Polyurethanes from Polyols Obtained by ADMET Polymerization of a Castor Oil-Based Diene: Characterization and Shape Memory Properties

E. DEL RIO,[1] G. LLIGADAS,[1] J. C. RONDA,[1] M. GALIA ,[1] M. A. R. MEIER,[2] V. CADIZ[1]

[1] Departament de Quımica Analıtica i Quımica Organica, Universitat Rovira i Virgili, Campus Sescelades, Marcel.lı´ Domingo s/n, Tarragona 43007, Spain

[2] Karlsruhe Institute of Technology, Institute of Organic Chemistry, Fritz-Haber-Weg 6, Karlsruhe, Germany

ABSTRACT: The acyclic diene metathesis polymerization (ADMET) of 1,3-di-10-undecenoxy-2-propanol, a castor oil based diene, is reported. 10-Undecenol was used as renewable comonomer to end-cap polymer chains and limit the molecular weight. The polyols obtained in this way were reacted with 4,4'-methylenebis(phenylisocyanate) (MDI) to yield a series of amorphous and semicrystalline polyurethane networks. The thermal stability and the thermomechanical and mechanical properties of these thermosets have been studied and showed good shape memory properties for the semicrystalline polymer.

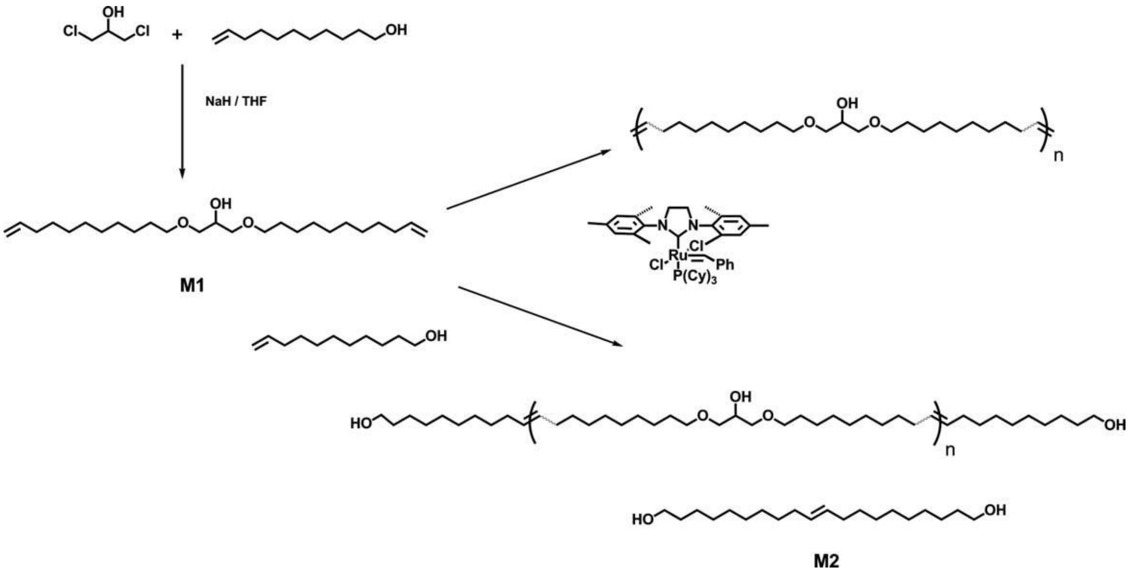
KEYWORDS: ADMET; metathesis; polyols; polyurethanes; renewable resources; shape memory

INTRODUCTION

Recently, the use of plant oils as renewable feedstock for the development of designed polymeric materials has received particular attention due to environmental concerns.[1] The main components of vegetable oils are triglycerides, which are the product of esterification between a molecule of glycerol and three fatty acids. The chemical modification of their structure enables the synthesis of a wide variety of derivatives which can be used in different fields such as surfactants, cosmetics, and lubricants.[2] Moreover, together with the well known applications in polymer science, new routes are being developed that enable access to value added polymer building blocks and controlled polymer architectures.[3] The increasing importance of polymeric materials from renewable resources has put polyols and polyurethanes derived from plant oils in the spotlight, especially due to their simple preparation yet greatly promising application.[4,5] To extend the application possibilities of vegetable oils, we focused on converting these renewable resources into useful bioderived polymers. We described the synthesis of polyether polyols through the combination of cationic ring opening[6] or ionic-coordinative[7] polymerization of epoxidized methyl oleate (EMO) and the reduction of carboxylate groups to hydroxyl moieties. These polyols were reacted with 4,4^{0}methylenebis(phenylisocyanate) (MDI) to obtain thermosetting polyurethanes,[8] with L-lysine diisocyanate (LDI) and 1,3-propandiol to obtain biodegradable segmented polyurethanes[9] or with a biobased silicon-containing polyol to obtain silicon-containing polyurethanes with enhanced flame retardant properties.[10]

Olefin metathesis takes advantage of the synthetic potential of oleochemicals by using the inherent double bond functionality of fatty acids. Acyclic diene metathesis (ADMET) polymerization of α,ω-dienes has been shown to be an efficient tool for the synthesis of a wide variety of linear polymers and polymer architectures that are not available using other polymerization methods.[11] Essentially, ADMET is a step growth polycondensation in which two terminal olefins react to form new internal carbon–carbon double bonds and ethylene, thus affording strictly linear unsaturated polymers. It has been demonstrated that ADMET polymerization can proceed in the presence of heteroatoms, as long as the terminal olefins are far enough apart from them.[12] There are many examples of ADMET of heteroatom-containing a,x-dienes in the literature, since the introduction of CAC double bonds in the backbone of the polymers provides different properties and permits further modifications.[13] When chain stoppers are used during the polymerization, it is possible to control the molecular weight of the final polymers.[3]

Castor oil is one of the most exploited vegetable oil as raw material for the chemical industry. From castor oil processing, like from other applications of vegetable oils as in biodiesel, glycerol is obtained as byproduct, being a platform chemical with widespread application possibilities.[14] Sebacic acid and 10-undecenoic acid are produced from castor oil via caustic fusion and pyrolisis, respectively.[15,16] Derivatives with a terminal double bond such as undecenoic acid, methyl undecenoate, undecenol, allyl undecenoate, or undecylenyl undecenoate are well suited renewable raw materials for olefin metathesis reactions and other chemical transformations.[17,18] In previous studies, we synthesized a series of phosphorus-containing linear polyesters through the ADMET copolymerization of a phosphorus-based α,ω-diene with different amounts of a castor oil derived diene.[19,20]



SCHEME 1 Synthesis of monomer M1 and ADMET polymerization.

Moreover, castor oil's unique structure, where most of the fatty acid chains bear a hydroxyl group, makes it especially attractive and a wide variety of polyurethanes have been prepared by taking advantage of the hydroxyl groups.[21] Numerous polyurethanes have been found to posses shape memory effects.[22] Generally, shape memory polymers (SMP) are stimuli-responsive materials that have the ability to store a secondary shape after deformation and restore to the originally primary shape when an external trigger is applied.[23,24] The most extensively investigated group of SMPs are thermally induced, which are triggered by heat: the shape memory is induced when a certain switching temperature is exceeded. The features of a polymer that allow for good shape memory behavior include a sharp transition that can be used to promptly fix the secondary shape and trigger shape recovery and high deformability above the transition temperature that leads the shape recovery.

The present work describes the synthesis of several polyols using ADMET chemistry. These polyols are based on a castor oil-based diene, 1,3-di-10-undecenoxy-2-propanol (M1, Scheme 1) and 10-undecenol to end-cap the polymer chains and limit the molecular weight during the ADMET polymerization. The polyols obtained in this way were reacted with MDI to yield a series of polyurethane networks that were characterized by infrared spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and thermodynamic mechanical analysis (DMA). In this study, we also investigated the shape memory properties of these materials.

EXPERIMENTAL

Materials

10-Undecenol, 1,3-dichloro-2-propanol, sodium hydride, ethyl vinyl ether (EVA), benzylidene[1,3-bis(2,4,6-trimethylphenyl)2-imidazolidinylidene]-dichloro (tricyclohexylphosphine)ruthenium (Grubbs catalyst second generation), [1,3-bis(2,4,6trimethylphenyl)-2-imidazolidinylidene]-dichloro(o-isopropoxyphenylmethylene)ruthenium (Hoveyda-Grubbs catalyst second generation), [1,3-Bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(phenylmethylene)bis(3-bromopyridine)ruthenium (II) (Grubbs third generation), 1,3-Bis(2,4,6-trimethylphenyl)4,5-dihydroimidazol-2-ylidene[2-(i-propoxy)-5-(N,N-dimethylaminosulfonyl)phenyl]methyleneruthenium(II) dichloride (Zhan Catalyst), 4,4′-methylenebis(phenylisocyanate) (MDI) were supplied by Aldrich. Anhydrous hexane and tetrahydrofuran (THF) were prepared by refluxing with sodium before used.

Synthesis of 1,3-Di-10-undecenoxy-2-propanol (M1)

12 g of a 60% dispersion of NaH in mineral oil (0.30 mmol) were introduced in a 250 mL two-neck round-bottom flask under argon atmosphere and equipped with magnetic stirring. The NaH was washed with anhydrous hexane twice. Then, 60 mL of anhydrous THF was added and under vigorous stirring, 65 mL of 10-undecenol (0.32 mmol) were slowly added at 25 ^{o}C. When the addition was finished, the temperature was increased to reflux for 2 h and then, 11.3 mL of 1,3-dichloro-2-propanol (0.12 mmol) were added dropwise. The reaction was maintained at reflux for 15 h under argon atmosphere and magnetic stirring. Finally, the reaction was allowed to reach room temperature and 10 mL of water were added, and the reaction mixture was transferred into a diethyl ether/water mixture, the organic layer was separated and the aqueous one extracted with diethyl ether. The organic phases were combined and washed with HCl 5%, $NaHCO_3$ saturated solution and brine. The organic phase was dried with anhydrous $MgSO_4$ powder filtered and the solvent evaporated under reduced pressure. The product obtained was purified by crystallization in hexane at 20 ^{o}C (hexane/product = 1/1). The final yield was 65% as a light yellow liquid.

^{1}H NMR ($CDCl_3$, TMS, δ in ppm): 5.84–5.75 (m, CH_2 =CH), 4.96 (d, CH_2 =CH, J_{trans} = 26.2 Hz), 4.93 (d, CH_2 =CH, J_{cis} = 20.0 Hz), 4.0–3.9 (m, CH-OH), 3.55–3.35 (m, CH_2-O), 2.49 (s, -OH), 2.03 (m, CH_2-CH=), 1.65–1.50 (m, CH_2-CH_2O), 1.45–1.10 (m, aliphatic backbone).

^{13}C NMR ($CDCl_3$, TMS, δ in ppm): 139.3 (CH_2 =CH), 114.3 (CH_2 =CH), 72.0 (CH_2-O), 71.8 (CH_2-O), 69.6 (CH-OH), 34.0 (CH_2-CH=), 29.9–29.0 (aliphatic backbone), 26.3 (CH_2ACH_2AO).

ADMET Polymerization (Catalysts Test)

0.50 g (1.26 mmol) of 1,3-di-10-undecenoxy-2-propanol and 1% of catalyst were introduced in a 3-mL conic vial. The reaction was equipped with magnetic stirring, screw cap with septum and needle to allow relaxing of the ethene evolved. The reaction was homogenized at room temperature for 10 min and then heated at 80 °C with stirring for 5 h. The reaction was stopped by adding ethylvinylether (EVE) in a EVE:catalyst ratio of 50:1.

^{1}H NMR ($CDCl_3$, TMS, δ in ppm): 5.5–5.25 (m, CH=CH), 4.0–3.85 (m, CH-OH), 3.55–3.35 (m, CH_2-O), 2.6–2.4 (m, OH), 2.1–1.9 (m, CH_2-CH=), 1.65–1.5 (m, CH_2-CH_2O), 1.4–1.2 (m, aliphatic backbone), 1.0–0.8 (m, CH_3).

Self Metathesis of 10-Undecenol

The same conditions as above were used starting from 0.50 g (2.94 mmol) of 10-undecenol, and 0.5% of catalyst were introduced in a 3-mL conic vial.

^{1}H NMR ($CDCl_3$, TMS, δ in ppm): 5.5–5.25 (m, CH=CH), 3.65 (t, CH_2OH, J = 6.6 Hz), 2.1–1.9 (m, CH_2-CH=), 1.7–1.5 (m, CH_2-CH_2O), 1.4–1.2 (m, aliphatic backbone), 1.0–0.8 (m, CH_3).

Synthesis of the Polyols

1,3-di-10-undecenoxy-2-propanol (M1) and 10-undecenol were mixed (2 g scale) in the desired molar ratio (Table 2) in a 3-mL conic vial. Then, 0.1% of catalyst per mol of double bond was added, and the reaction was equipped with magnetic stirring, screw cap with septum and needle to allow relaxing of the ethene evolved. The reaction was homogenized at room temperature for 10 min and then heated at 80 °C with stirring for 5 h. The reaction was stopped by adding EVE in a EVE:catalyst ratio of 50:1.

1H NMR (CDCl3, TMS, δ in ppm): 5.5–5.25 (m, CH¼CH), 4.0–3.85 (m, CHOH), 3.63 (t, CH2OH, J ¼ 6.6 Hz), 3.55–3.35 (m, CH2-O), 2.6–2.4 (m, OH), 2.1–1.9 (m, CH_2-CH=), 1.65–1.5 (m, CH_2-CH_2O), 1.4–1.2 (m, aliphatic backbone), 1.0–0.8 (m, CH3 Iso).

Determination of the mmol of Hydroxyl Groups per Gram of Polyol

The milimols of hydroxy groups per gram of polymer were determined by ^{1}H-NMR using 2-phenylethanol as internal standard. Primary hydroxyl content was determined from signal centered at 3.63 ppm, while secondary one was calculated from signal centered at 3.92 ppm. The following equation was used:

mmol of OH per gram of P-OH = (mmol IS x Int P-OH/Int IS)/g P-OH

where P-OH is the Polyol, IS is the internal standard, mmol IS is the quantity of internal standard added to the sample in millimoles and g P-OH is the quantity of sample measured in grams.

Synthesis of the Polyurethanes

Polyol was dissolved in anhydrous toluene (50% solution) under argon atmosphere, heated at 50 °C and added to a 50% dispersion of MDI in toluene. The solution was homogenized and casted over silanized glass preheated at 90 °C. The polyurethane was maintained at 90 °C 2 h and at 130 °C for 3 h.

Instrumentation

^{1}H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded in $CDCl_3$ using a Varian Gemini 400 spectrometer. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) and $CHCl_3$ as internal standards. Calorimetric studies were carried out on a Mettler DSC822e thermal analyzer using N_2 as a purge gas (100 mL/min) at a scan rate of 20 °C/min. Thermal stability studies were carried out on

---

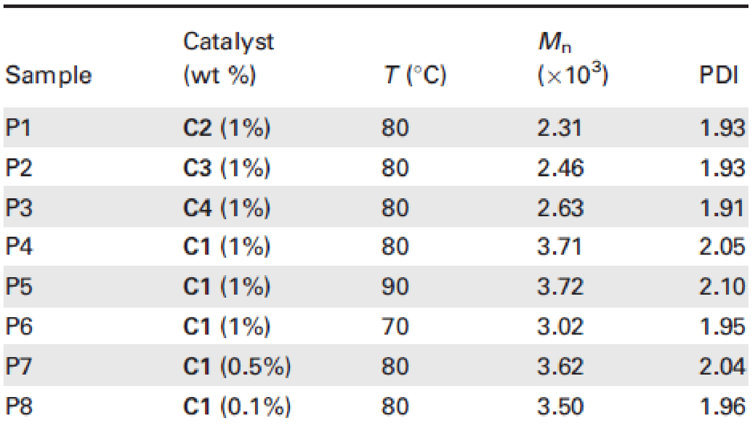
a Mettler TGA/SDTA851e/LF/1100 with N_2 or synthetic air as purge gases. The studies were performed in the 30– 800 °C temperature range at a heating rate of 10 °C/min.

The IR 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) accessory with thermal control and a diamond crystal (Golden Gate heated single-reflection diamond ATR, SpecacTeknokroma) was used to determine FTIR spectra.

Size exclusion chromatography (SEC) analysis was carried out with an Agilent 1200 series system with PLgel 3-µm MIXED-E, PLgel 5-µm MIXED-D, and PLgel 20-µm MIXED-A columns in series, and equipped with an Agilent 1100 series refractive-index detector. Calibration curves were based in polystyrene standards having low polydispersities. THF was used as an eluent at a flow rate of 1.0 mL/min, the sample concentrations were 5–10 mg/mL, and injection volumes of 100 µL were used.

Dynamic mechanical thermal analysis (DMTA) and tensile tests properties were measured with a TA DMA 2928 dynamic mechanical thermal analyzer. Specimens 0.6 mm thick, 3 mm wide, and 8 mm long were tested in a tension film configuration. For DMTA the temperature range was from 100 to 150 °C, at a heating rate of 3 °C/min and at a fixed frequency of 1 Hz. The tensile assays were performed by triplicate measuring the strain while applying a stress ramp of 1 N/min at 25 °C.

TABLE 1 ADMET Polymerization of **M1** in Bulk for 5 h



Sample	Catalyst (wt %)	T (°C)	M_n ($\times 10^3$)	PDI
P1	C2 (1%)	80	2.31	1.93
P2	C3 (1%)	80	2.46	1.93
P3	C4 (1%)	80	2.63	1.91
P4	C1 (1%)	80	3.71	2.05
P5	C1 (1%)	90	3.72	2.10
P6	C1 (1%)	70	3.02	1.95
P7	C1 (0.5%)	80	3.62	2.04
P8	C1 (0.1%)	80	3.50	1.96

Shape-memory properties of the polyurethanes were studied in the force-controlled setup. The sample was equilibrated at 70 °C and to achieve the suitable strain, a force ramp of 0.5 N/min was applied to a previously measured stress (by a stress-strain experiment at 70 °C). Maintaining the stress applied, the sample was cooled down to 25 °C at 10 °C/min and equilibrated at this temperature for 10 min more. Then, the stress was released and the temperature maintained at 25 °C for 5 min. Finally, the temperature was increased at 5 °C/min to 70 °C. Three consecutive cycles were applied to each sample. Strain fixity and strain recovery ratios were measured for the three cycles.

RESULTS AND DISCUSSION

1,3-Di-10-undecenoxy-2-propanol (M1) was synthesized by reaction of 1,3-dichloro-2-propanol with two equivalents of sodium 10-undecenolate, prepared by reacting 10-undecenol and sodium hydride (Scheme 1).[25] It must be pointed out that 1,3-dichloro-2-propanol can be obtained directly from glycerol[14] and 10-undecenol can obtained from castor oil, thus, both reagents are potentially plant oil derived, thus M1 can be considered as 100% renewable. The compound was obtained as a yellow liquid in 65% yield. Its ^1H NMR spectrum showed the expected signals at 5.8 and 4.9 ppm (CH_2 =CH), at 4.0 ppm (CHAO), at 3.4 ppm (CH_2-O), and at 2.5 ppm (OH).

The polymerization of M1 was investigated with several metathesis catalysts to obtain aliphatic polyether-polyols with internal C¼C double bonds (Table 1). Polymerizations were carried out in bulk under a continuous flow of nitrogen to remove the ethylene released during the metathesis reaction. SEC analysis confirmed that M1 conversion was quantitative in all cases, as were the yields of the polymers after precipitation. Alcohol containing dienes have been polymerized via ADMET before using Grubbs 1st generation catalyst, [26] but our previous studies showed that oligomerization and poor conversion occurs probably due to catalyst degradation in presence of hydroxyl groups.[20] Second (C1) and third-generation (C2) Grubbs catalysts, the Hoveyda-Grubbs second generation catalyst (C3), and Zhan catalyst (C4) were also tested in the present work at 1% catalyst loading at 80 °C (Table 1). The molecular weights of the ADMET polyethers were measured by SEC using PS standards. As can be seen the highest M_n was obtained using C1. When using this catalyst, no increase in M_n could be observed by increasing the reaction temperature, while lower M_n was obtained when conducting the reaction at 70 °C. Decreasing the catalyst loading led to a small decrease of M_n. On the basis of these results, polymerizations were carried out using a low catalyst loading of 0.1% of C1 at 80 ºC. The reactions could be monitored by the disappearance of the terminal olefin signals at 5.8 and 4.9 ppm together with the appearance of a multiplet at 5.4 ppm in the ^{1}H NMR spectrum (Fig. 1). Moreover, new signals at 0.9 and 1.7 ppm were observed. Second generation ruthenium metathesis catalysts are known to promote olefin isomerization side reactions that in the case of ADMET polymerizations lead to polymers with irregular repeating units and ill-defined end-groups.[27] The signals observed at 0.9 and 1.7 ppm can thus be attributed to CH_3 end groups formed by isomerization of terminal double bonds.

We synthesized a series of polymers by performing ADMET polymerization with 10-undecenol as a monofunctional chain stopper. In this way, telechelic polymers of different molecular weight are obtained, containing mainly primary alcohols as end groups (Scheme 1). First, the metathesis of 10-undecenol was investigated using the established reactions conditions. Using 0.1% of C1 at 80 ºC, a 70% of conversion was obtained. Isomerization of the double bond was detected in an amount of 27%, leading to internal olefins. Due to the higher reactivity of terminal olefins, if compared to the internal double bonds, the isomerized products remained unaltered in the reaction conditions employed.

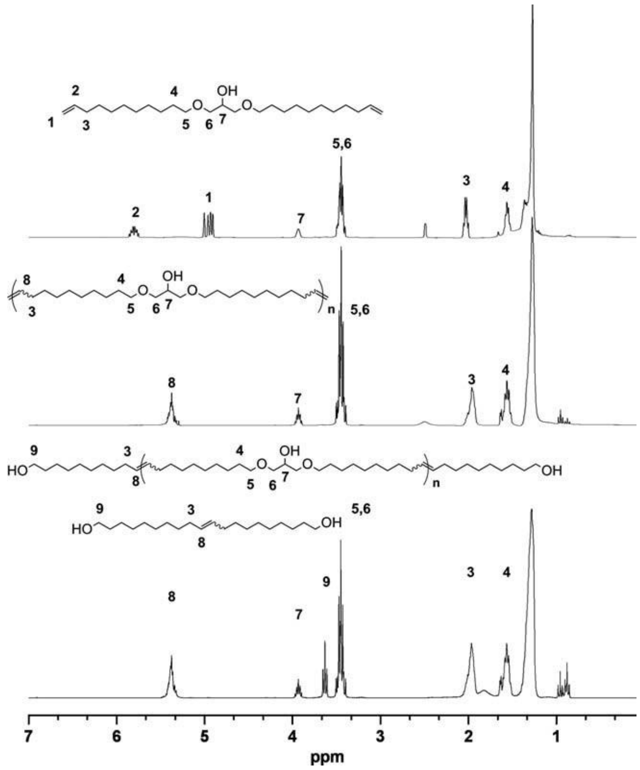


FIGURE 1 ^{1}H NMR spectra of M1, POH0, and POH2 (CDCl3, TMS, 400 MHz).

In the synthesis of polyols, the amount of chain stopper was varied to increase M1/chain stopper ratio from 1:0.1 to 1:5 (Table 2). As expected, isomerization of terminal double bonds took place and thus the reaction mixture was vacuum distilled at 70 ºC to remove the low molecular weight by-products. The distillation residue was analyzed by SEC, and the percentage of self-metathesis of chain stopper was found to increase as the amount of 10-undecenol does, as expected. Moreover, the molecular weights decrease as the amount of chain stopper increases as reported previously.[19,28] The total hydroxyl content as well as the percentage of primary and secondary alcohols were determined by ^{1}H NMR spectroscopy. The total hydroxyl content and the percentage of CH_2-OH increase while the percentage of CH-OH decreases when the amount of chain stopper increases. DSC traces for the polyols are collected in Figure 2. As can be seen, POH0 exhibits multiple melting endotherms centered at 3, 20, and 40 ºC that should be ascribed to different oligomers. When the amount of chain stopper increases, the number of lower temperature peaks increases and the enthalpy of the peak at higher temperature decreases, according to the existence of a lower molecular weight species.

The ADMET of M1 in the presence of 10-undecenol is a pathway to mixtures of polyether polyols of different molecular weights that include different amounts of the self-metathesis product M2 (Scheme 1). Novel biobased polyurethanes were prepared by reacting these mixtures with MDI. The polyurethanes were synthesized by dissolving the reactants under argon atmosphere in anhydrous toluene, mixing at 50 ºC and casting the mixture over a silanized glass plate preheated to 90 ºC. The polyurethanes were then cured at 90 ºC for 2 h and post-cured at 130 °C for 3 h. FTIR analysis demonstrated the urethane formation reaction during polymer synthesis by the disappearance of the band at 2240 cm^{-1} ascribed to the -N=C=O stretching of the isocyanate moiety and the appearance of the characteristic absorbances of the urethane link at 1730 cm^{-1}. Moreover, the broad band centered at 3500 cm^{-1}, corresponding to the OAH stretching, shifts to lower frequencies and shows a maximum at 3315 cm^{-1}, characteristic of the N-H stretching of urethanes.

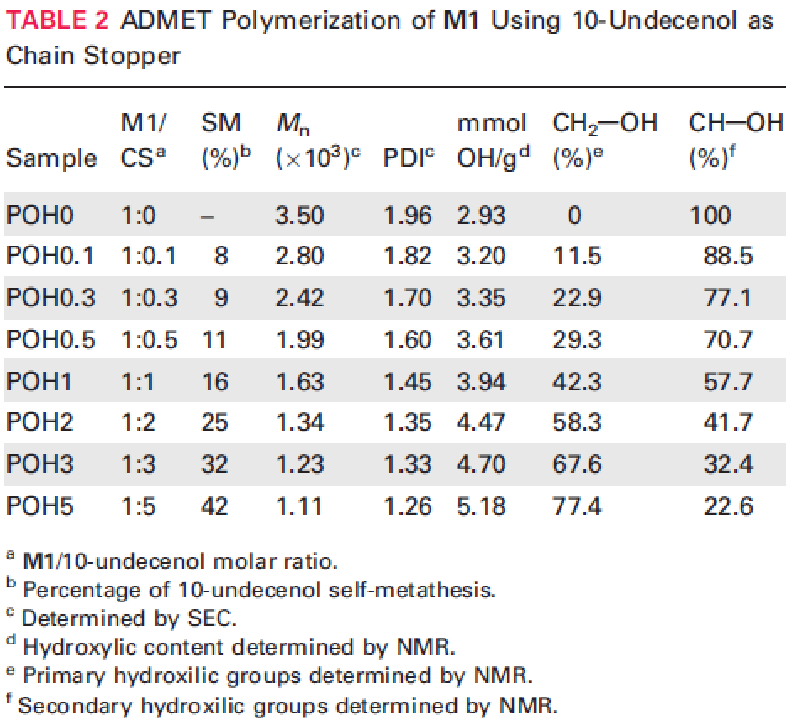


TABLE 2 ADMET Polymerization of **M1** Using 10-Undecenol as Chain Stopper

Sample	M1/ CS[a]	SM (%)[b]	M_n ($\times 10^3$)[c]	PDI[c]	mmol OH/g[d]	CH_2—OH (%)[e]	CH—OH (%)[f]
POH0	1:0	–	3.50	1.96	2.93	0	100
POH0.1	1:0.1	8	2.80	1.82	3.20	11.5	88.5
POH0.3	1:0.3	9	2.42	1.70	3.35	22.9	77.1
POH0.5	1:0.5	11	1.99	1.60	3.61	29.3	70.7
POH1	1:1	16	1.63	1.45	3.94	42.3	57.7
POH2	1:2	25	1.34	1.35	4.47	58.3	41.7
POH3	1:3	32	1.23	1.33	4.70	67.6	32.4
POH5	1:5	42	1.11	1.26	5.18	77.4	22.6

[a] **M1**/10-undecenol molar ratio.

[b] Percentage of 10-undecenol self-metathesis.

[c] Determined by SEC.

[d] Hydroxylic content determined by NMR.

[e] Primary hydroxilic groups determined by NMR.

[f] Secondary hydroxilic groups determined by NMR.

The thermal behavior of polyurethanes was investigated by DSC (Fig. 3). The glass transition temperature of the polyurethane PU0 measured by DSC is 8 °C. The most notable result of increasing the M2 content in the mixture and decreasing the molecular weight of the polyols is an upward shift in the T_g and the appearance of a melting endotherm for PU5. The lower molecular weight of the polyols and the increasing of crosslinking would cause a restriction of segmental mobility, therefore, an increasing of T_g values. Since the starting material in the preparation of the polyurethanes is a mixture of polyether polyol and diol, with primary and secondary hydroxyl groups, the relative reactivity of functional groups is not equal. As a result, structurally inhomogeneous systems containing various domains with different sizes are obtained, which consist of alternate polyol or diol isocyanate sequences. Part of the domain is chemically crosslinked, with covalent bonds between polyol and isocyanate and part results from the physical crosslinking of the linear diol-isocyanate segments through hydrogen bonding. The chemical crosslinks would reduce the mobility of molecular chains and restrict the effective packing into crystals. When increasing amounts of a shorter diol are employed, the effective packing of polymer chains into crystals seems to be promoted and a semicrystalline material is obtained for PU5. When this sample was run a second time after melting, no melting peaks were observed, probably as a result of the miscibility of polyol and M2 fragments above the melting point. To check this, PU5 was annealed at 40 °C for several hours and left to cool slowly to room temperature to promote phase separation and crystallization. In the DSC thermograms after annealing a small endotherm appears, that shifted to a higher temperature and increased in enthalphy as the annealing time increased.

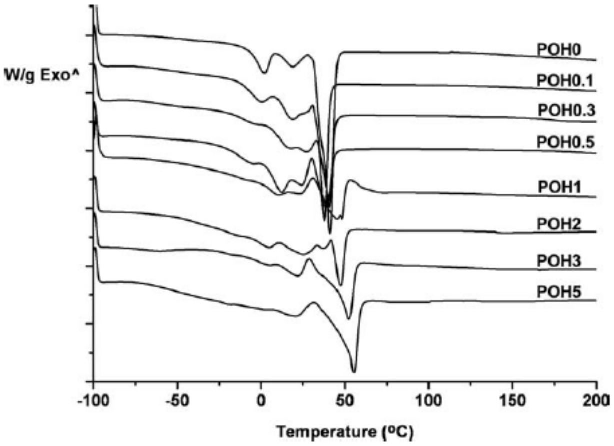


FIGURE 2 DSC thermograms (20 °C/min) of the polyols.

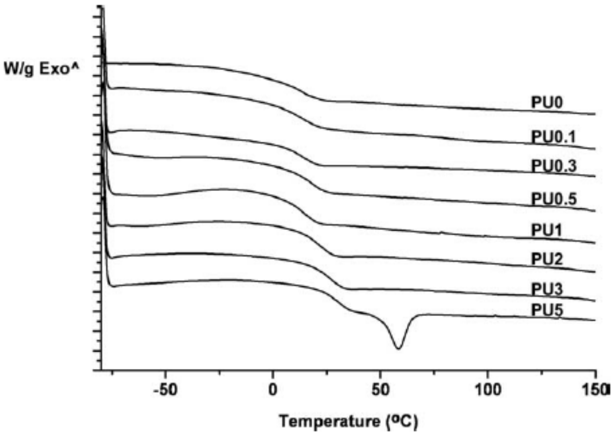


FIGURE 3 DSC thermograms (20 °C/min) of the polyurethanes.

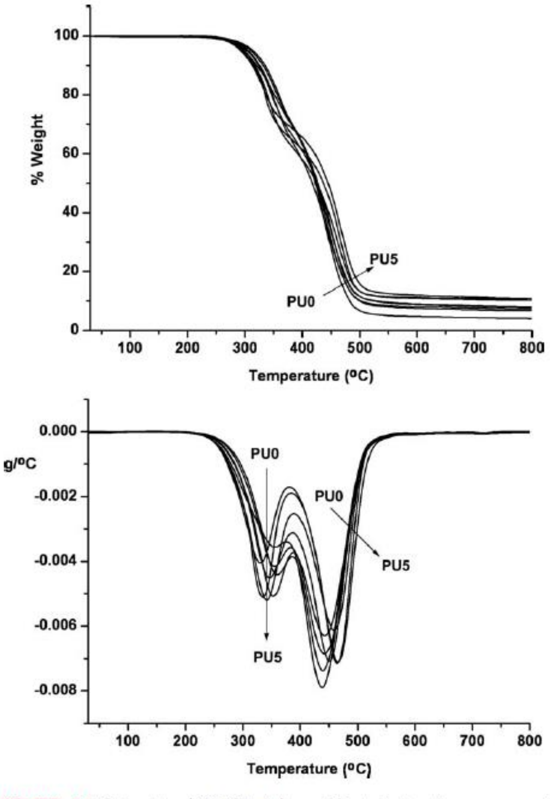


FIGURE 4 TGA plots (10 °C/min) and first derivative curves of polyurethanes.

The thermal stability of polyurethanes was studied by TGA in a nitrogen atmosphere and the obtained data are shown in Figure 4 and Table 3. The shapes of the weight-loss curves of all the polyurethanes are almost identical and the differences in the thermal stability appear to be small. The decomposition of the polyurethanes in a nitrogen atmosphere does not take place below 290 ºC. The derivative curves reveal that more than one process occurs during thermal degradation: a first drop below 400 ºC is followed by the main loss weight above 400 ºC. The first weight loss is related to the decomposition of urethane bonds, which takes place through the cleavage to isocyanate and alcohol, the formation of primary amines and olefins or the formation of secondary amines.[29] The main decomposition process is attributed to the polyether polyol chain scission, and occurs at about 450 °C. The weight loss in the first step increases as the hydroxyl content of the polyol increases, which is in accordance to the existence of a higher amount of weaker urethane bonds.

TABLE 3 Thermal Properties of Polyurethanes

	T_g (°C)		TGA (N_2)				Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
Polyurethane	1/2 ΔC_p	tan δ_{max}	$T_{5\%}$ (°C)	$T_{max\ 1}$ (°C)	$T_{max\ 2}$ (°C)	$Yield_{800\ °C}$ (%)			
PU0	8	36	298	356	438	4	7.3	6.5	96
PU0.1	12	39	314	360	439	7	9.7	7.0	120
PU0.3	13	39	310	355	442	8	6.5	4.5	100
PU0.5	9	41	306	353	443	7	8.8	7.6	140
PU1	10	37	303	347	451	8	4.7	9.3	171
PU2	23	46	299	341	459	11	11.4	8.0	120
PU3	25	51	295	335	464	10	25.0	11.8	120
PU5	28	54	293	331	466	11	90.0	19.0	121

The dynamomechanical behavior of these polyurethanes was investigated by DMTA. Figure 5 shows the elastic modulus and the dissipation factor as a function of the temperature. Like crosslinked polymeric networks, at low temperatures there is a glass state with E′ at a high modulus plateau and at higher temperatures there is a rubbery state with a lower E′. The storage moduli at the rubbery plateau decrease when the low molecular weight diol M2 content increase according to a lower crosslinking density. As can be seen, all the polymers behave like homogeneous networks.

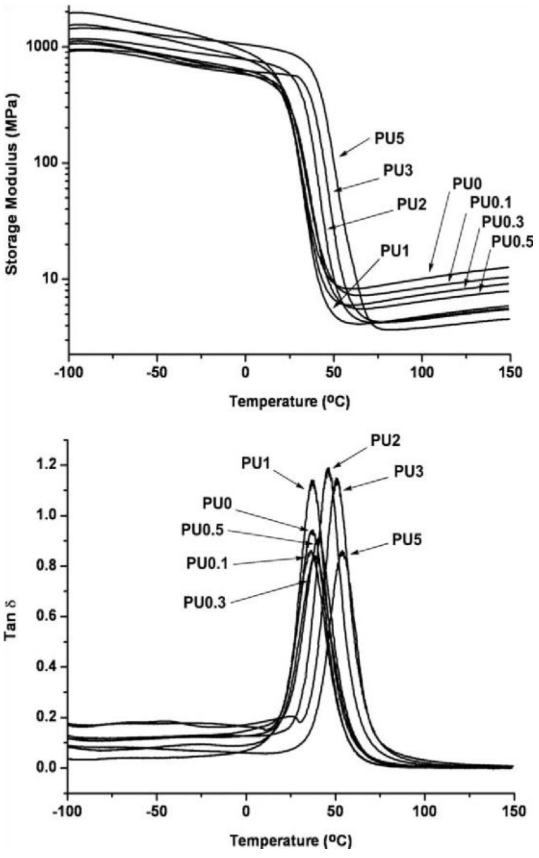


FIGURE 5 Storage moduli and loss factor of polyurethanes.

A unique broad transition is observed for semicrystalline PU5, which according to DSC results must correspond to the glass transition and the melting of the crystalline phase.

The glass transition temperature determined from the peak of tan d is higher than the one determined by DSC (Table 3), which can be related to the heat transporting hysteresis for large scale samples in DMTA. Consistent with DSC results, this peak shows a shift of maxima when increasing the M2 content in the mixture and decreasing the molecular weight of the polyols. The height of the tan d peak increases as the content of M2 increases, according to the lower crosslinking density that causes lower limitations on freedom of chain mobility. However, the peak value of tan d for PU5 is lower even though its M2 content is higher. This can be explained by the presence of microcrystalline domains in the polymer, as has been observed by DSC, which restricts the chain mobility.

Figure 6 shows the stress-strain curves of the polyurethanes, and Table 3 summarizes the values of the mechanical properties of all the obtained polyurethanes. Young's Modulus and tensile strength at break increase while strain at break decreases when increasing the M2 content in the mixture and decreasing the molecular weight of the polyols.

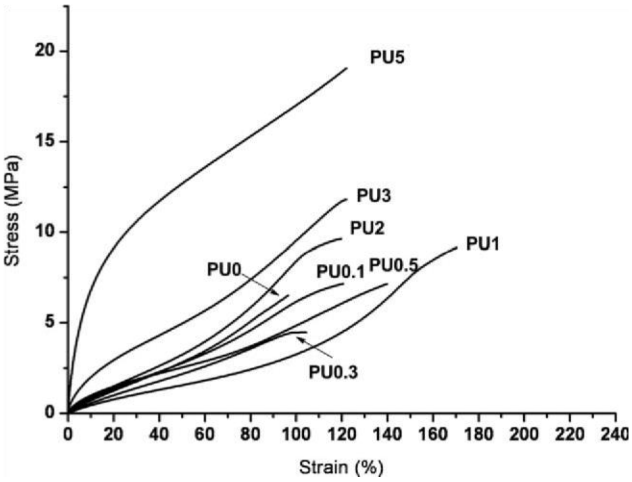


FIGURE 6 Stress-strain plots of the polyurethanes.

What is most notable is the enhanced modulus and tensile strength at break of PU5 as expected from its semicrystalline nature. The shape memory properties have been evaluated with cyclic tensile tests (Fig. 7). In such tests, samples were heated above the switching temperature and stretched to the desired temporary shape. In the next step, the materials are cooled down to 25 °C to fix the temporary shape, and shape recovery is triggered by heating the sample above the transition temperature. The tensile test was performed consecutively for two more times on the same sample.

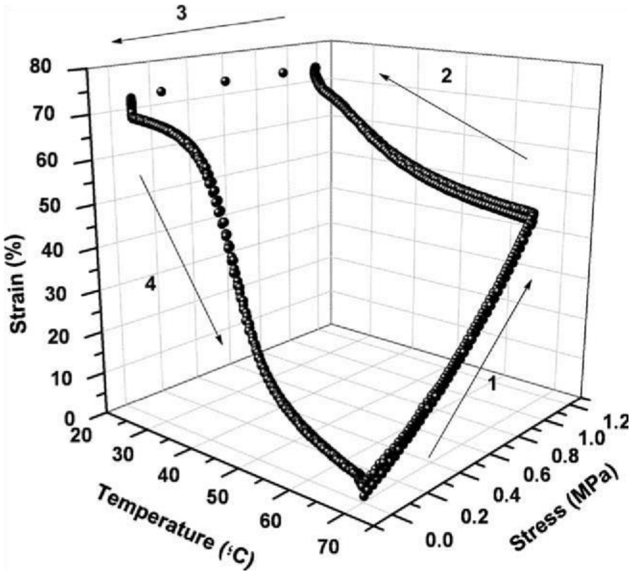


FIGURE 7 Stress-temperature-strain plot showing the shape memory cycle of PU5.

Samples PU0 to PU3 showed no capability to fix strain, that is, the strain diminished to zero as the stress was released. In contrast, semicrystalline PU5 showed a sharp recovery only after heat was applied. Below the switching temperature the sample keeps its shape because of the crystallinity of the switching segments and after reaching the melting temperature the material restores under entropic force.

Two main parameters define the quality of the shape memory material: the strain recovery rate R_r and strain fixity rate R_f.

$$\mathbf{R_r = (L_u\text{-}L_f)/(L_t\text{-}L_i) \times 100}$$

$$\mathbf{R_f = (L_u\text{-}L_i)/(L_t\text{-}L_i) \times 100}$$

where L_i is the initial length, L_t is the temporary length, L_u is the unloaded length, and L_f is the final recovered length. R_r indicates the quality of the restoration of the primary shape after reheating, and R_f expresses how well the material can maintain the total strain of the secondary shape after releasing the force on the sample. Strain fixity and recovery in the first experiment are high (R_f = 94% and R_r = 88%) and subsequent two cycles are superimposable with both parameters remaining high (R_f = 93% an R_r = 93%), thus showing remarkably shape memory properties.

CONCLUSIONS

A castor oil based α,ω-diene containing hydroxyl groups (M1) has been successfully polymerized via ADMET polymerization using the second generation Grubbs catalyst. The molecular weight of the polyols has been reduced using 10undecenol as renewable chain stopper, and mixtures of varying amounts of polyether polyols and diol M2 have been obtained. Novel biobased polyurethanes were prepared by reacting these hydroxyl containing mixtures with MDI. The most notable result of decreasing the molecular weight of the polyols and increasing the M2 content in the mixture is an upward shift in the T_g and the switch to a semicrystalline material for the highest M2 content (PU5). The shape memory properties of polyurethanes have been evaluated with cyclic tensile test and PU5 showed outstanding values of strain fixity and recovery.

The authors thank MICINN (Ministerio de Ciencia e Innovacion, MAT2008-01412) for the financial support for this work.

REFERENCES AND NOTES

1 Belgacem, M. N.; Gandini, A. Monomers, Polymers and Composites from Renewable Resources; Elsevier: Oxford, 2008.

2 Meier, M. A. R.; Metzger, J. O.; Schubert, U. S. Chem Soc Rev 2007, 36, 1788–1802.

3 Meier, M. A. R. Macromol Chem Phys 2009, 210, 1073–1079.

4 Petrovic, Z. S. Polym Rev 2008, 48, 109–155.

5 Lligadas, G.; Ronda, J. C.; Galia, M.; Cadiz, V. Biomacromolecules 2010, 11, 2825–2835.

6 Lligadas, G.; Ronda, J. C.; Galia, M.; Biermann, U.; Metzger, J. O. J Polym Sci Part A: Polym Chem 2006, 44, 634–645.

7 Del Rio, E.; Galia, M.; Cadiz, V.; Lligadas, G.; Ronda, J. C. J Polym Sci Part A: Polym Chem 2010, 48, 4995–5008.

8 Del Rio, E.; Lligadas, G.; Ronda, J. C.; Galia, M.; Cadiz, V. J Polym Sci Part A: Polym Chem 2010, 48, 5009–5017.
9 Lligadas, G.; Ronda, J. C.; Galia, M.; Cadiz, V. Biomacromolecules 2007, 8, 686–692.

10 Lligadas, G.; Ronda, J. C.; Galia, M.; Cadiz, V. Biomacromolecules 2006, 7, 2420–2426.

11 Baughman, T. W.; Wagener, K. B. Adv Polym Sci 2005, 176, 1–42.

12 Wagener, K. B.; Brzezinska, K.; Anderson, J. D.; Younkin, T.; Steppe, K.; de Boer, W. Macromolecules 1997, 30, 7363–7369.

13 Terada, k.; Berda, E. B.; Wagener, K. B.; Sanda, F.; Masuda, T. Macromolecules 2008, 41, 6041–6046.

14 Zhou, C. H.; Beltramini, J. N.; Fan, Y. X.; Lu, G. Q. Chem Soc Rev 2008, 37, 527–549.

15 Ogunniyi, D. S. Bioresour Technol 2006, 97, 1086–1091.

16 Van der steen, M.; Stevens, C. V. ChemSusChem 2009, 2, 692–713.

17 Lligadas, G.; Callau, L.; Ronda, J. C.; Galia, M.; Cadiz, V. J Polym Sci Part A: Polym Chem 2005, 43, 6295–6307.

18 Lluch, C.; Ronda, J. C.; Galia, M.; Lligadas, G.; Cadiz, V. Biomacromolecules 2010, 11, 1646–1653.

19 Montero de Espinosa, L.; Ronda, J. C.; Galia, M.; Cadiz, V.; Meier, M. A. R. J Polym Sci Part A: Polym Chem 2009, 47, 5760–5771.

20 Montero de Espinosa, L.; Meier, M. A. R.; Ronda, J. C.; Galia, M.; Cadiz, V. J Polym Sci Part A: Polym Chem 2010, 48, 1649–1660.

21 Sharma, V.; Kundu, P. P. Prog Polym Sci, 2008, 33, 1199–1215.

22 Mather, P. T.; Luo, X.; Rousseau, I. A. Annu Rev Mater Res 2009, 39, 445–471.

23 Liu, C.; Qin, H.; Mather, P. T. J Mater Chem 2007, 17, 1543–1558.

24 Behl, M.; Razzaq, M. Y.; Lendlein, A. Adv Mater 2010, 22, 3388–3410.

25 Doyle, M. P.; Tedrow, J. S.; Dyatkin, A. B.; Spaans, C. J.; Ene, D. G. J Org Chem 1999, 64, 8907–8915.

26 Valenti, D. J.; Wagener, K. B. Macromolecules 1998, 31, 2764–2773.

27 Fokou, P.; Meier, M. A. R. J Am Chem Soc 2009, 131, 1664–1665.

28 Ryback, A.; Meier, M. A. R. ChemSusChem 2008, 1, 542–547.

29 Levchik, S. V.; Weil, E. D. Polym Int 2004, 53, 1585–1610.