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Modulating molecular weight and crosslinking in thiol-ene polymerization of renewable monomer limonene

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Abstract

Limonene, a renewable material derived from citrus fruit peels, can be used as monomer in thiol-ene polymerization with dithiols and tetrathiols to form linear or crosslinked polymers, respectively. The effect of using a thermal- or photoinitiator on polymer properties was evaluated, with the photoinitiator significantly increasing the conversion of the internal unsaturation of limonene with 1,4-butanedithiol (>90%), resulting in higher molecular weights (9,000 g/mol). With pentaerythritiol tetrakis(3-mercaptopropionate), the gel content remained below 15% in thermally initiated reactions (28,000 g/mol) but increased to above 90% in photoinitiated ones. Finally, combining both thiols resulted in an intermediate molecular weight (~13,000 g/mol) for thermal initiation, and a gel content of about 85% for the photoinitiated ones. Thus, thiol-ene reactions stand out as an effective approach for the synthesis of polymers from limonene, with molecular weight and gel content being fine-tuned by the type/ amount of initiator, and by the combination of di- and tetrathiol.

Keywords: *green chemistry, photopolymerization, renewable monomers, thiol-ene polymerization.*

Data Availability: All data supporting the findings of this study are available from the corresponding author upon request.

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1. Introduction

(R)-(+)-Limonene is one of the most common natural terpenes[1] found in citrus peels, with orange peel containing 85–95% of it in its essential oil[2]. Brazil, the world's largest orange producer with around 17 million tons (primarily for juice), leads global production, followed by China, India, and the United States of America[3]. This terpene is an abundant, inexpensive, and versatile chemical feedstock used as a solvent and in the production of fragrances, pharmaceuticals, and flavors. The extraction and use of limonene from orange peels aligns with Goal 12 (Ensure Sustainable Consumption and Production Patterns) of the 2030 Agenda for Sustainable Development of the United Nations[4]. With two double bonds (an internal – endocyclic, and a terminal – exocyclic), it becomes a well-suited monomer for polymerization. However, due to the sterically hindered ene structure of terpenes, they are primarily ineffective in traditional chain-growth homopolymerization[5]. To overcome this limitation, free-radical-mediated thiol-ene reactions were explored and demonstrated to be a successful alternative[5,6].

Thiol-ene chemistry, although already known for over 100 years[7], studies involving thiol-ene polymerizations of terpenes remain scarce. It proceeds via a free radical chain mechanism and primarily yields anti-Markovnikov products[8]. Figure 1 illustrates this mechanism, where limonene reacts with 1,4-butanedithiol. The polymerization occurs according to the following steps. Initiation (1): A hydrogen atom is abstracted from a thiol group, forming a thiyl radical. This step can be induced by either a thermal initiator or a photoinitiator[9]. Propagation (2): The thiyl radical attacks the terpene double bond forming an intermediate carbon-centered radical. This C–S bond formation is a reversible reaction that also depends on the structure of the olefin. Thus, the addition of thiols to terminal olefins, monosubstituted alkynes, and olefins leading to resonance-stabilized radical intermediates is less reversible than the addition to internal olefins[8]. Therefore, terminal double bonds are generally more reactive than internal ones[10]. This intermediate radical, in turn, easily captures an electron-poor hydrogen from another thiol group, thus characterizing the chain transfer step (3). Finally, the termination step (4) occurs by the combination of two radicals[10,11].

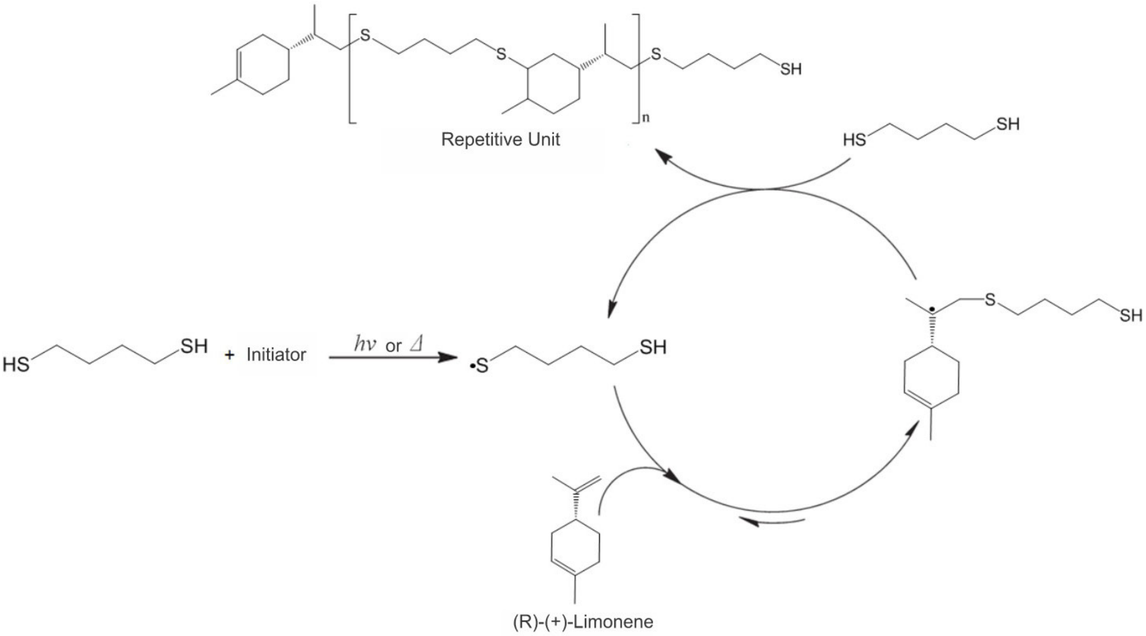

Figure 1. Scheme of thiol-ene polymerization of limonene with 1,4-butanedithiol. Adapted from Claudino et al.[10].

Thiol-ene polymerizations are used in UV-curable coatings[12], flame-retardant polymers[13], crosslinking[14], and polymerization of monomers derived from renewable sources[6,11,15-19], among others. The thiol-ene addition of limonene was used to synthesize alcohol and/or ester-functionalized monomers[8], as well as diamine monomers, for the production of polyamides and polyurethanes[15]. Additionally, sunlight-triggered thiol-ene reactions of D-limonene with poly[(mercaptopropyl)methylsiloxane] were used to produce luminescent films[20], while high Tg networks of poly(limonene carbonates) were prepared by thiol-ene reactions using a multifunctional thiol[21]. Beyond these applications, thiol-ene photopolymerization (TEP) has been employed to synthesize photocured organogels for artwork cleaning, utilizing bio-based monomers functionalized with thiol or allyl groups, particularly limonene[22]. Claudino et al.[10] studied the kinetics of thiol-ene reactions between D-limonene and mono-or tri-functional thiol monomers and observed that the coupling at the external double bond occurred about seven times faster than at the internal ones, with reaction rates unaffected by thiol functionality. In a subsequent study, Claudino et al.[6] synthesized limonene-terminated precursors using tri- and tetra-functional thiols for later UV-curing. However, studies involving thiol-ene polymerization of limonene remain scarce.

In light of the scarce findings reported in the literature and the growing demand for bio-based polymers with specific characteristics, the modulation of molecular weight and gel content in the thiol-ene polymerization of (R)-(+)-limonene was investigated by the combination of a dithiol and a tetrathiol, as well as by using different concentrations and types of initiators (photoinitiator or thermal initiator).

2. Materials and Methods

2.1 Reagents

(R)-(+)-Limonene (97%, CAS: 5989-27-5), 1,4-butanedithiol (dithiol) (≥97%, CAS: 1191-08-8) and pentaerythritol tetrakis(3-mercaptopropionate) (tetrathiol) (>95%, CAS: 7575-23-7) were purchased from Sigma-Aldrich. The thermal initiator α, α′-azobisisobutyronitrile (AIBN) (98%, CAS: 78-67-1) was purchased from Sigma-Aldrich, and the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) (CAS: 24650-42-8) was kindly donated by IGM Resins (Brazil). All reagents were used as received, except for AIBN, which was recrystallized from methanol.

2.2 Experimental procedure

Reactions were carried out in batch in a 10 mL glass reactor. Limonene and the initiator were stirred at room temperature for 10 min to complete initiator solubilization. Immediately afterward, the thiol (dithiol, tetrathiol, or both) was added, and the reaction medium was purged with nitrogen for 5 min. Limonene is miscible with dithiol; therefore, when the dithiol is used, the reactions occur in a homogeneous medium. In contrast, it is immiscible with tetrathiol, resulting in a heterogeneous system. However, in the presence of both thiols, dithiol acts as a miscibility-enhancing compound, and the system becomes homogeneous.

When the thermal initiator AIBN was used, the polymerizations were carried out for 4 h at 80 °C under magnetic stirring, as the half-life of AIBN at this temperature is approximately 80 min[23]. The polymerizations with the photoinitiator DMPA were performed in a UV chamber with two 26 W fluorescent black light lamps. These reactions were conducted for 2 h at 40 °C without stirring, with a distance of 4 cm between the reaction medium and one of the UV lamps, which corresponds to an average light intensity of 3.83 mW/cm^2 (measured using a Solar Light radiometer PMA2100, equipped with a digital UVA+B sensor PMA2107).

Table 1 presents the formulations for all reactions. The ratio of functional groups (thiol:double bond) was kept at 1:1, and all reactions were performed in duplicate.

2.3 Characterization

The conversions of the double bonds of limonene were calculated based on Nuclear Magnetic Resonance (^{1}H NMR) analyses. The ^{1}H NMR analyses were performed in deuterated chloroform ($CDCl_3$, CAS: 865-49-6, 99.8 atom% D) using a BRUKER AC 200 spectrometer operated at 200 MHz. Chemical shifts (δ) were reported in parts per million (ppm), related to tetramethylsilane (TMS, δ = 0.00 ppm). The conversions were calculated based on the concentration of TMS in the deuterated chloroform (0.05% v/v). ^{1}H NMR (200 MHz, $CDCl_3$, δ): 0.00 ppm (TMS, 12H, 4x-CH_3), 4.70 ppm (external unsaturation, 2H, C=CH_2), 5.41 ppm (internal unsaturation, 1H, C=CH). The yield was determined by gravimetric analysis at 90 °C under reduced pressure until a constant mass was achieved.

The gel content was determined after solubilization in tetrahydrofuran (THF) for 48 h and filtration using a syringe filter (0.45 µm). The bottle and the filter, which retained the insoluble polymer, were dried in a forced convection oven at 60 °C for 48 h and weighed to determine gel content by comparing the final dry mass to the original sample mass.

The molecular weight distributions and the corresponding weight average (M_W) and number average (M_N) molecular weights of the soluble polymer fractions were measured by gel permeation chromatography using a high-performance liquid chromatograph (HPLC, model LC 20-A, Shimadzu) equipped with a PL gel MiniMIX pre-column (5 µm, 50 × 4 mm), two MiniMIX PL gel columns (5 µm, 250 × 4.6 mm) in series, and a RID-10A refractive index detector. THF was used as the eluent with a flow rate of 0.3 mL/min flow rate at 40 °C. Polystyrene standards with molecular weights ranging from 580 to 9.835 × 10^6 g/mol were used for the calibration curve.

Thermal degradation was studied by thermogravimetric analysis (TGA, STA 449 F3 Jupiter, NETZSCH). Approximately 10 mg of the sample was weighed into an alumina pan and heated from 30 to 700 °C at a heating rate of 10 °C/min under a nitrogen flow rate of 60 ml/min.

3. Results and Discussions

3.1 Thiol-ene polymerizations using a bifunctional thiol

Limonene has an asymmetric structure, and its double bonds exhibit different reactivities[10]. The conversions of the double bonds with 1,4-butanedithiol were determined by ^{1}H NMR and are presented in Table 2. All polymerizations performed with dithiol at 80 °C (R1, R2, and R3) showed yields above 85% after 4 h of reaction, even R1, which was performed without initiator.

The external double bond of limonene showed a near-complete conversion when AIBN was used (R2 and R3). In contrast, the reaction without AIBN (R1) achieved a conversion of 80%, corroborating the yield determined by gravimetry.

The conversion of the internal double bond was notably lower than that of the external ones, increasing with the amount of initiator and reaching 65% with 4% of AIBN. This difference in the conversion of double bonds was described by Claudino et al.[10], who noted that the external unsaturation reacts about seven times faster than the internal one. Low chain growth was observed for all concentrations of AIBN, resulting in the formation of oligomers with a molecular weight of about 2,000 g/mol (R1, R2, and R3).

Table 1. Formulations of thiol-ene polymerizations of limonene (Lim) with 1,4-butanedithiol (Di) and/or pentaerythritiol tetrakis (3-mercaptopropionate) (Tetra), using AIBN or DMPA as initiator†.

Entry	Lim:Di:Tetra	Initiator	
	(mol:mol:mol)	type	(mol%)†
R1	1:1:0	AIBN	-
R2			1
R3			4
R4		DMPA	-
R5			1
R6			4
R7	1:0:0.5	AIBN	-
R8			1
R9			4
R10		DMPA	-
R11			1
R12			4
R13	1:0.5:0.25	AIBN	1
R14			4
R15		DMPA	1

†In relation to limonene.

Table 2. Thiol-ene polymerizations of limonene with 1,4-butanedithiol and/or pentaerythritiol tetrakis(3-mercaptopropionate).

Reaction[†]	Initiator (mol%)[‡]	Yield (%)	Double bond conversion (%)		Molecular Weight of soluble fraction (g/mol) × 10^{-3}		Gel Content (%)
			Ext.	Int.	M_n	M_w	
Limonene:Dithiol (1:1)							
R1	- (Δ)	85 ± 9	80	18	-[§]	-[§]	-
R2	1 (Δ AIBN)	96 ± 1	100	43	1.40 ± 0.20	1.98 ± 0.40	-
R3	4 (Δ AIBN)	98 ± 1	100	65	1.49 ± 0.12	2.34 ± 0.26	-
R4	- (⚡)	94 ± 4	100	57	1.27 ± 0.15	1.85 ± 0.31	-
R5	1 (⚡ DMPA)	99 ± 1	100	>90	2.66 ± 0.28	5.00 ± 0.95	-
R6	4 (⚡ DMPA)	97 ± 1	100	>90	3.55 ± 1.53	9.01 ± 2.41	-
Limonene:Tetrathiol (1:0.5)[¥]							
R8	1 (Δ AIBN)	75 ± 3	83	50	1.28 ± 0.34	1.99 ± 0.10	< 15
R9	4 (Δ AIBN)	95 ± 1	100	72	2.24 ± 0.36	28.08 ± 16.38	< 15
R11	1 (⚡ DMPA)	99 ± 1	-	-	-	-	97 ± 4
R12	4 (⚡ DMPA)	92 ± 5	-	-	-	-	90 ± 5
Limonene:Dithiol:Tetrathiol (1:0.5:0.25)							
R13	1 (Δ AIBN)	78 ± 10	95	47	1.38 ± 0.01	2.23 ± 0.01	< 15
R14	4 (Δ AIBN)	92 ± 1	100	63	2.29 ± 0.17	12.67 ± 1.13	< 15
R15	1 (⚡ DMPA)	98 ± 1	-	-	-	-	86 ± 9

[†]Results of R7 and R10 are not shown in this table due to sample heterogeneity that did not allow the determination of representative results. [‡]In relation to limonene. [§]Molecular weights were not presented due to the large amount of oligomers (out of the calibration curve). [¥]The reactions took place in a heterogeneous medium. Standard deviation refers to duplicate reactions.

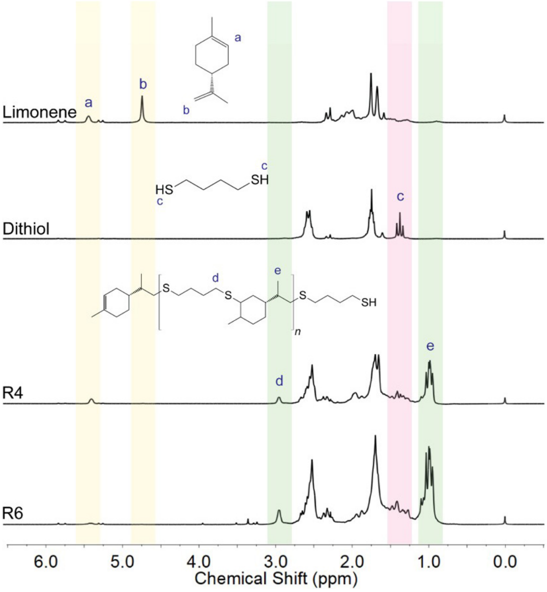

Figure 2. ^{1}H NMR spectra of polymers obtained by thiol-ene photopolymerization (reactions R4 and R6), along with the spectra of limonene and dithiol (at the same concentration as in the initial reaction medium).

To increase the conversion of the internal unsaturation and, thus, the growth of the polymer chain, photopolymerizations were performed with DMPA as a photoinitiator. Yields above 90% were reached for all evaluated DMPA concentrations (R5 and R6), even for R4, which was performed without photoinitiator. It was previously reported that thiol monomers are also photopolymerizable with a wide variety of vinyl monomers in the absence of photoinitiator[24] and that thiol oxidation by air may significantly contribute to the self-initiation of thiol-ene polymerizations performed in the absence of an initiator, but also mentioned that the formation of thiyl radicals by the molecule-assisted homolysis of thiols may not be ruled out[25]. Using the radical photoinitiator 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one (I2959, 3 wt% with respect to the terpene–dithiol mixture), Tarablsi et al.[5] related limiting ene conversions of 90% in the bulk photopolymerization of limonene with ethylene glycol dithiol.

Figure 2 shows the ^{1}H NMR spectra of limonene, dithiol, and the polymers resulting from thiol-ene photopolymerization (R4 and R6).

The absence of the chemical shift of the external double bond of limonene ('b') indicates its complete consumption, even in the reaction performed without DMPA (R4). Regarding the internal double bond of limonene (chemical shift 'a'), the photoinitiated reactions at 40 °C (R4, R5, and R6) showed considerably higher conversions than the respective reactions at 80 °C with AIBN (R1, R2, and R3), due to the significantly higher radical generation rate of the photoinitiator, even at lower temperatures. The conversion of internal double bond increased from 57% in R4 to over 90% in R5 and R6 with DMPA. In addition, the consumption of dithiol (chemical shift 'c') was observed, along with the appearance of peaks 'd' and 'e' corresponding to the formed polymer. Regarding the growth of the polymer chain, the reactions initiated with DMPA (R5 and R6), which showed high conversions of the internal unsaturation of limonene (above 90%), presented a considerable increase in molecular weight compared to those initiated with AIBN at the same concentration, even though the reaction was conducted at higher temperatures (80 °C). Increases of about 90% in M_N and 150% in M_W were obtained for reaction R5 compared to R2. These higher molecular weights achieved in the photoinitiated reactions are related to the higher conversions of the internal double bond. Furthermore, the increased concentration of the photoinitiator (R6) influenced the growth of the polymer chain, leading to a higher molecular weight ($M_W = 9.0 \times 10^3$ g/mol). This positive correlation between molecular weight and initiator concentration would be unexpected for a free radical chain growth polymerization. However, it is reasonable for free radical-mediated thiol-ene polymerization that follows a step-growth polymerization mechanism. In step-growth polymerizations, higher molecular weights are only reached when the conversions of the functional groups are very high, which, in the absence of solvents, may be hampered by diffusional limitations. Thus, in these thiol-ene polymerizations, higher initiator concentrations result in a greater concentration of thiyl radicals, which favors their reaction with the remaining double bonds and leads to higher molecular weights. When the photoinitiator replaces the thermal initiator, and when the concentration of the latter is increased, the molecular weight distribution (Figure 3) not only shifts towards higher molecular weights but also becomes broader while remaining unimodal. The effect of the initiator concentration is much more intense for the photoinitiator.

The thermal behavior of the polymer obtained under R6 photopolymerization conditions, which showed a broader molecular weight distribution, was evaluated by thermogravimetric analysis (Figure 4). This polymer presents thermal stability up to approximately 150 °C. After that, a mass loss (<5% at 350 °C) is observed, reaching complete decomposition at about 378 °C. Therefore, the thermal decomposition temperature of the polymer R6 is between 350 and 378 °C (applying a heating rate of 10 °C/min). Compared with the reaction carried out with AIBN (R2), no significant difference was observed in the thermal decomposition temperature of the polymer (Figure S1 in the Supplementary Information).

3.2 Thiol-ene polymerizations using a tetrafunctional thiol

A tetrathiol was used to evaluate the growth of the polymer chain and the formation of a gel (insoluble fraction), as the presence of four functionalities in the tetrathiol could lead to the formation of a polymer network with limonene. In these polymerizations the reaction medium was not completely homogeneous. Figure 5 shows the possible chemical structure of the crosslinked polymer, considering that all the symmetric thiol groups can eventually react with the double bonds of limonene. The products of reactions R11 and R12, using a limonene:tetrathiol molar ratio equal to 1:0.5, were solid. In contrast, a previous study involving the solution polymerization of limonene and tetrathiol with a molar ratio of 1:0.25 reported the obtention of a highly viscous liquid[22].

For reactions performed at 80 °C (R8 and R9) with AIBN, the yield increased with the amount of initiator used, from 75% for 1 mol% to 95% for 4 mol% initiator concentration (Table 2). Figure 6 shows the ^{1}H NMR spectra of limonene, tetrathiol, and the polymer resulting from the thiol-ene photopolymerization (R8 and R9). An increase in the amount of initiator increases the consumption of the external double bond, reaching virtually 100% conversion in R9 (with almost complete absence of the chemical shift 'b').

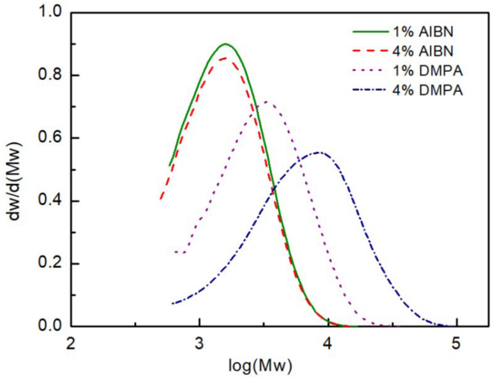

Figure 3. The molecular weight distribution of limonene polymerizations with 1,4-butanedithiol (R2 – 1% AIBN, R3 – 4% AIBN, R5 – 1% DMPA, and R6 – 4% DMPA) using different types and amounts of an initiator.

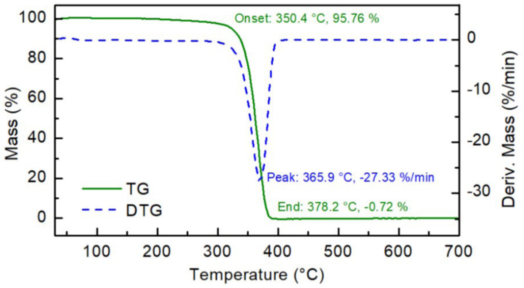

Figure 4. Thermogravimetric analysis (TG) and derivative thermogravimetric (DTG) curves of the polymer obtained from limonene polymerization with 1,4-butanedithiol (R6 – 4% DMPA).

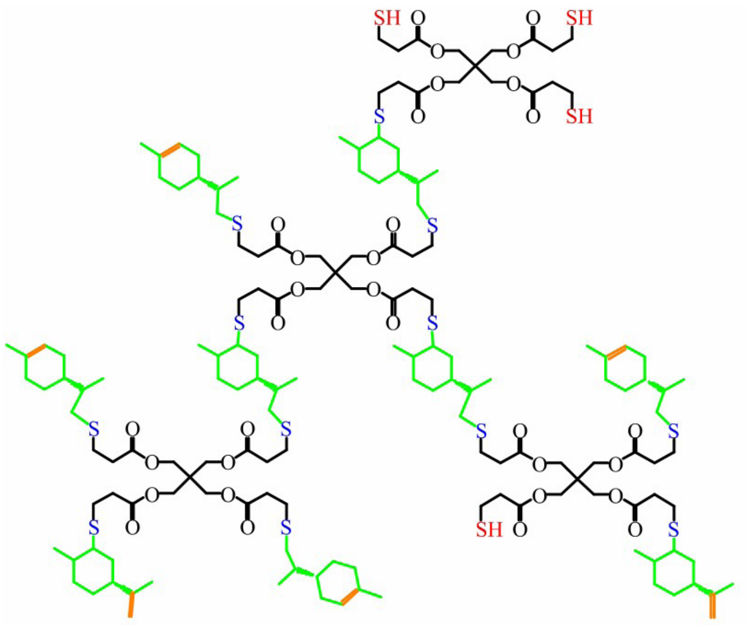

Figure 5. Possible chemical structure of the crosslinked polymer obtained from the reaction between limonene and pentaerythritiol tetrakis(3-mercaptopropionate).

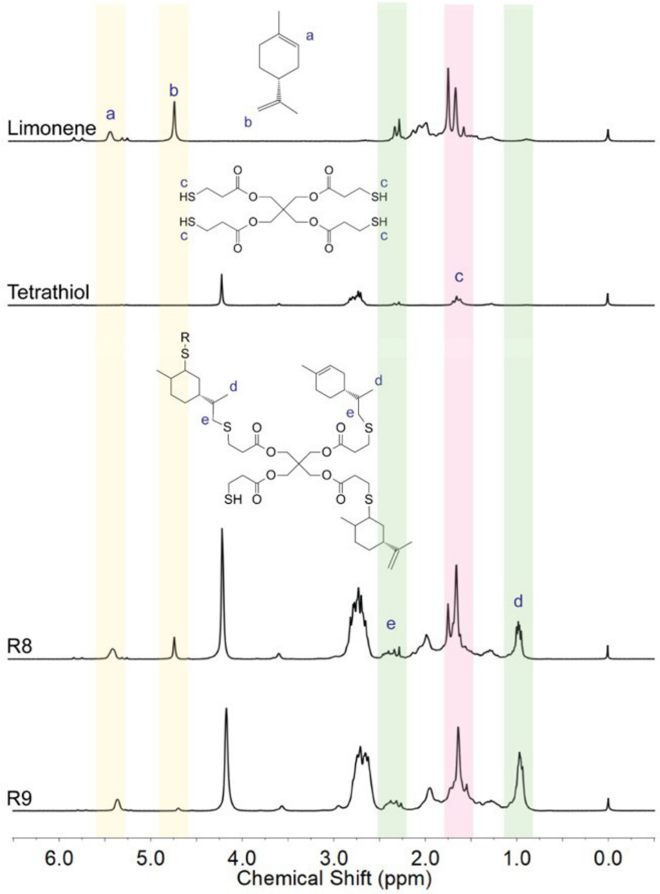

Figure 6. ^{1}H NMR spectra of polymers obtained by thiol-ene photopolymerization (reactions R8 and R9), along with the spectra of limonene and tetrathiol (at the same concentration as in the initial reaction medium).

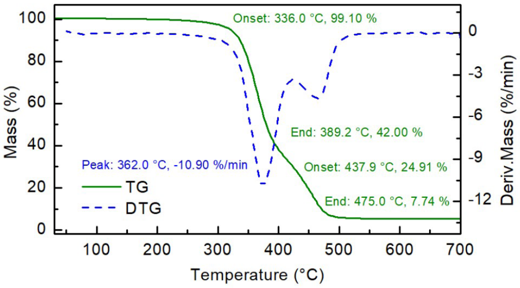

Figure 7. Thermogravimetric analysis (TG) and derivative thermogravimetric (DTG) curves of the polymer obtained from limonene polymerization with pentaerythritol tetrakis (3-mercaptopropionate) (R8 – 1% AIBN).

The reduction in the chemical shift ‘a’, referring to the internal double bond of limonene, indicates conversions of up to 72% (R9). It was not possible to identify the consumption of thiol (chemical shift ‘c’) due to its overlaps with the protons of the terminal methyl groups in limonene (1.6–1.8 ppm); however, the peaks ‘d’ and ‘e’ associated with the formed polymers, were observed.

Neither of these reactions, R8 nor R9, presented a considerable amount of gel content (< 15%), indicating the lower effectiveness of the thermal initiator AIBN, which resulted in branched rather than highly crosslinked polymers. Regarding the average molecular weight of the fraction of soluble polymer (>85%), a very expressive increase is observed with the increase in the amount of initiator used (from R8 to R9), reaching 28 × 10^3 g/mol. The reaction at 80 °C without an initiator (R7 in Table 1) yielded a heterogeneous material, and its characterization was not representative.

Given the positive effect of the photoinitiator DMPA on the conversion of the internal double bond of limonene and, consequently, on the molecular weight, photopolymerizations were also performed with the tetrathiol. For different DMPA concentrations (R11 and R12), yields and gel contents above 90% were obtained, indicating the formation of covalently crosslinked networks. Due to these high gel contents, GPC and ^{1}H NMR analyses were not performed. The high gel content in these reactions is due to the use of tetrathiol combined with high conversions of both double bonds of limonene, compared to the incomplete conversions observed in reactions R8 and R9 with the thermal initiator. Again, the reaction without DMPA (R10 in Table 1) resulted in heterogeneous samples.

Thermogravimetric analysis of the polymers obtained from photopolymerizations R8 and R12 showed two stages of thermal decomposition, as shown in Figure 7 and Figure S2 of the Supplementary Information. Thermal stability is also observed up to around 150 °C, with a mass loss of less than 3% before the first stage of decomposition begins, which occurs from 330 to 390 °C approximately, resulting in a mass loss of nearly 60%. The second stage of thermal degradation ranges from 425 to 475 °C, with a residual of almost 8%. Thus, the thermal decomposition temperature for reactions with tetrathiol has a broader range, divided into two stages, ranging from 330 to 475 °C.

3.3 Thiol-ene polymerizations using a bifunctional and a tetrafunctional thiol

The reactions between limonene and tetrathiol performed with DMPA as a photoinitiator (R11 and R12) showed a substantial increase in the gel content compared to reactions performed at 80 °C with AIBN, from <15% to up to above 90%. To modulate the formation of gel (insoluble fraction) and to evaluate the possibility of increasing the molecular weight without the formation of gel or with low gel content, reactions R13, R14, and R15 were performed, replacing part of the tetrathiol with dithiol (see Table 1).

Using AIBN at 80 °C (R13 and R14), the yield increases with the initiator amount, reaching 92%. These reactions also led to high external double bond conversion (≥95%) and a slight increase in internal double bond conversion, reaching up to 63% with 4% of AIBN (R14). The gel content for both reactions (R13 and R14) was lower than 15%. Regarding the molecular weight of the soluble polymer fraction (>85%), an important increase was observed again with the increase in initiator amount from 1% to 4% (R13 to R14) in these free radical-mediated thiol-ene polymerizations, which follow a step-growth mechanism. However, comparing the M_W from reactions R9 and R14, which used the same amount of initiator but in R14 partially replaced the tetrathiol with dithiol, the M_W decreased from 28.1 × 10^3 g/mol (R9) to 12.7 × 10^3 g/mol (R14). It is important to note that reactions with a higher tetrathiol concentration formed more branched polymers, thereby achieving higher molecular weights.

The results of reactions R13 and R14 showed that the yield, conversion of both double bonds of limonene, and molecular weight increased as the concentration of AIBN increased. The yield increased from 78% to 92%, the external double bond of limonene from 95% to 100% while the internal from 47% to 63%, and the molecular weight from 2.2 × 10^3 to 12.7 × 10^3 g/mol when the AIBN concentration increased from 1% to 4%. This behavior was similar to the reactions between limonene and tetrathiol (R8 and R9). The simultaneous use of both thiols allowed to reach an intermediate molecular weight (12.7 × 10^3 g/mol, R14) compared to reactions with either the dithiol (2.3 × 10^3 g/mol, R3) or the tetrathiol (28.1 × 10^3 g/mol, R9) with the same concentration of AIBN. Thermogravimetric analysis of the polymer produced during photopolymerization R13 (Figure S3 in the Supplementary Information) exhibited a behavior similar to that observed for the polymers synthesized in reactions R8 and R12.

Photopolymerization R15, performed with 1% DMPA as photoinitiator, presented yield and gel content above 95% and 85%, respectively, as shown in Table 2. The highly effective limonene thiol-ene photopolymerization yielded exceptionally high gel contents, even with 1% of initiator (DMPA) and a 2:1 dithiol:tetrathiol molar ratio.

4. Conclusions

Thiol-ene polymerizations of (R)-(+)-limonene have been successfully carried out with dithiol and/or tetrathiol. Increasing the initiator concentration and replacing the thermal initiator AIBN with the photoinitiator DMPA resulted in a higher conversion of the internal double bond of limonene, above 90%, leading to a higher molecular weight. Likewise, replacing the dithiol with tetrathiol increased the molecular weight, while the gel content remained relatively low (<15%) when AIBN was used. In contrast, the use of the photoinitiator DMPA resulted in high gel contents (above 90%). The degradation temperature of the obtained polymers ranged from 330 to 475 °C, being higher in the crosslinked polymers. Thus, polymerizing both thiols with limonene enabled the modulation of the polymer properties in terms of gel content, molecular weight, and thermal degradation, showing the versatility of limonene thiol-ene polymerization. These materials are considered promising for drug delivery systems; however, cytotoxicity and biocompatibility studies are essential for their safe implementation in biomedical applications.

5. Author's Contribution

- **Conceptualization** – Claudia Sayer; Pedro Henrique Hermes de Araújo; Débora de Oliveira; Bruno Augusto Mattar Carciofi.
- **Data curation** – Luiz Paulo Soares Pereira; Tamara Agner.
- **Formal analysis** – Débora de Oliveira; Marina de Souza Melchiors; Pedro Henrique Hermes de Araújo; Tamara Agner.
- **Funding acquisition** – Bruno Augusto Mattar Carciofi; Claudia Sayer.
- **Investigation** – Luiz Paulo Soares Pereira; Thayne Yasmin Vieira.
- **Methodology** – Luiz Paulo Soares Pereira; Marina de Souza Melchiors; Thayne Yasmin Vieira; Pedro Henrique Hermes de Araújo.
- **Project administration** – Bruno Augusto Mattar Carciofi.
- **Resources** – Claudia Sayer; Pedro Henrique Hermes de Araújo; Bruno Augusto Mattar Carciofi.
- **Software** – NA.
- **Supervision** – Claudia Sayer; Pedro Henrique Hermes de Araújo.
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Supplementary Material

Supplementary material accompanies this paper.

Figure S1. Thermogravimetric analysis (TG) and derivative thermogravimetric (DTG) curves of the polymer obtained from limonene polymerization with 1,4-butanedithiol (R2 – 1% AIBN).

Figure S2. Thermogravimetric analysis (TG) and derivative thermogravimetric (DTG) curves of the polymer obtained from limonene polymerization with pentaerythritol tetrakis(3-mercaptopropionate) (R12 – 4% DMPA).

Figure S3. Thermogravimetric analysis (TG) and derivative thermogravimetric (DTG) curves of the polymer obtained from limonene polymerization with 1,4-butanedithiol and pentaerythritol tetrakis(3-mercaptopropionate) (R13 – 1% AIBN).

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