

Synthesis of castor-oil based polyurethanes bearing alkene/alkyne groups and subsequent thiol-ene/yne post-modification

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Abstract

An efficient route to obtain allyl- and propargyl-containing diols from 10-undecen-1-ol, and their polymerization with isophorone diisocyanate to produce alkene- and alkyne-functionalized polyurethanes (PUs) is described. The bio-based PUs have been further modified by thiol-ene/yne coupling of thioglycerol into unsaturation to obtain a series of PUs with enhanced hydrophilicity. All the synthesized PUs were characterized by FTIR-ATR and NMR spectroscopy. As expected, the PUs were amorphous and DSC revealed glass transition temperatures in the range of 40 °C to 5 °C for the PUs before and after **modification**. **The PUs exhibited highly tunable** thermal and mechanical properties. The mechanical properties of these bio-based polymers (E modulus from 774 MPa to 6 MPa and at break from 45% to 401%) make the suitable materials for a large range of applications.

Introduction

The depletion of petroleum resources and the accumulation of plastic waste on land and in the oceans do not necessarily require that the essential plastics should be avoided. However, the use of renewable resources as starting materials for sustainable production technologies is certainly a step towards sustainable alternatives. Among others, natural oils, such as vegetable oils provide interesting feedstock -triglyceride fatty acids- that beyond their use in food allow additional chemistry that yields opportunities for replacing petrochemicals.

With a worldwide market expected by 2016 over 18 millions tons/year,¹ polyurethanes (PU)s are very interesting polymeric materials allowing a huge variety of applications in automotive, building and construction, flooring and packaging or in the medical field. They are synthesized from polyol and poly(isocyanate) reactants producing carbamate (urethane) bonds. In industry, only a few polyisocyanates are commonly used, while a variety of polyols are available. Therefore, the choice of polyol typically determines the properties of the created polyurethane. The conversion of unsaturated oils into polyols has been widely investigated to prepare PUs with different physical and chemical properties.²⁻⁹ Vegetable oils, such as soybean oil,¹⁰⁻¹³ canola oil,^{14,15} rapeseed oil,¹⁶ palm oil,¹⁷⁻²⁰ sunflower oil,^{21,22} corn oil²³ and linseed oil,^{24,25} have been extensively studied as platforms for various polyols used for the manufacture of PUs with high thermal stability and mechanical properties. There are several approaches to introduce the hydroxyl group into the vegetable oils structure. However, almost all polyols have been prepared by ring-opening of epoxidized vegetable oils with petroleum-based small molecules. Nowadays, only few examples of commercial PU produced from vegetable oils can be found. Among them, partially biobased thermosets polyurethanes are produced from polyol like castor oil, which naturally contains hydroxyl groups (approximately 2.7 per triglyceride), and has therefore been employed extensively in polyurethane manufacturing.²⁶

Fatty acids which can be easily isolated from oils are also attractive platform chemicals for polyurethane industry since they can be used as building blocks for the synthesis of polyols. Fatty acids with a rather low reactivity of their unsaturated aliphatic chains makes them ineffective monomers when used as such, but this drawback can be

overcome by functionalizing them with polymerizable moieties, for instance to introduce hydroxyl groups leading to polyols, which can be used for polyurethane synthesis. Ricinoleic acid is the main fatty acid in castor oil (> 90%) and its pyrolysis leads to 10-undecenoic acid,²⁷ a key substrate for the synthesis of precursors for the preparation of sustainable polyurethanes.²⁸²⁹⁻³⁴

For many high-tech applications PU materials should bear functionalities enabling tuning final material properties. The functionalization of PUs can be accomplished by introducing functional groups into oligodiols and further polymerization, post-polymerization modification, or by combining both strategies. Although the former approach is more experimentally feasible for the ease of incorporating functional groups into low or medium molecular weight oligodiol, in practice the functionalization is achieved by a variety of methods including the synthesis of polyols bearing reactive pendant groups to prepare novel comb-type, grafted structural functional polymers through post-modification.³⁵ So far, there have been a few reports focusing on the preparation of novel functional bio-based PUs bearing reactive pendant groups. Existing PUs are highly hydrophobic, thus practically leading to limitation in their biomedical applications due to the lack of desirable hydrophilicity. Therefore, new functional bio-based PUs bearing hydrophilic reactive pendant groups such as hydroxyl, carboxyl, amino, and so forth become attractive.

In this study, we will present a new facile and versatile strategy based on the incorporation of allyl- and propargyl-groups to diols, step-growth polymerization and the thiol-ene/thiol-yne coupling^{36,37} to prepare aliphatic bio-based PUs bearing reactive hydroxyl pendant groups under mild conditions. This was achieved by ring-opening of 10,11-epoxyundecan-1-ol by unsaturated secondary amines to obtain diols that were polymerized with isophorone diisocyanate to produce PUs with pendant alkene and alkyne groups. Finally, these unsaturated side groups have been used as modification sites for further functionalization with thioglycerol as hydrophilic compound.

EXPERIMENTAL

Materials

The following chemicals were obtained from Aldrich and used as received: 10-undecen-1-ol, 3-chloroperoxybenzoic acid, N-allylmethylamine, N-methylpropargylamine, allylamine, propargyl chloride, tin(II) 2-ethylhexanoate (Aldrich), isophorone diisocyanate (IPDI), thioglycerol, 3-tert-butyl-4-hydroxy-5-methylphenyl sulphide (Santonox®), boron trifluoride ethylamine complex and 2,2-dimethoxy-2-phenylacetophenone (DMPA). All solvents were purified by standard procedures.

Synthesis of 10,11-epoxyundecan-1-ol

10-undecen-1-ol (17 g, 0.10 mol), 3-chloroperoxybenzoic acid (19 g, 0.11 mol), Santonox (10^{-4} mol) as radical inhibitor, and 500 mL of 1,2-dichloroethane were placed into 1L two-necked round-bottom flask equipped with condenser and a teflon coated stirring bar. The reaction mixture was gently stirred and heated at 80°C for 1 h. The resulting yellow solution was cooled to room temperature and washed several times with 5% (w/w) $\text{Na}_2\text{S}_2\text{O}_3$ and 5% (w/w) NaOH solutions. The organic layer was dried over anhydrous MgSO_4 , the solvent was removed in the rotary evaporator and the product was dried under vacuum at room temperature for 24 h. The resulting colourless oil was used without further purification in the next step. Yield 91%.

^1H NMR (CDCl_3 , TMS, δ ppm): 3.61 (2H, t, $-\text{CH}_2\text{-OH}$), 2.90 (1H, m, CH in oxirane ring), 2.73 (1H, dd, $J_{\text{cis}} = 5.2$ Hz, H cis in CH_2 of the oxirane ring), 2.45 (1H, dd, $J_{\text{trans}} = 2.4$ Hz, H trans in CH_2 of the oxirane ring) and 1.53-1.27 (16H, $-\text{CH}_2-$).

^{13}C NMR (CDCl_3 , δ ppm): 66.77 (t), 59.27 (d), 56.79 (t), 34.80 (t), 32.75 (t), 29.75 (t), 29.50 (t), 29.47 (t), 29.38 (t), 25.72 (t) and 25.66 (t).

Synthesis of N-allylpropargylamine.

Propargyl chloride (7 g, 6.8 mL, 95 mmol) was added slowly to allylamine (38 g, 50 mL, 0.67 mol) into 100 mL round-bottom flask and the resulting solution was allowed to stir for a period of 48 h at 60°C. The reaction was then cooled to room temperature

and then extracted several times with diethyl ether. The combined extracts were dried over MgSO_4 , the solvent was removed in the rotary evaporator and the resulting oil was distilled at atmospheric pressure to yield a colourless oil (yield 45%).

^1H NMR (CDCl_3 , TMS, δ ppm): 5.42 (1H, m, $\text{CH}_2=\text{CH}-$), 5.04 (2H, m, $\text{CH}_2=\text{CH}-$), 3.36 (2H, dd, $-\text{CH}_2-\text{C}\equiv\text{CH}$), 3.19 (2H, dd, $-\text{CH}_2-\text{CH}=\text{CH}_2$) and 2.24 (1H, t, $-\text{C}\equiv\text{CH}$).

^{13}C NMR (CDCl_3 , δ ppm): 135.25 (d), 117.76 (t), 78.47 (s), 73.45 (t), 56.47 (t) and 32.94 (t).

Synthesis of diols: 11-allylmethylaminoundecan-1,10-diol (D1), 11-methylpropargylaminoundecan-1,10-diol (D2), 11-allylpropargylaminoundecan-1,10-diol (D3)

A 25 mL round-bottom flask was charged with the corresponding amine (1.3 mmol), boron trifluoride ethylamine complex (0.7 mmol) and 10,11-epoxyundecan-1-ol (1.3 mmol). The mixture was stirred and heated at 80°C for 15 h. The resulting oil was purified by column chromatography using silicagel and hexane/ethyl acetate 1/1 as eluent.

11-Allylmethylaminoundecan-1,10-diol (D1). Colourless oil. Yield 91%.

^1H NMR (CDCl_3 , TMS, δ ppm): 5.82 (1H, m, $\text{CH}_2=\text{CH}-$), 5.14 (2H, m, $\text{CH}_2=\text{CH}-$), 3.62 (2H, t, CH_2-OH), 3.62 (1H, m, $-\text{CH}-\text{OH}$), 3.19 (1H, dd, $-\text{CH}_2-\text{CH}=\text{CH}_2$), 2.98 (1H, dd, $-\text{CH}_2-\text{CH}=\text{CH}_2$), 2.28 (2H, m, $-\text{N}-\text{CH}_2-$), 2.24 (3H, s, $\text{CH}_3-\text{N}-$) and 1.55-1.28 (16H, $-\text{CH}_2-$).

^{13}C NMR (CDCl_3 , δ ppm): 135.25 (d), 117.76 (t), 66.81 (d), 63.03 (t), 62.89 (t), 60.98 (t), 41.91 (q), 34.88 (t), 32.75 (t), 29.74 (t), 29.50 (t), 29.47 (t), 29.39 (t), 25.72 (t), 25.63 (t).

11-Methylpropargylaminoundecan-1,10-diol (D2). Yellow powder. Yield 90%.

^1H NMR (CDCl_3 , TMS, δ ppm): 3.62 (1H, m, $\text{CH}-\text{OH}$), 3.62 (2H, t, $-\text{CH}_2-\text{OH}$), 3.36 (2H, dd, $-\text{CH}_2-\text{C}\equiv\text{CH}$), 2.49 (1H, dd, $-\text{N}-\text{CH}_2-$), 2.34 (3H, s, $\text{CH}_3-\text{N}-$), 2.22 (1H, dd, $-\text{N}-\text{CH}_2-$), 2.24 (1H, t, $\text{CH}\equiv\text{C}$) and 1.55-1.28 (16H, $-\text{CH}_2-$).

^{13}C NMR (CDCl_3 , δ ppm): 78.47 (q), 73.45 (d), 67.15 (d), 63.05 (t), 61.89 (t), 46.14 (t), 41.67 (t), 34.99 (t), 32.92 (t), 29.89 (t), 29.66 (t), 29.64 (t), 29.54 (t), 25.88 (t), 25.74 (t).

11-allylpropargylaminoundecan-1,10-diol (D3). Yellow oil. Yield 87%.

^1H NMR (CDCl_3 , TMS, δ ppm): 5.78 (1H, m, $\text{CH}_2=\text{CH}-$), 5.19 (2H, m, $\text{CH}_2=\text{CH}-$), 3.61 (1H, t, $\text{CH}-\text{OH}$), 3.58 (2H, m, $-\text{CH}_2-\text{OH}$), 3.38 (2H, dd, $-\text{CH}_2-\text{C}\equiv\text{CH}$), 3.24 (1H, dd, $-\text{CH}_2-\text{CH}=\text{CH}_2$), 3.06 (1H, dd, $-\text{CH}_2-\text{CH}=\text{CH}_2$), 2.49 (1H, dd, $-\text{N}-\text{CH}_2-$), 2.26 (1H, dd, $-\text{N}-\text{CH}_2-$), 2.18 (1H, s, $\text{CH}\equiv\text{C}$) and 1.55-1.26 (16H, $-\text{CH}_2-$).

^{13}C NMR (CDCl_3 , δ ppm): 134.91 (d), 118.46 (t), 78.21 (q), 73.19 (d), 66.90 (d), 62.74 (t), 59.29 (t), 41.83 (t), 34.75 (t), 32.73 (t), 29.70 (t), 29.49 (t), 29.46 (t), 29.38 (t), 25.72 (t), 25.57(t).

Synthesis of polyurethanes (PUD1-3)

1.84 mmol of each different diol, D1-3, and tin (II) ethyl hexanoate (6 μL , 0.02 mmol) was placed in a 10 mL round-bottom flask equipped with a Teflon coated stirring bar and closed by septum. To the mixture were applied 6 cycles of vacuum/argon. Dried DMF (0.4 mL, 6.48 mmol) was injected into the flask and the solution was stirred and heated at 60°C for 20 minutes. IPDI (0.4 mL, 1.84 mmol) was injected and the reaction mixture was left for 24 h. After this time, the solution was precipitated into 250 mL of diethylether, filtered and dried under vacuum for 24h.

PUD1

Yield 93%.

^1H NMR (CDCl_3 , TMS, δ ppm): 5.81 (1H, m, $\text{CH}_2=\text{CH}-$), 5.13 (2H, m, $\text{CH}_2=\text{CH}-$), 4.82 (1H, broad signal, $\text{CO}-\text{NH}-\text{CH}_2-$, Z-IPDI), 4.81 (1H, m, $\text{CH}-\text{OCO}-$), 4.70 (1H, broad signal, $\text{CO}-\text{NH}-\text{CH}_2-$, E-IPDI), 4.50 (1H, broad signal, $\text{CO}-\text{NH}-\text{CH}-$), 4.03 (2H, t, $-\text{CH}_2-\text{OCO}$), 3.79 (1H, m, $-\text{CH}$ ring), 3.24 (2H, d, $-\text{CH}_2-\text{NH}-$, E-IPDI), 3.00 (2H, d, $\text{CH}_2-\text{CH}=\text{CH}_2$), 2.91 (2H, d, $-\text{CH}_2-\text{NH}-$, Z-IPDI), 2.49 (1H, m, $\text{N}-\text{CH}_2-\text{CH}$), 2.38 (1H, m, $\text{N}-\text{CH}_2-\text{CH}$), 2.26 (3H, s, $-\text{N}-\text{CH}_3$) and 1.79-0.63 (24H, $-(\text{CH}_2)_n-\text{CH}_3$).

^{13}C NMR (CDCl_3 , δ ppm): 157.18 (s), 155.72 (s), 135.85 (d), 117.30 (t), 65.03 (t), 64.79 (t), 62.56 (t), 58.74 (t), 58.74 (t), 46.03 (t), 44.43 (t), 42.23 (s), 36.44 (t), 35.06 (q), 33.02 (t), 32.68 (d), 31.75 (t), 31.69 (t), 31.43 (t), 29.37 (t), 29.17 (t), 27.57 (t), 25.72 (t), 25.20 (s) and 23.21 (s).

PUD2

Yield 93%.

^1H NMR (CDCl_3 , TMS δ ppm): 4,79 (1H, broad signal, CO-NH-CH_2 -, Z-IPDI), 4.78 (1H, m, CH-OCO-), 4.71 (1H, broad signal, CO-NH-CH_2 -, E-IPDI), 4,45 (1H, broad signal, CO-NH-CH-), 4,03 (2H, t, $-\text{CH}_2\text{-OCO}$), 3,79 (1H, m, $-\text{CH}$ ring), 3.40 (2H, dd, $\text{CH}_2\text{-C}\equiv\text{CH}$), 3.29 (2H, d, $-\text{CH}_2\text{-NH-}$, E-IPDI), 2.91 (2H, d, $-\text{CH}_2\text{-NH-}$, Z-IPDI), 2.49 (2H, d, $\text{N-CH}_2\text{-CH}$), 2.32 (3H, s, $\text{CH}_3\text{-N}$), 2.18 (1H, s, $\text{CH}\equiv\text{C-}$), and 1.71-0.86 (24H, $-(\text{CH}_2)_n\text{-CH}_3$).

^{13}C NMR (CDCl_3 , δ ppm): 162.57 (s), 156.81 (s), 78.38 (s), 73.39 (d), 71.90 (t), 64.95 (t), 56.03 (t), 54.88 (t), 46.95 (d), 44.53 (t), 42.92 (t), 41.86 (q), 35.06 (q), 32.80 (t), 31.83 (t), 31.43 (t), 29.44 (t), 29.24 (t), 29.03 (t), 27.61 (t), 25.84 (t), 25.33 (s) and 23.22 (s).

PUD3

Yield 91%.

^1H NMR (CDCl_3 , TMS, δ ppm): 5.81 (1H, m, $\text{CH}_2=\text{CH-}$), 5.12 (2H, m, $\text{CH}_2=\text{CH-}$), 4.80 (1H, broad signal, CO-NH-CH_2 -, Z-IPDI), 4.79 (1H, m, CH-OCO-), 4.68 (1H, broad signal, CO-NH-CH_2 -, E-IPDI), 4.48 (1H, broad signal, CO-NH-CH-), 4.01 (2H, t, $-\text{CH}_2\text{-OCO}$), 3.79 (1H, m, $-\text{CH}$ ring), 3.35 (2H, dd, $\text{CH}_2\text{-C}\equiv\text{CH}$), 3.26 (2H, d, $-\text{CH}_2\text{-NH-}$, E-IPDI), 2.95 (2H, d, $-\text{CH}_2\text{-NH-}$, Z-IPDI), 2.91 (2H, d, $\text{CH}_2\text{-CH=CH}_2$), 2.49 (2H, d, $\text{N-CH}_2\text{-CH}$), 2.21 (1H, s, $\text{CH}\equiv\text{C-}$), and 1.71-0.86 (24H, $-(\text{CH}_2)_n\text{-CH}_3$).

^{13}C NMR (CDCl_3 , δ ppm): 157.18 (s), 155.72 (s), 134.89 (d), 118.45 (t), 78.20(s), 73.18(d), 66.89 (t), 66.83(t), 62.73 (t), 60.88(t), 59.27 (t), 56.62 (t), 56.08 (t), 41.83 (t), 32.72 (t), 29.70 (t), 29.49 (t), 29.48 (t), 29.45 (t), 29.38 (t), 25.72 (t), 20.26 (s) and 11.76 (s).

Films preparation

The films were obtained using 0.5 g of dried PUD1-3, between two Teflon plates by compression moulding at 60 °C and 3 MPa for 10 min.

Polyurethane modification

PUD1-3 (1 mmol) and 5% (w/w) DMPA was added to a 10mL round-bottom flask with a Teflon coated stirring bar and was closed by septum. The mixture was degassed six times and was purged with argon through a needle using a vacuum/argon line and using a syringe, 2mL of anhydrous THF and the appropriate amounts of thioglycerol (2 mmol for PUD1, 4 mmol for PUD2 and 6 mmol for PUD3) were added, and the components were dissolved. The reaction was stirred at room temperature under UV irradiation (365 nm) for 2 hours and the polymer was precipitated into cold water and was washed with water three times. The polymer was dried under vacuum at 60°C during 24 hours.

INSTRUMENTATION

^1H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded using a Varian Gemini 400 spectrometer. Spectra were recorded at room temperature using 15-25 mg of sample, in CDCl_3 as solvent. Chemical shifts were reported in ppm relative to TMS as internal standards. FTIR spectra were recorded on a Bomem Michelson MB 100 FTIR spectrophotometer with a resolution of 4 cm^{-1} in the absorbance mode. An attenuated total reflection (ATR) device with thermal control and a diamond crystal (Golden Gate heated single-reflection diamond ATR, Specac-Tknokroma) was used. Raman spectra were recorded on a RENISHAW-INVIA spectrometer. A laser of wavelength 785 nm line filtered at 10% of its nominal power was used. Each spectrum was obtained by accumulation of two spectra recorded from 800 to 3200 cm^{-1} over 120 s.

Size exclusion chromatography (SEC) analysis in DMF was carried out with an Agilent 1200 series system equipped with three serial columns (PLgel $3\mu\text{m}$ MIXED-E, PLgel $5\mu\text{m}$ MIXED-D and PLgel $5\mu\text{m}$ MIXED-C from Polymer Laboratories) and an Shimatzu RID-6A refractive-index detector working at $60\text{ }^\circ\text{C}$ at a flow rate of 1.0 mL/min . The calibration curves for SEC analysis were obtained with polystyrene (PS) standards.

Calorimetric studies were carried out on a Mettler DSC821 differential scanning calorimeter using N_2 as a purge gas (20 mL/min) at scanning rate of 10°C/min . Glass transition temperatures and heat capacity changes were determined on the second

heating cycles. Thermal stability studies were carried out on a Mettler TGA/SDTA851e/LF/1100 with N₂ as purge gas. The studies were performed in the 30–600°C temperature range at a scan rate of 10°C/min

Dynamomechanical properties were measured using a dynamic mechanical thermal analysis (DMTA) apparatus TA DMA 2928 in the controlled force-tension Film mode. The tensile essays were performed on rectangular films (5 x 3 x 0.2 mm³) measuring the strain while applying a ramp of 3N/min at 20-80°C. Preload forces of 0.01N and soak time of 5 min were used. Tensile tests were performed with an Instron dynamometer (model 5942, USA) on films of 5 cm length (distance between the grips of about 30 mm) and 500 mm width at a crosshead rate of 10 mm/min and at room temperature. The Young's modulus was determined by the tangent of elastic region from stress-strain curve and toughness could be calculated by integrating the stress-strain curve.

Environmental scanning electron microscopy (ESEM) images were obtained with a FEI QUANTA 600 instrument using an accelerating potential of 10 KV.

The contact angle of deionized water against polymer surfaces was measured by the water drop method (3µL) at 25°C, using the OCA15EC contact angle setup (Neurtek Instruments).

RESULTS AND DISCUSSION

Synthesis of diols

The straightforward and upscalable synthesis of functionalized PUs presented in this work is based on obtaining of functional diols from 10-undecen-1-ol. Epoxidation of carbon-carbon double bonds in backbone chain of fatty acid followed by nucleophilic oxirane ring opening is one of the most important and widely studied reactions to produce diols with different functionalities. Thus, 10,11-epoxyundecan-1-ol was prepared in 90% yield by reaction of 10-undecen-1-ol with a slight molar excess of 3-chloroperoxybenzoic acid in 1,2-dichloroethane at 80 °C. The ¹H NMR spectrum of the epoxy compound displays multiplets at about 3.0, 2.8 and 2.5 ppm, corresponding to resonances of the three protons bonded directly to the oxirane ring, along with the complete absence of the vinylic proton signals near 5.8 and 5.0 ppm in the spectrum of

starting compound. The aminolysis of epoxides, catalyzed with boron trifluoride ethylamine complex, resulted highly regioselective and in good yields (87-91%) (Figure 1). Allyl and propargyl amines were used in the reaction with 10,11-epoxyundecan-1-ol for preparing functional aminodiols. Their ^1H NMR spectra and the corresponding peak assignments are shown in Figure 1, with resonances (ppm) for D₁: one CH_3 peak at 2.24 ppm and the $\text{CH}_2=\text{CH}$ insaturation at 5.14 ppm and 5.82 ppm. For D₂: one CH_3 peak at 2.34 ppm and the $\text{C}\equiv\text{CH}$ triple bond insaturation at 2.24 ppm and for D₃ both $\text{CH}_2=\text{CH}$ insaturations at 5.19 ppm and 5.78 ppm and the $\text{C}\equiv\text{CH}$ triple bond insaturation at 2.18 ppm. As can be seen, only the ring-opening of the oxirane by the amine nucleophilic attack on the less substituted carbon of the oxirane ring is observed, and in all cases one CH attached to the OH group at 3.62 ppm appears.

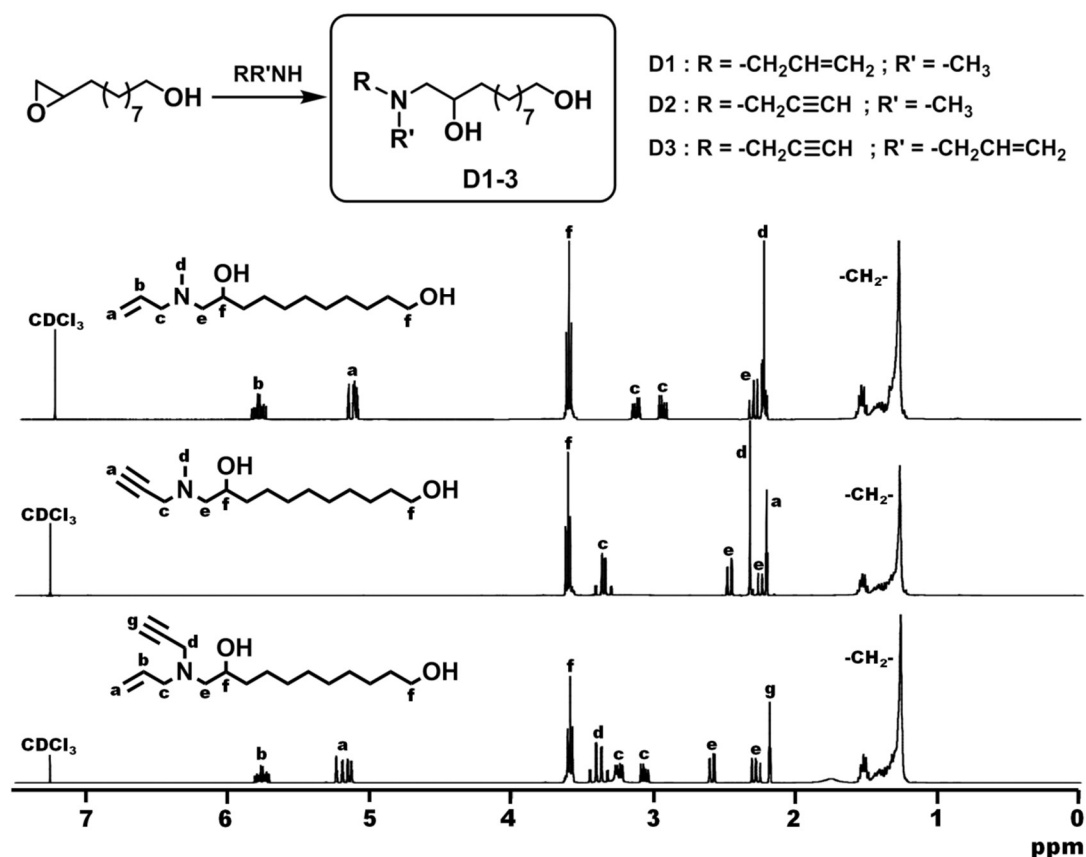


Figure 1. ^1H NMR spectra of diols D1-3

Polyurethane synthesis

A series of polyurethanes (PUD1-3) were prepared from equimolar amounts of the synthesized diols and commercially available IPDI in DMF solution at 60 °C for 24 h using tin(II) 2-ethylhexanoate as catalyst. IPDI was used owing to its lower toxicity

compared to the other commercially available diisocyanates. Moreover, due to its cyclic and asymmetric structure, IPDI is known to enhance the solubility of the PUs, which has been explained as resulting from increasing the free volume between polymer chains.²⁹ The possibility to form side products depends on the reaction conditions and the diisocyanate used to prepare the polyurethane. Generally, urea, allophanate, biuret, and isocyanurate are the side products that may form during the reaction, but in this case they are not detected under these conditions. PUs were obtained in high yields (86-95%) and showed good solubility in commonly used organic solvents. The molecular weights of PUs were evaluated by SEC and resulted similar in the three cases: Mw PUD1 about 45000 Da, Mw PUD2 48000 Da, Mw PUD3 46000 Da and dispersity ($D = 1.4$). SEC data indicate the formation of reasonably high molar mass polymers. However, the molar mass values provided by SEC should not be taken as absolute values as the SEC calibration was carried out using polystyrene standards.

The structural characterization of PUs was carried out by NMR and FTIR spectroscopy. IPDI is an asymmetric cycloaliphatic diisocyanate and contains Z and E isomers in a 3:1 ratio. The two-isocyanate groups are chemically different; one is bonded directly to cycloaliphatic ring (NCO_{sec}) and the other is bonded through a primary carbon (NCO_{prim}). The molecule consists of a mixture of two isomers, *cis* (Z) and *trans* (E), corresponding to the R and S configuration at C-5, respectively. For each of these isomers, the reactivity of the two NCO groups is different. Thus, different types of NCO groups and urethane moieties are formed during the reaction of the IPDI-diols prepolymers, and are present in the reaction mixture at same time. Now, by ^1H NMR spectroscopy we are able to distinguish and quantify the Z and E isomers that are present in the PU.³⁸

In Figure 2 the ^1H NMR spectrum of polyurethane from D1 and IPDI is shown as a mixture of both isomers. Signals corresponding to both isomers have unequivocally been identified by means of 2-D NMR gCOSY and HSQCAD spectra. Protons corresponding to the cyclic IPDI were identified: at 3.79 ppm signal (h) corresponding to methine ring undistinguishable for both isomers, and at 3.24 and 2.91 ppm signals (s and i) corresponding to methylene linked to urethane of E and Z isomers. Moreover, while the urethane proton signals from the isocyanate bonded directly to

cycloaliphatic ring (j) are undistinguishable for both isomers, the urethane proton signals from the isocyanate bonded through a primary carbon are distinguished, and appears at 4.82 and 4.70 ppm (k and o) for E and Z isomers. The ratio Z/E isomers was 3:1 calculated from signals (s and i) corresponding to methylene linked to urethane.

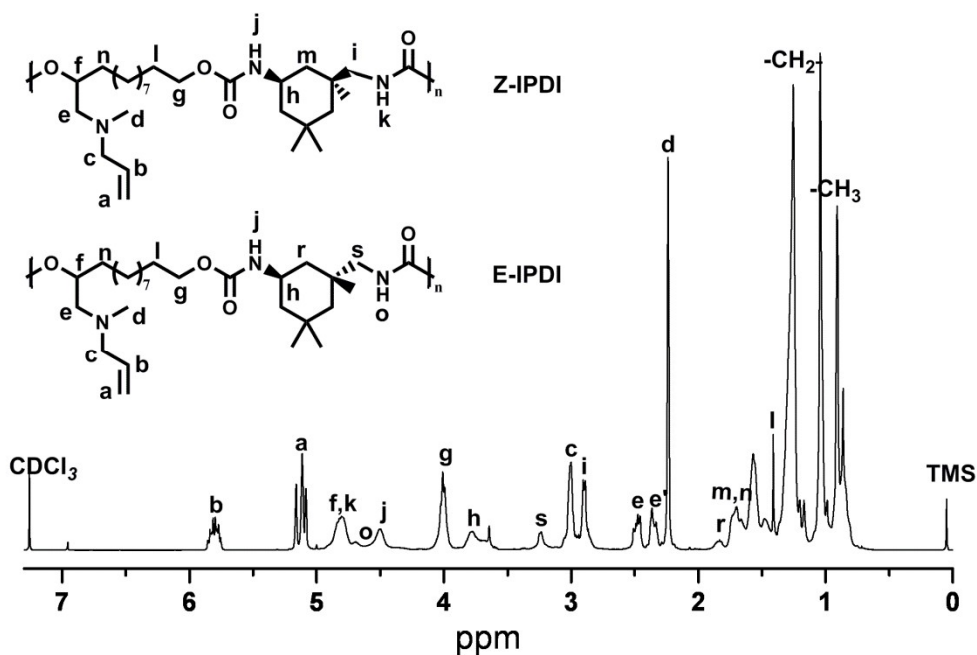


Figure 2. ^1H NMR spectrum of polyurethane from D1 and IPDI.

FTIR spectroscopic characterization revealed the expected structural features, including the disappearance of the vibrational band of NCO function, located at 2235 cm^{-1} and the appearance absorption bands of the main chain about 1694 , 3320 and 1522 cm^{-1} arising from urethane linkages corresponding to C=O stretching and NH stretching and bending bands respectively.

Polymer modification with thioglycerol

To access the highly functional polyurethanes, thiol-ene (TEC) and thiol-yne (TYC) couplings could be associated. Thiol-ene/yne chemistry was used for grafting functional groups onto polyurethanes bearing double and/or triple bonds that are very reactive.^{35,39} Thioglycerol in excess was both added on terminal double bond by TEC and terminal propargylic unsaturation by TYC. The TYC splits in two cycle mechanism

taking place the 1,2 double addition to the alkyne. The photoinduced radical addition of thioglycerol into unsaturation carried out at room temperature in presence of DMPA photoinitiator for 2h. Thanks to a simple work-up, the highly functional moieties: 2OH (diol) from PUD1, 4OH (tetraol) from PUD2 and 6OH (hexaol) from PUD3, (Figure 3), were successfully synthesized in good yields in all cases (about 80 %).

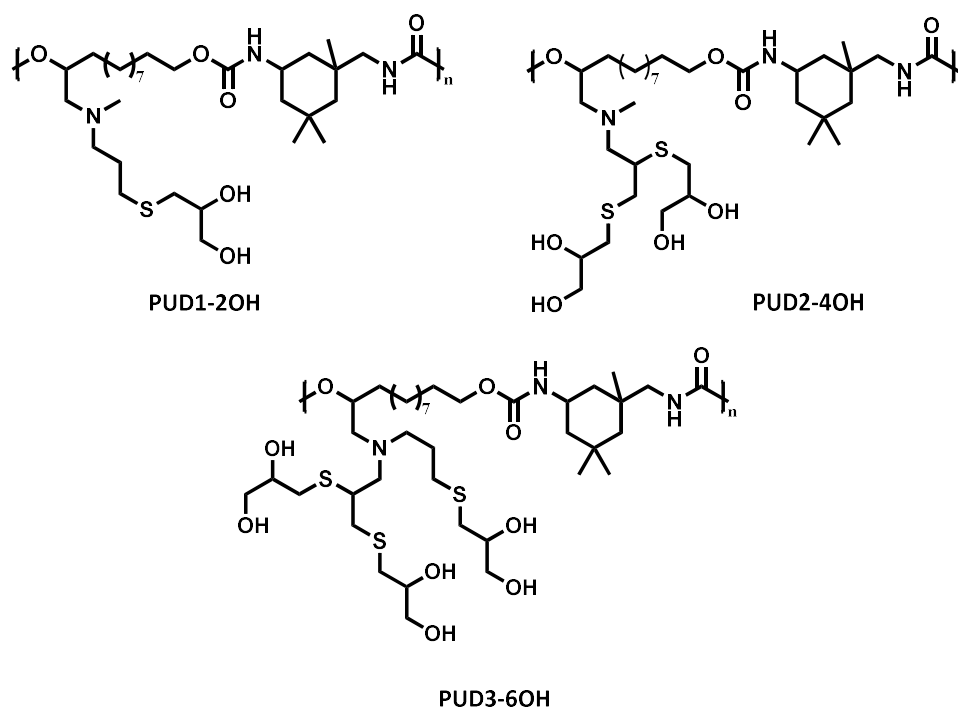


Figure 3. Structure of modified PUD1, PUD2 and PUD3 with thioglycerol

SEC analysis of modified PDUs gave slightly higher molecular weight values than PDUs. Mw PUD1-2OH about 50000 Da, Mw PUD2-4OH 55000 Da, Mw PUD3-6OH 52000 Da and polydispersity index = 1.5, showing that no degradation occurs along the thiol-ene or thiol-yne coupling.

The ^1H NMR spectra confirmed the chemical structure of modified PUs as illustrated in Figure 4 of a representative modified PUD1. The occurrence of thiol-ene reaction was evidenced by the disappearance of characteristic double bond signals at 5.81 and 5.13 ppm and the appearance of new signals corresponding to the coupled thioglycerol, i.e. a complex signal between 2.75 and 2.45 ppm for both methylene directly bonded to

sulphur (p and q) and at 3.80 ppm and 3.65 ppm signals of the methane (u) and methylene (t) directly bonded to hydroxyls (assigned by gHSQCAD spectrum).

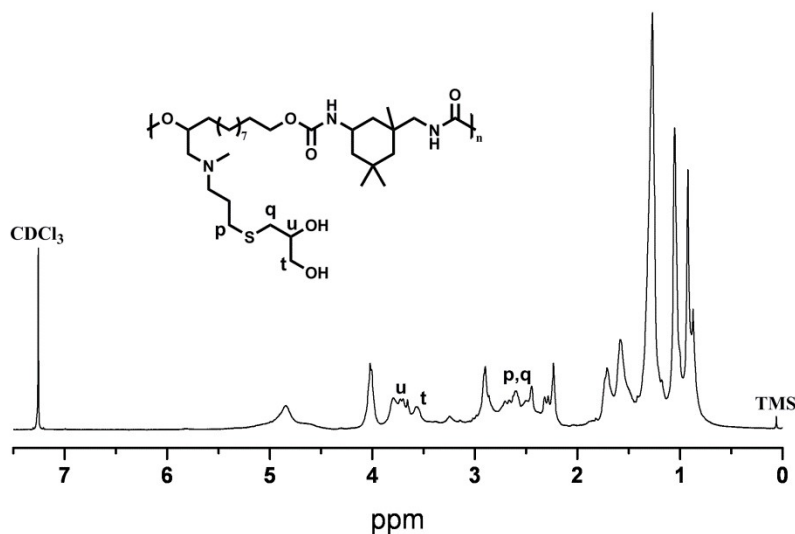


Figure 4. ^1H NMR spectrum of PUD1 after thiol-ene reaction with thioglycerol

For modified PUD2 and PUD3 although their ^1H NMR spectra show broad signals, the disappearance of the ^1H NMR signal of the propargyl methylene protons around 3.35-3.40 ppm, along with the appearance of the signals to the coupled thioglycerol are observed. For all reactions performed, the ^1H NMR results indicated the occurrence of double addition of thiol molecules to the reacted alkyne groups. The absence of a monothiol adduct and thus the absence of double bonds in the final products after the coupling reaction is in accordance with earlier observations on thiol-yne reactions.⁴⁰ It was previously described that the addition of the first thiol to the alkyne is the rate-limiting step, which is followed by the fast second thiol addition to the intermediate thiol-alkene.⁴¹

To confirm the occurrence of thiol-ene/yne reactions on PUD2 and PUD3, Raman spectra were registered at different times. **Figure 5 shows spectra as a function of time of reaction** of PUD3 with thioglycerol. At first, the characteristic peaks of double and triple bonds of PUD3 at 1644 and 2105 cm^{-1} respectively, clearly appear. After 15 min, only the thiol-ene coupling appears to be started, as signal of triple bond remained unchanged but at 30 min triple bond peak is scarcely observed. The spectrum at 60

min shows the total disappearance of double and triple bond confirming thiol-ene/yne occurred.

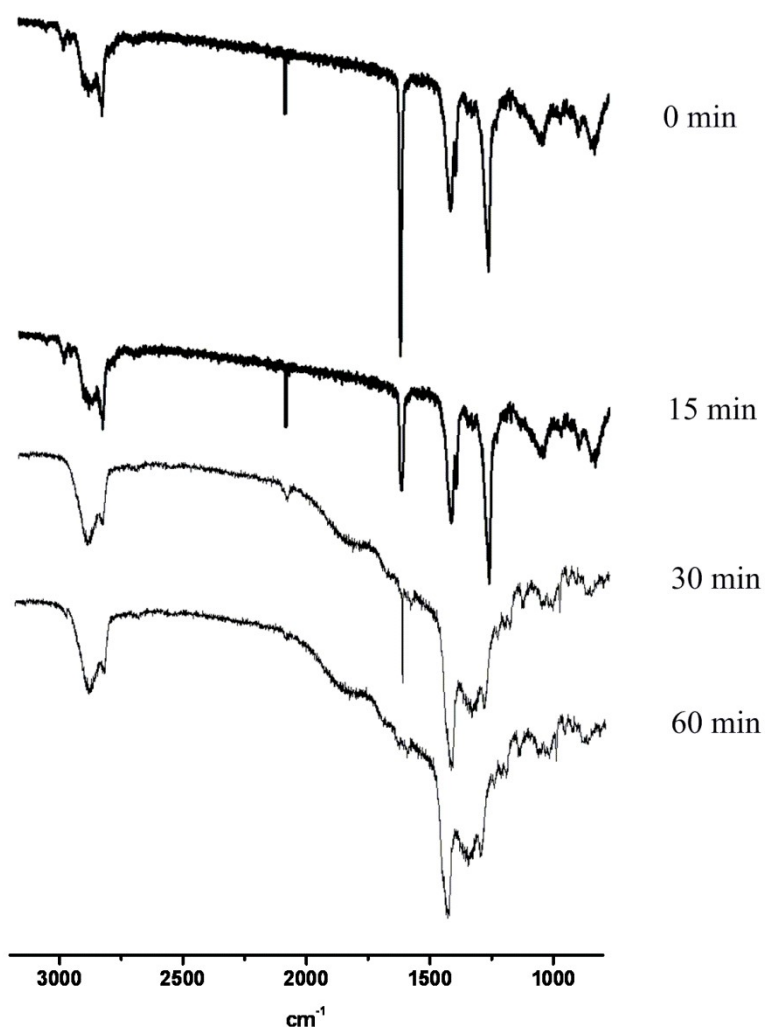


Figure 5. Raman spectra of PUD3 and thiol-ene/yne reaction with thioglycerol at different times

Thermal, mechanical and contact angle properties

Thermal characterization of PUDs and modified PUDs was carried out by DSC, DMA and TGA under N₂ atmosphere at a heating rate of 10 °C/min. The DSC traces are shown in Figure 6 and the data are summarized in Table 1. No melting peaks were

observed thus PUs are not semicrystalline. As expected, the presence of cycloaliphatic ring, pendant alkyl chains or asymmetry of the monomer enhances the free volume and hence hinders the packing of the polymer chains. The glass transition temperatures (T_g s) of the three PUD (Figure 6 a) were near 40 °C and lower T_g s, between 5 °C and 18 °C, were found for the modified PUD-OH (Figure 6 b). Indeed the presence of high density hydrogen bonding due to the presence of tertiary amine, increases the rigidity and thus strongly suppresses the mobility of the polymer chains. Besides the presence of the dangling chains after the modification of PUD with thioglycerol could act as plasticizers decreasing their T_g values. On the other hand the possibility of hydrogen bonding in PUD3-6OH is higher than in PUD1-2OH increasing its T_g around 13 °C.

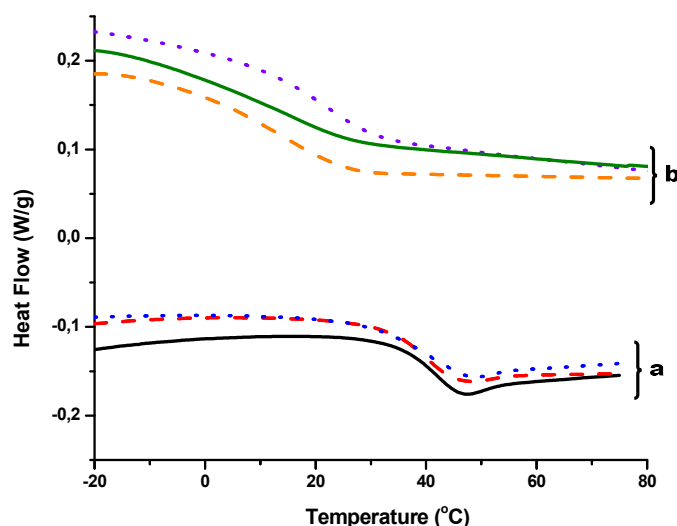


Figure 6. DSC traces of amorphous PUD1-3 (a): PUD1 (—), PUD2 (---) and PUD3 (···) and the modified PUD1-3 with thioglycerol (b): PUD1-2OH (—), PUD2-4OH (---) and PUD3-6OH (···).

Table 1. Thermal properties for the PUD1-3 and the modified PUD1-3 with thioglycerol

Sample	DSC	DMA	TGA	
	T_g (°C)	T_g (°C)	$T_{5\%}$ (°C) ^a	T_d (°C) ^b
PUD1	41	51	281	319/441
PUD2	39	53	282	315/421
PUD3	40	53	290	317/453
PUD1-2OH	5	21	223	312/420
PUD2-4OH	11	26	203	301/423
PUD3-6OH	18	31	186	303/431

^aTemperature at which 5% weight loss was observed.

^bTemperature for maximum degradation rate.

The dynamic mechanical behaviour was also investigated as a function of temperature. DMA results are summarized in Table 1 and correlated with the data from DSC analysis. The curves of $\tan \delta$ *versus* temperature, of the three PUD (a) and the modified PUD-OH (b) are shown in Fig. 7. The glass transition temperatures, **estimated from DMA as** the maximum of $\tan \delta$, are in good agreement with the DSC values as $\frac{1}{2} \Delta C_p$. The observed differences are explainable by the way of measurement. Indeed, DSC and DMA measure changes of the heat capacity and the mechanical response of the polymer chains during the transition, respectively.

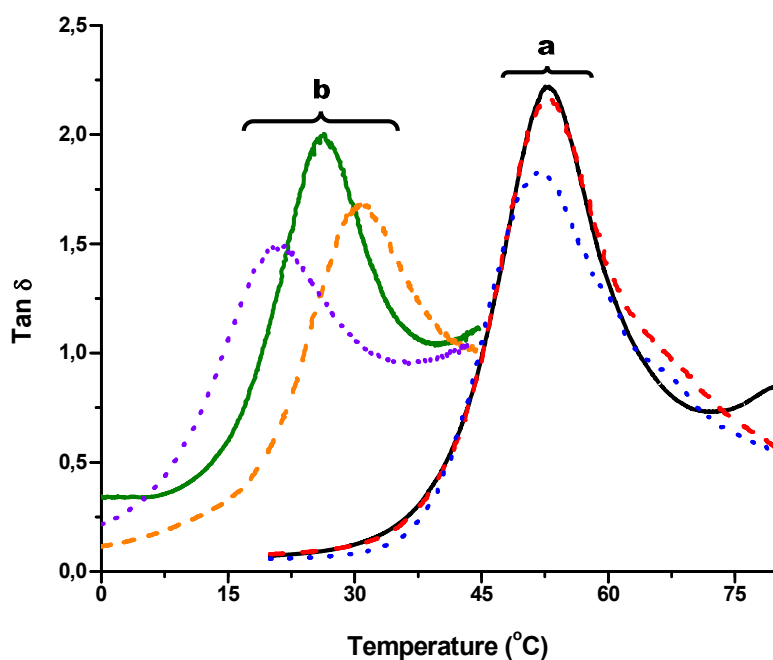


Figure 7. $\tan \delta$ as a function of temperature for PUD1-3 (a): PUD1 (—), PUD2 (---) and PUD3 (···) and the modified PUD1-3 with thioglycerol (b): PUD1-2OH (—), PUD2-4OH (---) and PUD3-6OH (···).

Thermal stability of PDU1-3 and modified PUD1-3 with thioglycerol was investigated by TGA in a nitrogen stream and data are summarized in Table 1. In general, PUs present low heat resistance due to the presence of thermo-labile urethane linkage. Overall, the

PUs were found to have a typical complex decomposition behavior as clearly displayed by the TGA derivatives of the weight loss as a function of temperature. (Fig. 8). All polymers showed an initial weight loss in the range of 180- 280 °C, suggesting that degradation starts at the urethane bond. Studies on the decomposition of the urethane bond indicate that decomposition initial temperature of the urethane bond depends on the structure of both the isocyanate and the diol, and it takes place through dissociation to isocyanate and alcohol, the formation of primary amines and olefins and the formation of secondary amines and carbon dioxide.⁴² It can be observed that the initial degradation temperatures are shifted to lower temperature with increasing polyol OH-functionality, i.e for modified PUD-OH (plots b).

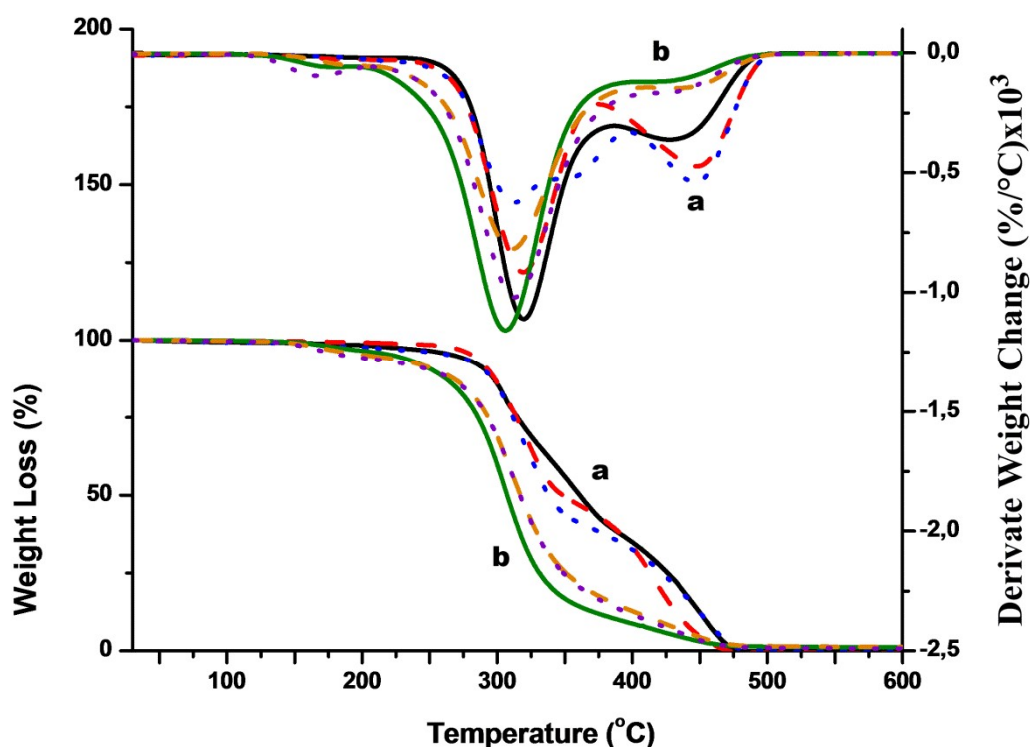


Figure 8. TGA and first derivative traces of PUD1-3 (a): PUD1 (—), PUD2 (---) and PUD3 (···) and the modified PUD1-3 with thioglycerol (b): PUD1-2OH (—), PUD2-4OH (---) and PUD3-6OH (···).

The main degradation step is associated with the aliphatic moieties of the remaining structure and occurs at similar temperatures for all PUs (300-320 °C). This degradation

is produced at lower temperature than the **one** described for conventional oil-derived aliphatic PUs (i.e castor oil- derived PU)⁴³ and could be related with the dissociation of the amine and thioether bonds⁴⁴ that confer lower stability to the prepared PUs. Finally, the third degradation stage (over 400 °C) is more prominent in the case of the unmodified PUs (a) but occurs at similar temperatures and corresponds to the gasification of any remaining components.³⁹

Tensile tests were performed on PUDs and PUD-OHs: the Young 's modulus, elongation at break, stress at break and toughness **and their standard deviation** are given in Table 2. The stress-strain curves are depicted in Figure 9.

Table 2. Mechanical properties of PUD1-3 and the modified PUD1-3 with thioglycerol

Sample	Young Modulus (Mpa)	Elongation at break (%)	Stress at break (MPa)	Toughness (MJ/m3)
PUD1	683±9	48.0±0.6	6.72±0.20	456±7
PUD2	726±9	47.0±0.6	5.88±0.18	450±6
PUD3	774±9	45.0±0.6	7.51±0.21	412±6
PUD1-2OH	6.0±0.0	401±6	0.17±0.00	352±4
PUD2-4OH	19.0±0.1	255±3	1.17±0.01	426±5
PUD3-6OH	24.0±0.1	153±2	1.47±0.06	375±4

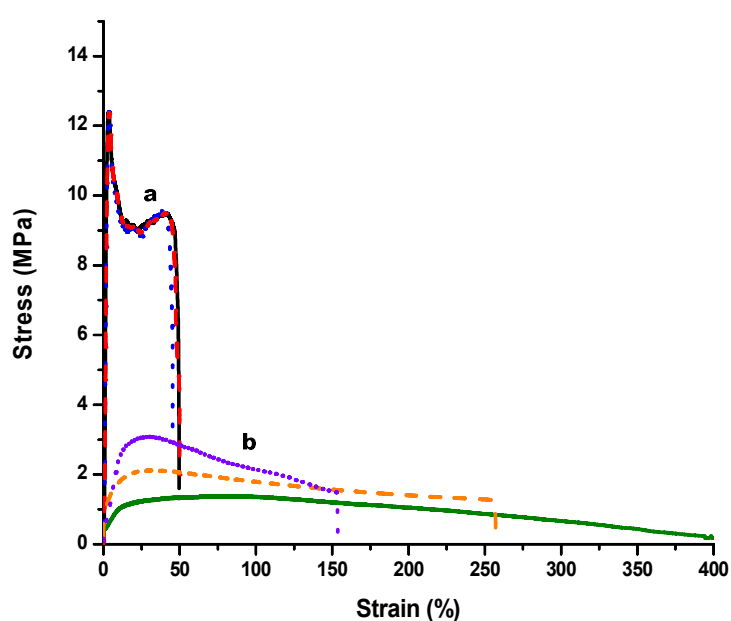


Figure 9. Tensile stress *versus* strain curves of PUD1-3 (a): PUD1 (—), PUD2 (---) and PUD3 (···) and the modified PUD1-3 with thioglycerol (b): PUD1-2OH (—), PUD2-4OH (---) and PUD3-6OH (···).

Similar high Young's modulus was observed for the three PUDs (a) but **significantly lower moduli were obtained** for the modified PUD-OHs (b). The last ones show a behavior similar to slightly crosslinked amorphous rubbers with low modulus and smooth transition in their stress-strain behaviour. In addition the elongation at break is similar for the three PUDs and higher than that for PUD-OHs. The mechanical properties of these bio-based polymers (E modulus from 683-774 MPa to 6-24 MPa and at break from 45% to 401%) make them suitable materials for a large range of applications.

Hydrophilicity/hydrophobicity balance strongly affects the material applications. PUs prepared from vegetable oils are expected to exhibit a non-wetting surface due to the hydrophobic nature of triglycerides. Contact angle measurements demonstrated the high hydrophobicity of the synthesized PUDs (PUD1: 108 °; PUD2: 110 °; PUD3: 104 °). Modified PUD-OHs were more hydrophilic showing contact angle values of PD1-2OH: 89 °; PUD2-4OH: 83 °; PUD3-6OH: 77 °). These results agree with the increase of the dangling hydroxyl moieties. Pictures of the contact angle measurements of the PDU3 and PUD3-6OH, after modification with thioglycerol, are shown in Figure 10, and confirm the change of the surface properties of both films. When hydrophilic treatment was undertaken (pictures on the bottom left), the drop of water spreads over the PU film due to a higher interaction between water and the newly modified PU material.

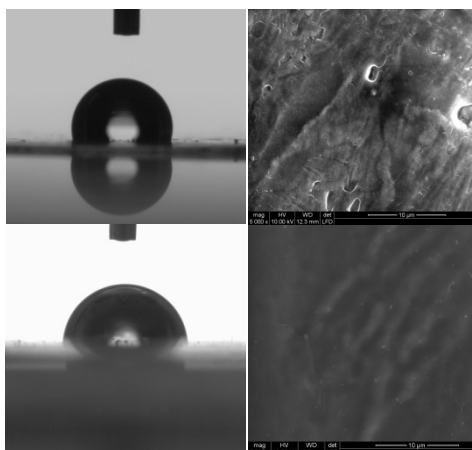


Figure 10. Contact angle and ESEM images of PUD3 (a) and PUD3-6OH (b)

ESEM images of the surface structures show the morphology of surface-modified samples compared to unmodified samples. As an example ESEM images of PDU3 and PDU3-6OH are collected in Figure 10 a) and b) respectively. The first is accounted for by roughness or heterogeneous composition that is, a surface composition characterized by domains of different surface tensions. The rough hydrophobic surface **makes it difficult for water to penetrate** the crevices and cracks. After modification, the micrograph of PDU3-6OH shows a more homogeneous distribution on the surface.

The results, also interpreted on the basis of SEM micrographs, show that not only hydroxyl terminated bond is the reason of hydrophilic nature of the film, but its homogeneous composition helps a great deal in achieving a greater hydrophilicity of the film.

Conclusions

In this study we reported the synthesis of functionalized aliphatic bio-based PUs bearing reactive hydroxyl pendant groups under mild conditions. We describe an efficient route to obtain allyl- and propargyl-containing diols, that were then polymerized with IPDI to produce alkene- and alkyne-functionalized PUs. By thiol-ene/yne coupling of thioglycerol into unsaturation a series of PUs with enhanced hydrophilicity were obtained. Water contact data shows that modified PUD-OHs have a greater hydrophilic stability than precursors PUDs. All the synthesized PUs were characterized and revealed good thermal and mechanical properties. The mechanical properties of these bio-based polymers (E modulus from 683-774 MPa to 6-24 MPa and at break from 45% to 401%) make the suitable materials for a large range of applications.

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REFERENCES

- ¹ Bassam, N.; Candy, L.; Blanco, J-F.; Guerin, C.; Raoul, Y.; Mouloungui, Z. From Petrochemical Polyurethanes to Biobased Polyhydroxyurethanes. *Macromolecules*, **2013**, *46*, 3771-3792.
- ² Garrison, T. F.; Kessler, M. R. Plant oil-based polyurethanes in Bio-based Plant Oil Polymers and Composites, Madbouly, S.; Zhang, C.; Kessler, M. R. Eds. Elsevier, Amsterdam, **2016** pp.37-55.
- ³ Li, Y.; Luo, X.; Hu, S. Bio-based Polyols and Polyurethanes. Springer International Publishing Ag Switzerland, **2015**, pp.15-39.
- ⁴ Zhang, C; Madbouly, S. A.; Kessler, M. R. Biobased polyurethanes prepared from different vegetable oils. *ACS Appl. Mater. Interfaces*, **2015**, *7*, 1226-1233.
- ⁵ Alagi, P.; Hong, S. C. Vegetable oil-based polyols for sustainable polyurethanes. *Macromol. Research*, **2015**, *23*, 1079-1086.
- ⁶ Desroches, M.; Escouvois, M.; Auvergne, R.; Caillol, S; Boutevin, B. From vegetable oils to polyurethanes: synthetic routes to polyols and main industrial products. *Polym. Rev.* **2012**, 38-79.
- ⁷ Pfister, D. P.; Xia, Y.; Larock, R. C. Recent advances in vegetable-oil based polyurethanes. *ChemSusChem* **2011**, *4*, 703-717.
- ⁸ Lligadas, G.; Ronda, J. C.; Galià, M.; Cádiz, V. Plant Oils as Platform Chemicals for Polyurethane Synthesis: Current State-of-the-art. *Biomacromolecules* **2010**, *11*, 2825-2835.
- ⁹ Hojabri, L.; Kong, X.; Narine, S. S. Functional thermoplastics from linear diols and diisocyanates produced entirely from renewable lipid sources. *Biomacromolecules* **2010**, *11*, 911–918.
- ¹⁰ Campanella, A.; Bonnaillie, L. M.; Wool, R. P. Polyurethane foams from soyoil-based polyols. *J Appl Polym Sci*, **2009**, *112*, 2567-2578.
- ¹¹ Tan, S.; Abraham, T. ; Ference, D.; Macosko, C. W. Rigid polyurethane foams from a soybean oil-based polyol. *Polymer*, **2011**, *52*, 2840–2846.

-
- ¹² Zhang, C.; Xia, Y.; Chen, R.; Huh, S.; Johnston, P. A.; Kessler, M. R. Soy-castor oil based polyols prepared using a solvent-free and catalyst-free method and polyurethanes therefrom. *Green Chem.*, **2013**, *15*, 1477-1484
- ¹³ Caillol, S.; Desroches, M.; Carlotti, S.; Auvergne, R.; Boutevin, B. Synthesis of new polyurethanes from vegetable oil by thiol-ene coupling. *Green Materials*, **2012**, *1*, 16-26.
- ¹⁴ Kong, X.; Narine, S. S. Physical properties of polyurethane plastic sheets produced from polyols from canola oil. *Biomacromolecules*, **2007**, *8*, 2203-2209.
- ¹⁵ Kong, X.; Yue, J.; Narine, S. S. Physical Properties of Canola Oil Based Polyurethanes Networks. *Biomacromolecules*, **2007**, *8*, 3584-3589.
- ¹⁶ Desroches, M.; Caillol, S.; Lapinte, V.; Auvergne, R.; Boutevin, B. Synthesis of Biobased Polyols by Thiol-Ene Coupling from Vegetable Oils. *Macromolecules*, **2011**, *44*, 2203-2209.
- ¹⁷ Chian, K. S.; Gan, L. H. Development of a rigid polyurethane foam from palm oil. *J. Appl. Polym. Sci.* **1998**, *68*, 509-515.
- ¹⁸ Tanaka, R.; Hirose S.; Hatakeyama, H. Preparation and characterization of polyurethane foams using a palm oil-based polyol. *Bioresource Technol*, **2008**, *99*, 3810-3816.
- ¹⁹ Noor, N. M.; Ismail, T. N. M. T.; Kian, Y. S.; Hassan, H. A. Synthesis of palm-based polyols: effect of K10 montmorillonite catalyst. *J. Oil Palm Research*, **2013**, *25*, 92-99.
- ²⁰ Adnan, S.; Ismail, T. N. M. T.; Noor, N. M.; Din, N. S. M. N. M.; Hanzah, N. A.; Kian, Y.S.; Hassan, H. A. Development of Flexible Polyurethane Nanostructured Biocomposite Foams Derived from Palm Olein-Based Polyol. *Adv. Mater. Sci. Eng.*, **2016** doi.org/10.1155/2016/4316424.
- ²¹ Palaskar, D. V.; Boyer, A.; Cloutet, E.; Le Meins, J-F.; Gadenne, B.; Alfes, C.; Farcet, C.; Cramail, H. Original diols from sunflower and ricin oils: synthesis, characterization, and use as polyurethane building blocks. *J. Polym. Sci. Part A Polym. Chem.* **2012**, *50*, 1766-1782.
- ²² More, A. S.; Maisonneuve, L.; Lebarbé, T.; Gadenne, B.; Alfes, C.; Cramail, H. Vegetable-based building-blocks for the synthesis of thermoplastic renewable polyurethanes and polyesters. *Eur. J. Lipid Sci. Tech.* **2013**, *115*, 61-75.

-
- ²³ De Souza, V.H.R.; Silva, S.A.; Ramos, L.P.; Zawadzki, S. F. Synthesis and Characterization of Polyols Derived from Corn Oil by Epoxidation and Ozonolysis. *J. Am. Oil Chem. Soc.* **2012**, *89*, 1723-1731.
- ²⁴ Sharma, V.; Banait, J. S.; Kundu, P. P. Swelling kinetics of linseed oil-based polymers. *J. Appl. Polym. Sci.* **2009**, *111*, 1816-1827.
- ²⁵ Zlatanovic, A.; Lava, C.; Zhang, W. Z.; Petrovic, S. Effect of structure on properties of polyols and polyurethanes based on different vegetable oils. *J. Polym. Sci. Pol. Phys.* **2004**, *42*, 809-819.
- ²⁶ Hablot, E.; Zheng, D.; Bouquey, M.; Avérous, L. Polyurethanes Based on Castor Oil: Kinetics, Chemical, Mechanical and Thermal Properties. *Macromol. Mater. Eng.* **2008**, *293*, 922-929.
- ²⁷ Van Steen, M.; Stevens, C. V. Undecylenic Acid: a Valuable and Physiologically Active Renewable Building Block from Castor Oil. *ChemSusChem* **2009**, *2*, 692-713.
- ²⁸ Bigot, S.; Daghrir, M.; Mhanna, A.; Boni, G.; Pourchet, S.; Lecamp, L. Plasseraud, L. Undecylenic acid: A Tunable Bio-based Synthon for Materials Applications. *Eur. Polym. J.* **2016**, *74*, 26-37.
- ²⁹ Maisonneuve, L.; Lebarbé, T.; Nga Nguyen, T. H.; Cloutet, E.; Gadenne, B.; Alfos, C.; Cramail, H. Hydroxyl telechelic building blocks from fatty acid methyl esters for the synthesis of poly(ester/amide urethane)s with versatile properties. *Polym. Chem.*, **2012**, *3*, 2583-2595.
- ³⁰ Gonzalez-Paz R. J.; Lluch, C.; Lligadas, G.; Ronda, J. C.; Galià, M.; Cádiz, V. Thiol-yne reaction of alkyne-derivatized fatty acids: biobased polyols and cytocompatibility of derived polyurethanes. *Polym. Chem.*, **2012**, *3*, 2471-2478.
- ³¹ Lligadas, G.; Ronda, J. C.; Galià, M.; Cádiz, V. *Biobased Monomers, Polymers, and Materials*, ACS Symposium Series, **2012**, 1105, 17, 269-280.
- ³² Lligadas, G.; Ronda, J. C.; Galià, M.; Cádiz, V. Oleic and undecylenic acids as renewable feedstocks in the synthesis of polyols and polyurethanes. *Polymers* **2010**, *2*, 440-453.

-
- ³³ Lluch, C.; Ronda, J. C.; Galià, M.; Lligadas, G.; Cádiz. V. Rapid approach to biobased telechelics through two one-pot thiol-ene click reactions. *Biomacromolecules*, **2010**, *11*, 1646-1653.
- ³⁴ Gonzalez-Paz R. J.; Lluch, C.; Lligadas, G.; Ronda, J. C.; Galià, M.; Cádiz. V. A green approach toward oleic- and undecylenic acid-derived polyurethanes. *J. Polym. Chem. Part A Polym. Chem.*, **2010**, *11*, 1646-1653.
- ³⁵ Basko, M.; Bednarek, M.; Nguyen, L-T. T.; Kubisa, P.; Du Prez, F. Functionalization of polyurethanes by incorporation of alkyne side-groups to oligodiols and subsequent thiol-yne post-modification. *Eur. Polym. J.* **2013**, *49*, 3573-3581.
- ³⁶ Ott, C.; Easton, C. D.; Gengenbach, T. R.; McArthur, S. L. Gunatillake, P. A. Applying "click" chemistry to polyurethanes: a straightforward approach for glycopolymer synthesis. *Polym. Chem.* **2011**, *2*, 2782-2784.
- ³⁷ Lowe, A. B. Thiol-yne click/coupling chemistry and recent applications in polymer and material synthesis and modification. *Polymer* **2014**, *55*, 5517-5549.
- ³⁸ Prabhakar, A.; Chattopadhyay, D. H.; Jagadeesh, B.; Raju, K. V. S. N. Structural investigations of polypropylene glycol (PPG) and isophorone diisocyanate (IPDI)-based polyurethane prepolymer by 1D and 2D NMR spectroscopy. *J. Polym. Chem. Part A Polym. Chem.*, **2005**, *11*, 1196-1209.
- ³⁹ Pham, P. D.; Lapinte, V.; Raoul, Y.; Robin, J-J. Lipidic polyols using thiol-ene/yne strategy for crosslinked polyurethanes. *J. Polym. Chem. Part A Polym. Chem.*, **2014**, *52*, 1597-1606.
- ⁴⁰ Hoogenboom, R. Thiol-yne chemistry: A powerful tool for creating highly functional materials. *Angew. Chem. Int. Ed.*, **2010**, *49*, 3415-3417.
- ⁴¹ Fairbanks, B. D.; Sims, E. A. Anseth K. S.; Bowman, C. N. Reaction Rates and mechanisms for radical, photoinitiated addition of thiols to alkynes, and implications for thiol-yne photopolymerizations and click reactions. *Macromolecules*, **2010**, *43*, 4113-4119.
- ⁴² Javni, I.; Petrović, Z. S.; Guo, A.; Fuller R. Thermal stability of polyurethanes based on vegetable oils. *J. Appl. Polym. Sci.*, **2000**, *77*, 1723-1734.

-
- ⁴³ Ristic, I. Bjelovic, Z. D.; Holló, B.; Szécsenyi, K. M.; Budinski-Simendic, J.; Lazic, M.; Kicanovic, M. Thermal stability of polyurethane materials based on castor oil as polyol component. *J. Therm. Anal. Calorim.*, **2013**, *111*, 1083-1091.
- ⁴⁴ Calle, M.; Lligadas, G.; Ronda, J. C.; Galià, M.; Cádiz, V. Non-isocyanate route to biobased polyurethanes and polyureas via AB-type self-polycondensation. *Eur. Polym. J.*, **2016**, <http://dx.doi.org/10.1016/j.eurpolymj.2016.04.022>.