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Use of hydroxytelechelic *cis*-1,4-polyisoprene (HTPI) in the synthesis of polyurethanes (PUs). Part 1. Influence of molecular weight and chemical modification of HTPI on the mechanical and thermal properties of PUs

Nasreddine Kébir[a], Irène Campistron[a], Albert Laguerre[a], Jean-François Pilard[a,*], Claude Bunel[b,**], Jean-Pierre Couvercelle[b], Christian Gondard[c]

[a]*L.C.O.M. Chimie des polymères (UCO2M, UMR CNRS 6011), Université du Maine, Avenue Olivier Messiaen, F-72085 Le Mans Cedex 9, France*
[b]*UMR CNRS 6522, Polymères, Biopolymères, Membranes, Laboratoire de Matériaux Macromoléculaires, Institut National des Sciences Appliquées de Rouen, Place Emile Blondel, BP 08, 76131 Mont-Saint-Aignan Cedex, France*
[c]*ISPA Alençon, Pôle Universitaire de Mont Foulon, 61250 Alençon Damigny, France*

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Abstract

New telechelic *cis*-1,4-polyisoprene oligomers bearing an hydroxyl group at the end of the polyisoprene backbone and possessing controlled molecular weights were used as soft segments in the elaboration of polyurethane elastomers. Besides, the well defined hydroxytelechelic *cis*-1,4-polyisoprene (HTPI) structure obtained through a controlled methodology, was chemically modified leading to hydrogenated and epoxidized oligomers based polyurethanes. The influence of the structural changes of these precursors on the polyurethanes properties have been studied. Thus, mechanical parameters as well as glass transition and mechanical transition temperature measurements indicated an increase in PUs hardness when the length of soft segment decreases and when the degree of epoxidized and hydrogenated isoprenic moieties increases. Moreover, based on thermogravimetric analysis (TGA), a linear relationship was established between the weight loss in the urethane stage degradation and the amount of hard segments in the PUs. Otherwise, the hydrogenated soft segments were found more thermally stable than the epoxidized and the non modified ones. By comparison with similar investigations developed from commercial oligodienes (PBHT R20 LM® and EPOL®), this study mainly showed that the PUs based on hydrogenated hydroxytelechelic *cis*-1,4-polyisoprenes were more thermally stable and softer than the EPOL® based analogues.

Keywords: Polyurethanes; Telechelic polymers; *cis*-1,4-Polyisoprene

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1. Introduction

Since their discovery in the 40's by Bayer [1], polyurethanes have found a growing interest for wide applications in shipbuilding, cars, footwear and building industries, etc… [2,3]. Polyurethanes are based, mainly, on the exothermic reaction between polyisocyanates and telechelic oligomers containing hydroxyl groups (polyols). Relatively few basic isocyanates and a range of polyols of different molecular weights and functionalities are used to produce the whole spectrum of polyurethane materials [2]. Among the wide different polyols used (mostly with polyesters and polyethers backbone), hydroxytelechelic polydienes, specially, hydroxytelechelic polybutadienes based PUs were found to present particular interest both in industry and public research in regards to their physico-chemical and mechanical properties [4–18]. They are widely used as solid propellants, explosives, adhesives, sealants, electric and electronic devices, high frequency acoustic and/or mechanical insulatings, elastic coatings, biocompatible medical devices etc… [9–17]. However, despite their extensive uses, microstructures and functionalities of these oligomers are not well controlled due to their synthetic approach. Actually, hydroxytelechelic polydienes

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* Corresponding authors. Tel.: +33 2 43 83 35 40; fax: +33 2 43 83 37 54.
** Tel.: +33 2 35 52 84 46; fax: +33 2 35 52 84 46.
E-mail addresses: jean-francois.pilard@univ-lemans.fr (J.-F. Pilard), claude.bunel@insa-rouen.fr (C. Bunel).

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Table 1
Characteristics of hydroxyoligomers

Oligomer	$\bar{M}_n$ (SEC)	PDI	$\bar{M}_n$ (NMR)	f_{OH}	Backbone microstructure	T_α (°C)	$T_{liq-liq}$ (°C)	Thermal degradation steps					
								1st step		2nd step		3rd step	
								T_{max} (°C)	Weight loss (%)	T_{max} (°C)	Weight loss (%)	T_{max} (°C)	Weight loss (%)
HTPI, 1600	2400	1.80	1600	2.00	100% of *cis*-1,4-PI units	−54	−49	380	93.1	539	6.7	–	–
HTPI, 3600	5000	1.90	3600	2.00	100% of *cis*-1,4-PI units	−43	−26	383	92.5	538	6.6	–	–
HHTPI, 90%	2700	2.10	1500	2.00	10% of *cis*-1,4-PI units 90% of hydrogenated units	−48	−38	458	97.0	497	2.9	–	–
EHTPI, 10%	2400	1.90	1700	2.00	90% of *cis*-1,4-PI units 10% of epoxide	−42	−34	305	5.8	390	80.4	588	8.1
EHTPI, 15%	2700	1.96	1780	2.00	85% of *cis*-1,4-PI units 15% of epoxide	−40	−27	297	7.4	402	85.7	688	8.1
EHTPI, 20%	2600	1.90	1840	2.00	80% of *cis*-1,4-PI units 20% of epoxide	−34	−24	270	9.9	441	82.6	556	6.7
PBHT R20 LM®	2400	2.49	1600[a]	2.56[a]	25% of 1,2 units; 23% of *cis*-1,4 units; 52% of trans-1,4 units; 1,4% of epoxide[a]	−60	−51	489	92.8	530	6.6	–	–
EPOL®	4600	2.02	2600[b]	2.35[b]	6% of 1,2 units; 6% of 3,4 units; 32% of *cis*-1,4 units; 56% of trans-1,4 units 90% of hydrogenated units[b]	−36	−25	428	97.2	505	2.5	–	–

[a] Refs. [30–34].
[b] Refs. [28,29,35,36].

are mainly synthesized by the classical radical polymerization leading to oligomer characteristics strongly depending to the reaction conditions (temperature, time, solvent nature, monomer ratios, stirring frequency) [19–22].

Strongly involved in the obtaining of telechelic polyisoprenes through an original degradation of high molecular weight *cis*-1,4-polyisoprene with controlled microstructures and functionalities [23,24], our laboratory investigated their reaction with TDI for the elaboration of new polyurethanes. Focusing on a comparative mechanical and thermal study, polyurethanes based on commercial hydroxytelechelic polybutadiene (PBHT R20 LM®) and hydrogenated hydroxytelechelic polyisoprene (EPOL®) were also synthesized.

2. Experimental section

2.1. Materials

cis-1,4-Polyisoprene (Acros Organics, 98% *cis*, $\bar{M}_w = 800,000$), *meta*-chloroperbenzoic acid (*m*CPBA, JANSSEN, 70% by titration), periodic acid (Acros, 99%), sodium borohydride (Acros, 98%), dibutyl tin dilaurate (DBTL, Aldrich), toluene diisocyanate (TDI, Aldrich, 95%), palladium on activated carbon (18%, Acros) were used without further purification.

Hydroxytelechelic polybutadiene (Poly Bd R20 LM® or PBHT R20 LM®), hydrogenated hydroxytelechelic polyisoprene (EPOL®) were kindly supplied by ATOFINA. The main characteristics of these commercial oligomers are shown in Table 1. Ethyl acetate, dichloromethane and tetrahydrofurane were used after distillation.

2.2. Instrumentation

2.2.1. Size exclusion chromatography (SEC)

Average molecular weights and molecular weight distributions of the different oligomers were measured using Size Exclusion Chromatography (SEC) on a system equipped with a SpectraSYSTEM AS1000 autosampler, with a guard column (Polymer Laboratories, PL gel 5 μm Guard, 50×7.5 mm) followed by 2 columns (Polymer Laboratories, 2 PL gel 5 μm MIXED-D columns, 2×300×7.5 mm), with a SpectraSYSTEM RI-150 and a SpectraSYSTEM UV2000 detectors. The eluent used is THF at a flow rate of 1 ml min^{-1} at 35 °C. Polystyrene standards (580–483×10^3 g mol^{-1}) were used to calibrate the SEC and molar mass are given in polystyrene equivalent (PS. Eq.).

2.2.2. NMR analysis

^{1}H and ^{13}C NMR spectra were recorder on a Bruker 400 Fourier Transform spectrometer at 400.13 and 100.62 MHz respectively, in $CDCl_3$ solutions using tetramethylsilane (TMS) as internal standard.

2.2.3. FTIR analysis

IR spectra were recorded on a FTIR Perkin–Elmer spectrophotometer, having a diamond ATR device (attenuated total reflection), between 4000 and 500 cm^{-1}.

2.2.4. *Dynamic mechanical thermal analysis (DMTA)*

The storage modulus (E') and loss tangent (tan δ) were measured by dynamic mechanical thermal analysis (DMA 7 Perkin–Elmer) in compression mode with stainless steel parallel plate probe (1 mm diameter), at 1 Hz, on small samples ($5\times5\times1.5$ mm^3) regularly taken from the polymer plate. The dynamic and static forces applied were 1000 and 1100 mN, respectively. Measurements were carried out in the range of −100–200 °C, at a rate of 10 °C/min. Standard calibration was performed with *n*-decane ($T_m=-29.7$ °C) and indium ($T_m=156.6$ °C). The α transition, which can be understood as the mechanical manifestation of the glass transition phenomenon, was characterized by the T_α temperature taken at the maximum of the tan $\delta=f(T)$ curve.

2.2.5. *Differential scanning calorimetry (DSC)*

Differential scanning calorimetry (DSC) determinations were performed on a Perkin–Elmer DSC-7 with a heating rate of 10 °C/min under nitrogen atmosphere. The sample weight was about 20 mg. Calibration was achieved with indium as reference material.

2.2.6. *Thermogravimetric analysis (TGA)*

Polymer thermal stabilities were checked by Thermo-Gravimetric Analysis (TGA-7 Perkin–Elmer). Experiments were carried out in air (20 ml/min). A 50–750 °C range was scanned at a heating rate of 20 °C/min. For each weight loss, a characteristic temperature (T_{max}), which correspond to the maximum rate of degradation, was determined from the minimum of the peak observed on the derived curve.

2.2.7. *Polyurethane density determination*

The density of the solid cast polyurethanes was measured using specific gravity bottle.

2.3. *Syntheses*

2.3.1. *Synthesis of hydroxytelechelic cis-1,4-polyisoprene (HTPI)*

Synthesis of $\bar{M}_n=1600$ g mol^{-1} HTPI (HTPI, 1600) and $\bar{M}_n=3600$ g mol^{-1} HTPI (HTPI, 3600): *m*-chloroperbenzoic acid (5.14 g, 20.9 mmol for HTPI, 1600; 2.68 g, 10.9 mmol for HTPI, 3600) in CH_2Cl_2 (0.1 mol L^{-1}) were added dropwise to a solution of *cis*-1,4-polyisoprene (24.00 g, 349 mmol for HTPI1600; 31.26 g, 460 mmol for HTPI, 3600) in CH_2Cl_2 (0.7 mol L^{-1}) into a jacketed reaction flask cooled at 0 °C (reaction time: 6 h). To the purified epoxidized *cis*-1,4-polyisoprene [23,24] (23.34 g, 339 mmol, 5% epoxidized for HTPI, 1600; 29.8 g, 436 mmol, 2% epoxidized for HTPI, 3600) dissolved in THF (0.85 mol L^{-1}), periodic acid (H_5IO_6) (4.25 g, 19 mmol for HTPI, 1600; 2.19 g, 9.6 mmol for HTPI, 3600) in THF (0.4 mol L^{-1}) was added dropwise in a jacketed reaction flask at 30 °C (reaction time: 6 h) (yield = 91%). The purified carbonyltelechelic *cis*-1,4-oligoisoprene [23,24] (20.58 g, $\bar{M}_n=1600$ g mol^{-1}; 25.33 g, $\bar{M}_n=3600$ g mol^{-1}) in THF (0.07 mol L^{-1}) was added dropwise to sodium borohydride ($NaBH_4$), (1.88 g, 49.6 mmol for HTPI, 1600; 1.06 g, 28 mmol for HTPI, 3600) in THF (0.3 mol L^{-1}) into a jacketed reaction flask at 30 °C. After stirring for 6 h at 60 °C, hydrolysis was performed after cooling by dropwise addition of 100 mL of THF with ice. The reaction mixture was washed with saturated aqueous NaCl (250 mL) and dried ($MgSO_4$). The solvent was evaporated under vacuum to give the product (yield = 90%).

2.3.1.1. *Characterization.* ^{1}H NMR and ^{13}C NMR chemical shifts ($CDCl_3$) are reported in Scheme 1.

2.3.1.2. *FTIR.* Disappearing of $\nu_{C=O}$ at 1721 cm^{-1}; appearance of ν_{OH} at 3350 cm^{-1}.

2.3.1.3. *SEC.* HTPI, 1600: $\bar{M}_n=2400$ g mol^{-1} (PS. Eq.), PDI = 1.80.

HTPI, 3600: $\bar{M}_n=5000$ g mol^{-1} (PS. Eq.), PDI = 1.90.

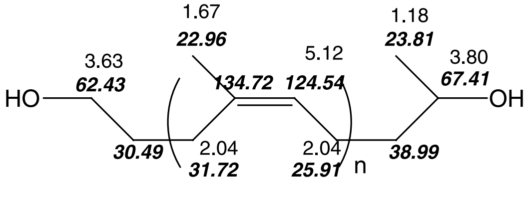
2.3.2. *Synthesis of hydrogenated hydroxytelechelic cis-1,4-polyisoprene (HHTPI)*

Hydroxytelechelic *cis*-1,4-polyisoprene ($\bar{M}_n=1600$ g mol^{-1}, 0.83 g, 0.5 mmol) in ethyl acetate (50 ml), and palladium on activated carbon (500 mg) were introduced into a catalytical hydrogenation device with mechanical stirring under 3.2 bar of hydrogen pressure at room temperature. After stirring 16 h, the pressure dropped to 2.5 bar, the reaction mixture was filtered to remove the catalyst. The solvent was removed under vacuum to give the product (yield: 80%, hydrogenated degree determined by ^{1}H NMR: 90%).

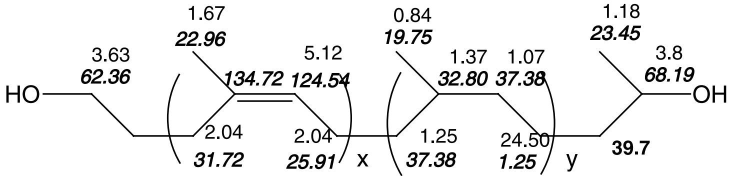
2.3.2.1. *Characterization.* ^{1}H NMR and ^{13}C NMR chemical shifts ($CDCl_3$) are reported in Scheme 2.

2.3.2.2. *FTIR.* Disappearance of the isoprenic double bond C=C bands after hydrogenation.

2.3.2.3. *SEC.* $\bar{M}_n=2700$ g mol^{-1} (PS. Eq.), PDI = 1.90.



Scheme 1. Chemical shifts of HTPI (^{1}H NMR and ^{13}C NMR).



Scheme 2. Chemical shifts of HHTPI (^{1}H NMR and ^{13}C NMR).

2.3.3. Synthesis of epoxidized hydroxytelechelic cis-1,4-polyisoprene (EHTPI)

m-Chloroperbenzoic acid (1.37 g, 5.55 mmol, for 10% of epoxidation; 2.03 g, 8.25 mmol, for 15% of epoxidation; 2.71 g, 11 mmol, for 20% of epoxidation) in 30 mL of CH_2Cl_2 were added dropwise to a solution of hydroxytelechelic *cis*-1,4-polyisoprene (HTPI, 1600, 4 g, 2.5 mmol) in 30 mL of CH_2Cl_2 (0.084 mol L^{-1}) into a three-necked round bottom flask with magnetic stirring at 0 °C. After stirring 3 h, the reaction mixture was washed with saturated NaCl aqueous solution. The organic layer was separated and dried ($MgSO_4$). The solvent was removed under vacuum to give the product (yield: 90%).

2.3.3.1. Characterization. ^{1}H NMR and ^{13}C NMR chemical shifts ($CDCl_3$) are reported in Scheme 3.

2.3.3.2. FTIR. Intensity decrease of the isoprenic double bond C=C bands with increasing amount of epoxide; appearance of $\nu_{C\text{–}O(epoxide)} = 870\ cm^{-1}$.

2.3.3.3. SEC. EHTPI, 10%: $\bar{M}_n = 2400\ g\ mol^{-1}$ (PS. Eq.), PDI = 1.80.

EHTPI, 15%: $\bar{M}_n = 2700\ g\ mol^{-1}$ (PS. Eq.), PDI = 1.96.

EHTPI, 20%: $\bar{M}_n = 2600\ g\ mol^{-1}$ (PS. Eq.), PDI = 1.90.

2.3.4. Synthesis of polyurethane materials

Hydroxytelechelic oligomers were dissolved in THF (1 g mL^{-1}) after drying at 60 °C under vacuum. The catalyst (DBTL) was added to the solutions in a ratio of [DBTL]/ [OH] = 0.045. TDI was added in last with a ratio of [NCO]/ [OH] = 1.2. The different solutions were cast in PTFE moulds under argon atmosphere for 2 h.

The materials formed after solvent evaporation were cured for 12 h at 60 °C. Characteristics of the different polyurethanes prepared are shown in Table 2.

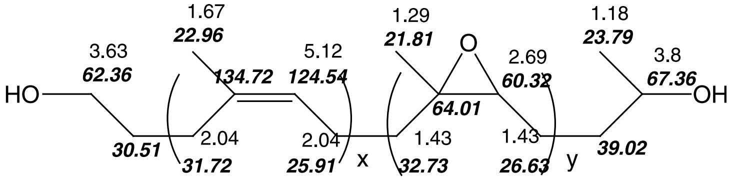
3. Results and discussion

3.1. Hydroxytelechelic oligomers synthesis

The structures of the different commercial hydroxytelechelic oligomers used are shown in Scheme 4. EPOL® is a hydrogenated hydroxytelechelic polyisoprene synthesized by radical polymerization of isoprene. PBHT R20 LM® is a hydroxytelechelic polybutadiene synthesized by radical polymerization of butadiene. Hydroxytelechelic *cis*-1,4-polyisoprene (HTPI) (Scheme 1) was obtained by selective reduction of carbonyltelechelic *cis*-1,4-polyisoprene resulting from controlled degradation of high molecular weight polyisoprene according to a method previously described [23,24]. Briefly, high molecular weight *cis*-1,4-polyisoprene was epoxidized by reaction of *m*-chloroperbenzoic acid in two different ratios leading to 2 and 5% epoxidized polyisoprenes. Cleavage of oxirane units was performed with periodic acid. Reduction of carbonyl end-groups was performed by sodium borohydride to get HTPI of $\bar{M}_n = 3600\ g\ mol^{-1}$ (HTPI, 3600) and $\bar{M}_n = 1600\ g\ mol^{-1}$ (HTPI, 1600), respectively.

HTPI, 1600 were hydrogenated under 3.2 bar hydrogen pressure at room temperature during 16 h leading to 90% hydrogenated *cis*-1,4-polyisoprene (HHTPI, 90%). The degree of hydrogenation was found independent to the hydrogen pressure and to the reaction time. This hydrogenation degree was determined by ^{1}H NMR analysis (Scheme 2) according to the signals of the methylic protons of the hydrogenated and non-hydrogenated units ($\delta = 0.84$, 1.67 ppm, respectively).

Reactions of HTPI with different amounts of *m*-chloroperbenzoic acid lead to partially epoxidized hydroxytelechelic polyisoprenes (10, 15, 20%). The degrees of epoxidation were determined by ^{1}H NMR analysis (Scheme 3) according to the signals of the oxirane proton of the



Scheme 3. Chemical shifts of EHTPI (^{1}H NMR and ^{13}C NMR).

Table 2
Composition and physical properties of prepared polyurethanes

Notation	Precursors	% Hard block[a]	% of Catalyst[b]	Appearance	T_α (°C)	T_g (°C)	Density
PU1	HTPI1600	12.6	2.9	Yellowish, soft	−40	−58	0.994
PU2	HTPI3600	5.7	1.4	Yellowish, soft	−46	< −58	0.939
PU3	HHTPI90%	13.7	3.3	Yellowish, soft	−40	−58	0.945
PU4	EHTPI10%	11.1	2.7	Brownish, soft	−27	−42	1.010
PU5	EHTPI15%	10.7	2.6	Brownish, soft	−24	−39	1.013
PU6	EHTPI20%	10.3	3.0	Brownish, soft	−18	−37	1.024
PU7	PBHT R20 LM®	19.4	3.7	Yellowish, soft	−42	< −58	0.990
PU8	EPOL®	14.9	2.0	Yellowish, soft	−32	−45	0.934

[a] % Hard segment = [wt. of (TDI)/wt. of (TDI + oligomer + catalyst)] × 100.

[b] % Catalyst = [wt. of (catalyst)/wt. of (TDI + oligomer + catalyst)] × 100.

epoxidized unit at $\delta = 2.69$ ppm and of the ethylenic proton of the non epoxidized unit at $\delta = 5.12$ ppm.

3.2. Comparative study of hydroxytelechelic oligomers

Average molecular weights and molecular weight distributions of the different oligomers were determined by SEC with standards polystyrene calibration. The values are reported in Table 1 and are compared with those obtained by ^{1}H NMR using the following formulas:

$$\bar{M}_n(\text{HTPI}) = \left[\frac{\text{I(C = CH)}}{\text{I(CHOH)}}\right] \times 68 + 104$$

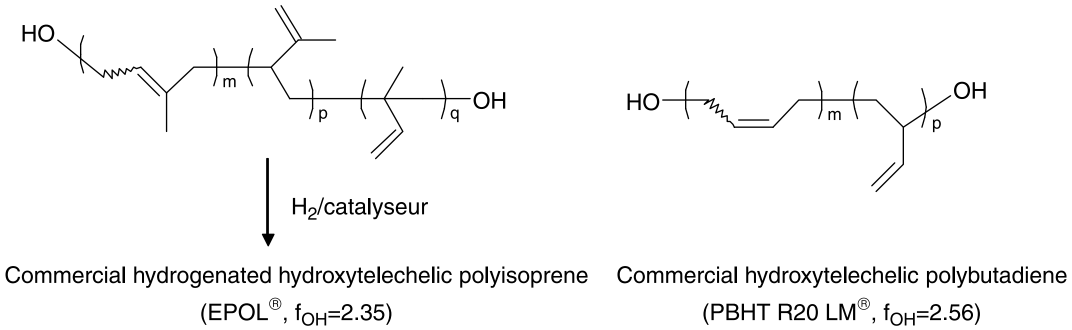
$$\bar{M}_n(\text{EHTPI}) = \left[\frac{\text{I(C = CH)}}{\text{I(CHOH)}}\right] \times 68 + \left[\frac{\text{I(CH epoxide)}}{\text{I(CHOH)}}\right] \times 84 + 104$$

$$\bar{M}_n(\text{HHTPI}) = \left[\frac{\text{I(C = CH)}}{\text{I(CHOH)}}\right] \times 68 + \left[\frac{\text{I(CH}_3\text{ hydrogenated units)}}{\text{I(CHOH)}} \times 3\right] \times 70 + 104$$

The $\bar{M}_n$(NMR)/$\bar{M}_n$(SEC) average ratio is about 0.67 for unsaturated and epoxidized oligomers. This is in agreement with Benoît factor [25,26] $B = 0.67$ according to $M_{PI} = BM_{PS}$ where M_{PS} is the polystyrene standardized molecular weight and M_{PI} is the corresponding *cis*-1,4-polyisoprene molecular weight. Otherwise, for hydrogenated oligomers this ratio is about 0.56.

3.2.1. Thermo-mechanical behavior

The evolutions of E' and tan δ versus temperature of some oligomers are shown in Fig. 1. All Mechanical transition (T_α) and liquid–liquid transition temperatures are shown in Table 1. As expected, one can observe an increase in rubbery plateau-limited by the liquid–liquid transition at $T_{\text{liq–liq}}$- and mechanical transition temperature T_α for HTPIs with increasing molecular weight. Likewise, T_α increases with epoxydation degree for the series EHTPI due to higher backbone rigidity and chain interactions. Moreover, a linear relationship was obtained between T_α and epoxidation degree (Fig. 2). An increase in T_α and rubbery plateau was also observed in the case of hydrogenated oligomer (HHTPI, 90%; Fig. 1 curve 3) compared with non-hydrogenated one (HTPI, 1600; Fig. 1 curve 1). It is interesting to note firstly that disordered oligobutadiene, PBHTR20LM® (Fig. 1 curve 7), has lower T_α than HTPI, 1600 and secondly that the mechanical behavior of EPOL® (Fig. 1 curve 8) is well explained by its higher molecular weight compared to HHTPI, 90% (Fig. 1 curve 3), effect mentioned above for HTPI series.



Scheme 4. Structure of the available hydroxypolydienes used for the synthesis of polyurethanes.

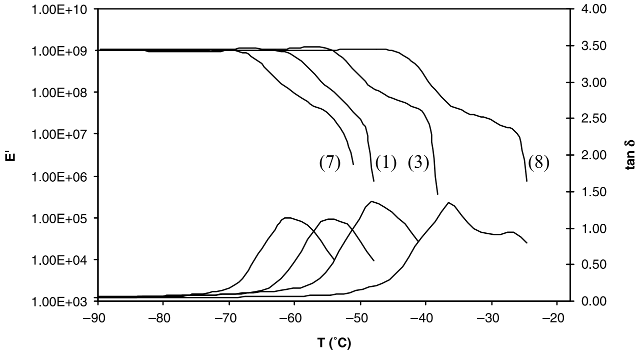


Fig. 1. Thermo-mechanical behavior of: (1) HTPI,1600; (3) HHTPI, 90%; (7) PBHT R20 LM®; (8) EPOL®.

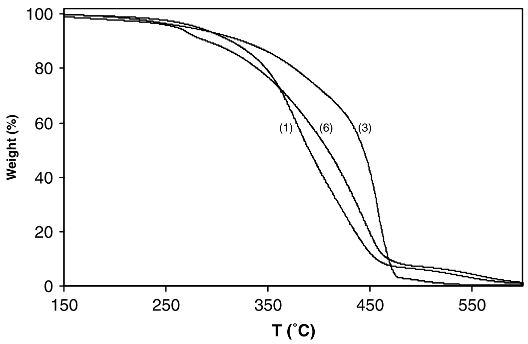


Fig. 3. Thermal degradation under air: (1) HTPI, 1600; (6) EHTPI, 20%; (3) HHTPI, 90%.

3.2.2. Thermal stability

Examples of TGA curves of oligomers are shown in Fig. 3. For each weight loss, the characteristic temperature ($T_{\max}$), which corresponds to the maximum rate of degradation, was determined from the minimum of the peak observed on the derived curve. The main TGA parameters are shown in Table 1.

For HTPI, 1600, the curves show two steps (Fig. 3, curve 1).

The first step corresponds to polyisoprene backbone degradation of oligomers. It is difficult to explain all the phenomena which contribute to last step degradation. Most likely, the oligomer residues decompose slowly by oxidation and justify the quasi disappearance of this step under nitrogen atmosphere.

It is noteworthy that there is no influence of molecular weight on thermal degradation of HTPIs, HTPI, 3600 exhibiting the same curve.

The thermal degradation of HHTPI shows also two steps (Fig. 3, curve 3). In the first one, $T_{\max}$ is noticeably higher for these hydrogenated isoprenic moieties even though the curve is similar to HTPI one up to 300 °C. The second step is the oxidation step which contribution is lower than for HTPI; this is probably due to the decrease of C=C double bonds ratio.

In the case of EHTPI series, the thermal degradation curves show a first additional step, i.d. three steps (e.g. EHTPI, 20%: Fig. 3, curve 6), which probably corresponds to the degradation of epoxidized moieties located near the end-groups of the oligomer chain or to the degradation of neighbouring epoxides leading, in each case, to evaporation of small molecules. Crosslinking reactions between the remaining epoxide moieties can possibly occur to lead to the increase in thermal stability observed in the second step.

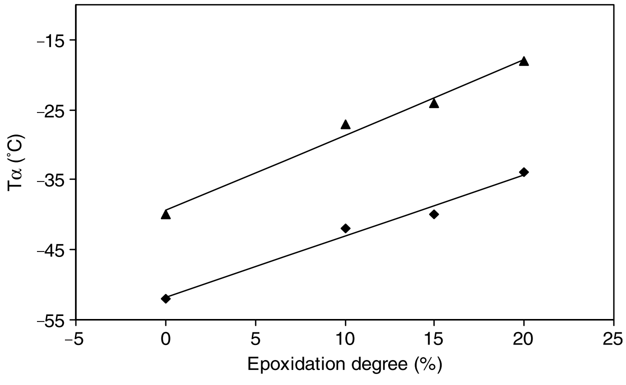


Fig. 2. T_{α} versus epoxydation degree (%): (◆) oligomers; (▲) polymers.

At 700 °C, all the oligomers are totally degraded.

Fig. 4 shows EPOL® and PBHTR 20 LM® thermogravimetry curves compared with HHTPI and HTPI ones, respectively. Thermal stability is strongly dependent of oligomer micro-structures. PBHT R20 LM® (Fig. 4, curve 7) is the more stable due to absence of methylic group in its repeating units. Inversely, the less thermally stable is EPOL®, less stable than HHTPI, 90% and similar to HTPI, 1600, probably because of the hydrogenated pending groups (alkyl and hydroxy alkyl groups) resulting from the 1,2 and 3,4 repeating units of the polyisoprene precursor.

3.3. Comparative study of polyurethane materials

Polyurethanes are synthesized by solvent evaporation process under argon atmosphere at room temperature. The materials obtained are next cured for 12 h at 60 °C (Scheme 5).

No molecular weight measurement could be carried out. In the case of 'linear PUs', either isocyanate secondary reactions such as allophanate formation or high aggregation

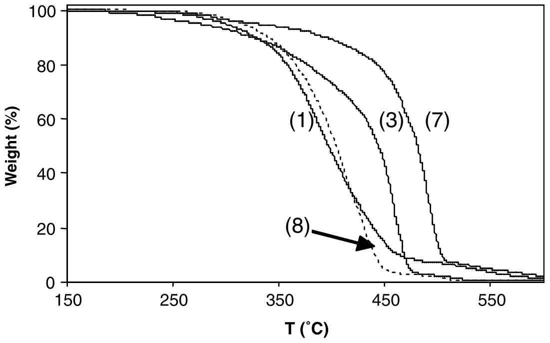
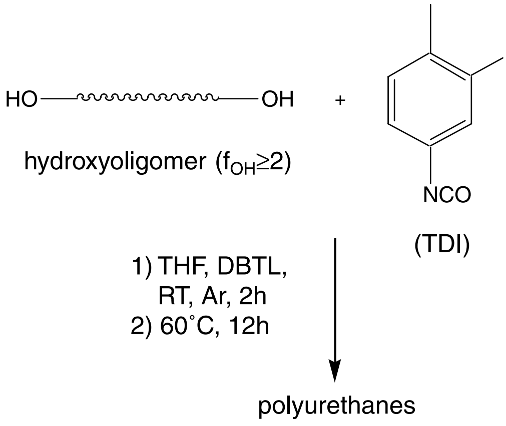


Fig. 4. Thermal degradation under air: (1) HTPI, 1600; (3) HHTPI, 90%; (7) PBHT R20 LM®; (8) EPOL®.



Scheme 5. Polyurethane syntheses.

of hard segments in addition to probably high molecular weight could be the reason of a partial solubility, even in the best solvents of oligomer precursors. In fact, the presence of microgels in the medium, despite LiCl addition to improve solubility by breaking hydrogen bonds, allows neither reproducible viscosimetric measurements nor the filtration of the medium for size exclusion chromatography.

The FTIR spectra of all the polyurethanes show the existence of absorption at nearly 3300 and 1700 cm^{-1} corresponding, respectively, to N–H and C=O stretching vibrations of urethane functions. No NCO absorption was observed at 2270 cm^{-1} which indicated that the reactions were complete. On the other hand, when HTPI chain length decreases, the ratio of urethane moieties (hard segments) in the polymer increases leading, as expected, to an increase in urethane band intensities in the FTIR spectra.

3.3.1. Thermo-mechanical behavior

The evolutions of E' and $\tan\delta$ versus time of some polyurethanes are reported in Figs. 5–8.

Fig. 5 shows the influence of the chain length of HTPI soft segment on the PU mechanical behaviors. The results are opposite to polyol ones, i.e. when the length of the soft segment increases, the molecular weight between urethane physical crosslinks increases too and therefore, E' at the rubbery plateau and T_α decrease. Moreover, the increase in $\tan\delta_{max}$ value attests a higher damping efficiency. This is in consistency with Lee et al. [27] results in term of modulus of elasticity increase with hard segments content.

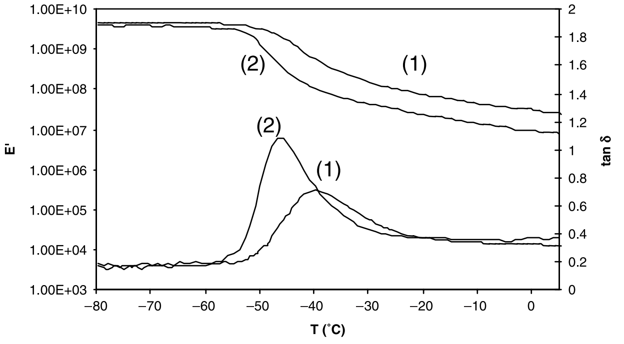


Fig. 5. Thermo-mechanical behavior of: (1) PU1; (2) PU2.

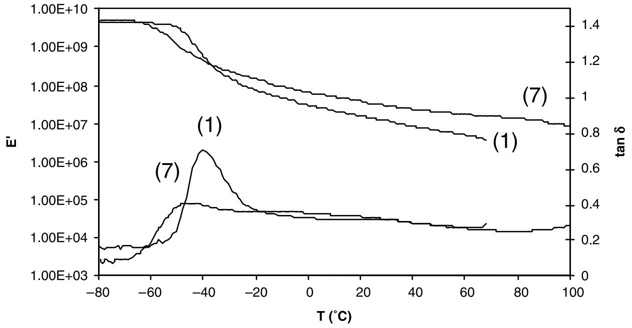


Fig. 6. Thermo-mechanical behavior of: (7) PU7; (1) PU1.

The influence of HTPI epoxidation degree is shown in Table 2. The mechanical behaviors are in agreement with polyol series, with a 16 °C increase in T_α due to the lowering of molecular motion after polymerization (Fig. 2). As expected, when the epoxydation degree increases, E' at the rubbery plateau and T_α increase linearly with epoxidation degree (Fig. 2) owing to intermolecular interactions and backbone rigidity.

In the case of the PU based on PBHT R20 LM® (PU7) compared to the one based on HTPI (PU1), the hydroxyl functionality (fn > 2) of PBHT R20 LM® leads to a crosslinked material and DMTA curves (Fig. 6) exhibit a higher E' at the rubbery plateau and, above all, no mechanical failure as observed at 70 °C for PU1. However, compared to PU1 (same molecular weight), a lower value of T_α is still observed for PU7 with, nevertheless, a smaller T_α difference with regard to corresponding polyols (Fig. 1). Damping efficiency is greater for PU1 with a narrower $\tan\delta$ peak owing to better defined HTPI micro-structure.

After double bond hydrogenation of PU1 (PU3, Fig. 7), only an increase in E' at rubbery plateau is observed with a slight decrease of $\tan\delta$ value, T_α being similar. For the PU based on EPOL® (PU8, Fig. 8), the result was difficult to predict because of a competition between its crosslinked structure, its higher molecular weight and its disordered micro-structure. PU8 exhibits an E' at the rubbery plateau equal to PU3 one, despite its higher molecular weight, but without mechanical failure as observed at 50 °C for PU3.

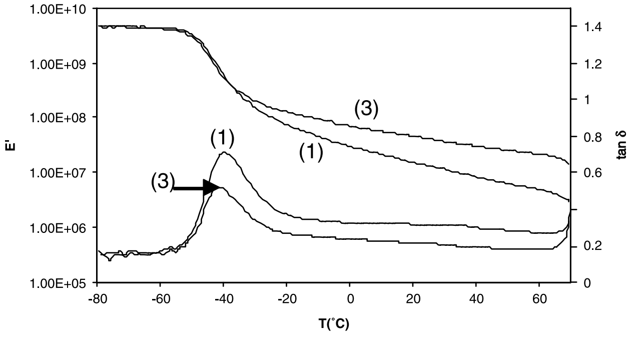


Fig. 7. Thermo-mechanical behavior of: (1) PU1; (3) PU3.

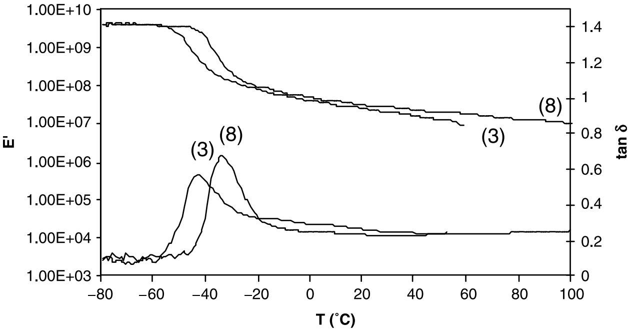


Fig. 8. Thermo-mechanical behavior of: (3) PU3; (8) PU8.

Owing to crosslinked structure, a higher T_α is observed for PU8 comparing to PU3 which is softer.

Glass-transition temperatures (T_g) of the different polyurethanes, obtained by DSC, are shown in Table 2. The T_g values are in agreement with mechanical-transition temperatures (T_α), with an average deviation of 16 °C.

3.3.2. Thermal stability

A three-step degradation was observed for all polyurethanes (e.g. for PU2, Fig. 9). The curves indicate that all polyurethanes remain stable up to 260 °C, after that the first step of degradation occurs. This first step corresponds mainly to the urethane degradation. Moreover, as mentioned in oligomer study, it corresponds also to the probable degradation of epoxide moieties located at the end of the soft segments or of two neighbouring epoxides in the case of polyurethanes based on EHTPIs. The second and the third steps correspond perfectly to the soft segment degradations. Otherwise, as observed for oligomers, the third steps do not occur under a nitrogen atmosphere (e.g. for PU2, Fig. 9).

Table 3 shows weight loss, and characteristic temperatures (T_{max}), determined from the minimum of the peak observed on the derived curve, for each polyurethane and for each step.

Assuming only the degradation of urethane function in the first step, one should observe a linear relationship between theoretical weight loss and percentage of hard segments (Fig. 10: dashed line). Experimentally, for linear PUs (PU1, PU2 and PU3), the results are slightly above due to the contribution of polyisoprene backbone degradation in this temperature range, as observed for oligomers in TGA curves (Fig. 3). On the other hand, for crosslinked PUs (PU7 and PU8), lower weight loss is observed that can be explained by a higher stability of the urethane linkage for which degradation happened later, and/or by lack of polyisoprene contribution observed for the HTPI based samples. The case of epoxidized PUs (PU4, PU5 and PU6) is different in that the corresponding points move away from the linear curve (Fig. 10) when the amount of epoxide units increases. These results are due to the supplementary step mentioned above in the case of EHTPI oligomers which is concomitant with urethane degradation.

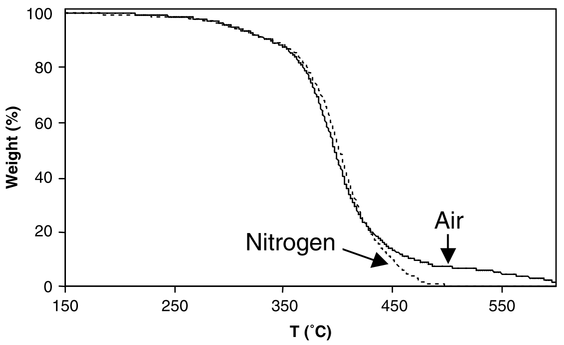


Fig. 9. Thermal degradation of PU2 under air and nitrogen.

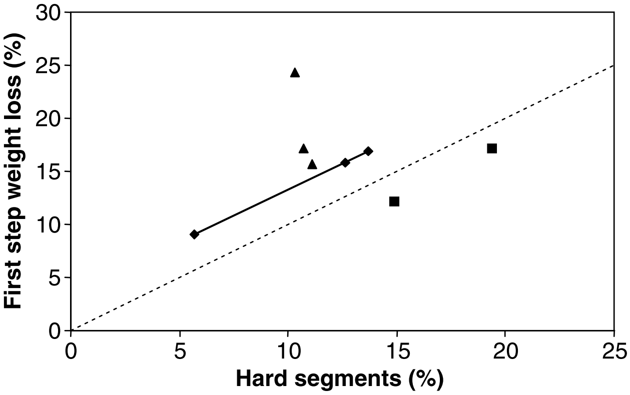


Fig. 10. First step weight loss (%) versus hard segments percentage (%): (◆) linear PUs; (▲) linear epoxidized PUs; (■) crosslinked PUs; (- - - -) theoretical curve.

Otherwise, Flandrin et al. [28] have investigated the thermal ageing at 150 °C for 1 month of a hydrogenated hydroxytelechelic polyisoprene (EPOL®) and of polyurethanes based on EPOL®, showing that these oligomers and their polyurethanes were more stable than the corresponding unsaturated hydrocarbons (HTPI and HTPB). This ageing behavior can be extrapolated to HHTPI based polyurethanes.

4. Conclusion

In this work, we have described the use of hydroxytelechelic *cis*-1,4-polyisoprene (HTPI) in the synthesis of polyurethanes. The influence of molecular weight, as well as the chemical structure of the polyisoprene backbones (including hydrogenated and epoxidized moieties) on the thermo-mechanical and thermal behavior of the synthesized polyurethanes was studied, and compared to commercially available hydroxytelechelic polydienes (PBHT R20 LM® and EPOL®). The study of thermo-mechanical properties shows that materials flexibility reduce with decrease of HTPI molecular weight or with increase in epoxidation degree (increase in T_α and E' at the rubbery plateau, decrease of tan δ_{max}). The same variations of tan δ_{max} and E' are observed for hydrogenated PU but without evolution of T_α.

Table 3
Characteristic temperatures (T_{max}) and weight loss of the different polyurethanes

Notation	Thermal degradation steps					
	1st step		2nd step		3rd step	
	T_{max} (°C)	Weight loss (%)	T_{max} (°C)	Weight loss (%)	T_{max} (°C)	Weight loss (%)
PU1	323	15.8	399	75.8	569	6.6
PU2	323	9.1	397	83.3	596	6.7
PU3	323	16.9	461	73.6	570	7.7
PU4	316	15.7	400	70.9	564	9.5
PU5	313	17.2	404	70.2	564	10.6
PU6	312	24.3	403	63.3	567	11.7
PU7	326	17.1	492	71.1	612	11.3
PU8	345	12.2	451	81.5	565	5.8

Thus, on the base of HTPI and by using either hydrogenation or epoxidation, it was shown that we are able to control and to modulate the PUs structure in such a way to obtain lower to higher thermo-mechanical properties (T_α, E' at the rubbery plateau, tan δ_{max}) than the ones of polyurethanes based on commercial polydienes.

Whatever the PUs (linear or crosslinked), the thermal stability is always controlled by urethane function degradation which starts at about 260 °C, the first step weight loss being proportional to hard segment content, except for PUs based on EHTPI series where concomitant epoxide degradation occurs.

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