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## RESEARCH ARTICLE

## Ring-opening (co)polymerization of cardanol glycidyl ether

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## Abstract

The anionic ring-opening copolymerization of commercially available bio-based cardanol glycidyl ether (CGE) was investigated without any prior purification. As a first step, anionic-ring-opening homopolymerization was attempted through active chain-end and monomer-activated mechanisms. Both strategies were unsuccessful. Conversely, in a second step, the anionic alternating ring-opening copolymerization (AAROP) of CGE with the renewable *N*-acetyl homocysteine thiolactone (NHTL) was successfully carried out in the presence of a strong base. Anisole, a solvent classified as sustainable and rarely used in anionic ring-opening polymerization, proved to be a suitable for the AAROP. This polymerization is an unusual example of synthesis of linear polyesters with cardanol-based monomers. The copolymers were carefully characterized by <sup>1</sup>H, <sup>13</sup>C, COSY, HSQC, <sup>1</sup>H-<sup>15</sup>N NMR and MALDI-ToF, demonstrating an alternating structure. Then, CGE was copolymerized with NHTL and another additional epoxide. The cardanol-derived monomers enable the preparation of functionalizable poly(ester-*alt*-thioether) bearing multiple allyl and alkene groups. The AAROP method in anisole offers new opportunity for green anionic polymerization through the use of sustainable chemicals, witnessed by the valorization of cardanol-derived compounds and expands the scope of synthesized renewable polyesters.

## KEYWORDS

alternating copolymerization, bio-based polymers, cardanol glycidyl ether, ring-opening copolymerization

## 1 | INTRODUCTION

Cardanol is directly derived from anacardic acid, the main component of abundant and low-cost cashew nutshell liquid (CNSL), which is considered as one of the most promising renewable feedstock.<sup>1</sup> CNSL is a co-product and a non-edible oil with no-impact on the food supply chain. Therefore, CNSL has been intensively investigated for many

years and has been used to prepare a large variety of chemicals and materials.<sup>2</sup> For example, cardanol-derived polyols have been reacted with water-based polyisocyanates, to produce crosslinked polyurethane films.<sup>3</sup> Various chemical modifications, such as etherification, esterification, thiol-ene addition, nitration, sulfonation or epoxidation, have been performed on CNSL in order to introduce reactive moieties and prepare various additives, (multi)functional monomers or polymers having great industrial potential.<sup>4,5</sup> Epoxy-, amino-, (meth)acrylic, or carbonate monomers derived from CNSL have been investigated in

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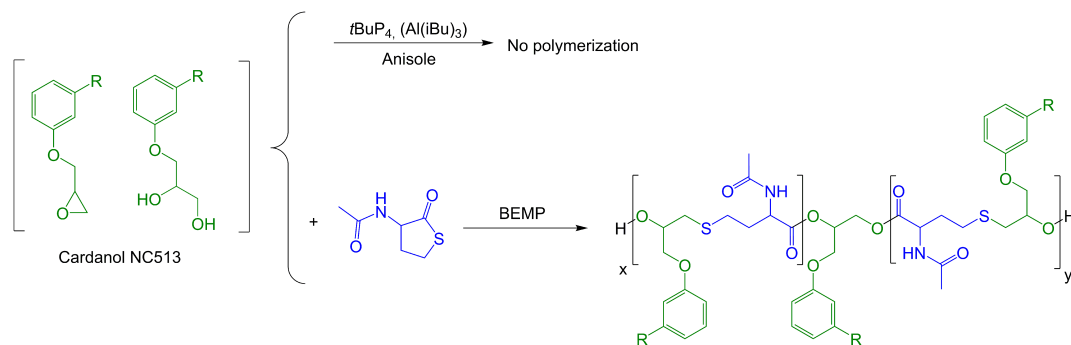
order to prepare various materials, such as polyurethanes or thermosets. Epoxidized cardanol compounds are produced by the epoxidation of the unsaturation(s) in the alkenyl side chain, while cardanol glycidyl ether (CGE) is obtained by the functionalization of the phenolic hydroxyl group. Eventually, epoxidized cardanol glycidyl ether compounds have undergone both processes. Epoxide-containing cardanols have shown interesting properties and have been highly investigated. For example, epoxidized cardanol is a high-performance non-toxic plasticizer for PVC and is therefore a promising substituent to phthalates.<sup>6,7</sup> CGE was also used as reactive diluent for epoxy resins.<sup>8</sup> However, cardanol-based epoxy monomers have been mainly used to synthesize various polyepoxide networks, such as epoxy-anhydride networks with high thermal properties.<sup>9</sup> They are promising bio-based alternatives to petroleum-based chemicals to produce thermosets with various industrial applications, such as anti-corrosion paints,<sup>10</sup> or bio-based coatings.<sup>11</sup> Epoxy cardanol derivatives have also been suggested as a replacement of bisphenol A in epoxy resin for coating applications.<sup>12</sup>

The use of cardanol derivatives as monomer unit in thermoplastic polymers is much less common compared to their incorporation in thermosetting polymers. Cardanol-derived difunctional monomers have been used in polycondensation or polyaddition reactions to synthesize polymers with aromatic moieties in the main chain or as side substituents. For example, cardanol diol derivatives were reacted with diisocyanates in order to prepare linear polyurethanes.<sup>13</sup> Cardanol diacylhydrazide derivatives were used with dianhydride compounds to synthesize poly(amideimides).<sup>14</sup> Polymers with favorable mechanical properties were prepared by reacting allyl-containing cardanol derivatives with bismaleimide compounds by addition copolymerization.<sup>15</sup> Unmodified cardanol was directly used as a comonomer in the radical suspension polymerization of methyl methacrylate or styrene, however the poor reactivity of the alkyl chain unsaturations limited its incorporation in the final copolymer.<sup>16,17</sup> Linear poly(cardanol) was also obtained from unmodified cardanol using a Friedel-Crafts alkylation polymerization mechanism.<sup>18</sup> Cardanyl acrylate was polymerized in solution using free radical polymerization<sup>19–21</sup> or controlled ATRP.<sup>22</sup> Lee et al. carried out the free radical copolymerization of 2-hydroxy-3-cardanylpropyl methacrylate with various functional methacrylates for the preparation of filtration membranes,<sup>23</sup> and antibacterial coating applications.<sup>24</sup> The same group synthesized star-shaped polymers and antibacterial and biocompatible ABA-triblock copolymers by ATRP of 2-hydroxy-3-cardanylpropyl methacrylate initiated by star-PEG and perfluoropolyether macroinitiator, respectively.<sup>25,26</sup> Latex were prepared by homo- or copolymerization of cardanol-based (meth)acrylates with various comonomers in direct or mini-emulsions.<sup>27–29</sup> Cardanol ethyl vinyl ether was homo- and copolymerized using a carbocationic mechanism and well-defined linear (co)polymers with  $M_n$  up to 34 kg mol<sup>-1</sup> were obtained.<sup>30</sup> Very few linear polymers were prepared using CGE as monomer. Epoxy cardanol oligomers were obtained by autoxidation of the unsaturated group of the side chain of CGE.<sup>31</sup> Low molar mass polyethers ( $\approx 3000$  g mol<sup>-1</sup>) were obtained by cationic polymerization of CGE.<sup>32</sup> To the best of our knowledge, the anionic ring-opening polymerization of CGE has never been reported.

Our group has a long expertise in the field of anionic ring-opening polymerization (AROP), whether based on an active end-of-chain mechanism<sup>33–35</sup> or an activated monomer mechanism.<sup>36,37</sup> We have also reported the synthesis of poly(ester-*alt*-thioether)s by organocatalyzed anionic ring-opening copolymerization of thiolactones and epoxides or cyclocarbonates under mild conditions.<sup>38–41</sup> Recently, this technique was used to prepare fully bio-based poly(ester-*alt*-thioether)s using eugenol-derived glycidyl ether and *N*-acetyl homocysteine thiolactone (NHTL).<sup>42</sup> In this study, experiments were performed to assess the feasibility of applying various ROP pathways to a commercially available cardanol glycidyl ether (Cardolite NC-513). Working under sustainable and up-scalable conditions was a requirement. Therefore, the commercial monomers were used as received without any purification or drying steps. Furthermore, the experiments were carried out either in the bulk or in anisole, which is widely recognized as a sustainable solvent.

## 2 | DISCUSSION

The CGE NC513 is industrially produced by reaction of cardanol with epichlorohydrin under basic conditions. According to Jaillet et al. cardanol NC513 also contains opened epoxy groups (Figures 1 and S1).<sup>43</sup> In this work, these hydroxy containing cardanol molecules were supposed to be used as initiator but also to limit the achievable molar masses. In the supplier technical data sheet, the epoxy equivalent weight (EEW) ranges between 425 and 575 g.eq<sup>-1</sup> with a typical value of 490 g.eq<sup>-1</sup>, corresponding to a number of epoxy functions per molecules from 0.61 to 0.83 (typical value of 0.72). First, we investigated the anionic ring-opening homopolymerization of CGE. Several factors guided our choice of anisole as a solvent. It is a commercially available, low-cost, high-boiling point, non-toxic and biodegradable aromatic compound with a structural similarity to cardanol (*like-dissolve-like principle*). It is classified as a green or recommended alternative to conventional solvents in various solvent selection guides published by several organizations and companies such as IMI-CHEM21, Pfizer, Sanofi, and GlaxoSmithKline.<sup>44–47</sup> According to the Globally Harmonized System of Classification and Labeling of Chemicals (GHS), anisole is harmless to the human body or the environment. Eventually, anisole can be obtained from renewable sources, such as lignin and guaiacol.<sup>48–50</sup> The first CGE homopolymerization was carried out in anisole under chain-end mechanism conditions using benzyl alcohol-*t*BuP<sub>4</sub> as initiating system (Table 1, run 1). *t*BuP<sub>4</sub> was used due to its very high basicity and weak nucleophilicity. *t*BuP<sub>4</sub> deprotonates benzyl alcohol and the protonated bulky phosphazanium cation formed in the deprotonation process generates highly reactive ion pairs.<sup>51</sup> After 91 h at 90°C, no homopolymerization of CGE was measured. The second experiment was carried out under typical monomer activated conditions in the presence of 3 equivalents of Al(*i*Bu)<sub>3</sub> Lewis acid. Here again, no homopolymerization occurred after 65 h at 60°C. This lack of reactivity could be explained by the presence of a significant amount of opened epoxy groups in the starting monomer, resulting in a large excess of alcohol functions compared to the *t*BuP<sub>4</sub> base.



**FIGURE 1** Anionic ring-opening (co)polymerization of cardanol derivative NC513.

**TABLE 1** Experimental conditions and molecular characteristics of the polymers synthesized by ROP using CGE as monomer.

Run	Base	[CGE] <sub>0</sub> <sup>b</sup> / [NHTL] <sub>0</sub> / [Base]	[CGE] <sub>0</sub> (g l <sup>-1</sup> )	Solvent	T (°C)	Time (h)	Cv <sub>CGE</sub> (%)	Cv <sub>NHTL</sub> (%)	M <sub>n,th(1)</sub> <sup>c</sup> (g mol <sup>-1</sup> )	M <sub>n,th(2)</sub> <sup>d</sup> (g mol <sup>-1</sup> )	M <sub>n,SEC</sub> <sup>e</sup> (g mol <sup>-1</sup> )	Đ <sup>e</sup>
1 <sup>a</sup>	tBuP <sub>4</sub>	35/0/1	202	Anisole	90	91	0	–	–	–	–	–
2 <sup>a</sup>	tBuP <sub>4</sub>	35/0/1 + 3 eq. Al(iBu) <sub>3</sub>	196	Anisole	60	65	0	–	–	–	–	–
3	BEMP	20/20/1	170	Anisole	60	96	100	97	10,500	1700	2950	1.65
4	BEMP	50/50/1	175	Anisole	60	96	100	95	26,000	1700	2800	1.77
5	BEMP	20/20/1	170	THF	50	96	100	97	10,500	1700	3150	1.61
6	BEMP	20/20/1	170	Toluene	60	96	99	97	10,500	1680	2900	1.65
7	BEMP	20/20/1	170	–	100	4	100	60	10,500	1700	2600	1.70
8	BEMP	20/20/1	170	–	100	4	100	98	10,500	1700	2700	1.73
9	BEMP	18/25/1	150	Anisole	60	96	100	70	9500	1700	2900	1.74
10	BEMP	18/25/1	150	Anisole	100	72	100	66	9500	1700	2700	1.68
11	BEMP	18/25/1	150	Toluene	100	96	100	66	9500	1700	3200	2.60

<sup>a</sup>These experiments have been performed in duplicate.

<sup>b</sup>Using the typical epoxy equivalent weight (EEW) value equal to 490.

<sup>c</sup>The initiation of one macromolecules per base is assumed and the theoretical molar mass is calculated according to the

equation:  $M_{n,th(1)} = \frac{[CGE]_0}{[Base]_0} * Cv_{CGE} * (M_{CGE} + M_{NHTL}) + M_{opened\ CGE}$ .

<sup>d</sup>A fast equilibrium between alcohol and alcoholate species is assumed and thus, each opened epoxy cardanol molecule initiated one macromolecules. The theoretical molar mass is calculated according to the equation:  $M_{n,th(2)} = \frac{0.72}{0.28} * Cv_{CGE} * (M_{CGE} + M_{NHTL}) + M_{opened\ CGE}$ .

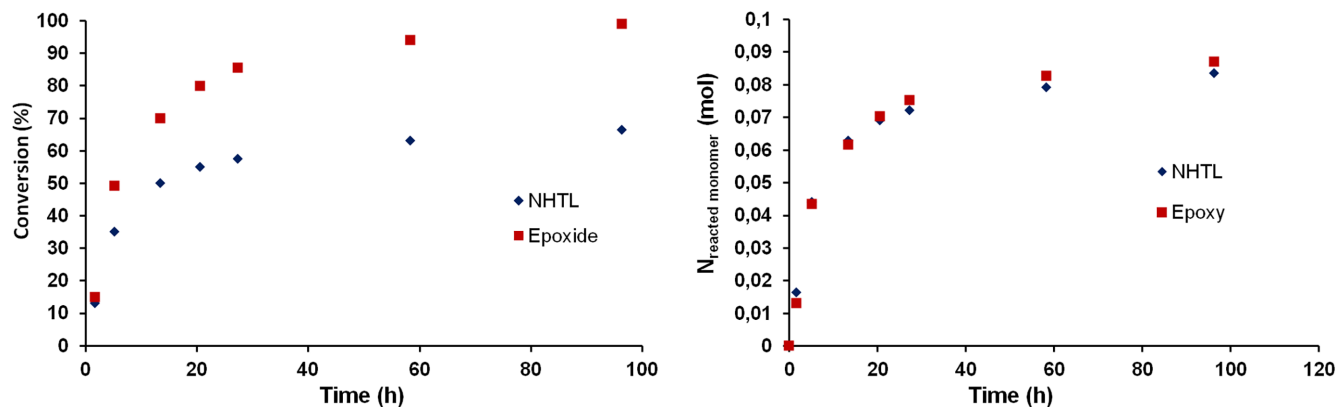
<sup>e</sup>Determined by SEC (THF, 40°C, poly(methyl methacrylate) standards).

However, doubling the amount of tBuP<sub>4</sub> base did not enabled the polymerization.

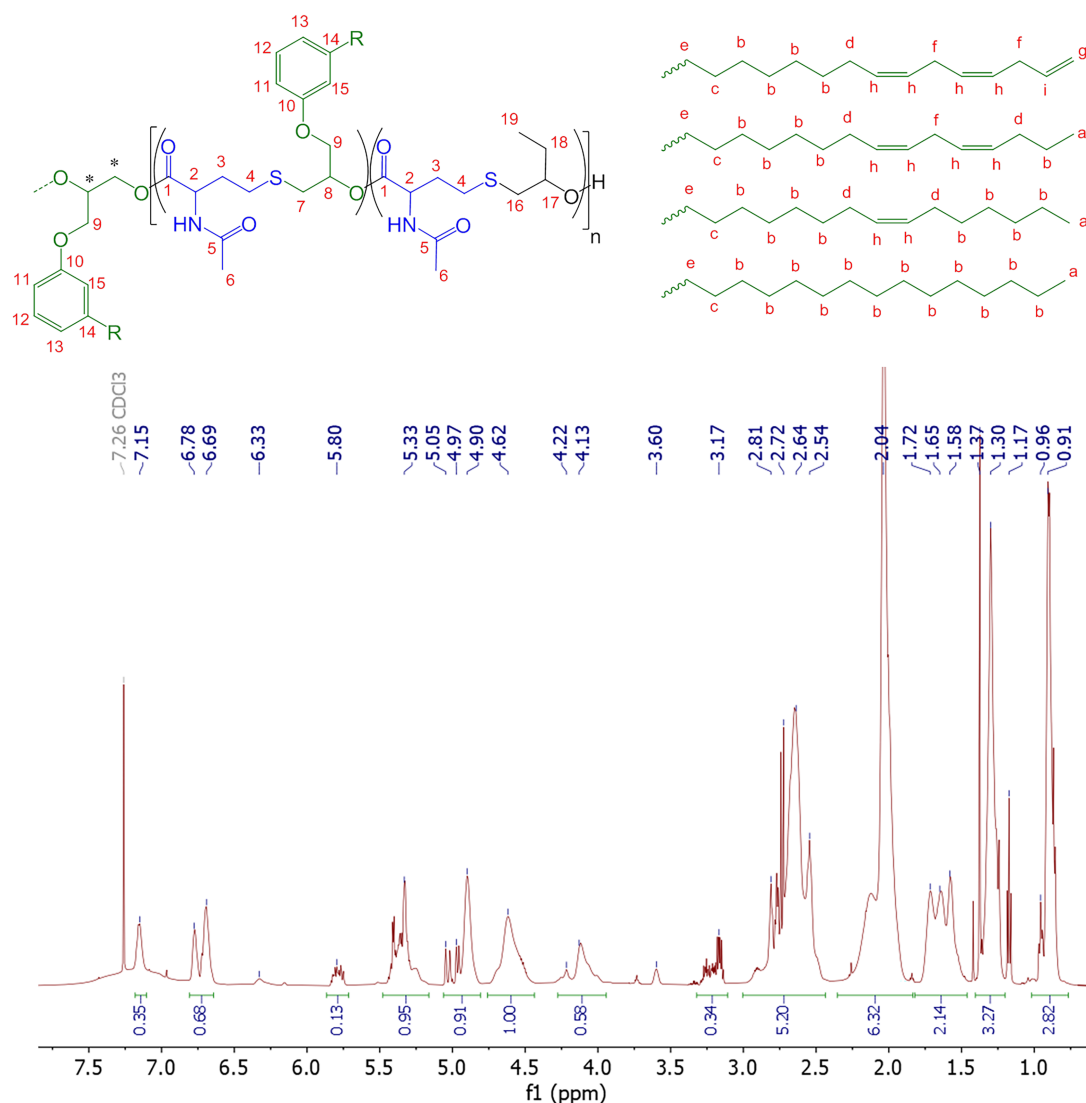
In a second step, the copolymerization of CGE with NHTL was investigated. NHTL was previously demonstrated as a non-homopolymerizable monomer and BEMP was chosen as a base according to previously reported conditions.<sup>39</sup> Two experiments were carried out in anisole at 60°C at the stoichiometry between thiolactone and epoxy groups (Table 1, runs 3 and 4). In each case, an increase in the viscosity of the reaction mixture was observed with time. Full conversions were determined for both monomers by <sup>1</sup>H NMR after 96 h (monomer conversion calculations are detailed in Figure S2). As both monomers do not homopolymerize, an alternating mechanism is strongly suggested. The experimental M<sub>n</sub> determined by SEC was significantly lower than the theoretical ones calculated by assuming that the number of macromolecules is equal to the amount of added tBuP<sub>4</sub> base (M<sub>n,th(1)</sub>). Only oligomers (≈3000 g.mol<sup>-1</sup>) were obtained and the [Epoxy]<sub>0</sub>/[NHTL]<sub>0</sub>/[Base]

ratio has no influence on the M<sub>n</sub>. This result is logical since cardanol NC513 is a mixture of closed and opened epoxy rings, and the latter acts as bifunctional alcohol initiators. A second value of the theoretical number-average molar mass (M<sub>n,th(2)</sub>) was calculated assuming that cardanol NC523 contained 0.28 equivalents of opened epoxy (diols) per molecule and that rapid exchange between alcohol and alcoholate groups occurred. The resulting value is closer to M<sub>n,SEC</sub>.

Oligomers with similar M<sub>n</sub> and Đ were obtained in THF (Table 1, run 5), in toluene (Table 1, run 6) and even in the bulk (Table 1, runs 7 and 8). It is noteworthy that when the polymerization reaction was performed in the bulk at 100°C, full monomer conversions were achieved after only 4 h. Runs 9–11 (Table 1) were performed in the presence of an excess of NHTL. However, the molar consumptions of both monomers remained strictly equal as shown in Figure 2. This result also argues in favor of an alternating incorporation of both monomers.



**FIGURE 2** (A) Time-conversion plot and (B) Time-reacted monomer amounts of the copolymerization of 25 eq. of *N*-acetyl homocysteine thiolactone with 18 eq. of cardanol glycidyl ether in toluene at 100°C (Table 1 run 11).



**FIGURE 3** <sup>1</sup>H NMR spectrum of poly(NHTL-*alt*-CGE) in CDCl<sub>3</sub> at 25°C (Table 1, run 7).

After purification by dialysis in a regenerated cellulose membrane of 1 kDa molecular cut-off against THF, all the oligomers were carefully characterized by <sup>1</sup>H, <sup>13</sup>C NMR, <sup>1</sup>H-<sup>1</sup>H COSY and <sup>1</sup>H-<sup>13</sup>C HSQC.

They displayed very similar spectroscopic data. An assignment of the signals observed in <sup>1</sup>H, <sup>13</sup>C, and COSY NMR could be made and is available directly on the spectra (Figures 3 and S3–5). The <sup>1</sup>H NMR

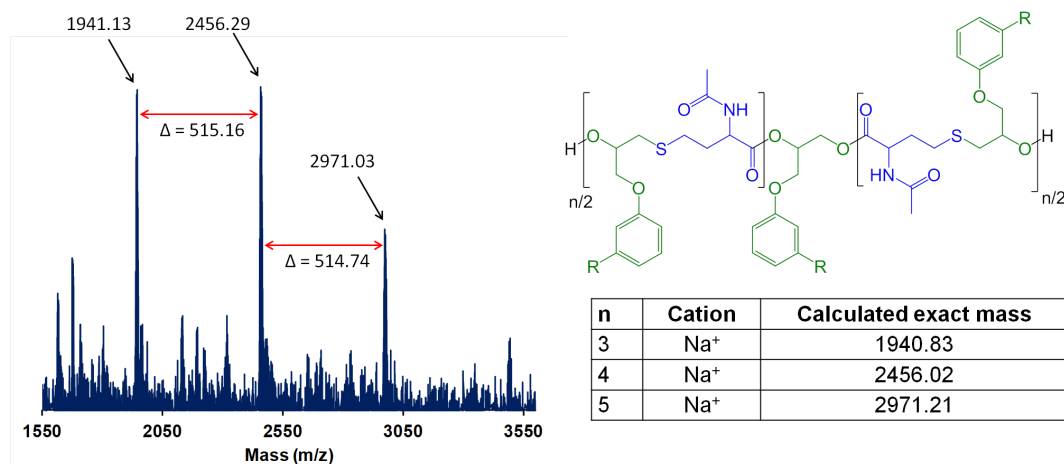
signal with a chemical shift at 5.4 ppm correlates in HSQC NMR with a signal at 72.9 ppm in  $^{13}\text{C}$  NMR, and can be attributed to the —CHR— group of the oxirane monomer next to an ester group, which is consistent with an alternating structure of the chains. It is also relevant to notice that the alkene and allyl groups remained unmodified during the polymerization.

The MALDI-ToF spectrum corresponding to the poly(NHTL-*alt*-CGE) obtained in Table 1 run 5 is shown in Figure 4. Cardanol is a mixture of four different molecules with a variable number of side chain unsaturations. According to Jaillet et al., cardanol is composed of 37% of tri-unsaturated chain, 33% of di-unsaturated chain, 29% of mono-unsaturated chain and 1% of saturated chain.<sup>43</sup> In accordance with this composition, we consider the exact molar mass of cardanol glycidyl ether equal to 356.15 mass unit. The MALDI-ToF spectrum displayed one major distribution, corresponding to oligomers cationized by a sodium ion, initiated by difunctional hydrolyzed cardanol glycidyl ether, end-terminated by two hydroxy groups and for which the molar mass difference between two peaks is strictly equal to the molar mass of one alternating repeat unit (515.19 mass unit).

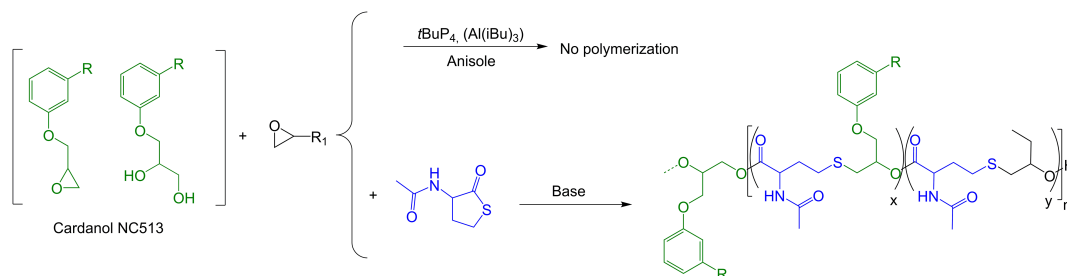
The unsaturation sites in the side-chain of the CGE units could be used for further functionalization or cross-linking reactions. In fact, they can be modified by a large range of well-known reactions, such

as hydrogenation,<sup>1</sup> epoxidation,<sup>7,52</sup> thiol-ene coupling reaction,<sup>53</sup> methathesis,<sup>54</sup> or phenolation.<sup>55</sup> In a preliminary experiment, the allyl groups of poly(NHTL-*alt*-CGE) (Table 1, run 7) were reacted with difunctional dithiothreitol by thiol-ene addition in the presence of AIBN at 70°C in toluene. The disappearance of the allyl groups was followed by  $^1\text{H}$  NMR spectroscopy (Figure S6). After 24 h of reaction a fully insoluble gel was obtained and dried under vacuum.

In the second part, the monomer cardanol NC513 was copolymerized in the presence of a second epoxide (Figure 5). As previously, active chain-end and activated monomer mechanism were tested (Table 2, runs 12–13) without any polymerization being observed after 96 h reaction time. On the contrary, the copolymerization of 4 eq. cardanol glycidyl ether and 20 eq. *tert*-butyl glycidyl ether (tBuGE) with 25 eq. NHTL was observed using BEMP as the base in anisole at 60°C (Table 2, run 14) or in toluene at 100°C (Table 2 run 15, Figure S10). For both reactions, near full monomer conversions were achieved after 24 h. The polymer was characterized by SEC in DMF,  $^1\text{H}$ ,  $^{13}\text{C}$ , COSY, HSQC and DOSY NMR. The poly(NHTL-*alt*-CGE/tBuGE) in anisole had a  $M_n$  determined by SEC equal to 6200 g.  $\text{mol}^{-1}$  in good agreement with  $M_{n,\text{th}(2)}$  and a large dispersity ( $\mathcal{D} = 2.43$ ). The copolymers displayed spectroscopic data consistent with the postulated alternating structure. All the signals observed in



**FIGURE 4** Matrix-assisted laser desorption and ionization time-of-flight mass spectrum (reflectron mode) of a poly(NHTL-*alt*-CGE) synthesized in the bulk (Table 1, run 5).



**FIGURE 5** Anionic ring-opening copolymerization of cardanol derivative NC513 and a second epoxide with or without *N*-acetyl homocysteine thiolactone.

TABLE 2 Experimental conditions and molecular characteristics of the polymers synthesized by ring-opening polymerization using a mixture of epoxides.

Run	Base	Epoxide 2	$[CGE]_0^a/[Epoxide\ 2]/[NHTL]_0/[Base]$	$[CGE]_0$ (g l <sup>-1</sup> )	Solvent	T (°C)	Time (h)	C <sub>VCGE</sub> (%)	C <sub>Vepo2</sub> (%)	C <sub>VNHTL</sub> (%)	$M_{n,th(1)}^b$ (g mol <sup>-1</sup> )	$M_{n,th(2)}^c$ (g mol <sup>-1</sup> )	$M_{n,SEC}^d$ (g mol <sup>-1</sup> )	Đ
12	tBuP <sub>4</sub>	tBuGE	20/20/0/1	178	Anisole	60	96	0	0	-	-	-	-	-
13	tBuP <sub>4</sub>	tBuGE	20/20/0/1 + 3 eq. Al( <i>i</i> Bu) <sub>3</sub>	173	Anisole	60	96	0	0	-	-	-	-	-
14	BEMP	tBuGE	4/20/26/1	140	Anisole	60	24	≈95	100	≈95	8100	5350	6200	2.43
15	BEMP	tBuGE	4/20/26/1	140	Toluene	100	24	95	99	82	8050	5300	4900	2.20
16	DBU	tBuGE	4/20/26/1	140	Anisole	60	24	94	100	88	7750	5350	5000	1.50
17	BEMP	BO	4/20/26/1	140	Anisole	60	24	100	100	≈88	5850	4700	5800	2.66

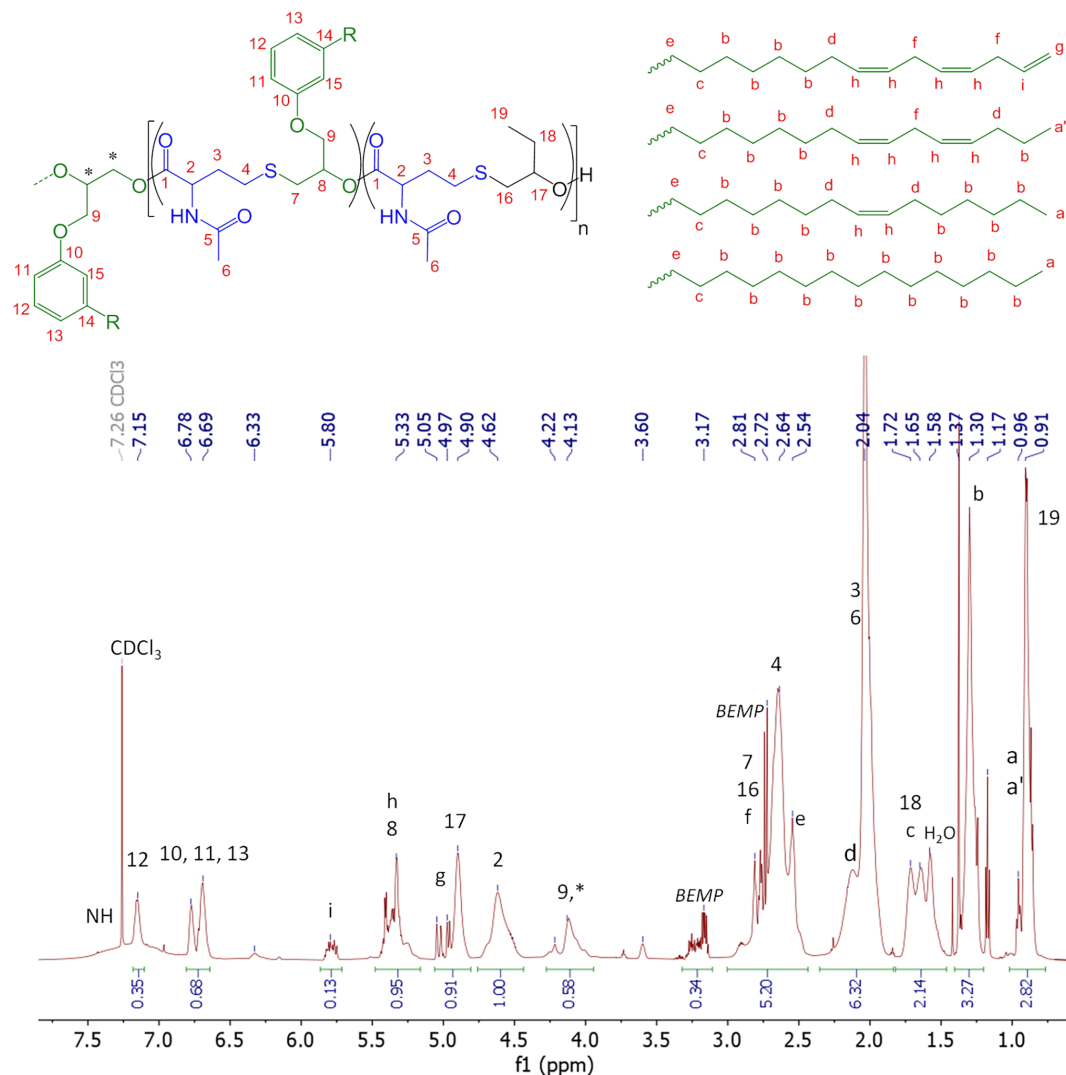
<sup>a</sup>Using the typical epoxy equivalent weight (EEW) value equal to 490.

<sup>b</sup>Theoretical molar mass calculated considering the initiation of one macromolecules par base according to the equation:  $M_{n,th(1)} = \frac{[CGE]_0 \cdot CV_{CGE}}{[Base]_0} + \frac{[Epoxide\ 2]_0}{[Base]_0} \cdot CV_{Epoxide\ 2} \cdot (M_{Epoxide\ 2} + M_{NHTL}) + M_{opened\ CGE}$ .

<sup>c</sup>A fast equilibrium between alcohol and alcoholate species is assumed and thus, each opened epoxy cardanol molecule initiated one macromolecules. The theoretical molar mass is calculated according to the equation:  $M_{n,th(2)} = \frac{0.72}{0.28} \cdot CV_{CGE} \cdot (M_{CGE} + M_{NHTL}) + \frac{0.72 \cdot [Epoxide\ 2]_0}{0.28 \cdot [CGE]_0} \cdot CV_{Epoxide\ 2} \cdot (M_{CGE} + M_{NHTL}) + M_{opened\ CGE}$ .

<sup>d</sup>Determined by SEC (THF, 40°C, poly(methyl methacrylate) standards).





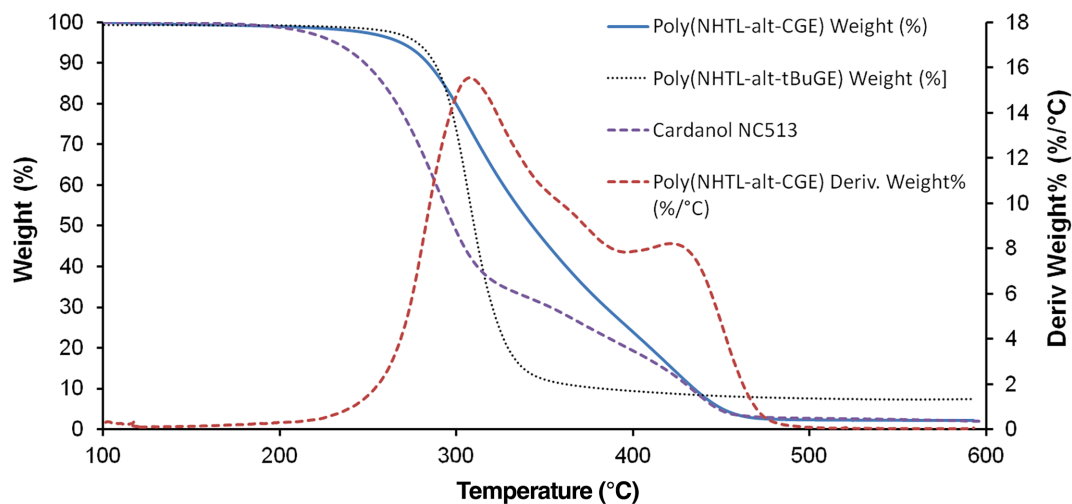
**FIGURE 6**  $^1\text{H}$  NMR spectrum of poly(NHTL-*alt*-CGE/tBuGE) in  $\text{CDCl}_3$  at  $25^\circ\text{C}$  (Table 2, run 15).

$^1\text{H}$  and  $^{13}\text{C}$  NMR could be assigned to the expected polymers (Figures 6, S7–S9). The replacement of the BEMP base by the non-nucleophilic 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) has no influence on the kinetic and on the  $M_n$  (Table 2, run 16). Only the dispersity was reduced ( $\text{Đ} = 1.50$ ). DOSY NMR characterization was conducted on poly(NHTL-*alt*-CGE/tBuGE) (Figure S11). As expected, the signals of the three monomer units of the copolymers provided a similar diffusion coefficient confirming that both epoxide units belong to the same alternating macromolecules. Lastly, a poly(NHTL-*alt*-CGE/BO) was synthesized in run 17 (Table 2). In that case, the experimental  $M_n$  was in good agreement with the theoretical one and the structure was confirmed by the NMR analyses (Figures S12–S14).

A poly(NHTL-*alt*-CGE), a poly(NHTL-*alt*-CGE/tBuGE) and a poly(NHTL-*alt*-CGE/BO) were characterized by thermogravimetric analysis (TGA, Figures 7 and S15–S17) and differential scanning calorimetry (DSC). The results of these analyses were compared with the previously reported thermal behaviors of poly(NHTL-*alt*-tBuGE) and poly(NHTL-*alt*-BO).<sup>39</sup> The thermal stabilities and characteristics are

summarized in Table 3. Although poly(ester-*alt*-thioether)s typically have a one-step degradation profile as seen, for example, on the TGA trace of a poly(NHTL-*alt*-tBuGE), a two-step degradation profile centered at 305 and  $422^\circ\text{C}$  was observed for poly(NHTL-*alt*-CGE) as shown in Figure 7. The first step in the degradation temperature is typical for polythioethers and is due to the degradation of the backbone at the carbon-sulfur bond, which is the weakest linkage in the polymer structure. We assume that the second step of the degradation was due to the degradation of the cardanol substituents. Poly(NHTL-*alt*-CGE/tBuGE) and poly(NHTL-*alt*-CGE/BO) have similar two-step degradation profiles. Logically, the proportion of the second degradation step was lower than the one of Poly(NHTL-*alt*-CGE) due to the lower proportion of CGE units in the copolymer structure. Poly(NHTL-*alt*-CGE) is amorphous, only displaying an only glass transition temperature ( $T_g$ ) at  $-2^\circ\text{C}$  (Table 3). This  $T_g$  value is significantly lower than those of the reference polymers poly(NHTL-*alt*-BO) and poly(NHTL-*alt*-tBuGE) ( $37$  and  $44^\circ\text{C}$ , respectively). This result can be easily explained by the pentadecyl side-chain of cardanol, which





**FIGURE 7** TGA curve and its first derivative measured under a stream of nitrogen between 100 and 600°C with a heating rate of 20°C/min for a poly(NHTL-*alt*-CGE) (Table 1, run 5). The dotted curve correspond to the TGA curve of a poly(NHTL-*alt*-tBuGE) analyzed under the same conditions. The dashed curve corresponds to the TGA curve of the monomer cardanol glycidyl ether NC513.

**TABLE 3** Thermal properties of the alternating copolymers.

Entry	Run	Chemical structure	$T_{\text{deg},10\%}$ (°C)	$T_{\text{deg},\text{max}}$ (°C)	$T_g$ (°C)
1	Table 1, run 5	Poly(NHTL- <i>alt</i> -CGE)	283	307	−2
2	Table 2, run 14	Poly(NHTL- <i>alt</i> -CGE/tBuGE)	264	287	17
3	Illy et al. <sup>39</sup>	Poly(NHTL- <i>alt</i> -tBuGE)	288	307	44
4	Table 2, run 17	Poly(NHTL- <i>alt</i> -CGE/BO)	265	283	14
5	Illy et al. <sup>39</sup>	Poly(NHTL- <i>alt</i> -BO)	296	318	37
6	–	Poly(NHTL- <i>alt</i> -CGE) after cross-linking <sup>a</sup>	230	320	8

<sup>a</sup>Cross-linking by thiol-ene addition with dithiothreitol.

decreases intermolecular interactions and is well-known to provide flexibility to materials through the plasticizing effect.<sup>1</sup> As expected, the cross-linking of poly(NHTL-*alt*-CGE) with dithiothreitol under thiol-ene addition conditions led to an increase of the  $T_g$  (8°C). The  $T_g$  value of poly(NHTL-*alt*-CGE/BO) is equal to 14°C, a value that lies as expected between that of poly(NHTL-*alt*-CGE) and that of poly(NHTL-*alt*-BO). A similar result was obtained with a  $T_g$  equaled to 17°C for poly(NHTL-*alt*-CGE/tBuGE).

### 3 | CONCLUSION

The alternating copolymerization of cardanol glycidyl ether with NHTL was carried out in anisole, a solvent with a high sustainability ranking or in the absence of any solvent. This resulted in the formation of di-hydroxy-terminated oligo(ester-*alt*-thioether)s with cardanol lateral substituents. Polyesters originated from renewable resources are attractive materials that can be used as building blocks for the preparation of environmentally friendly and potentially biodegradable products. In particular, the alkyl chains of cardanol could provide interesting coating properties, such as flexibility, hydrophobicity, chemical resistance, flame retardant and anti-corrosion properties. In addition, due to their pendant alkene and alkyl groups cardanol-based

polymers have the potential to be modified or cross-linked for example using efficient thiol-ene reactions. These oligomers might also be used as diol macromonomers for step-growth polymerization or poly-addition reactions.

The alternating ring-opening copolymerization of thiolactones and epoxides is a very robust technique allowing to work with commercially-available reactants without prior purification or drying steps. Bio-based epoxides, especially those from oleochemistry, are hard to purify. Therefore, the alternating ring-opening copolymerization with thiolactones, which has a low susceptibility to proton impurities, appears to be an interesting method to valorize them as monomers.

## 4 | EXPERIMENTAL PART

### 4.1 | Materials

Phosphazene base 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP) solution (1.0 mol.L<sup>−1</sup> in hexane, Sigma-Aldrich), 1-*tert*-Butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylideneamino]-2λ5,4λ5-catenadi(phosphazene) (tBuP<sub>4</sub>) solution (0.8 mol.L<sup>−1</sup> in hexane, Sigma-Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-ene

(DBU, 98%, Sigma-Aldrich), triisobutylaluminum solution ( $1.0 \text{ mol.L}^{-1}$  in hexane, Sigma-Aldrich), anisole (anhydrous 99.7%, Sigma-Aldrich), DL-N-acetylhomocysteine thiolactone (98%, Sigma-Aldrich), 2,2-dimethoxy-2-phenylacetophenone (99%, Sigma-Aldrich), dithiothreitol (97%, Roche) were used as received. Cardanol NC-513 was kindly provided by Cardolite. THF and toluene were dried with an MBRAUN MB SPS-800 solvent purification system under nitrogen.

## 4.2 | Instruments

$^1\text{H}$ ,  $^{13}\text{C}$ ,  $^1\text{H}$ - $^1\text{H}$  COSY and  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectra were recorded in  $\text{CDCl}_3$  or  $\text{DMSO}-d_6$  using a Bruker 400 MHz NMR spectrometer or a Bruker 600 MHz NMR spectrometer.

The diffusion-ordered spectroscopy (DOSY) experiment was carried out on a Bruker Avance 600 MHz at 300 K using the ledbpgp2s. mod pulse sequence with a linear gradient of 32 steps between 2% and 98%. Before each diffusion experiment, the length of the gradient  $\delta$  and the diffusion time  $\Delta$  were optimized. The softwares used for data analysis were Topspin and Dynamics Center. Size exclusion chromatography experiment (SEC) were carried out on three PL gel Mixed-C  $5 \mu\text{m}$  columns ( $7.5 \times 300 \text{ mm}$ ; separation limits: 0.2 to  $2000 \text{ kg.mol}^{-1}$ ) maintained at  $40^\circ\text{C}$  and sample Viscotek GPCmax delivery module and 2 modular detectors: a Viscotek 3580 differential refractive index (RI) detector and a Shimadzu SPD20-AV diode array UV detector. THF was used as the mobile phase at a flow rate of  $1 \text{ mL.min}^{-1}$ , and toluene was used as a flow rate marker. All polymers were injected ( $100 \mu\text{L}$ ) at a concentration of  $5 \text{ mg mL}^{-1}$  after filtration through a  $0.45 \mu\text{m}$  pore-size membrane. The OmniSEC 4.6.2 software was used for data acquisition and analysis. Number-average molar masses ( $M_n$ ), weight-average molar masses ( $M_w$ ) and dispersities were determined by SEC with a calibration curve based on poly(methyl methacrylate) standard, using the RI detector. The thermal decomposition was evaluated by thermogravimetric analysis (TGA) using a TA Q50 apparatus. Data were collected using a  $20^\circ\text{C}/\text{min}$  ramp to  $600^\circ\text{C}$ . The experiment was run under a stream of nitrogen. DSC measurements were carried out using a TA DSC Q2000 calibrated with indium standard. The sample (ca  $15 \text{ mg}$ ) was placed in an aluminum cell and initially cooled at  $-70^\circ\text{C}$ . Two heating ( $10 \text{ K min}^{-1}$ )—cooling ( $10 \text{ K min}^{-1}$ ) cycles were then applied in the  $-70$  to  $200^\circ\text{C}$  temperature range.

Matrix-assisted laser desorption and ionization time-of-flight mass spectrometry (MALDI-TOF MS). Mass spectra were recorded by MALDI-TOF MS using trans-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile ( $\geq 99\%$ ) as a matrix and NaI as cationizing agent using a Bruker Autoflex Speed mass spectrometer, equipped with a laser that produces pulses at  $337 \text{ nm}$  or using an Applied Biosystems 4700 Proteomics Analyzer instrument. Spectra were recorded in reflectron mode at an accelerating potential of  $20 \text{ kV}$ . Samples were prepared by dissolving the polymer in THF at a concentration of  $5 \text{ mg.mL}^{-1}$ . A  $10 \mu\text{L}$  aliquot of this solution was mixed with  $20 \mu\text{L}$  of matrix solution and  $10 \mu\text{L}$  of NaI solution (both at  $20 \text{ mg.mL}^{-1}$  in THF). Poly(ethylene oxide) standards (Polymer Standards

Service) of known structures,  $M_n = 1500 \text{ g.mol}^{-1}$  were used to calibrate the mass scale. In all cases, to determine  $m/z$ , the molar mass of the sodium cation was added.

## 4.3 | Polymerization protocols

All polymerization were carried out under nitrogen in a glass reactor equipped with a stirring bar and closed with a septum.

## 4.4 | Homopolymerization

The polymerization was carried out according to the following typical procedure.  $0.52 \text{ g}$  of Cardanol NC-513 was weighted into a glass reactor under an ambient atmosphere. Then, in a glovebox,  $2.0 \text{ mL}$  of anisole was introduced under nitrogen into the reactor. Then,  $35 \mu\text{L}$  of  $t\text{BuP}_4$  solution were added using a microsyringe. After closure of the reaction flask, the reaction mixture was stirred at  $50^\circ\text{C}$  and left to react for the required period of time (Table 1). A small portion of the reaction mixture was sampled through a septum at various reaction times for NMR analyses. For polymerization carried out in the presence of Lewis acid,  $85 \mu\text{L}$  of  $i\text{Bu}_3\text{Al}$  ( $1.0 \text{ mol.L}^{-1}$  in hexane) was added just after  $t\text{BuP}_4$ .

## 4.5 | General copolymerization procedure

The copolymerization was carried out according to the following typical procedure.  $0.32 \text{ g}$  of NHTL ( $2.04 \text{ mmol}$ ),  $0.5023 \text{ g}$  of cardanol NC513 ( $2.04 \text{ mmol}$  of epoxide) and  $2.0 \text{ mL}$  of anisole were introduced into a polymerization tube fitted with a natural rubber folding skirt stoppers. Then,  $102 \mu\text{L}$  of BEMP solution ( $0.100 \text{ mmol}$ ) was added through the septum using microsyringes. The reaction mixture was stirred at  $60^\circ\text{C}$  and left to react for the required period of time. The progress of the reaction was monitored by removing samples from the polymerization reactor through a septum at various reaction times for  $^1\text{H}$  NMR analyses. After removing residual monomers and solvent by rotary evaporation, the polymer was dissolved in THF and dialyzed in regenerated cellulose membrane (Repligen Spectra/Por 6 dialysis tubing, flat width =  $45 \text{ mm}$ , molecular cutoff =  $1 \text{ kDa}$ ) against THF for  $24 \text{ h}$ . After removing the solvent under vacuum at  $50^\circ\text{C}$ , an orange viscous oil was obtained. Yield: 85%. Deviations from this general procedure are summarized in Tables 1 and 2.

## 4.6 | Thiol-ene addition

$0.2 \text{ g}$  of poly(NHTL-*alt*-CGE) (Table 1, run 7;  $0.3898 \text{ mmol}$  of repeating units,  $0.145 \text{ mmol}$  of allyl groups),  $0.087 \text{ g}$  of dithiothreitol ( $0.564 \text{ mmol}$ ,  $7.8$  thiol equivalents per allyl groups) and  $0.018 \text{ g}$  AIBN ( $0.11 \text{ mmol}$ ,  $0.75$  equivalents per allyl groups) were dissolved in dry toluene ( $30 \text{ mL}$ ). After  $1 \text{ h}$  of nitrogen bubbling, the stirred

homogeneous reaction mixture was heated at 70°C and stirred for 24 h. A small portion of the reaction mixture was sampled through a septum at various reaction times for NMR analyses until the full cross-linking of the reaction mixture.

## DATA AVAILABILITY STATEMENT

Data are available upon request to the corresponding author.

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## SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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