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Terpolymers derived from Limonene Oxide and Carbon Dioxide: Access to Cross-Linked Polycarbonates with Improved Thermal Properties

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ABSTRACT: The formation of bio-derived materials is gaining momentum in academic and industrial research as a consequence of depleting petroleum resources, providing mid- and long-term alternative sustainable materials. In this context, we have prepared a series of terpolymers derived from the renewable terpene limonene producing polycarbonates with a controlled and variable ratio of incorporated nonfunctional cyclohexene oxide (CHO) and functional limonene oxide (LO) monomers. As catalyst, a simple binary combination of an Al(III) aminotriphenolate complex and PPNCI (PPN = bis(triphenyl)phosphine-ammonium) has been used to afford the targeted, partially bio-based polycarbonates with typically high carbonate content (>95%), good conversions and a controllable amount of olefinic groups in the terpolymer backbone. Cross-linked polymers (CLP) have been easily obtained from these terpolymers through thiol-ene click reactions allowing for the preparation of interconnected networks with improved thermal properties with their T_d in the range of 250–280°C and with glass transitions (T_g) of up to 150°C. A detailed analysis of the cross-linked polycarbonates demonstrates a clear relation between the percentage of potential cross-linking groups in the terpolymer precursors and the physico-chemical properties including solubility, rigidity and thermal stability.

INTRODUCTION

Polymers are ubiquitous building blocks for a range of consumer-based products providing the necessary plastics, coatings and fibers that increase the quality of life. Therefore, the development of new (catalytic) strategies to obtain synthetic polymers with new and improved properties continues to attract huge interest. The conversion of natural resources into value-added polymers¹ is gaining momentum due to environmental issues, fore-casted depleting fossil resources and more strict waste legislation. The use of carbon dioxide (CO₂) as a carbon feed stock in organic synthesis² and the replacement of fossil fuel feed stocks for natural, renewable ones³ in polymer synthesis have become mature areas of research. In the latter context, polycarbonates produced by ring-opening copolymerization of epoxides and CO₂ represent promising a type of materials.⁴ For instance, epoxide/CO₂ coupling processes have led to the synthesis of new polymers through the use of bio-based monomers based on terpenes⁵ or fatty acids.⁶ These new approaches enable the synthesis of polymers with diverse, new architectures and properties potentially useful in applications that go beyond bench-scale. Thus, beside the conventional alternating copolymerization of epoxides and CO₂ (copolymers, Figure 1a), novel polymers have been synthesized by sequential epoxide addition (CO₂-based block copolymers, Figure 1b)^{7,8} or by random incorporation of multiple epoxide monomers (terpolymers; Figure 1c).^{9,10,11} Interestingly, these block copolymers and terpolymers have been prepared with the idea to use the pendant functional groups for post-polymerization modifications. A wide range of such functional (ter)polymer examples exist incorporating different polymer side chain groups such as alcohols, carboxylic acids, amines, ionic fragments and alkenes. The latter category has been popular in this respect as it allows for easy conversion by thiol-ene “click” chemistry” to modify the polymer properties.^{8,10,12}

Figure 1. Structures of different CO₂-based polycarbonates: (a) Co-polymers, (b) Block copolymers and (c) Terpolymers. The red circles represent the carbonate units, whereas the black and white circles are different incorporated epoxide monomers.

The easy click chemistry and other post-polymerization reactions can be used to prepare new functionalized polymers but also offer opportunities towards the formation of cross-linked polymers by interconnecting different polymer chains (intermolecular process) or fragments (intramolecular process). Such cross-linking may give polymers with improved mechanical strength and thermal stability, as well as polymer nanoparticles with many applications including data storage technology.^{13,14} However, examples of cross-linked polycarbonates based on functional monomers remain rather limited to date. An interesting example was reported by the Coates group, describing the efficient transformation of a linear polycarbonate with pendent alkene groups into organic nanoparticles through well-established olefin cross-metathesis reactions (Figure 2a).⁹ The group of Darensbourg utilized a radical initiated thiol-ene approach to prepare cross-linked materials using a rigid pentaerythriol tetrakis(mercaptoacetate) (Figure 2b).¹⁵ Another recent example of this thiol-ene chemistry is the formation of a rigidified polymer reported by Pescarmona *et al.* that exhibited a high glass transition temperature ($T_g = 130^\circ\text{C}$, Figure 2c).¹⁶ In this latter example a flexible dithiol linker was employed to connect the olefin fragments present in the oligomeric carbonates. All these cross-linked polymers are based on

petroleum feed stocks, and thus the development of new cross-linked materials derived from natural resources remains an interesting target to provide more sustainable alternatives.

Figure 2. Schematic drawings of cross-linked polymers derived from petroleum sources (a-c) and a functional terpolymer derived from the naturally occurring limonene (d). Note that here the black and red units represent a full repeat unit based on an epoxide monomer and CO₂.

As mentioned before, there are only few examples of 100% bio-based polycarbonates known in the literature where natural oils have been used as co-monomers.^{5,6} In this regard, the first copolymerization reaction using terpene-derived epoxides (*i.e.*, limonene oxide, LO) and CO₂ was described by Coates and co-workers utilizing highly active β -diiminate (BDI) zinc catalysts, and they succeeded in the stereoselective conversion of *trans*-LO.^{5a} Furthermore, we recently communicated the use of Al(aminotrisphenolate)/PPNCl [PPN = bis(triphenylphosphine)-iminium] binary catalysts for stereoregular LO/CO₂ copolymerization.¹⁷ As far as we know, the synthesis of CO₂-based terpolymers derived from renewable terpenes is still an unexplored area. Inspired by our previous results in LO copolymerization, we set out to extend this approach towards the preparation of (partially) renewable terpolymers. Here we disclose an efficient catalytic method for the synthesis of new terpolymers based on cyclohexene oxide (CHO), LO and CO₂ with controllable incorporation of both functional (LO) and nonfunctional (CHO) monomers in the polymer backbone. The olefin groups in the resultant terpolymers allow for post-polymerization cross-linking by thiol-ene click chemistry, and our modular strategy provides networks derived from terpenes with high thermal stability and rigidity, and offers alternatives for polycarbonate based materials.

EXPERIMENTAL SECTION

General Considerations. All water sensitive operations were carried out under a nitrogen atmosphere using an MBraun glovebox, standard vacuum-line and Schlenk techniques. Solvents were purchased from Sigma-Aldrich as HPLC grade and dried by means of an MBraun MBSPS800 purification system. All reagents were purchased from commercial suppliers (Aldrich and Acros) and used as received unless stated otherwise. FT-IR measurements were

performed on a Bruker Optics FTIR Alpha spectrometer equipped with a DTGS detector, KBr beam-splitter at 4 cm^{-1} resolution. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed by the Research Support Group at ICIQ on a BRUKER Autoflex spectrometer (more details are provided in the Supporting Information). NMR spectra were recorded on a Bruker AV-400 spectrometer and referenced to the residual NMR solvent signals. Glass transition temperatures (T_g) were measured under N_2 atmosphere using a Mettler Toledo equipped, model DSC822e. Samples were weighed into $40\text{ }\mu\text{L}$ aluminum crucibles and subjected to three heating cycles covered the range from 20°C to $150\text{--}190^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$. Thermo-gravimetric analyses were recorded under a N_2 atmosphere using a Mettler Toledo equipped; model TGA/SDTA851 with a heating rate of $10^\circ\text{C}/\text{min}$. Molecular weights (M_n) and their distributions ($\mathcal{D}$) of the terpolymers were determined by gel permeation chromatography (GPC) at the Instituto de Ciencia y Tecnología de Polímeros (CSIC), Madrid. GPC analyses were carried out with Styragel ($300\times 7.8\text{ mm}$, $5\text{ }\mu\text{m}$ nominal particle size) water columns. Measurements were performed at 35°C at a flow rate of $1\text{ mL}/\text{min}$ using a RI detector (Waters, model 410) and using THF as solvent. Samples were analyzed at a concentration of $4\text{ mg}\cdot\text{mL}^{-1}$ after filtration through a $0.22\text{ }\mu\text{m}$ pore-size. M_n , M_w and M_w/M_n ($\mathcal{D}$) data were derived from the RI signal by a calibration curve based on polystyrene standards.

Reagents and Catalyst. Commercial CO_2 was obtained from Praxair and used without further purification. The commercially available epoxide substrates 1,2-epoxy-cyclohexane (CHO) and (*R*)-limone oxide (LO) were used after distillation over calcium hydride, CaH_2 . *Cis*-limonene¹⁸ oxide was obtained following a literature procedure and purified by distillation over CaH_2 . Commercially available nucleophilic additives bis(triphenylphosphine)iminium chloride (PPNCl) was purified by recrystallization from dichloromethane and dried in vacuo at 40°C for

24 h. Tris(3,5-dimethyl-2-hydroxybenzyl)amine and its aluminium complex (Al^{Me}) were prepared as described previously¹⁹ and used after drying under vacuum at 40°C for 24 h.

General Catalytic Procedure for the Copolymerization of CO_2 and Epoxides. All reactions were prepared in a glovebox using a 30 mL stainless-steel Berghof reactor. In a typical experiment, the catalyst (0.05 mmol), co-catalyst/nucleophile (0.025 mmol) and 10 mmol of epoxide (0.98 g of CHO or 1.52 g of LO) were added into the teflon reaction vessel. Three cycles of pressurization and depressurization of the reactor (5 bar) were carried out before finally stabilizing the pressure at 15 bar. The reaction was stirred at 45°C (40°C inside the reactor) for 48 h. Finally, the reaction was stopped and the autoclave was allowed to cool down to room temperature before venting. The crude reaction mixture was analyzed by ^1H NMR spectroscopy to determine the conversion to polymer and the amount of ether linkages.

General Catalytic Procedure for the CHO-LO- CO_2 Terpolymerization Reactions. The experiments were performed as mentioned above for the copolymerization processes using 0.05 mmol of catalyst, 0.025 mmol of co-catalyst and 10 mmol of the corresponding mixture of LO and CHO. For example, the terpolymer containing 30% of the LO monomer incorporated was prepared from a mixture of 5 mmol of CHO (0.49 g) and 5 mmol of LO (0.76 g) at 15 bar, 45°C (40 °C inside the reactor) during 48 h.

Kinetic Experiments. All reactions for the polymerization control experiments and kinetic studies were prepared in the glovebox using a 30 mL stainless-steel Berghof reactor. The teflon reaction vessel was charged with 0.50 mol % of Al^{Me} catalyst, 0.25 mol % of co-catalyst (PPNCl) and 3.5 mmol of the epoxide mixture (1:1 ratio; 0.17 g of CHO and 0.27 g of LO). Three cycles of pressurization and depressurization of the reactor (5 bar) were carried out before finally stabilizing the pressure at 15 bar. Parallel reactions were stirred at 45°C (40°C inside the

reactor) for different reaction times (from 2 to 48 h). For each reaction time, stirring was stopped and the autoclave was cooled down to room temperature before venting. The conversion of the substrate was examined by ^1H NMR spectroscopy (CDCl_3) of an aliquot taken from the crude reaction mixture and using as internal standard 1,4-dimethoxybenzene (typically 5.0 mol % with respect to the epoxide substrate).

Isolation of the Polymers. The crude reaction mixture was extracted with dichloromethane and the solution allowed to evaporate. The crude mixture was then re-dissolved in a minimal amount of dichloromethane and the polymer precipitated with a 1 M solution of hydrochloric acid in methanol. Upon settling, the supernatant solution was decanted and discarded. Then the polymer was washed with a solution of methanol. Finally the purified polymer was dried *in vacuo* at 40°C overnight and analyzed by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR, IR, DSC, TGA and GPC. The MALDI-TOF assignment for various terpolymers was done taking into account the relative ratios of CHO/LO monomers incorporated as determined by ^1H NMR spectroscopy.

General Procedure for the Cross-Linking Process through Thiol-Ene Click Chemistry. All reactions were carried out under inert conditions using standard vacuum-line and Schlenk techniques. A radical initiator (0.20 equiv. of AIBN; 2,2'-azobis(2-methylpropionitrile) *vs* olefins units in polymers) and 150 mg of the corresponding polymer were transferred into a Schlenk tube equipped with a Teflon stirring bar. Then, the solvent (tetrahydrofuran, 1.0 mL) and 1,2-ethanedithiol (0.50 equiv. *vs* olefin units in the polymers) were added.²⁰ The reaction mixture was heated in an oil bath at 70°C and after 12 h the volatiles were removed in *vacuo*. Afterward, the crude reaction mixture was washed three times with methanol. Finally, the purified polymer was dried in *vacuo* and analyzed by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR, IR, GPC, DSC, TGA.

Figure 3. Previously developed LO/ CO_2 copolymerization process using the binary catalyst Al^{Me} /PPNCI.

RESULTS AND DISCUSSION

Terpolymer Synthesis using the Binary Catalyst Al^{Me} /PPNCI. Previously we reported the use of Al-based amino(triphenolate) complexes with PPNCI as binary catalysts for the coupling reaction between CO_2 and limonene oxide (LO) (Figure 3).¹⁷ The aluminum complex with peripheral methyl substituents has proven to be an efficient catalyst for the synthesis of stereoregular LO-based polycarbonates with M_n 's up to around 10.6 kg/mol ($\bar{D} \sim 1.4$) after 24 h at 45°C and 5 bar operating pressure under neat conditions using 1.0 mol % of Al^{Me} and 0.50 mol % of PPNCI with respect to the substrate. Furthermore, the use of this catalytic system has shown kinetic differences between the conversions of the *cis*- and *trans*-LO monomer, with the latter one being more slowly consumed. Based on these observations, we decided to probe a similar approach towards terpolymers based on CO_2 , CHO and the renewable substrate *cis*-LO. Initially we assessed the potential terpolymerization process under similar conditions used for the LO/ CO_2 copolymerization process, *i.e.* using 1.0 mol % of Al^{Me} and 0.50 mol % of PPNCI, and performing the reaction at 45°C and 10 bar pressure. Upon using a starting ratio of 1:1 between both epoxides, we clearly observed the formation of a polymer having both monomers

incorporated. The conversion (24 h; 75 %) of the substrate and the percentage of LO incorporated (30%; by signal integration) could be calculated by ^1H NMR spectroscopic analysis of an aliquot taken from the reaction mixture (Supporting Information, Figure S23). Thermal analysis showed several glass transition temperatures for this CO_2 -based terpolymer ($T_g = 54, 72$ and 126°C , respectively, Supporting Information Figure S57). The presence of different T_g values observed by differential scanning calorimetry analysis (DSC) may be a result of a poor control over the terpolymerization process leading to a rather heterogenous combination of terpolymeric species. With the aim to gain improved control over the coupling product between CO_2 and both epoxides, we decided to use lower amounts of Al^{Me} and PPNCl (0.50 and 0.25 mol %, respectively) as well as a slightly lower reaction temperature (40°C) and higher initial pressure ($p(\text{CO}_2)^\circ = 15$ bar). Under these latter conditions, the reaction seems to proceed more selectively though a longer reaction time was necessary to obtain appreciable monomer conversions. Importantly, the selective formation of a polycarbonate containing 30% of incorporated LO and with only one T_g (95°C) was noted. However, the molecular weight that was observed was rather modest $M_n = 4.0$ kg/mol with a narrow polydispersity ($D = 1.48$; see Table 1 entry 4). On the basis of this result, we used similar conditions to access various CHO/LO based terpolymers with different percentages of LO incorporated (Table 1). Variation of the relative concentrations of both CHO and LO monomers in reactions led to different polycarbonates with percentages of incorporated LO monomer ranging from 10–40% (Table 1). Additionally, the CHO/ CO_2 and LO/ CO_2 copolymers were also prepared under the same conditions to compare their properties with the terpolymer ones.²¹

The data in Table 1 show that the percentage of LO incorporated in these terpolymers has a significant effect on the molecular weight (M_n) as well as on the glass transition temperature (T_g). At higher percentages of LO incorporated in the terpolymer products, lower molecular weights are found and concomitantly lower T_g values. These observations are to be expected when the amount of LO is increased in the initial reaction mixture as this monomer typically shows lower conversion kinetics compared to CHO.

In order to gain more insight into the terpolymerization process, the CO₂/CHO/LO coupling process was followed in time. Such kinetic experiments are usually performed to assess whether diblock copolymers or terpolymeric structures are formed.²² This type of analysis is useful to get more detailed information about the reactivity of all involved monomers and the monomer composition in the chain as to discriminate between a homogeneous or a gradient type of terpolymer.^{15,23} We thus carried out a set of experiments with an equimolar CHO/LO mixture at 40°C and 15 bar and followed the terpolymerization process in time. Reactions were stopped at different time intervals and the reaction mixtures were analyzed by ¹H NMR spectroscopy to determine the consumption of each epoxide monomer (Supporting Information, Table S1). Figure 4 shows the conversion of both CHO and LO in this terpolymerization process. Clearly, CHO reacts much faster than LO, delivering a polycarbonate with an incorporation ratio CHO/LO of 74:26 determined by ¹H NMR signal integration. Despite the fact that CHO reacts significantly faster in this terpolymerization, LO incorporation into the polymer backbone occurs from the early stage (12% on average; after 2 h, 14% total monomer conversion) to the end of the process (26% on average; after 48 h with a 70% total monomer conversion). Therefore, the polymer seemingly has the functional monomer LO reasonably distributed throughout the entire chain. To further substantiate a random distribution of the LO monomer, the ratio between the

net consumption of CHO and LO monomers was followed in time providing relative incorporation kinetics (Figure 5). This graph thus gives an impression of the relative rates of incorporation of both monomers, and the terpolymer that was produced has apparently a high CHO/LO incorporation ratio (7:1) at the initial stage of the reaction (first 2 h period), which then quickly decays to lower CHO/LO incorporation rates in subsequent one hour time intervals ($t = 3, 4, 5$ and 6 h).

Figure 4. Kinetic profiles for the CHO and *cis*-LO (denoted as LO) consumption and the terpolymer formation. In green, the average % of LO incorporation throughout the reaction. Reaction conditions: CHO/LO (1:1 ratio, 3.5 mmol in total), Al^{Me} 0.50 mol %, PPNC1 0.25 mol %, $p(\text{CO}_2)^0 = 15$ bar, neat, 40°C. Polycarbonate conversion, and CHO and LO consumption were determined by ^1H NMR analysis of the crude reaction mixture using 1,4-dimethoxybenzene as internal standard.

Notably, after a 10 h reaction time the overall reaction kinetics become rather slow likely as a consequence of the observed increasing viscosity of the mixture. It is thus clear that the terpolymer starts with a low content of incorporated LO monomer (12%) but after 10 h, when the CHO monomer conversion reaches around 95% (Figure 4) this becomes significantly higher with CHO/LO incorporation ratios < 0.5 (for more details see Table S2, Supporting Information). Overall, this results in a terpolymer structure with a clear gradient in the pendant olefin groups.

Figure 5. The change in the relative CHO/LO incorporation kinetics in time for the terpolymerization process carried out at 40°C, 15 bar and using 1:1 ratio of CHO and LO (3.5 mmol in total).

Figure 6. MALDI-TOF mass spectrum recorded for terpolymer **T-30**. The upper part shows the 1000–5000 m/z region, whereas the lower part displays an enlarged portion between 1700–3400 with some of the assigned peaks explained together with the most dominant end-groups observed.

The terpolymer structures **T-*m*** (*m* = 10, 20, 30 or 40; Table 1 entries 2-5) were further investigated by MALDI-TOF mass spectrometry (Figure 6, and Supporting Information: Figures S53-S56) using similar conditions that were previously successfully used for LO/CO₂ copolymers.¹⁷ As a representative example the characteristics of **T-30** (having an approximate 30% average of LO/CO₂ carbonate repeat units) are discussed here.²⁴ The full trace (Figure 6, upper part) and the selected, enlarged MALDI-TOF region (*m/z* 1700–3400) show a complicated combination of peaks. Despite this complexity, we were able to assign most of the peaks by considering (1) the preference for specific end-groups such as –OH and those having H₂O eliminated (see terpolymer schematic insets at the top of Figure 6),²⁵ and (2) the average % of LO incorporated in the terpolymer **T-30** determined by ¹H NMR analysis. For instance, the peak at *m/z* = 1722 could be readily assigned to a terpolymer based on seven CHO/CO₂ and three LO/CO₂ repeat units with a cyclohexanol end-group (calculated: *m/z* = 1721), and subsequent incorporation of four CHO/CO₂ fragments (*m/z* = 1864, 2006, 2147 and 2291; Δm = 142, equal to a CHO/CO₂ repeat unit) was recognized. At various stages also the incorporation of new LO/CO₂ repeat units (196) was detected, for instance from *m/z* = 1722 to 1918 and from *m/z* = 2291 to 2485.

Apart from all the possible combinations of *n* and *m* (*i.e.*, the ratio of CHO/CO₂ vs LO/CO₂ repeat units for **T-30** being an average of around 30%), also the presence of different end-groups in these polymer distributions add to the complexity of the analysis. The peak at *m/z* = 1756 (calculated: 1757) was assigned to a terpolymer having the same *n/m* ratio as found for the peak at *m/z* = 1722 but with a different end-group based on a dehydrated LO fragment (upper part of Figure 6, green schematic inset). Propagation through consecutive CHO/CO₂ insertions is again easily recognized giving rise to polymers with increasing *n* up to 11 (*m/z* = 2323, calculated:

2324), and the incorporation of LO/CO₂ repeat units can also be observed from, for instance, the peak at $m/z = 2038$ ($n = 9, m = 3$) to give a polymer chain with increasing m ($n = 9, m = 4$: $m/z = 2236$, calculated: 2234).

In the higher mass region up to m/z 3300 similar type of distributions can be found, and the MALDI-TOF analysis therefore provides evidence for a complex mixture of polymer structures with distinct n/m ratios, but more importantly it provides further proof for the early incorporation of the functional monomer LO into the polymer backbones. This corroborates with the kinetic profiles for CHO and LO consumption and the synthesis of terpolymeric structures with a clear gradient in the presence of the olefin groups from relatively low (12% in the first 2 h) to high (>26%) at the end of the terpolymerization process.

Scheme 1. Synthesis of Cross-Linked Polymers through Radical-Initiated Thiol-Ene Click Chemistry. Here m Denotes the % of LO/CO₂ Repeat Units determined in the Different Terpolymers by ¹H NMR, whereas **T- m** is the Terpolymer Substrate and **CLP- m** the Cross-Linked Polymer.

Terpolymer Cross-Linking Reactions. Having prepared a varied range of polycarbonates containing a controlled number of the functional monomer LO, we next turned our focus on post-

polymerization modifications with the aim to improve their thermic properties. Since the pendent olefin groups are reasonably distributed throughout the polymer structures, we envisioned that cross-linking of the alkene units by thiol-ene chemistry would be an ideal strategy to prepare thermally more stable terpolymeric architectures. Thus, the partial bio-based terpolymers described in Table 1 were treated with 1,2-ethanedithiol in the presence of 2,2'-azobis(2-methylpropionitrile) (AIBN) used as radical initiator in catalytic amounts (0.20 equiv. *vs* amount of olefin groups) in THF. The thiyl radicals generated by heating the reaction mixture to 70°C should attack the least hindered carbon center of the olefin unit (Scheme 1) and enable the connection of two separate LO/CO₂ repeat units either *via* intra- or inter-molecular pathways. It should be noted that the reaction stoichiometry is likely a decisive factor to control the ratio between mono- and di-reacted dithiol linkers which may influence the overall polymer properties.

The thiol-ene addition reaction leads to a gradual disappearance of the olefin groups in the polymer backbone, a change that could be easily followed and confirmed by IR and NMR spectroscopy (see Figures 7 and 8). For instance, evidence for thioether formation is provided by changes in the typical IR bands for the copolymer **P-100** substrate located at 1645 cm⁻¹ (C=C) and 887/837 cm⁻¹ (C=C-H) that disappear in time (Figure 7).

¹H NMR analysis of **T-20** treated with 1,2-ethanedithiol to give **CLP-20** provided additional confirmation of olefin to thioether conversion in the polymer structure (Figure 8). For example, the appearance of a peak at 0.98 ppm can be ascribed to thioether linkage formation causing a clear upfield shift of the methyl resonance of the incorporated LO unit (colored green; in the yellow sphere). Also, the presence of various peaks in the region 2.5–3.0 ppm supports the presence of thioether linkages.²⁶ When a (larger) excess of 1,2-ethanedithiol is used, a peak with

increasing intensity at 2.73 ppm is noted which can be ascribed to the presence of cumulative amounts of mono-coupled dithiol species (*cf.*, presence of $-\text{CH}_2\text{SH}$ pendant fragments). In addition to these observation done by ^1H NMR, the disappearance of the quaternary and secondary carbon peaks pertinent to the olefin groups at 148.6 and 108.6 ppm, respectively, of **T-20** was also noticed in the ^{13}C NMR (see Supporting Information: Figure S25).

Figure 7. Comparative IR spectra for the copolymer **P-100** and its corresponding cross-linked polymer **CLP-100** (top) after the thiol-ene reaction.

Figure 8. Comparative ¹H NMR spectra in CDCl₃ at 25°C for: (a) isolated **T-20** terpolymer, and (b–d) prepared cross-linked polymers **CLP-20** using different 1,2-ethanedithiol molar equiv. in the cross-linking process: (b) 0.50 equiv., (c) 0.70 equiv. and (d) 1.5 equiv. The colored spheres represent the relevant protons attached to the indicated carbon centers in the schematic structure above.

The optimal reaction conditions for the cross-linked polymer synthesis were then further examined with particular attention dedicated to influence of the cross-linking reagent on the polymer properties (Table 2). We performed a series of reactions with terpolymer **T-20** and varied the concentration of 1,2-ethanedithiol. Moreover, reactions were performed under concentrated conditions to maximize intermolecular cross-linking (*i.e.*, 1.0 mL of solvent per 150 mg of polymer substrate). The final product may incorporate thiol pendant groups (*m'* repeat units in Scheme 1). Indeed, we were able to detect such pendant groups by ¹H NMR spectroscopy (Figure 8) and their amount depended on the molar equiv. of 1,2-ethanedithiol used in the cross-linking process. Figure 8 suggest that the percentage of free, unreacted –SH groups should be minimal upon using a stoichiometric amount of dithiol reagent (*i.e.*, 0.50 equiv.).

The post-modified **CLP**'s were analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). These thermal analyses showed that interconnected networks **CLP-20a** and **CLP-20b** derived after the cross-linking using an excess (> 0.50 molar equiv.) of dithiol reagent exhibited the lowest *T_g* and *T_d* values among the series (Table 2, entries 1 and 2). Conversely, the use of a stoichiometric amount of dithiol (0.50 equiv., entry 3) resulted into the formation of a cross-linked polymer **CLP-20c** with better thermal properties. The reaction was then also carried out in the presence of a smaller than stoichiometric amount of dithiol (0.30 equiv., entry 4). Under these conditions, the resulting **CLP-20d** did not show any improvement relative towards **CLP-20c**. Additionally, no observable reaction was noted under dithiol-free conditions in the presence of AIBN as radical initiator (entry 5, Table 2). From the combined results it can be concluded that the use of a stoichiometric amount of dithiol produces a cross-linked polymer with optimized thermal features.

Table 2. Synthesis of Cross-Linked Polymers *via* Thiol-Ene Click Chemistry varying the Amount of Dithiol and using Terpolymer **T-20**.^{a,b}

Entry	dithiol (equiv) ^c	CLP ^d	T_g (°C) ^e	ΔT_g (°C) ^f	T_d (°C) ^g	ΔT_d (°C) ^h
1	1.5	CLP-20a	107	7	264	16
2	0.70	CLP-20b	109	6	272	24
3	0.50	CLP-20c	118	18	279	31
4	0.30	CLP-20d	112	9	272	24
5	0	—	100	—	248	—

^aReaction conditions: 150 mg of terpolymer **T-20**, AIBN (0.20 equiv. *vs* olefin groups), 12 h, THF (1.0 mL), 70°C. ^b T_g and T_d values for the sample **T-20** used in these studies were 100°C and 248°C, respectively. ^cEquivalents of 1,2-ethanedithiol used *vs* amount of olefin groups. ^dCross-linked polymer (**CLP**) containing a maximum *m* % of linkages. ^eDetermined by differential scanning calorimetry (DSC). ^f ΔT_g is the difference between the T_g of the cross-linked polymer and the **T-20** terpolymer substrate. ^gDecomposition temperature (T_d) determined by thermogravimetric analysis (TGA) at 10% weight loss of the polymer. ^h ΔT_d is the difference between T_d values of the cross-linked polymer and the **T-20** terpolymer substrate.

With these optimized conditions (0.50 equiv. dithiol, 0.20 equiv. of AIBN, 12 h, 70°C, THF), we then further investigated the formation of cross-linked terpolymers with different amount of olefin groups (**T-*m***; *m* = 10, 20, 30, 40% and **P-100**; Table 3).²⁷ For the **CLP**'s derived from **T-10** and **T-20** we observed the quantitative conversion of the olefin groups and formation of soluble networks **CLP-10** and **CLP-20**.²⁸ However, a further increase in reactive olefin groups in the ter/copolymer substrate (**T-30**, **T-40** and **P-100**) resulted in the formation of materials that

are virtually insoluble in organic solvents. From Table 3 it can be deduced that the cross-linking reaction had a pronounced positive effect on the thermal stability of the resultant **CLP** polymers increasing the decomposition temperatures (T_d) up to 54°C (for **CLP-30**, entry 3). Interestingly, this cross-linking process also enhanced the glass transition temperature and the **CLP**'s exhibited single T_g 's from 116°C (**CLP-30**, entry 3) up to 150°C (**CLP-100**, entry 5). As expected, the T_g values increased as a function of the amount of cross-linkable olefin groups with **CLP-40** (entry 4) and **CLP-100** (entry 5) displaying the highest T_g . In the latter case, the T_g increased from 73 to 150°C ($\Delta T_g = 77^\circ\text{C}$) despite the rather modest molecular weight ($M_n = 3.69$ kg/mol; Table 1, entry 6) of the copolymer substrate **P-100**. Copolymer **P-100** was also reacted with an excess of dithiol (Table 3, entry 6) towards the formation of a CLP with a larger amount of unreacted thiol groups as observed for **T-20** (*cf.*, formation of **CLP-20a** and **CLP20b**, entries 1 and 2 in Table 2). The resulting cross-linked polymer **CLP-100a** showed a much lower T_g and also a lower T_d values than obtained for **CLP-100** thus supporting the view that stoichiometric amounts (0.50 molar equiv.) of the dithiol reagent are also ideal for converting polymers substrates with higher cross-linkable olefin densities into thermally more stable materials. Under more dilute conditions (entry 7), the **CLP-100b** produced from **T-100** was fully soluble and showed virtually no change in the T_g value. This indicates that most of the olefin groups had either reacted in an intramolecular fashion and/or had led to a considerable concentration of unreacted mono-thiol groups in the polymer backbone. GPC analysis of this post-modified polymer **CLP-100b** showed a considerable increase in molecular weight ($M_n = 9.51$ kg/mol) and polydispersity ($\mathcal{D} = 3.15$) compared with **P-100** ($M_n = 3.69$ kg/mol, $\mathcal{D} = 1.34$). Thus, the cross-linking process carried out under diluted conditions favors to a larger extent olefin functionalization and/or introduction of intramolecular linkages though some level of intermolecular cross-linking is maintained.

Table 3. Synthesis of Various Cross-Linked Polymers (CLPs) *via* Thiol-Ene Click Chemistry.^a

Entry	T-<i>m</i> ^b	<i>T</i> _g (°C) ^c	<i>T</i> _d (°C) ^d	CLP-<i>m</i> ^e	<i>T</i> _g (°C) ^c	ΔT_g (°C) ^f	<i>T</i> _d (°C) ^d	ΔT_d (°C) ^g
1	T-10	102	263	CLP-10	117	15	282	19
2	T-20	100	248	CLP-20	118	18	279	31
3	T-30	100	210	CLP-30	116	16	264	54
4	T-40	97	228	CLP-40	119	22	256	28
5	P-100	73	226	CLP-100	150	77	245	19
6 ^h	P-100	73	226	CLP-100a	83	10	239	13
7 ⁱ	P-100	75	226	CLP-100b	74	0	233	7

^aReaction conditions: 150 mg of terpolymer, 1,2-ethanedithiol (0.50 equiv. *vs* olefin groups), AIBN (0.20 equiv. *vs* olefin groups), 12 h, 70°C. ^bTerpolymer containing *m* % of LO monomer incorporated. ^cDetermined by differential scanning calorimetry (DSC). ^dDecomposition temperature (*T*_d) determined by thermogravimetric analysis (TGA) at 10% weight loss of the polymer. ^eCross-linked polymer (**CLP**) containing a maximum of *m* % of linkages. ^f ΔT_g is the difference between the *T*_g values of the cross-linked polymer **CLP** and the terpolymer **T-*m*** substrate. ^g ΔT_d is the difference between the *T*_d values of the cross-linked polymer **CLP** and the terpolymer **T-*m*** substrate. ^hUsing 1.0 equiv. of 1,2-ethanedithiol *vs* olefin groups. ⁱUsing 20 mL of THF as solvent.

The increase of the rigidity in the **CLP**'s with increasing cross-linking density could be observed by DSC analysis as shown in Figure 9. The **CLP**'s having a higher amount of linker units (*i.e.*, **CLP-30**, **CLP-40** and **CLP-100**) displayed more flattened glass transitions and this

behavior may be expected of highly rigid²⁹ and intermolecular connected polymer chains, in line with the poorer solubility observed for the **CLP**'s.

Figure 9. Selected region of the differential scanning calorimetry (DSC) analysis of **CLP-10**, **CLP-20**, **CLP-30**, **CLP-40** and **CLP-100**. The heating rate was 10°C/min. In each case, the trace of the second cycle is shown.

CONCLUSION

In summary, we describe here the first catalytic process towards the formation of terpolymers based on the naturally occurring terpene limonene oxide (LO) with a controlled number of functional repeat units. The control over the number of olefin units enables the post-modification of these terpolymers through thiol-ene chemistry providing materials with improved thermal properties exhibiting much higher T_g and T_d values than their corresponding terpolymer precursors. These new cross-linked polymers (CLP's) thus provide a partial bio-based alternative for those systems that are derived from fossil fuel based feed stocks only. The combined analytical data (IR, NMR, TGA, DSC and GPC) shows good control in the radical initiated thiol-ene cross-linking process when stoichiometric amount of dithiol reagent (0.50 equiv. vs olefin groups) is utilized and emphasizes the importance of the appropriate reaction stoichiometry, and the influence of the amount of functional groups present in the ter/copolymer backbone enabling the synthesis of new cross-linked materials with T_g 's of up to 150°C. Due to the vast increase in bio-renewable materials in industry and academic settings, our current focus is now on the design of new and stable (partially) bio-based co- and terpolymers with different architectures and novel properties using terpenes as accessible and modular scaffolds.³⁰

ASSOCIATED CONTENT

Supporting Information. Further experimental details, spectra of isolated polymer samples (NMR and IR), and relevant GPC, MALDI-TOF-MS, DSC and TGA traces. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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(28) The soluble cross-linked polymer **CLP-10** was analyzed by GPC to assess the influence of the cross-linking process compared to the parent terpolymer **T-10** ($M_n = 8.22$ kg/mol, $D = 1.24$). After cross-linking both the M_n (14.6 kg/mol) and polydispersity ($D = 2.94$) significantly increased.

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