Lipidic Polyols Using Thiol-ene/yne Strategy for Crosslinked Polyurethanes

Phuoc Dien Pham,[1] Vincent Lapinte,[1] Yann Raoul,[2] Jean-Jacques Robin[1]
[1]Institut Charles Gerhardt Montpellier UMR5253 CNRS-UM2-ENSCM-UM1 - Equipe Ingénierie et Architectures Macromoléculaires, Université Montpellier II – Bat 17 – cc1702, Place Eugène Bataillon 34095 Montpellier Cedex 5
[2]Société Interoléagineuse d'Assistance et de développement (S.I.A.), 11, rue de Monceau CS 60003 75378 Paris cedex 08, France
Correspondence to: V. Lapinte (E-mail: Vincent.Lapinte@univ-montp2.fr)

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ABSTRACT: Oleic acid and α,ω-diacid were converted into propargylic esters followed by thiol-ene/yne coupling (TEC/TYC) functionalization in presence of mercaptoethanol. The multiradical addition on fatty esters leads to the formation of lipidic polyols (OH1 and OH2), as judged by ^{1}H NMR and mass spectroscopies as well as by size exclusion chromatography. The crosslinking reaction between TEC/TYC-based polyols and 4,4′-methylene bis(phenylisocyanate) isocyanate reactant was monitored by FTIR experiment and reaction parameters were optimized. By differential scanning calorimetry, relatively high glass transitions are measured corresponding to structure with little or without dangling chain. Moreover, the thermal stability of the resulting plant oil-based polyurethane materials (PU1 and PU2) were found to be fully consistent with that of other lipidic PUs respecting a three-step process. Thanks to TYC methodology, fatty α,ω-diacid produces lipidic polyol without dangling chain and lipidic thermoset PU with relatively high T_g. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 1597–1606

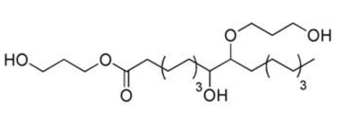
KEYWORDS: fatty acid; polyol; polyurethanes; renewable resources; thiol-yne coupling; thermosets

INTRODUCTION With growing concerns over sustainable development and environmental impact of petrochemical polymer products, researchers are paying more attention to biobased materials. The main biobased materials are vegetable oils, polysaccharides, sugars, and woods[1] that are chemically modified for the development of chemicals, plasticizers,[2] polymers,[3] blends,[4] composites, and coatings.[5] In particular, vegetable oils and their derivatives (fatty alcohols, esters, and acids) have been extensively modified to generate biobased materials[6] such as polyamides,[7] nonisocyanate polyurethanes,[8,9] surfactants,[10] and epoxy resins.[11–13]

Polyurethanes (PU)s are very interesting polymeric materials allowing a huge variety of industrial applications from paints, coatings, adhesives, sealants and insulation foams. They are synthesized from polyol and poly(isocyanate) reactants producing carbamate (urethane) bonds. The conversion of unsaturated oils into polyols has been widely investigated to prepare PUs with different physical and chemical properties. There are several approaches to introduce the hydroxyl group into the vegetable oils structure. To date, the synthesis of lipidic polyols has been mainly accomplished from epoxy vegetable oils or fatty esters intermediate (Table 1). The ring-opening of oxirane by various nucleophiles like alcohol (methanol[14] and propylene glycol[15] or carboxylic acid (lactic acid[16] was described. An alternative approach consists in the oligomerization of fatty ester by ring-opening of epoxy groups in presence of catalyst based on aluminum.[17] Ozonolysis of oils and further reduction of terminal acid groups also lead to lipidic polyols.[18] Cadiz et al. explored another strategy by hydrosilylation of methyl 10-undecenoate with phenyl tris(dimethylsiloxy) silane (PTDS).[19] Additionally, polyols were prepared by radical pathway: thiol-ene coupling (TEC) using mercaptoethanol in presence of raw oil[20] or fatty esters.[21,22] One drawback of plant oil-based PU is the low T_g value (<40 °C) due to both the low functionality of polyols and the presence of dangling chains which act as plasticizers.

Herein, we report a new synthetic approach for the facile synthesis of lipidic polyols via thiol-ene/yne coupling (TEC/TYC) using 2-mercaptoethanol (Scheme 1).[23] The TYC splits in two cycle mechanism.[24] In the first cycle, the thiyl radicals generated from thiol groups were added on the ethynyl groups to form a vinyl sulfide radical, which could attract a hydrogen atom from a thiol group, producing the vinyl sulfide and generating another thiyl radical at the same time. In the second cycle, a thiyl radical adds on the double bond of the vinyl sulfide, generating a dithioether radical, which attracts a hydrogen atom from a thiol groups and forms the disubstituted

TABLE 1 Comparison of Polyols Synthesized in This Work and in the Literature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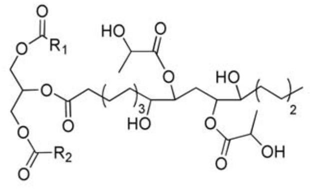
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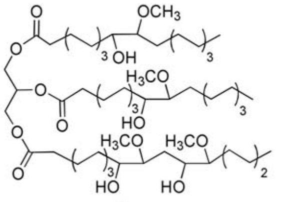
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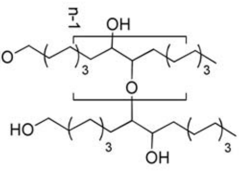
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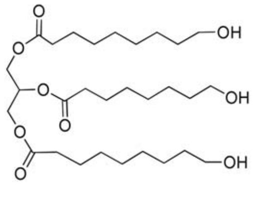
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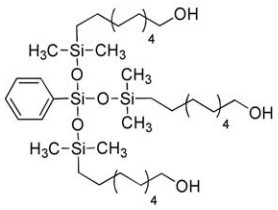
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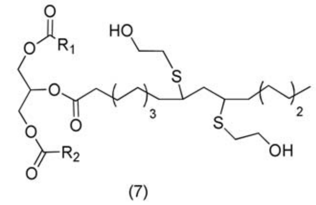
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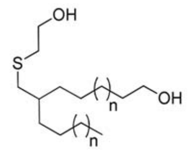
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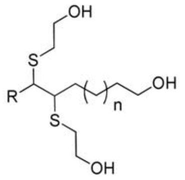
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Reference	Lipidic Precursor	Structure	Strategy	Reactant
[1]	Various VO	FA	ROEG and esterification	Propylene glycol
[2]	Soybean	TAG	ROEG	Lactic acid
[3]	Various VO	TAG	ROEG	Methanol
[4]	Methyl oleate	oligomer	ROEG and reduction	$LiAlH_4$
[5]	Various VO	TAG	Ozonolysis and reduction	O_3 and $NaBH_4$
[6]	Methyl oleate	TAG	Hydrosylilation and reduction	PTDS and $AlLiH_4$
[7]	Rapeseed oil	TAG	TEC	$HS\text{-}(CH_2)_2OH$
[8]	Methyl oleate	FA	Allylation + TEC	$HS\text{-}(CH_2)_2OH$
[9]	Methyl oleate	FA	Dehydrobromation + TYC	$HS\text{-}(CH_2)_2OH$
OH1	Oleate acid	FA	Eesterification + TYC	$HS\text{-}(CH_2)_2OH$
OH2	Oleate diacid	FA	Esterification + TYC	$HS\text{-}(CH_2)_2OH$

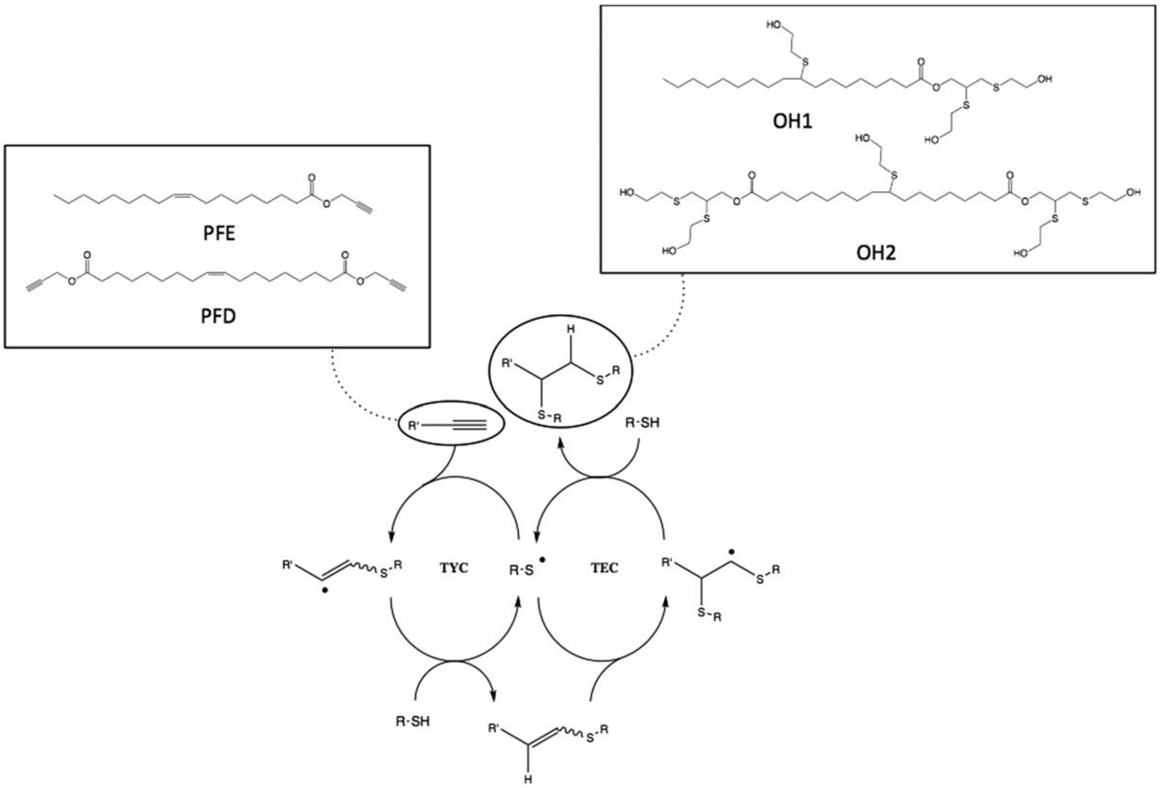
FA: fatty acid; PTDS: phenyl tris(dimethylsiloxy)silane; ROEG: ring-opening epoxy group; TAG: triacyl glycerol; VO: vegetable oil.

product. This synthetic strategy leads to high-functional polyols since one ethynyl group turns into two thioether groups. By this methodology, propargylic fatty acid (PFE), and α,ω-diacid (PFD) were converted into lipidic polyols (OH1) and (OH2), respectively. Cadiz et al. have already synthesized lipidic polyols by thiol-yne coupling after bromination, dehydrobromination of 10-undecenoic and 9-octadecenoic acids.[25,26] However, the ethynyl group is in internal position, along the fatty chain whereas in our case it is in terminal position via propargylic precursor. The advantage of our strategy is to obtain, in the case of α,ω-diacid, a polyol without dangling chain and plant oil-based PUs with relatively high T_g value. The polyols were carefully characterized by NMR and mass spectroscopies as well as size exclusion chromatography (SEC). Finally, crosslinked PUs from lipidic polyols (OH1 and OH2) and 4,4′-methylene bis(phenylisocyanate) (MDI) isocyanate reactant were investigated in terms of thermal properties and stability by differential scanning calorimetry (DSC) and thermogravimetric analyzer (TGA) techniques.

EXPERIMENTAL

Materials

Triethylamine, 2-mercaptoethanol, *p*-toluenesulfonic acid, thionyl chloride, propargylic alcohol, 2,2-dimethoxy-2-phenylacetophenone (DMPA), oleic chloride (purity 85%), and MDI



SCHEME 1 General mechanism of thiol-ene and thiol-yne couplings between alkene and alkyne and thiol - Application to PFE and PFD and mercaptoethanol.

were purchased from Aldrich and were used as received. *N,N*-dimethylformamide (DMF) and chloroform were dried and distilled according to standard procedures. C18:1 α,ω-diacid [(9Z)-octadec-9-enedioic acid] (purity 95 %) was generously gifted by S.I.A.. Deuterated solvents were purchased from SDS and were used without further purification. 2,2′-Azobisisobutyronitrile was purified twice by recrystallization in methanol and dried under vacuum. Commercially available reagents and solvents were purified and dried, when necessary, by standard methods prior to use.

Analytical Techniques

^{1}H and ^{13}C NMR spectra were recorded using a Bruker AC 300 and 400 MHz with $CDCl_3$ as solvent. Chemical shifts (^{1}H NMR) were referenced to the peak of residual $CHCl_3$ at 7.26 ppm. Chemical shifts (^{13}C NMR) were referenced to $CDCl_3$ at 77 ppm. Fourier Transform Infrared (FTIR) spectra were recorded with a Perkin–Elmer Spectrum 100 spectrometer equipped with an attenuated total reflectance crystal made of ZnSe. SEC analyses were performed in DMAc (0.1% LiCl) as eluent. Two PL-gel mix C columns were used at 50 °C with a flow rate of 0.8 mL min^{-1}, calibrated using PS standards. DSC analyses of the samples were carried out on 5–10 mg samples in aluminum pans, using a Mettler Toledo apparatus. The DSC heating and cooling schedules used were as follows: the samples were heated at 10 °C min^{-1} and cooled at the same rate to room temperature. LC/ESI-MS chromatograms were acquired in the positive ion mode with the capillary voltage set at 3000 V and cone voltage at 30 V while the dry temperature was set at 350 °C and dry gas flow was maintained at 13 mL min^{-1}. The mass acquisition range was from m/z 50 to 1000. The thermo-oxidative stability of the PU materials was examined using a Q50 TGA from TA Instruments®. The experiments consisted in registering the weight loss of the sample under nitrogen flow (60 mL min^{-1}) as a function of temperature from the ambient up to 550 °C. Different experiments were heated at 10 °C min^{-1}.

Conversion of α,ω-Diacid into Fatty α,ω-Diacid Chloride (DCl)

In a 500 mL two-necked flask equipped with a reflux condenser and a dropping funnel, 53.5 g (171.2mmol) of α,ω-diacid were dissolved in 150 mL of dry chloroform. The chloroform solution (200 mL) containing thionyl chloride was added dropwise over a period of 1 h. The mixture was heated gently on an oil bath held at 60°C for 16 hours. The mixture was evaporated under pressure in order to remove any excess of thionyl chloride. The product was used without any further purification in 97% yield.

^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 1.16–1.48 (16H, $H_{4\text{-}7}$, $H_{12\text{-}15}$), 1.55–1.82 (4H, H_3, H_{16}), 1.86–2.12 (4H, H_8, H_{11}), 2.79–2.98 (4H, H_2, H_{17}), 5.25–5.41 (2H, H_9, H_{10}).

Synthesis of Propargylic Esters

Propargylic Fatty Ester (PFE)

Propargylic alcohol (4.04 g, 72 mmol) and triethylamine (7.28 g, 72 mmol) were dissolved in dry dichloromethane

(80 mL). The solution was cooled in an ice bath under N_2 for 15 min. At 0 °C, dichloromethane solution (80 mL) of oleoyl chloride (18.05 g, 60 mmol) was added dropwise to the previous solution over 1 h. The stirring was continued for one additional hour. Then, the mixture refluxed for 16 h. The solution was washed with water (3× 150 mL) and brine (2×100 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure to yield a brown oil (15.57 g, 81 %).

23.35 g, 81%; yield.^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.79–0.95 (3H, H_1), 1.15–1.44 (20H, $H_{2\text{-}7}$, $H_{12\text{-}15}$), 1.52–1.72 (2H, H_{16}), 1.87–2.11 (4H, H_8, H_{11}), 2.27–2.39 (2H, H_{17}), 2.45–2.50 (2H, H_{21}), 4.60–4.72 (4H, H_{19}), 5.26–5.41 (2H, H_9, H_{10}); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.04 (C_1), 22.64 (C_2), 24.74 (C_{16}), 27.10 and 27.16 (C_8, C_{11}), 28.99-29.72 ($C_{4\text{-}7}$, $C_{12\text{-}15}$), 31.87 (C_3), 33.88 (C_{17}), 51.63 (C_{19}), 74.61 (C_{21}), 77.74 (C_{20}), 129.62 and 129.89 (C_9, C_{10}), 172.72 (C_{18}); IR: ν = 3312 (O-H), 2923 and 2853 (C-$H_{\text{stretching}}$), 1744 cm^{-1} (C=$O_{\text{ester stretching}}$).

Propargylic Fatty Diester (PFD)

Dichloride route

Propargylic alcohol (7.71 g, 137.4 mmol) and triethylamine (13.9 g, 137.4 mmol) were dissolved in dry dichloromethane (100 mL). The solution was cooled in an ice bath under N_2 for 15 min. At 0 °C, dichloromethane solution (100 mL) of DCl (20 g, 57.2 mmol) was added dropwise to the previous solution over 1 h. The stirring was continued for one additional hour. Then, the mixture refluxed for 16 h. The solution was washed with water (3× 200 mL) and brine (2×100 mL), dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure to yield a brown oil (19.2 g, 86 %).

Diacid route

In a 500-mL flask, 13.55 g of α,ω-diacid (43.38 mmol) and 25 mL of propargylic alcohol (433.8 mmol, 10 equiv) were dissolved in 200 mL of toluene. The mixture is vigorously stirred and 0.77 g of p-toluenesulfonic acid monohydrate (4.338 mmol, 0.1 equiv) was added. In a Dean–Stark apparatus the resulting suspension refluxed for 16 h. The organic solution was washed successively with saturated aqueous sodium bicarbonate (3 × 50 mL) and brine (2 × 50 mL) then dried over anhydrous $MgSO_4$, filtered, and finally concentrated under reduced pressure to yield an oil (15.35 g, 91 %).

^{1}H NMR (300 MHz, $CDCl_3$, δ): 1.17–1.41 (16H, $H_{4\text{-}7}$, $H_{12\text{-}15}$), 1.61–1.71 (4H, H_3, H_{16}), 1.88–2.08 (4H, H_8, H_{11}), 2.24–2.40 (4H, H_2, H_{17}), 2.45–2.49 (2H, H_{21}), 4.60–4.70 (4H, H_{19}), 5.26–5.38 (2H, H_9, H_{10}); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 24.27 (C_3, C_{16}), 26.10 (C_8, C_{11}), 27.97, 28.01, 28.08 ($C_{4\text{-}7}$, $C_{12\text{-}15}$), 32.80 (C_2, C_{17}), 50.61 (C_{19}), 73.86 (C_{21}), 76.85 (C_{20}), 128.73 (C_9, C_{10}), 171.51 (C_1, C_{18}); IR: ν = 3294 (O-H), 2926 and 2854 (C-$H_{\text{stretching}}$), 1739 cm^{-1} (C=$O_{\text{ester stretching}}$).

TEC/TYC Between Mercaptoethanol and Propargylic Fatty Esters

Polyol Derivating from PFE (OH1)

In a 50 mL flask, PFE (10 g, 31.2 mmol) was reacted with 2-mercaptoethanol (21.9 g, 280.8 mmol) in presence of the radical initiator DMPA (2.4 g, 9.36 mmol) under N_2 atmosphere. An amount of DMF (5 mL) was added to dissolve the photoinitiator. The reaction carried out under UV irradiation (365 nm) at room temperature for 8 h. DMF was then removed under reduced pressure. The mixture was dissolved in $CHCl_3$ (200 mL), then washed with water (3x200 mL), and brine (2x200 mL), dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure to yield a dark yellow oil. The product was purified by column chromatography using AcOEt/CH_2Cl_2 3/7, as eluent, to afford a viscous light yellow product (11.78 g, 68%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.81-1.02 (3H, H_1), 1.15–1.76 (29H, $H_{2\text{-}16}$), 2.27–2.44 (2H, H_{17}), 2.53–3.23 (11H, H_{20}, H_{21}, H_{22}, H_{24}), 3.63–3.91 (6H, H_{23}, H_{25}), 4.06–4.43 (2H, H_{19}); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 13.52 (C_1), 22.05 (C_2), 24.23 (C_{16}), 26.02–29.01 ($C_{4\text{-}8}$, $C_{12\text{-}15}$), 31.25 (C_3), 32.77 (C_{17}), 33.56–35.27 (C_9, C_{11}, C_{21}, C_{22}), 44.43 (C_{10}), 45.32 (C_{20}), 60.54, 60.86 (C_{19}, 2 × C_{23}), 64.77 (C_{25}), 173.15 (C_{18}); IR: ν = 3389 (O-H), 2930 and 2858 (C-$H_{\text{stretching}}$), 1736 cm^{-1} (C=$O_{\text{ester stretching}}$).

Polyol Derivating from PFD (OH_2)

In a 50 mL flask, PFD (5 g, 12.86 mmol) was reacted with 2-mercaptoethanol (15.07 g, 193 mmol) in presence of the radical initiator DMPA (1.65 g, 6.43 mmol) under N_2 atmosphere. An amount of DMF (2.4 mL) was added to dissolve the photoinitiator. The reaction carried out under UV irradiation (365 nm) at room temperature for 8 h. DMF was then removed under reduced pressure. The mixture was dissolved in $CHCl_3$ (200 mL), then washed with water (3 x 200 mL), and brine (2 x 200 mL), dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressure to yield a dark yellow oil. The product was purified by column chromatography using AcOEt/CH_2Cl_2 3/7, as eluent, to afford a viscous light yellow product (6.59 g, 66%).

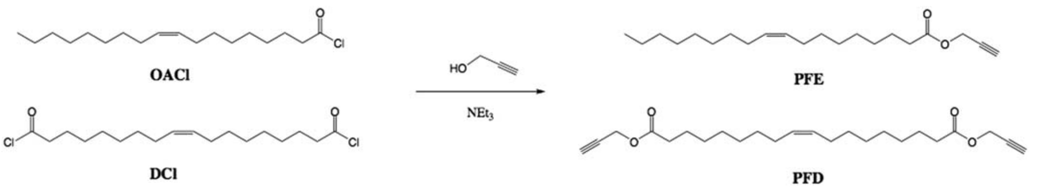
^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.14-1.65 (27H, $H_{2\text{-}16}$), 2.21-2.36 (4H, H_2, H_{17}), 2.64–2.93 (18H, H_{21}, H_{22}, H_{24}), 2.99–3.16 (2H, H_{20}), 3.43 (OH), 3.61–3.80 (10H, H_{23}, H_{25}), 4.13–4.39 (4H, H_{19}); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 24.27 (C_3, C_{16}), 26.06–28.88 ($C_{4\text{-}8}$, $C_{12\text{-}15}$), 32.86 (C_2, C_{17}), 33.61, 34.36, 35.41, 32.77 (C_9, C_{11}, C_{21}, C_{22}), 44.51 (C_{10}), 45.33 (C_{20}), 60.50, 60.84 (C_{19}, 4 × C_{23}), 64.84 (C_{25}), 173.20 (C_1, C_{18}); IR ν = 3375 (OH), 2931 and 2856 (C-$H_{\text{stretching}}$), 1731 cm^{-1} (C=$O_{\text{ester stretching}}$); ESI-MS ($m/z$): calcd for $M+H^+$ 779.33; found: 779.40, calcd for M-$(C_7H_{15}O_3S_2)^+$ 567.30; found: 567.3.

General Procedure for Crosslinked Polyurethanes (PU1 and PU2)

The PU materials were prepared by mixing OH1 or OH2 with MDI at 60 °C in an aluminum mold. The [NCO]/[OH] ratio ranged from 1/1 to 1.1/1. The vacuum was applied to remove bubbles. The mixture was cured at 60 °C for 24h and post-cured at 110 °C for 24h. The resulting PU materials were peeled off from the mold for characterization tests.

RESULTS AND DISCUSSION

The various approaches described in the literature to synthesize lipidic polyols are summarized in Table 1. Herein, we



SCHEME 2 Synthesis of propargylic fatty ester: PFE and PFD.

focus the discussion on the lipidic polyols used in thermoset PUs in presence of MDI isocyanate. Three lipidic structures are mentioned: i) the triacylglycerols (TAG) (**2, 3, 5** and **7**), ii) the linear fatty acid derivatives (FA) (**1, 8** and **9**), and iii) other structures like three-arm stars (**6**) and oligomers (**4**). It is interesting to note that the presence of dangling chain was observed in almost all structures, except for **5** and **6**. Otherwise, some structures carry primary alcohol groups (**1, 5, 6, 7, 8** and **9**) while others carry secondary ones (**2, 3** and **4**). This comparative study also highlights the presence of ester group in polyol structures apart from **4, 6, 8** and **9**. Herein, we proposed two types of polyol based on oleic acid and α,ω-diacid. From the first one, a triol (OH1) bearing an ester group and a dangling chain was elaborated whereas a pentaol (OH2) bearing a diester structure without dangling chain was synthesized using fatty α,ω-diacid.

Synthesis of Propargylic Fatty Ester and Diester

The synthesis of PFE and diester (PFD) starts from activated species of oleic (di)acids. The α,ω-diacid chloride (OACl) is marketed whereas the corresponding DCl is easily synthesized in 97% yield (see experimental part). Thus, the treatment of OACl and DCl with propargylic alcohol in presence of triethylamine in CH_2Cl_2 afforded PFE and PFD in a good yield (81 and 86%, respectively) (Scheme 2). The complete reaction was monitored by ^1H NMR experiment using in both cases the shift of $CH_2{-}C{=}O$ signal (H_{17}) from 2.88 to 2.34 ppm as well as the appearance of the propargylic signals corresponding to H_{19} and H_{21} at 4.65 and 2.45 ppm. Alternative route may be considered. For instance, PFD was also prepared in presence of α,ω-diacid using *p*-toluenesulfonic acid in good yield.

Photoinduced Thiol-ene/yne Reaction for an Efficient Synthesis of Polyols

To access the highly functional fatty polyols, thiol-ene and thiol-yne couplings could be both associated. In our case, the key step is the functionalization of propargylic fatty (di)esters (PFE and PFD) into fatty polyols (OH1 and OH2) by photoinduced TEC/TYC (Scheme 1). Mercaptoethanol was both added on internal double bond by thiol-ene coupling and terminal propargylic unsaturation by thiol-yne coupling. The photoinduced radical addition of thiol into unsaturation carried out at room temperature in presence of DMPA photoinitiator. Thanks to a simple work-up, the highly functional moieties OH1 (triol) and OH2 (pentaol) were successfully synthesized in good yields (66–68%). The ^1H NMR spectra confirmed the chemical structure of both polyols as illustrated in Figures 1 and 2. The total consumption of unsaturations: ethylenic ($H_{9\text{-}10}$) and propargylic (H_{19} and H_{21}) protons at 5.3, 4.7, and 2.4 ppm, respectively was observed in both cases. Moreover, the appearance of signals assigned

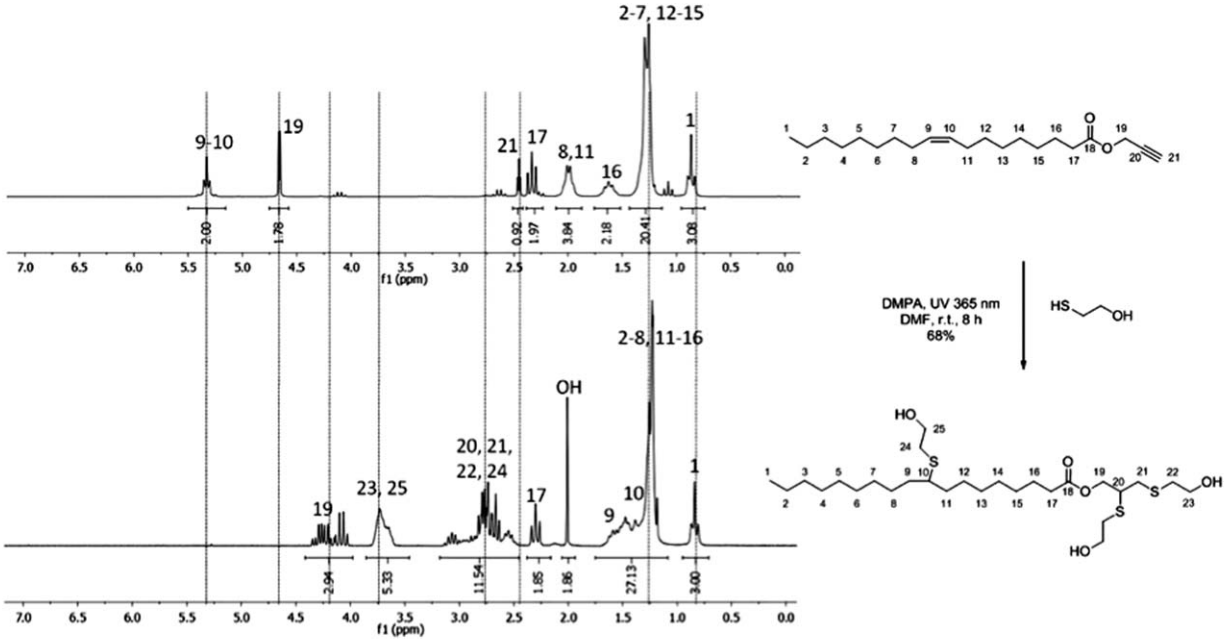


FIGURE 1 ^1H NMR spectra of PFE and OH1 in $CDCl_3$.

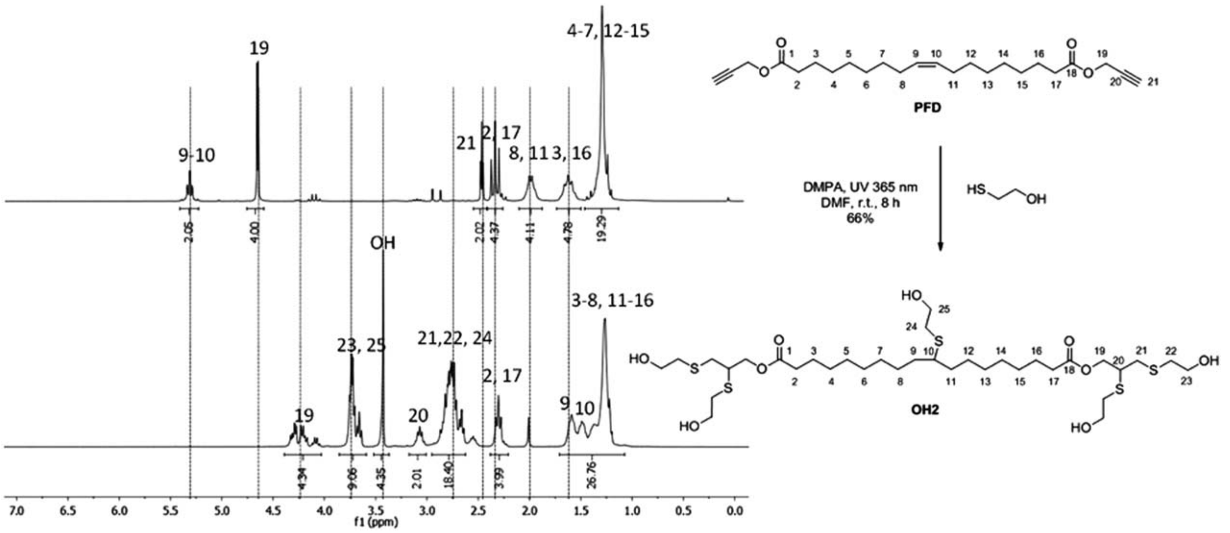


FIGURE 2 ^{1}H NMR spectra of PFD and OH2 in $CDCl_3$.

to CH_2—OH at 3.6–3.8 ppm (H_{23} and H_{25}) and thioether groups ($H_{20,\ 21,\ 22,\ 24}$) at 2.55–3.0 ppm attested the mercaptoethanol addition on fatty structures. It is interesting to notify that the both OH1 and OH2 polyols are soluble in common solvents such as $CHCl_3$, THF, and DMSO and insoluble in water.

Numerous synthetic methodologies of polyols including ring-opening epoxy group, ozonolysis, and hydrosylilation were described in the literature. Unfortunately, in many cases the side reactions accompany the polyol synthesis such as the oligomerization of unsaturated compounds into dimers, trimers, etc. The best way to observe this phenomenon is the utilization of gel permeation chromatography (GPC). By this technique, Curtis et al. detected 17% of oligomers during the epoxy ring-opening process by lactic acid followed by esterification in the case of **2**, described in Table 1.[15] Additionally, Pétrovic et al. estimated 18–25% of oligomers for **3** during oxirane ring-opening reaction of epoxidized vegetable oil in presence of methanol.[14] In our case, the synthesis of OH1 polyol happened without oligomer formation since no trace was observed at higher retention time whereas very little oligomers likely dimers appeared for OH2 polyol. In addition, the shift of the polyol traces related than those of PFD and PFE precursors confirmed the addition of three and five mercaptoethanol units into fatty structures. GPC analysis of OH1 and OH2 show an increase in molecular weight from 400 and 500 g mol^{-1} to 1400 and 2400 g mol^{-1} (Fig. 3). The large difference between targeted and experimental molecular weights can be attributed to large difference in hydrodynamic volume between the polyols and the polystyrene standards.

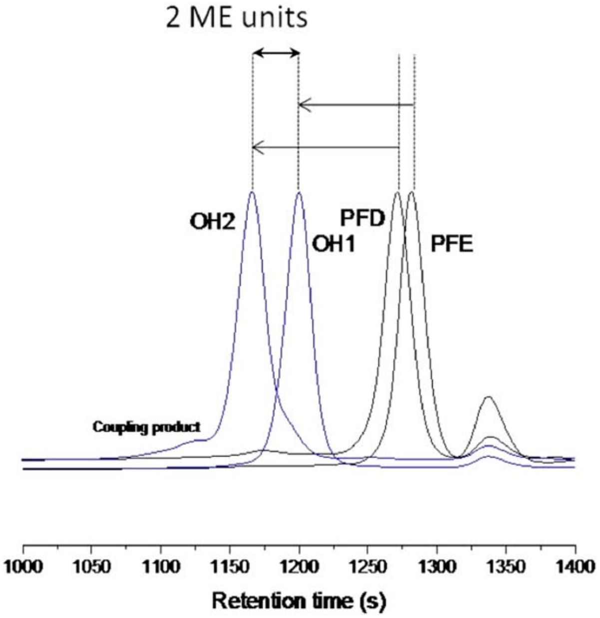


FIGURE 3 GPC traces in DMAc of PFE and PFD precursors and OH1 and OH2 polyols. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

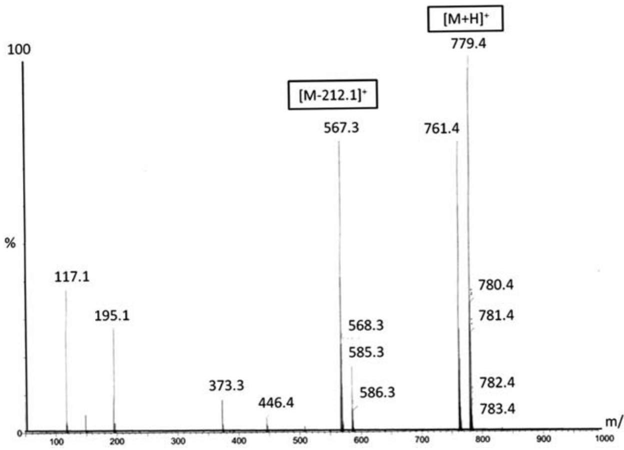
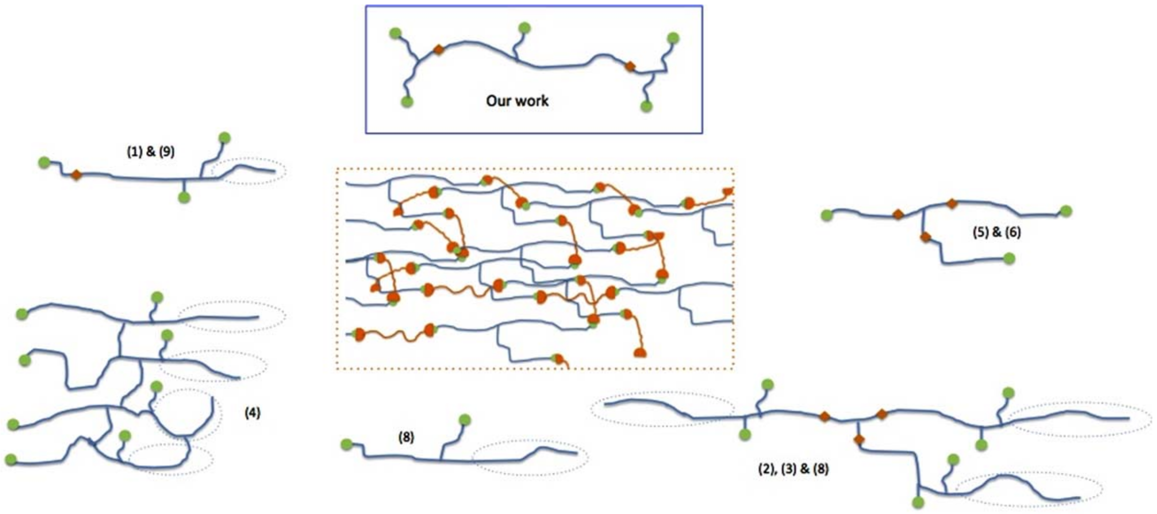


FIGURE 4 LC ESI/MS spectrum of PFD.



SCHEME 3 Schematic network based on various architectures of lipidic polyols. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The structure of OH2 polyol, alcohol highest functionality of both synthesized, was also explored by LC-ESI/MS technique (Fig. 4). As expected, the isomolecular peak $[M + H]^+$was detected at m/z of 779.40 in accordance with the m/z theoretical value of 779.33. Another peak was observed at m/z of 567.3 and corresponds to $[M\text{-}211]^+$, outcome of the breaking of the C—O bond's breaking of one of the two ester group.

Preparation of PU Materials Based on Lipidic Polyols

The polyol structure obviously impacts the density of PU network. Therefore, the T_g values and the thermal properties of the thermosets are influenced by the lipidic polyol structures described in Table 1. It is widespread that the dangling chains of the fatty polyols affect the physical properties of the resulting materials and act as plasticizers decreasing the their T_g values.[18] Apart from **5** and **6**, the polyols described in the literature carry one (**1, 8**, and **9**), three (**2, 3**, and **8**) or numerous (**4**) dangling chains as illustrated in Scheme 3. The design of our vegetable oil based polyols considers this aspect. Thus, thanks to fatty acid and α,ω-diacid precursors coming from oleic chain, OH1 and OH2 polyols were provided with three and five alcohol groups, respectively and without or one dangling chain using a simple and versatile TEC/TYC approach.

TABLE 2 Comparison of PUs Synthesized in This Work and in the Literature

Reference	[NCO]/[OH]	T_g (°C)	$T_{5\%\ loss}$ (°C)
1	1.1/1	69 − 114^{a}	–
2	1.05/1	96^{b}	273^{e}
3	1.02/1	30 − 77^{b}	–
4	1.02/1	−3 − 57^{d}	337 − 352
5	1.02/1	22 and 36	330 and 337^{e}
6	1.02/1	39	322^{f}
7	1.05/1	25^{c}	–
8	1/1	8 − 56	269 − 290
9	1/1	42 − 59	245
PU1	1/1	36	297
	1.1/1	45	295
PU2	1/1	68	279
	1.1/1	72	282

PU materials were curing at 110°C apart from
[a] 100 °C;
[b] 80 °C;
[c] 65 °C.
[d] T_g value determined by DMA experiment.
[e] Deduced from figure.
[f] Temperature of 10% of weight loss.

The comparative study gathers the thermoset PUs coming from MDI and various polyols as compiled in Table 2. The relationship between the polyol structure and the T_g value of

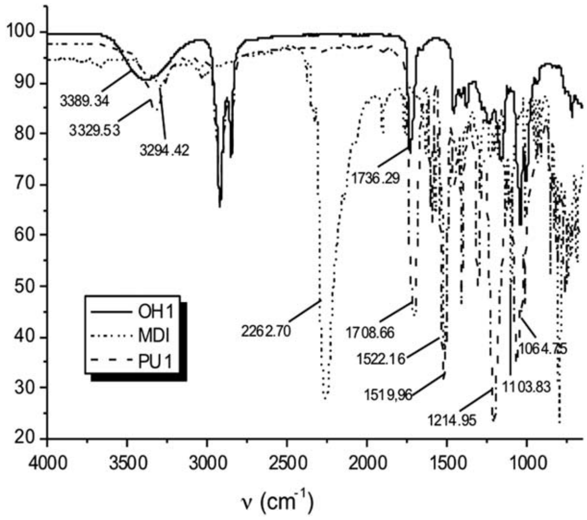


FIGURE 5 FTIR spectra of OH1, MDI and PU1 (NCO/OH = 1.1).

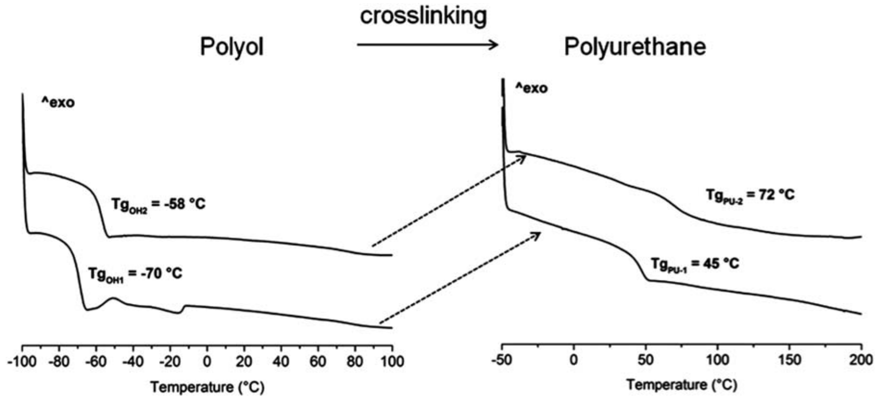


FIGURE 6 DSC thermograms of thermoset PUs (right) and the OH1 and OH2 precursors (left).

the resulting material was discussed. The T_g values were affected by the number of alcohol groups of each fatty chain. This value is directly related to the number of double bonds of precursors fatty chains. Note that the fatty chains are classified according to the number of carbon atoms (n) and of double bonds (m) such as Cn:m. For **1, 3**, and **5** polyols, several types of vegetable oils are employed carrying various contents in oleic (C 18:1), linoleic (C 18:2), and linolenic (C 18:3) chains.[14,15,18] For instance, **3**-based PU using canola oil (iodine index of 114) or linseed oil (iodine index of 182) have got a T_g value of 32 and 77 °C, respectively.[14] In short, as expected, the high level of unsaturations (iodine index closed to 220) favors the high T_g value in relation to the crosslinking density. The T_g values also depend on the strategy of incorporation of alcohol groups on fatty chains (TEC, ring-opening (RO) of oxirane). For instance, even if in all cases, fatty precursors are vegetable oils (TAG structure), PU based on **2** (RO), **3** (RO), and **7** (TEC) offered a large panel of T_g values ranging from 25 °C for **7** until 96 °C for **2**.[14,16,20] Thus, the nature of the functional alcohol unit (lactic acid for **2** and methanol for **3**) added on epoxidized vegetable oil influenced the T_g value. Interestingly, the three-arm star structure (**5** and **6**) having a terminal alcohol group exhibited low T_g values ranging from 22 and 39 °C.[18,19] This result can be explained by the flexibility of the alkyl chain bearing alcohol group and the long distance between two reactive alcohol functions producing a network with wide mesh.

As mentioned above, the presence of dangling chain in polyol structure decreased the T_g value by plasticization the T_g value. Besides the oligomer nature of **7**, low T_g values were measured (−3 and 57 °C) likely caused by the dangling chain.[27] By TEC functionalization, the same problem occurred with modified TAG (**7**) and modified fatty acid (**8**).[20,21] The T_g values varied between 25 and 56 °C. Surprisingly, the structure **1** exhibited the highest T_g value (114 °C) with 3 alcohol groups (2 secondary and 1 primary) with one dangling chain.[15] In order to enhance the alcohol density in polyol structure without dangling chain, Cadiz et al. reported the thiol-yne functionalization of 10-undecynoic and 9-octadecynoic acids after bromation of double bond, deshydrobromation into alkenic bond followed by esterification of acid group.[25] The resulting PU thermosets have a T_g value up to 59 °C. In our methodology, even if we kept TYC approach, a shorter strategy was used to incorporate an alkenyl group in fatty acid (PFE) and α,ω-diacid (PFD) structures. Unlike Cadiz, thiol-yne coupling led the introduction of terminal alkenyl group by esterification instead of bromation/deshydrobromation of internal double bond.

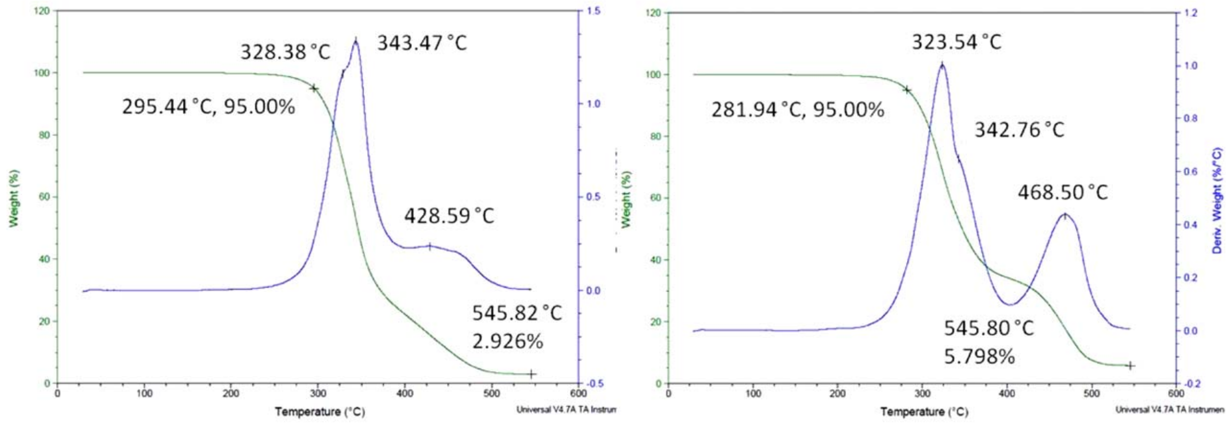


FIGURE 7 TGA chromatograms of PU1 (left) and PU2 (right) under nitrogen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The thermoset PU materials were prepared by mixing OH1 or OH2 with MDI at 60 °C in aluminum mold. The mixture was cured at 60 °C for 24 h and postcured at 110 °C for 24 h. The [NCO]/[OH] ratio ranged from 1/1 to 1.1/1 being careful to keep the NCO amount superior than OH amount to compensate the consumption of NCO species by side reactions. The PU crosslinking was confirmed by FTIR analysis as illustrated by the overlapping of OH1, MDI, and PU1 spectra in Figure 5. The total disappearance of —N=C=O stretching of the isocyanate moiety at 2240 cm^{-1} in PU1 means that the network was complete. Furthermore, the stretching vibration of C=O urethane appeared at 1708 cm^{-1} and overlapped with the C=O ester band at 1736 cm^{-1}. The N—H deformation as well as C—N stretching vibration occurred at 1520 and 1215 cm^{-1}, respectively. In addition, the broad band at 3500 cm^{-1} corresponding to O—H stretching, shifted to lower frequencies at 3350 cm^{-1}, characteristic of N—H stretching.

The thermal behaviors of PU1 and PU2 coming from OH1 and OH2 were investigated by DSC technique as shown in Figure 6. First, the glass transition temperatures of lipidic polyols (before crosslinking) were estimated. The T_g of OH1 and OH2 polyols were found to be −70 and −58 °C, respectively (Fig. 6, left). The larger number of alcohol groups reduced the mobility of fatty chain and increased the T_g value. Secondly, the same experiments were conducted on resulting thermoset PUs (Fig. 6, right). The influence of [NCO]/[OH] ratio on the crosslinking density and the T_g value was also investigated and reported in Table 2. For both polyols, the best results were observed for slight excess in isocyanate: 1.1/1 related than 1/1 as widely described in the literature. It is noteworthy that higher T_g value was measured for PU2 in comparison to PU1 (72 and 45 °C, respectively). This difference could be explained by the presence of dangling chain in the structure of OH1 in opposition to OH2 as well as the densification of the network resulting in higher functionality in alcohol groups in the latter case.

The thermal stability of PU1 and PU2 thermosets was investigated by TGA in nitrogen stream, and the results were collected in Figure 7. As previously reported, the thermal stability of PUs is relatively low. Our results were in accordance with other thermoset PUs coming from lipidic polyols and synthesized by TEC or TYC methodology. At weight loss of 5%, the degradation temperatures of PU1 and PU2 were 295 and 282 °C, respectively whereas those of Cadiz are 269–290 °C for TEC-based polyol (**8**) and 245 °C for TYC-based polyol (**9**) (Table 2).[21,25] Moreover, the well-known thermal degradation of PUs undergoes in a three-step process.[21] As described, our products degraded in two overlapping steps: (i) the first step around 325 °C results in the degradation of weak urethane bonds through the dissociation to isocyanate and alcohol and (ii) the second step occurs at 343 °C and corresponds to the decomposition and the char formation of crosslinked polymer networks. Finally, the third decomposition took place at 428–468 °C and corresponds to the gasification of any remaining components.

CONCLUSIONS

In this contribution, propargylic fatty ester of oleic acid and α,ω-diacid were synthesized in good yields. It has been showed that TEC/TYC is an effective approach to synthesize lipidic polyols without oligomers. For α,ω-diacid, polyol without dangling chain was prepared and produced PU materials with T_g value of 72 °C after optimization of the crosslinking parameters (temperature and [NCO]/[OH]). Comparing our results to those reported in the overview regarding to plant oil-based crosslinked PUs, it has been showed a typical thermal stability in a three-step process of plant oil-based thermoset PUs. Thus, through the synthesis of these lipidic polyols, we illustrated the opportunity of TYC/TEC functionalization in the synthesis of high functional monomers and branched polymers using biobased building blocks.

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