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Bio-based poly(ester-*alt*-thioether)s synthesized by organo-catalyzed ring-opening copolymerizations of eugenol-based epoxides and *N*-acetyl homocysteine thiolactone

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The anionic alternating ring-opening copolymerizations of three bio-based aromatic monomers, eugenol glycidyl ether (EGE), dihydroeugenol glycidyl ether (DEGE) and vanilin glycidyl ether (VGE), were carried out with renewable N-acetyl homocysteine thiolactone (NHTL) using benzyl alcohol and 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP) as initiating system. This polymerization is a rare example of eugenol-based monomers used to synthesize linear polyesters. Alternating poly(ester-*alt*-thioether)s are obtained with number-average molar masses M_n ranging from 1.1 to 10.8 kg mol^{-1} and dispersities as low as 1.20. The copolymer structures were carefully characterized by ^{1}H, ^{13}C, COSY, HSQC, ^{1}H-^{15}N NMR. It was found that the alternate copolymers were obtained selectively under different monomer feed ratios. In addition, the use of EGE and VGE monomers allows the preparation of multi-functional poly(ester-*alt*-thioether) respectively bearing allyl or aldehyde groups in each repeating unit. The copolymers display only clear glass transition temperatures higher than ambient temperature. This alternating copolymerization method offers a new chemical pathway for the valorization of bio-based aromatic compounds and expand the scope of renewable polyesters.

Introduction

Eugenol (4-allyl-2-methoxyphenol) is a commercially-available bio-based phenol that can be extracted from numerous essential oils,[1, 2] such as clove oil, nutmeg, cinnamon, basil, bay leaf, tulsi or pepper or synthesized by the allylation of naturally-occurring guaiacol.[3] This valuable compound can alternatively be obtained by depolymerization of abundant lignin. Hence, lignin is a phenolic macromolecule that accounts for roughly 15–30% of the dry weight of ligno-cellulosic biomass.[4] This is thus the second most abundant natural polymer and the biggest natural source of aromatics[5, 6] which uses was reported directly in phenolic resins for various applications such as plywood, foams, laminates…[7] However its use is also limited by some issues. Its chemical structure is very variable, depends on many parameters, which makes precise characterization and understanding of the reaction mechanism challenging. Finally, this biopolymer is also difficult to process.[8, 9] Hence, to overcome these limitations, lignin depolymerization to produce biobased aromatics seems to be a promising approach. Vanillin and syringaldehyde are the main commercial lignin-derived products,[10] but eugenol is also a very promising monomer derived from lignin. Indeed, the rise of increasingly efficient chemical or enzymatic depolymerization processes will likely establish eugenol as an economically realistic feedstock with a relatively low market price in a near future.[11-14] This biocompatible compound has found numerous applications in areas such as cosmetics, fragrance and pharmaceuticals.[15] For example, it has been widely used in dental materials for its antibacterial, analgesic and anti-inflammatory properties.[16, 17] Eugenol is also intensively investigated as a feedstock for the development of functional polymer materials. Eugenol and eugenol-derived compounds, such as isoeugenol, dihydroeugenol or vanillin, are potential natural substitutes for rigid aromatic monomers.[11] For example, two common pathways allow the preparation of eugenol-containing epoxide monomers. First, eugenol glycidyl ether (EGE) has been synthesized by reacting the phenolic hydroxyl group of eugenol with epichlorhydrin (glycidylation), a chemical that can be produced from renewable glycerin, for example according to the *Epicerol® technology of* TechnipFMC.[18,19] EGE has been be used as reactive diluent in order to lower the viscosity of epoxy resin formulation and extend onset of network formation without changing the glassy phase modulus.[20] Secondly, epoxydized

eugenol has been prepared in high yield by epoxidation of the eugenol allyl group.[21]
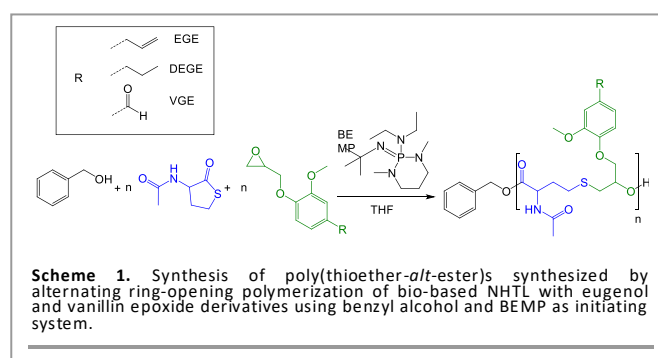
Numerous research papers are dealing with the preparation of various eugenol-containing thermosets. For example, eugenol derivatives containing more than one epoxy group are excellent non-toxic building blocks candidates for the substitution of the endocrine disrupting diglycidylether of bisphenol A (DGEBA) in the preparation of epoxy thermosets. The resulting networks often exhibit excellent thermo-mechanical properties similar to the ones from petroleum-based DGEBA counterparts.[21] Alternatively, eugenol derivatives, such as glycidyl ether eugenol or allyl-etherified eugenol derivatives, have been cured in the presence of multi-functional thiols by simultaneous thiol-ene / thiol-epoxy click reactions.[22-25] Glycidyl ether eugenol was also used to prepare hybrid non-isocyanate polyurethane thermosets.[26] Ultimately, a large variety of structurally diverse eugenol-containing thermosets displayed various promising properties, such as high thermal stability[27, 28] low electric permittivity and flame retardancy,[29] or antibacterial properties.[30] Although eugenol-based monomers have been mostly incorporated in thermosetting polymers, some research works have reported the synthesis of linear thermoplastic polymers. Several examples can be found where eugenol derivatives have been used in step-growth polymerizations, resulting in various polymer backbone natures, such as aromatic polyesters,[31] poly(ester-thioether)s,[32] polycarbonates,[33] or poly(anhydride)s.[34] However, polycondensation reactions only enable a limited control of the polymer structure with high dispersities and no control of the chain ends. Eugenol-based monomers have been scarcely used in chain-growth polymerization. The use of eugenol allyl bond directly as polymerizable group is rather uncommon and led to poorly-defined high-dispersity polymers.[35] Alternatively, eugenol was functionalized with other polymerizable groups, such as alkyne or methacrylate groups. These monomers were polymerized by coordination,[36] free radical polymerizations,[16, 39] suspension radical polymerization,[37, 38] or free radical precipitation polymerization.[17] However, for conversion higher than 10%, cross-linked insoluble networks were obtained due to the additional involvement of eugenol allyl group in the radical polymerization.

All these previously reported polymerizations of eugenol-derived monomers were poorly controlled and led to ill-defined polymer chains. The synthesis of well-defined linear polymers using monomers derived from eugenol remains a current challenge. Most of the polymers issued from sustainable aromatic monomers are either thermoset/cross-linked networks or polycondensates. While polycondensates stand in the thermoplastic family, the control of their molar mass and their high dispersity prevent from their use in some applications requiring well-defined structures, such as biomedical applications. Up to date, the use of eugenol as the

building block for the preparation of well-defined polymers has rarely reported. Only two examples of ring-opening copolymerization of eugenol-based epoxide monomers have also been reported. Hu et al. demonstrated that eugenol glycidyl ether could copolymerize with carbonyl sulfide to afford sustainable poly(monothiocarbonate) having a high refractive index and potential application as optical materials.[3] Very recently, a series of promising 100% bio-based polyesters has been prepared by the alternating ring-opening copolymerization of eugenol glycidyl ether with cyclic anhydrides.[40] The authors have also demonstrated that the pendant allyl groups provided an additional versatility for further functionalization and the resultant polyesters backbone was potentially biodegradable. However, this method still provides a limited control over the polymerization and requires high temperatures and the use of chromium complex catalysts.

Well-defined polyesters originated from renewable resources are very attractive materials for the preparation of environmentally-friendly and potentially biodegradable products. Our group recently reported the synthesis of well-defined poly(ester-*alt*-thioether)s by organo-catalyzed anionic ring-opening copolymerization of N-acetyl homocysteine thiolactone (NHTL) and various epoxides under mild conditions. NHTL is commercially-available at relatively low cost and can be synthesized from renewable resources. Thus, the resulting poly(ester-*alt*-thioether)s are partially bio-based. In this paper, we report the synthesis of fully bio-based poly(ester-*alt*-thioether)s by the alternating AROP of NHTL with eugenol glycidyl ether (EGE), dihydroeugenol glycidyl ether (DEGE) and vanilin glycidyl ether (VGE). This study was conducted to assess the feasibility of this polymerization pathway with such aromatic biobased monomers under different experimental conditions. In particular, the influence of the initial monomer ratio has been carefully studied. And the copolymer structures and thermal properties have been carefully characterized.

Results and discussion

Scheme 1. Synthesis of poly(thioether-*alt*-ester)s synthesized by alternating ring-opening polymerization of bio-based NHTL with eugenol and vanillin epoxide derivatives using benzyl alcohol and BEMP as initiating system.
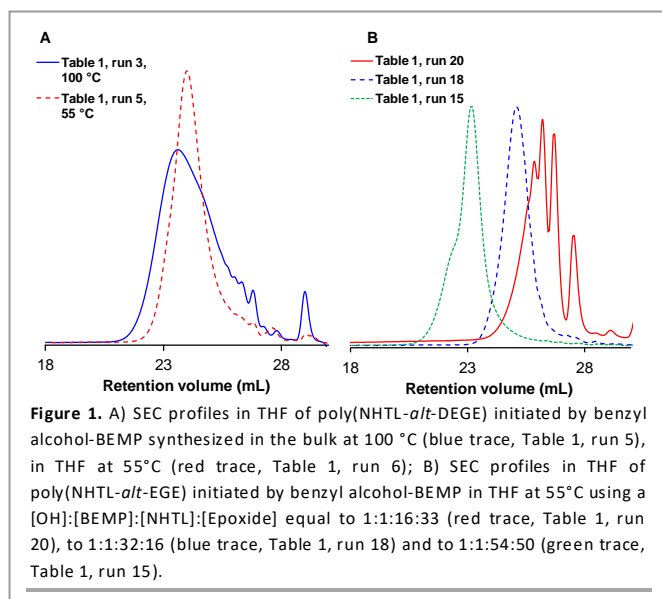
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Table 1. Experimental conditions and molecular characteristics of poly(thioether-*alt*-ester)s synthesized by alternating ring-opening polymerization of bio-based NHTL with eugenol and vanillin epoxide derivatives using benzyl alcohol and BEMP as initiating system.

Run	Epoxide	Solvent	Base	ROH^a:Base: NHTL^b:Epoxide	T° [°C]	Time [h]	Cv $_{NBTL}$ [%]	Cv $_{Epo}$ [%]	$M_{n, th}$ [g mol^{-1}]	$M_{n, NMR}$ [g mol^{-1}]	$M_{n, SEC}^c$ [g mol^{-1}]	Đ
1	-	THF	BEMP	1:1:25:0	55	24	-	-	-	-	-	-
2	DEGE	THF	BEMP	1:1:0:25	55	24	-	-	-	-	-	-
3	EGE	THF	BEMP	1:1:0:25	55	24	-	-	-	-	-	-
4	VGE	THF	BEMP	1:1:0:25	55	24	-	-	-	-	-	-
5	DEGE	-	BEMP	1:1:24:23	100	1	90	89	7850	8035	3550	2.12
6	DEGE	THF	BEMP	1:1:23:22	55	5.5	88	90	7600	7500	4400	1.47
7	DEGE	THF	*t*BuP$_4$	1:1:25:25	55	5.5	100	100	9600	8500	2700	2.39
8	DEGE	THF	DMAP	1:1:25:25	55	6	85	86	7750	8850	3160	2.31
9	DEGE	THF	BEMP	1:1:23^d:23	55	24	68	64	5750	6400	4000	1.49
10	EGE	THF	BEMP	1:1:23:23	55	17	97	93.5	8500	7600	4300	1.60
11	DEGE	THF	BEMP	1:1:12:12	55	2.25	91	89	4350	4300	3400	1.28
12	DEGE	THF	BEMP	1:1:47:47	55	46.5	84	90	15100	15800	6200	1.39
13	DEGE	THF	BEMP	1:0.5:50:50	55	23	80	83	15400	16900	9200	1.47
14	EGE	THF	BEMP	1:1:50:46	45	7	77	89	14680	14550	5650	1.67
15	EGE	THF	BEMP	1:1:54:50	40	24	92	99	18950	11100	10800	1.34
16	DEGE	THF	BEMP	1:1:17.6:8.6	55	2	43	92	2950	2550	2400	1.20
17	DEGE	THF	BEMP	1:1:35:17	55	23	45	92	6180	6250	4100	1.20
18	EGE	THF	BEMP	1:1:32:16	55	6	49	96	5600	5485	3900	1.31
19	DEGE	THF	BEMP	1:1:17:35	55	6	95	46	6250	5900	2250	1.42
20	EGE	THF	BEMP	1:1:16:33	55	6	99	48	6200	5500	1150	1.44
21	DEGE	-	BEMP	1:1:35:18	100	2	52	100	6800	7100	4600	1.82
22	DEGE	THF	BEMP	1:1:25:12+14	55	3.75 / 19	50 / 100	100/ 93	9600	9250	3800	1,92
23	VGE	THF	BEMP	1:1:23:25	55	4	73	89	5750	6200	2700	1.77
24	VGE	THF	BEMP	1:1:24:24	55	4	75	82	6300	5100	2350	1.71
25	VGE	THF	BEMP	1:1:50:44	45	23	56	69.5	10300	10750	2600	1.54

^{a} ROH = benzyl alcohol.
^{b} [NHTL]$_0$ = 1.05 mol.L^{-1}.
^{c} Determined by SEC (THF, 40°C, poly(methyl methacrylate) standards).
^{b} [NHTL]$_0$ = 0.72 mol.L^{-1}.

DEGE and EGE have been synthesized according to Ecochard *et al.*[26] procedure with a supplementary purification step by flash chromatography to obtain highly pure monomers for the ring-opening polymerization. As reported in Table 1, no homopolymerization of NHTL (Table 1, run 1), DEGE (Table 1, run 2), EGE (Table 1, run 3) and VGE (Table 1, run 4) occurred in THF at 55°C using benzyl alcohol - BEMP as initiating system. These results are in agreement with our previous work.[41] A first copolymerization attempt between NHTL and DEGE was carried out in the bulk at 100°C with a [OH]:[BEMP]:[NHTL]:[Epoxide] = 1:1:24:23 ratio (Table 1, run 5). No extensive drying protocol was applied to the monomers: NHTL was used as received from Sigma-Aldrich and DEGE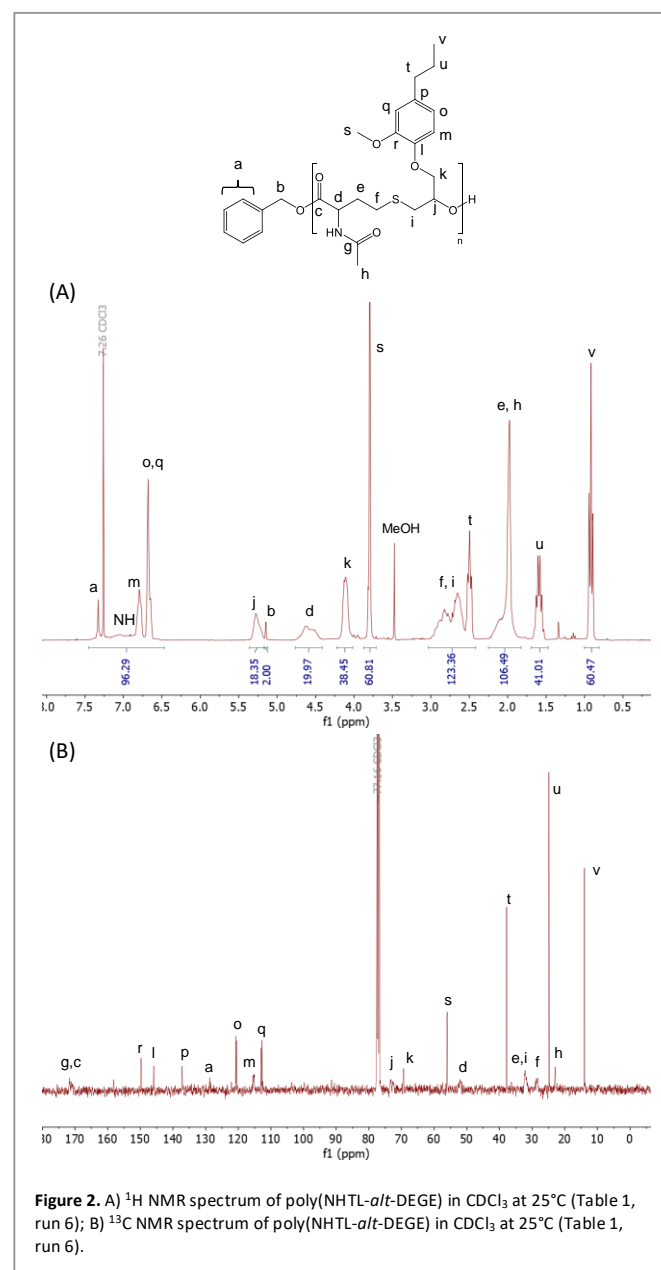 was only dried under vacuum after its synthesis. The water contents of THF and the monomers was determined by coulometric Karl Fischer titrations, showing that monomers contained significant amounts of water (Table S1). In addition, all the reactants and the solvent were introduced under air in the polymerization reactor. It is interesting to note that although the reaction was performed without taking any special precautions, almost full monomer conversions were obtained after only 1 h (an example of monomer conversion calculation using reaction mixture ^{1}H NMR is given in Figure S4). The experimental number-average molar mass (M_n) determined by ^{1}H NMR end-group analysis is in excellent agreement with the theoretical one, demonstrating a quantitative initiation by benzyl alcohol. However, the M_n determined by SEC (Figure 1.A, blue trace) is far lower than the

Figure 1. A) SEC profiles in THF of poly(NHTL-*alt*-DEGE) initiated by benzyl alcohol-BEMP synthesized in the bulk at 100 °C (blue trace, Table 1, run 5), in THF at 55°C (red trace, Table 1, run 6); B) SEC profiles in THF of poly(NHTL-*alt*-EGE) initiated by benzyl alcohol-BEMP in THF at 55°C using a [OH]:[BEMP]:[NHTL]:[Epoxide] equal to 1:1:16:33 (red trace, Table 1, run 20), to 1:1:32:16 (blue trace, Table 1, run 18) and to 1:1:54:50 (green trace, Table 1, run 15).

theoretical one and the dispersity is high (Đ = 2.12). This phenomenon has been previously found for the alternating ring-opening copolymerization of thiolactone with epoxides and was explained by undesired chain transfer reactions to water molecules and by transesterification reaction between the propagating alcoholate species and the ester groups of the main chain.[41, 42] Transesterification reactions are a well-recognized issue for organocatalyzed ring-opening polymerization of cyclic esters in the presence of phosphazene base.[43] In order to reduce the occurrence of side reactions, one solution is to add solvent and to decrease the reaction temperature. Thus, a NHTL-DEGE copolymerization with an identical reactant ratio was performed in THF at 55°C (Table 1, run 6). As expected, a longer reaction time was required to reach similar monomer conversions. Compared to the polymerization in the bulk, the resulting copolymer exhibits a lower molar mass distribution (Figure 1.A). A better agreement is also observed between the theoretical and experimental molar masses, even if a mass discrepancy is still present. Two other catalysts, *t*BuP$_4$ (Table 1, run 7) and DMAP (Table 1, run 8) have been used in place of BEMP. In both cases, lower M_n and higher dispersities Đ have been achieved. BEMP has therefore been used as catalyst for the following reactions. A polymerization was then performed at lower monomer concentration, but no significant improvement could be noticed (Table 1, run 9). A copolymerization between NHTL and EGE was performed under the same reaction conditions as those of Table 1, run 6 leading to comparable results (Table 1, run 10).

The obtained copolymers were characterized by ^{1}H, ^{13}C, COSY and HSQC NMR and display spectroscopic data consistent with the ring-opened alternating structures. All signals could be assigned and are provided directly on the spectra in Figures 2 an S6-S7 for poly(NHTL-*alt*-DEGE) and Figures S8-S11 for poly(NHTL-*alt*-EGE). After polymer purification by dialysis, using a membrane with a cutoff value of 1000 Da, the signals

associated with the protons of benzyl alcohol initiator are still observed. For all the copolymers produced by the copolymerization of NHTL with DEGE or EGE, the NHTL/DEGE or NHTL/EGE unit ratios were found to be very close to 1/1 and no conspicuous signals assignable to ether linkage can be observed. In addition, the intensity of the signals corresponding to the -CHR- of oxirane units in alpha position of ester groups (at 5.28 ppm for poly(NHTL-*alt*-DEGE) and at 5.29 ppm for poly(NHTL-*alt*-EGE)) correspond to the values expected for strictly alternating structures. The presence of alternating units were further supported by the ^{13}C NMR spectrum of poly(NHTL-alt-EGE) (Figure S9), where no characteristic resonance of the ether linkages in the range of 75–85 ppm was observed.[44] The NH of the lateral acetamido groups have very large ^{1}H NMR signals between around 6.6 and 7.6 ppm as demonstrated by ^{1}H-^{15}N HSQC NMR spectrum

Figure 2. A) ^{1}H NMR spectrum of poly(NHTL-*alt*-DEGE) in CDCl$_3$ at 25°C (Table 1, run 6); B) ^{13}C NMR spectrum of poly(NHTL-*alt*-DEGE) in CDCl$_3$ at 25°C (Table 1, run 6).

in Figure S12.

The effect of feed ratio of the two monomers on the copolymer structures was analyzed. For all the copolymerization reactions of NHTL with DEGE or EGE that were performed with stoichiometric amounts of thiolactone and epoxide, the final monomer conversions of both monomers are equal (Table 1, runs 5-13). In the case of the copolymerization of 23 equivalents of NHTL with 23 equivalents of DEGE at 55°C (Table 1, run 9), the conversions of both monomers were plotted against reaction time in Figure 3.A. As expected for strictly alternating copolymerization, they increased equally throughout the polymerization. When the copolymerization of NHTL and oxiranes were performed under different feed ratios (Table 1, runs 16-21), the molar consumptions of both monomers remained strictly equal as shown in Figures 3.B and 3.C. The nature of the monomer in excess does not interfere with the alternating mechanism. However, when alternating copolymerizations were carried out in the presence of a large excess of oxiranes (Table 1, runs 19 and 20), lower M_n and higher Đ were obtained compared to alternating copolymerizations having similar targeted M_n but which were performed in the presence of a large excess of thiolactone (Table 1, runs 17 and 18). For the alternating copolymerization of NHTL with EGE, the SEC profiles in the presence of an excess of EGE (red trace) or an excess of NHTL (blue trace) have been superimposed in Figure 1.B. A copolymerization of NHTL and DEGE, in which DEGE was sequentially added, was then carried out (Table 1, run 22). In the first step, 25 equivalents of NHTL and 12 equivalents of DEGE were introduced in the polymerization reactor. After 3.75 hours, monomer conversions are equal to 50 % for NHTL and 100 % for DEGE. Then, a second batch of 14 equivalents of DEGE in THF was added in the reaction mixture. The polymer chain continued to grow. Full NHTL conversion and 93 % DEGE conversion are reached after 19 hours. In order to increase the M_n of the copolymers, X_n values of 100 were targeted (Table 1, runs 12 and 14). In both cases, the experimental M_n determined by SEC were significantly lower than the theoretical ones. A decrease of the amount of BEMP to 0.5 eq. (Table 1, run 13) resulted in higher M_n, as previously described in the literature.[45-47] In addition, M_n higher than 10 000 g.mol^{-1} was achieved for the copolymerization of NHTL and EGE performed at 40°C in the presence of a slight excess of NHTL (Table 1, run 15).

Lastly, the copolymerization of vanillin glycidyl ether (VGE) was carried out using 1:1:25:25 (Table 1, runs 23 and 24) or 1:1:50:44 (Table 1, run 25) $[OH]_0:[BEMP]_0:[NHTL]_0:[Epoxide]_0$ ratios. VGE is a very promising bio-based monomer due to the presence of an aldehyde moiety on the aromatic ring. The synthesis of polymers bearing multiple aldehyde lateral substituents is of particular interest for further postpolymerization modification based on a large variety of chemical reactions under mild conditions.[48, 49] However, the synthesis of polymer chains bearing highly reactive aldehyde

lateral substituent by anionic polymerization remains challenging and usually requires protection and deprotection steps.[50] The copolymerization of NHTL and VGE occurred without functional protection. The structure of poly(NHTL-*alt*-VGE) was verified by FTIR and NMR spectroscopy (Figures 4 and S13-S16). The ^{1}H NMR spectrum in Figure S13 clearly shows the signal of the aldehyde proton at 9.8 ppm, the same
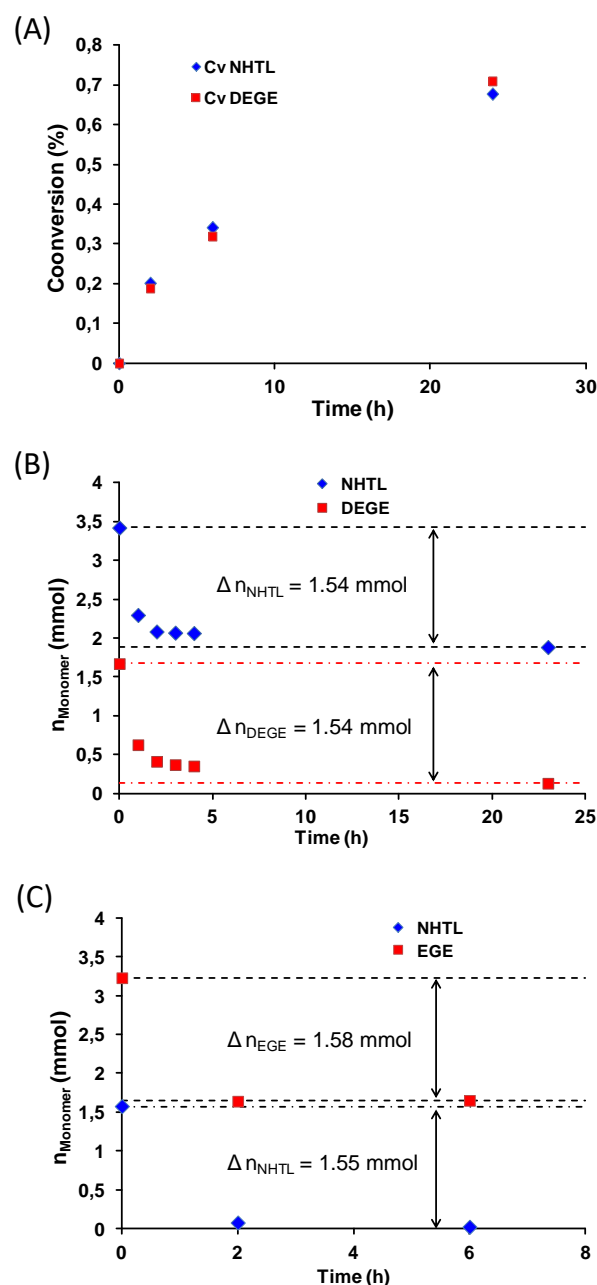
Figure 3. A) Time-conversion of the copolymerization of equivalent amounts of NHTL (2.22 mmol) and DEGE (2.20 mmol) using benzyl alcohol-BEMP as initiating system (0.97 mmol) in THF at 55°C (Table 1, run 9); B) Monomer amounts as a function of time of the copolymerization of NHTL (3.42 mmol) and DEGE (1.67 mmol) using benzyl alcohol-BEMP as initiating system (0.97 mmol) in THF at 55°C (Table 1, run 17); C) Monomer amounts as a function of time of the copolymerization of NHTL (1.57 mmol) and EGE (3.22 mmol) using benzyl alcohol-BEMP as initiating system (0.97 mmol) in THF at 55°C (Table 1, run 20).

shift as the one of the monomer (Figure S3). The integration area ratio of aldehyde proton vs the aromatic methoxy group in vanillin unit was 1.00:3.26 (to compare with 1.00:3.13 for the monomer) illustrating the essential absence of side-reaction on the aldehyde functionalities. The stability of the aldehyde groups can also be seen by the presence of the NMR peak at 190.99 ppm corresponding to the carbonyl in the ^{13}C and HSQC NMR spectra (Figures S14 and 4). In addition, the FTIR spectrum shows a carbonyl band at 1677 cm^{-1} (Figure S15e), a value in agreement with a α, β-unsaturated aldehydes, which is also visible in the FTIR spectrum of the monomer at 1682 cm^{-1} (Figure S15d).[51] However for all the copolymerization with VGE, only low molar-mass polymer chains (≤ 2700 g.mol^{-1}) have been measured by SEC (Figure S5). According to the technical data sheet of commercial VGE, its epoxy content is only 0.0040 eq/g while the theoretical value is 0.0048 eq/g for pure VGE. Thus, aromatic alcohols resulting from unmodified vanillin could act as additional initiator during the polymerization and strongly limit the achievable M_n.
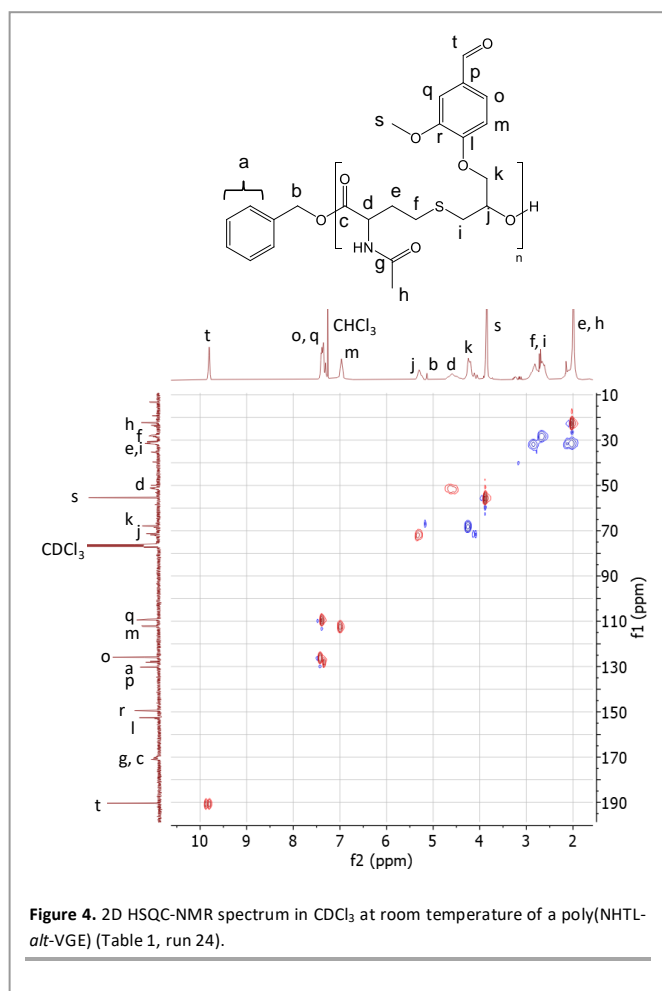
Figure 4. 2D HSQC-NMR spectrum in CDCl$_3$ at room temperature of a poly(NHTL-*alt*-VGE) (Table 1, run 24).

TGA and TGA derivative curves of poly(NHTL-*alt*-DEGE), poly(NHTL-*alt*-EGE) and poly(NHTL-*alt*-VGE) are shown in Figures S17-S19. The thermal properties (decomposition temperature after 10% weight loss and decomposition temperature at maximum degradation rate) are outlined in
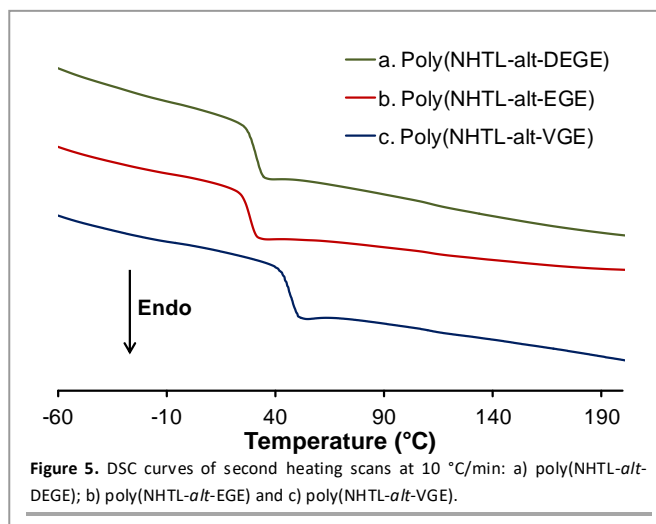
Figure 5. DSC curves of second heating scans at 10 °C/min: a) poly(NHTL-*alt*-DEGE); b) poly(NHTL-*alt*-EGE) and c) poly(NHTL-*alt*-VGE).

Table 2. All the copolymers exhibit single-step narrow degradation curves with T$_{d,10\%}$ in the range 273-285 °C. The substituent change on the aromatic group does not obviously change the thermal stability of the polymers. The low molar mass of poly(NHTL-*alt*-VGE) has probably to be taken into account when considering the slightly lower T$_{d,10\%}$. The good thermostability of the bio-based alternating copolymers is similar to the one of poly(NHTL-*alt*-PhGE), an alternating copolymer synthesized using petro-based phenyl glycidyl ether (PhGE).[41] More generally, similar degradation temperatures have been observed for polymers containing thioether bonds in their backbone, suggesting that carbon-sulfur bond is the weakest linkage in the structure.[33, 52] The remaining residual weights of poly(NHTL-*alt*-DEGE) and poly(NHTL-*alt*-EGE) at 600°C are equal to 8.0 and 11.9 %, respectively. Linear aliphatic sections are known to decompose almost completely compared to double bonds and aromatic sections under the same TGA conditions.[32] The difference between the char yields is consistent with the presence of an allyl group in para position of the aromatic ring in the case of EGE instead of a propyl group in the case of DEGE. In comparison, poly(NHTL-

Table 2. Thermal properties of the alternating copolymers.

Entry	Run	Chemical nature	T$_{d,10\%}$ [°C][a]	T$_{dm}$ [°C][b]	T$_g$ [°C]	Char yield (%)
1	Table 1, run 6	poly(NHTL-*alt*-DEGE)	285	310	31	8.9
2	Table 1, run 10	poly(NHTL-*alt*-EGE)	283	302	28	11.9
3	Tables 1, run 23	poly(NHTL-*alt*-VGE)	273	288	46	24.5
4	-	poly(NHTL-*alt*-PhGE) [c]	286	313	35	9.7

[a] Decomposition temperature after 10% weight loss.
[b] Decomposition temperature at maximum degradation rate (derivative thermogravimetry).
[c] Results from Illy et al.[41]

ARTICLE

alt-VGE) has a higher char yield (24.5 %), more than twice the value of the other alternating copolymers, which is probably due to thermal cross-linking reaction between aromatic aldehyde and aromatic groups.[53] The thermal behaviors of the copolymers were studied by DSC at a 10°C min^{-1} heating and cooling rate. The second heating DSC curves measured from -60 to 200°C are shown in Figure 5, and the corresponding thermal data are summarized in Table 2. All copolymers are amorphous with no indication of melting temperatures (up to 200 °C), exhibiting clear glass transition temperatures Tg. Melting temperatures were not expected since achiral monomers (epoxides and thiolactone) and initiating system were employed. In addition, the existence of methoxy group on the aromatic ring is detrimental to the structural symmetry. The Tg of poly(NHTL-*alt*-DEGE) (Tg = 31°C) and poly(NHTL-*alt*-EGE) (Tg = 28°C) are slightly lower than the one of poly(NHTL-*alt*-PhGE) (Tg = 35°C). The presence of substituents on the aromatic rings could increase the steric hindrance and interfere with the formation of hydrogen bonds between amide and carbonyl groups. On the contrary, poly(NHTL-*alt*-VGE) has a higher Tg (46°C) due to the presence of aromatic aldehydes, which are polar groups and thus, can participate to the formation of hydrogen bonds, dipole-dipole interactions and generate cross-linking points.[51]

It may be added that the allyl groups on the poly(NHTL-*alt*-EGE) scaffold afford a reactive platform for the functionalization of the poly(ester-*alt*-thioether). In order to demonstrate the feasibility of the functionalization, the coupling of 2-mercaptoethanol with the allyl groups of poly(NHTL-*alt*-EGE) (Table 1, run 14) has been investigated using a UV initiated free radical addition in the presence of 2,2-dimethoxy-2-phenylacetophenone as photoinitiator. The ^{1}H NMR spectrum is fully compatible with the expected structure for a quantitative thiol-ene modification: full disappearance of the signals corresponding to the allyl group at 5.00-5.10 ppm and 5.96 ppm and appearance of the signals corresponding to the grafted 2-mercaptoethanol lateral substituents (Figure S20). In addition, the experimental M_n determined by SEC is equal to the expected one for a fully modified polymer (7500 g.mol^{-1} compared to 6900 g.mol^{-1}).

Conclusions

This study introduces a new family of thermoplastic polymers based on sustainable phenols, one of the most abundant bio-based feedstock on earth. A series of fully renewable linear poly(ester-*alt*-thioether)s were synthesized via the alternating ring-opening copolymerization of NHTL with eugenol-based epoxides using benzyl alcohol-BEMP as initiating system. The present new copolymer family offers promising features compared to numerous thermoplastic from renewable resources. The polymerization process is organo-catalyzed and atom-economical, it occurs in the presence of moisture and air

at moderate temperatures from readily accessible monomers. One striking observation during the synthesis of these new copolymers from sustainable monomers is the fact that polymers with M_n up to 10 kg.mol^{-1} are prepared with monomers used as received, in opposition to other classical anionic polymerization. The absence of specific drying-purification of the monomers prior polymerization open the way to an easy scale-up of the synthesis. Copolymers with strictly alternating structures and rather low dispersities are obtained in high yields. In addition, initiation is also controlled and provide an access to new specific copolymers, different by their end functionality. These alternating copolymers are amorphous materials with Tg higher than ambient temperature. Moreover, these bio-based polyesters offer the possibility of a functional group every repeating unit, suitable for further post reaction: poly(NHTL-*alt*-EGE) and poly(NHTL-*alt*-VGE) scaffolds are reactive platforms that could be further functionalized using a wide range of mild chemical reactions. Eventually, one of the most promising points is the fact that this copolymer synthesis strategy allows for the production of polymer with one aldehyde function every repeating unit in a one step procedure without any protection-deprotection step. This unique feature opens various expectations in particular in the biomedical field or in the design of responsive materials/hydrogels that will be investigated in the near future.[50,55]

Author Contributions

Simon Le Luyer - Investigation. Baptiste Quienne - Investigation. Matthieu Bouzaid - Investigation. Philippe Guégan - Ressources, Supervision, Writing – review & editing. Sylvain Caillol - Conceptualization, Supervision, Writing – review & editing. Nicolas Illy - Conceptualization, Investigation, Supervision, Writing – original draft.

Conflicts of interest

There are no conflicts to declare.

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