properties as functional monomer [17,19–23]. One attractive method for the utilization of this monomer is to prepare polycarbonates by the catalyzed copolymerization with CO_2, leading to alternating poly(limonene carbonate)s (PLCs) carrying pendant isopropenyl groups. The resulting PLCs showed a T_g of up to 130 °C, excellent thermal resistance, hardness, transparency and full recyclability, and have been assessed as a green platform for functionalized polymers via chemical modification [20,23,24]. Since the first report on the alternating copolymerization of LO and CO_2 catalyzed by a β-diiminate (BDI) zinc complex, continuous efforts have been made to investigate potential applications of limonene-based polycarbonates [14,16,17,19]. We described the synthesis of α,ω-dihydroxyl-PLCs and their initial evaluation in coatings, in which a versatile two-step process was successfully used to prepare materials with desired low molecular weights and end groups [20]. The properties of the coatings were moderate, resulting from the low reactivity of the tertiary hydroxyl end group. However, the coating performance of the polymers were improved after post-modification of the pendant isopropenyl groups with mercaptoalcohols carrying primary OH functionalities via thiol-ene click chemistry, which prompted us to investigate the direct curing of PLCs with multifunctional thiols. Recently, polycarbonates prepared from cyclohexene oxide and alkenyl epoxides (e.g. vinyl cyclohexene oxide, limonene oxide) have been cured with a multifunctional thiol. The resulting networks showed promising properties such as good acetone resistance, high hardness or enhanced thermal properties [17,25]. However, no systematic investigation has been performed on the curing kinetics of these thiol-ene systems, in particular, under solvent-free conditions and the thermo-mechanical properties of the resulting TENs. Moreover, it has been demonstrated that the alicyclic ring structure in the final crosslinked network increases the rigidity and T_g (up to 150 °C) accordingly, and improves the weatherability due to the low UV absorbance [9,17,26]. In this paper we report our detailed investigations on fully bio-based PLCs as core polymers for the synthesis of new TENs under solvent-free conditions for thermoset coating applications.

2. Experimental section

2.1. Materials and methods

All reactions involving air- or water-sensitive compounds were carried out under dry nitrogen using MBraun glove boxes or standard Schlenk line techniques. The copolymerizations were performed in a 200 mL stainless steel reactor (Büchi). Toluene, tetrahydrofuran (THF), dichloromethane (CH_2Cl_2) and diethyl ether were purchased from Biosolve and purified using an activated alumina purification system. *cis/trans*-(*R*)-Limonene oxide (98% purity) was purchased from Aldrich, distilled from calcium hydride and stored under nitrogen. Polymercaptan 358 was a gift from Chevron Phillips. Carbon dioxide (99.999% purity) from Linde Gas was used without further purification. The caprolactam-blocked hexamethylene diisocyanate-based polyisocyanate (trade name: Desmodur BL3272) was a gift from Bayer AG. All other chemicals were also obtained from Aldrich and used as received. (Et-BDI)Zn [$N(SiMe_3)_2$] [Et-BDI = 2-((2,6-diethylphenyl)amido)-4-((2,6-diethylphenyl)imino)-2-pentene)] has been synthesized according to published procedures [19].

2.2. Methods

NMR spectra were recorded on a Varian Mercury Vx (400 MHz) spectrometer at 25 °C in chloroform-d_1 and referenced versus residual solvent shifts.

Gel permeation chromatography (GPC) analyses were carried out using a Waters Alliance system equipped with a Waters 2695 separation module, a Waters 2414 refractive index detector, a Waters 2487 dual absorbance detector, and a PSS SDV 5 m guard column followed by two PSS SDV linear XL columns in series of 5 m (8 × 300) at 40 °C·THF with 1% v/v acetic acid was used as eluent at a flow rate of 1.0 mL·min^{-1}. The columns were calibrated using a series of polystyrene standards (Polymer Laboratories, M_p = 580 Da up to 7.1 × 10^6 Da). Before analyses, the samples were filtered through a 0.2 µm PTFE filter (13 mm, PP housing, Alltech).

Curing reactions were followed using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) on a Varian FT-IR 3100 spectrophotometer equipped with a heat-controlled, single-reflection accessory unit (Golden Gate). All the IR measurements were performed in the reflection mode in a resolution of 4 cm^{-1}. The conversion at the time t, x(t) can be determined as x(t) = [A(0) − A(t)]/A(0), where A(0) and A(t) are the normalized areas (with respect to 1745 cm^{-1}) of the initial ene peak (C═C−H out-of-plane bending vibration $\delta_{=C-H}$ at 888 cm^{-1}) and ene peak at time t, respectively.

Differential Scanning Calorimetry (DSC) analyses of polymer samples were performed on a DSC Q100 from TA Instruments.