

New Crosslinked Polyurethane Elastomers with Various Physical Properties from Natural Rubber Derivatives

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ABSTRACT: New hydroxytelechelic *cis*-1,4-oligoisoprenes exhibiting variable values and distributions of the hydroxyl functionality were successfully prepared. The synthesis reactions involved chemical modifications of carbonyl telechelic *cis*-1,4-polyisoprene, which was obtained by controlled degradation of synthetic or natural rubber. These new oligomers were reacted with toluene diisocyanate to elaborate crosslinked polyurethane elastomers. The thermomechanical properties of the prepared polyurethanes were investigated. The results show

a strong relationship between the chemical structures and properties. This work mainly shows the potentiality of making new crosslinking polyurethane materials with controlled and various properties from natural rubber, a renewable resource. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1677–1687, 2011

Key words: crosslinking; mechanical properties; polyurethanes; rubber; structure-property relations

INTRODUCTION

Polyurethanes are a class of very useful and versatile materials, and they are attracting growing interest for wide applications, such as shipbuilding, footwear, construction, cars, abrasion-resistant coatings, and biomaterials.¹ Polyurethanes are mainly produced in their crosslinking form, such as foams, which exhibit 90% of the world production.¹ They are based 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 a whole spectrum of polyurethane materials.¹ Despite their large applications, polyurethanes are still the target of a lot of investigations. Indeed, over the last few years, a big number of chemical structures and/or properties of polyurethanes have been developed.^{2–12} For example, they have been used as imprinting polymers,²

semiinterpenetrating polymer networks,⁸ dendrimers,⁹ photocrosslinkable hyperbranched polymers,¹⁰ and nanocomposites.¹¹

In the polyurethane industry, conventional polyether polyols, which account for 80% of the total worldwide consumption of oligopolyols, are mostly produced from petroleum-based alkylene oxides. Because of uncertainty about the future cost of petroleum and the desire to move toward more environmentally friendly feedstocks, many recent efforts have focused on replacing all or part of conventional petroleum-based polyols with those made from renewable resources.^{13–15} For example, combined with isocyanates, vegetable-oil-based polyols produce polyurethanes that can compete in many ways with polyurethanes derived from petrochemical polyols, and their preparation for general polyurethane use has been the subject of many studies.^{3–7}

In this respect, telechelic liquid natural rubbers can be considered as potential precursors of a very wide range of polymers. These oligomers are prepared by the selective cleavage of high-molecular-weight natural rubber.^{16–18} During the last decade, our group has focused its attention on the selective degradation of *cis*-1,4-polyisoprene (*cis*-1,4-PI) using well-controlled oxidative chain-cleavage, which has led to a new carbonyl telechelic *cis*-1,4-polyisoprene (CTPI or oligomer 1)^{19–21} (Fig. 1). Chemical

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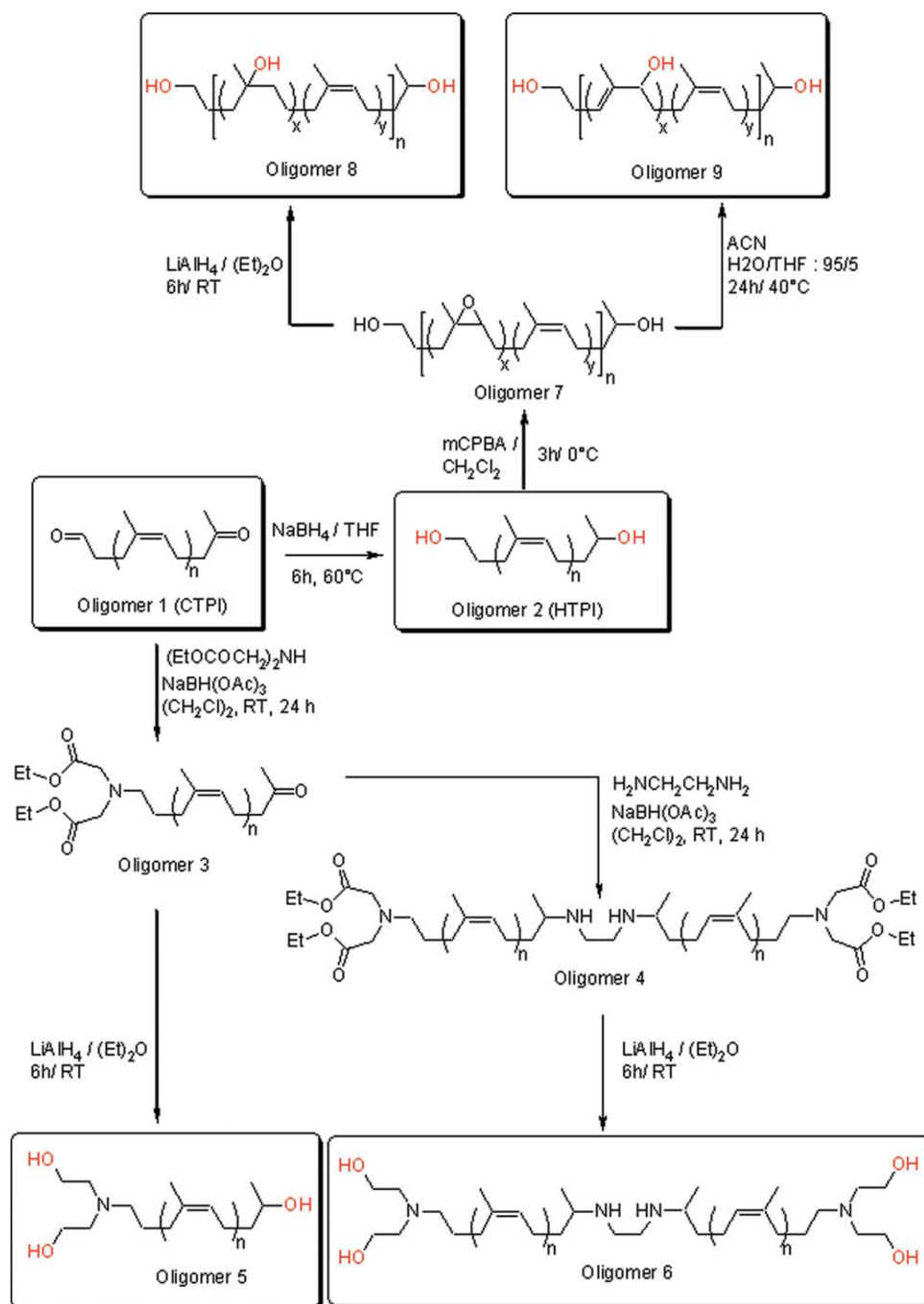


Figure 1 Chemical pathways of hydroxytelechelic oligomers synthesized from CTPI. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

modifications of carbonyl end groups and carbon-carbon double bonds at various ratios has led to new hydroxyl, amino, and quaternary ammonium telechelic *cis*-1,4-PIs.^{21–25} Thermoplastic polyurethanes with different soft- and hard-segment backbones based on some of these oligomers have been synthesized, and their thermomechanical properties have been investigated.^{21–24} Moreover, polyurethane materials with antibacterial properties have also been elaborated.²⁴

Here, we report the synthesis of new hydroxytelechelic *cis*-1,4-oligoisoprenes with variable values and distributions of hydroxyl functionalities. We also describe their use in the elaboration of new cross-linked polyurethane materials. Their chemical structures, thermomechanical properties, and thermal stabilities were studied with Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

cis-1,4-PI (Acros Organics, France, 98% *cis*, weight-average molecular weight = 800,000), *meta*-chloroperbenzoic acid (mCPBA; Janssen, France, 70% by titration), periodic acid (Acros, 99%), sodium borohydride (NaBH₄; Acros, 98%), lithium aluminum hydride (LiAlH₄) in an ether solution (1M, Aldrich), ammonium cerium(IV) nitrate (ACN; Acros, 99%), sodium triacetoxyborohydride [NaBH(OAc)₃; Acros, 97%], diethanolamine [(HOCH₂CH₂)₂NH; Aldrich, 99%], diethyl iminodiacetate [(EtOCOCH₂)₂NH; Acros, 99%], 1,2-dichloroethane (ClCH₂CH₂Cl; Aldrich, France, 99%), dibutyl tin dilaurate (DBTL; Aldrich), phenyl isocyanate (Janssen, 99%), and toluene diisocyanate (TDI; Aldrich, 95%) were used without further purification. Ethylenediamine (H₂NCH₂CH₂NH₂), dichloromethane (CH₂Cl₂), tetrahydrofuran (THF), and diethyl ether [(Et)₂O] were used after distillation.

Instruments

All of the measurements were performed at least three times.

Size exclusion chromatography (SEC)

The average molecular weights and molecular weight distributions of the different oligomers were measured with SEC on a system equipped with a SpectraSYSTEM AS1000 autosampler with a guard column (Polymer Laboratories, Marseille, France, PL, gel 5 μm guard, 50 × 7.5 mm²) followed by two columns (Polymer Laboratories, 2 PL gel 5 μm MIXED-D columns, 2 × 300 × 7.5 mm³) with SpectraSYSTEM RI-150 and SpectraSYSTEM UV2000 detectors. The eluent used was THF at a flow rate of 1 mL/min at 35°C. Polystyrene standards (580–483 × 10³ g/mol) were used to calibrate the SEC.

NMR analysis

¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker 400 Fourier transform spectrometer (France) at 400.13 and 100.62 MHz, respectively, in CDCl₃ solutions with tetramethylsilane as an internal standard. ¹H data are reported as follows: chemical shift (multiplicity: s, singlet; t, triplet; q, quadruplet; and m, multiplet; integration and peak assignments). ¹³C data are reported as follows: chemical shift (peak assignments). Chemical shifts of isoprenic moieties were similar for all oligomers and are described as follows.

¹H-NMR (CDCl₃, δ): 5.10 (t, =CH), 2.05 (m, CH₂), 1.70 (s, CH₃). ¹³C-NMR (CDCl₃, δ): 134.7 (C=CH),

124.5 (C=CH), 31.7 (CH₂C=CH), 25.9 (CH₂CH=C), 23.0 (CH₃).

Only chemical shifts of chain ends and modified moieties are detailed in the NMR data. The number-average molecular weight (M_n) and average hydroxyl functionality (\bar{f}_n) values of the different oligomers were also calculated by ¹H-NMR as follows:

α,ω-Dihydroxyl *cis*-1,4-polyisoprene (HTPI or oligomer 2) and oligomer 5:

$$M_n = [I_{(C=CH)}/I_{(CHOH)}] \times 68 + M_1$$

$$\bar{f}_n = 2 \quad (2)$$

$$\bar{f}_n = 3 \quad (5)$$

Oligomer 6:

$$M_n = 8 \times [I_{(C=CH)}/I_{(CH_2OH)}] \times 68 + M_2$$

$$\bar{f}_n = 4$$

Oligomer 8_10% and oligomer 8_20%:

$$M_n = [I_{(C=CH)}/I_{(CHOH)}] \times 68$$

$$+ [I_{(CH_3 \text{ of tertiary alcohol})}/(3 \times I_{(CHOH)})] \times 86 + 104$$

$$\bar{f}_n = \{ [I_{(CH_3 \text{ of tertiary alcohol})}$$

$$+ I_{(CH_3CHOH)} - 3 \times I_{(CHOH)}] / (3 \times I_{(CHOH)}) \} + 2$$

Oligomer 9_10%:

$$M_n = [I_{(C=CH)}/I_{(CHOH)}] \times 68$$

$$+ [I_{(CH_3 \text{ and } CH_2 \text{ of allylic alcohol})}/(5 \times I_{(CHOH)})] \times 84$$

$$+ 104$$

$$\bar{f}_n = [I_{(CH_3 \text{ and } CH_2 \text{ of allylic alcohol})}/(5 \times I_{(CHOH)})] + 2$$

where 68 is the molecular weight of the isoprenic moieties, M_1 is the molecular weight of the chain ends, M_2 is the molecular weight of the oligomer part not belonging to the repeating units, $I_{(C=CH)}$ is the signal intensity of CH of the isoprenic moieties (centered at 5.1 ppm), $I_{(CHOH)}$ is the signal intensity of CH of the chain-end secondary alcohol (centered at 3.80 ppm), $I_{(CH_3CHOH)}$ is the signal intensity of CH₃ of the chain-end secondary alcohol (centered at 1.18 ppm), $I_{(CH_2OH)}$ is the signal intensity of CH₂ of the chain-end primary alcohols (centered at 3.63 ppm), $I_{(CH_3 \text{ of tertiary alcohol})}$ is the signal intensity of CH₃ of the tertiary alcohol (centered at 1.15 ppm), and $I_{(CH_3 \text{ and } CH_2 \text{ of allylic alcohol})}$ is the signal intensity of CH₃ and CH₂ of the allylic alcohol moieties (centered at 1.59 ppm).

FTIR analysis

IR spectra were recorded on a Spectrum 2000 FTIR apparatus (PerkinElmer, France) equipped with a diamond attenuated total reflection device. Spectra

were obtained from 10 scans in the 4000–500-cm⁻¹ range. Characteristic bands of the isoprenic moieties were similar for all of the oligomers and are described as follows: $\nu_{\text{C}=\text{C}-\text{H}} = 3035 \text{ cm}^{-1}$; $\nu_{\text{CH}_2, \text{CH}_3} = 2900\text{--}2730 \text{ cm}^{-1}$; $\nu_{\text{C}=\text{C}} = 1664 \text{ cm}^{-1}$; $\nu_{\text{CH}_2, \text{CH}_3} = 1448, 1376 \text{ cm}^{-1}$; and $\delta_{\text{C}=\text{C}-\text{H}} = 834 \text{ cm}^{-1}$.

Dynamic mechanical analysis

The storage modulus (E') and loss tangent ($\tan \delta$) were measured by DMTA (DMA7, PerkinElmer) in compression mode with a stainless steel parallel-plate probe (1 mm in diameter) at 1 Hz on small samples ($5 \times 5 \times 1.5 \text{ mm}^3$) 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 to 200°C at a rate of $10^\circ\text{C}/\text{min}$. Standard calibration was performed with *n*-decane (melting temperature = -50°C) and indium (melting temperature = 156.6°C). The α transition, which can be understood as the mechanical manifestation of the glass-transition phenomenon, was characterized by the mechanical-transition temperature (T_α), which was taken to be the maximum of the $\tan \delta = f(T)$ curve ($f(T)$ means that $\tan \delta$ is a function of Temperature).

DSC

DSC determinations were performed on a PerkinElmer DSC-7 with a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. The sample weight was about 20 mg. Calibration was achieved with indium as a reference material.

TGA

Polymer thermal stabilities were checked by TGA (TGA-7, PerkinElmer). Experiments were carried out in air (20 mL/min). A $50\text{--}750^\circ\text{C}$ range was scanned at a heating rate of $20^\circ\text{C}/\text{min}$. For each weight loss, a characteristic temperature (T_{max} is the temperature corresponding to the maximum rate degradation) was determined from the minimum of the peak observed on the derived curve.

Density measurements

The density of the solid polymer materials was measured with a specific gravity bottle. Samples were weighed in air and in ethanol. The densities were calculated with the following formula:

$$\text{Density} = \frac{A}{\frac{A}{d_0} - B} \times d_0$$

where A is the sample weight in air, B is the sample weight in ethanol, and d_0 is the density of ethanol.

Synthesis

The syntheses of oligomers **1**, **2**, **3**, and **5** and partially epoxidized hydroxytelechelic *cis*-1,4-polyisoprene (oligomer **7**; Fig. 1) have been described elsewhere.^{21–25}

Preparation of oligomer **6** (Fig. 1)

First step. Oligomer **3** (1.235 g, 0.67 mmol) in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (10 mL) and $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (0.02 g, 0.34 mmol) were mixed in a three-necked, round-bottom flask with magnetic stirring under argon. The mixture was then treated with $\text{NaBH}(\text{OAc})_3$ (0.206 g, 0.94 mmol) at room temperature (RT). After 24 h of stirring under argon, the reaction mixture was washed with a 1N sodium hydroxide solution. The organic layer was separated and dried [magnesium sulfate (MgSO_4)]. The solvent was removed *in vacuo* to give oligomer **4** (yield = 83%).

¹H-NMR (CDCl_3 , δ): 1.26 (t, 3H, $\text{CH}_3\text{CH}_2\text{O}-\text{COCH}_2\text{NCH}_2$), 4.16 (m, 2H, $\text{CH}_3\text{CH}_2\text{COCH}_2\text{NCH}_2$), 3.54 (s, 2H, $\text{CH}_3\text{CH}_2\text{OCOCH}_2\text{NCH}_2$), 2.68 (t, 2H, $\text{CH}_3\text{CH}_2\text{COCH}_2\text{NCH}_2$), 1.04 (d, 3H, $\text{CH}_3\text{CHNHCH}_2$), 2.74 (m, 1H, $\text{CH}_3\text{CHNHCH}_2$), 2.61 (t, 2H, $\text{CH}_3\text{CHNHCH}_2$). ¹³C-NMR (CDCl_3 , δ): 10.88 ($\text{CH}_3\text{C H}_2\text{COCH}_2\text{NCH}_2$), 68.12 ($\text{CH}_3\text{CH}_2\text{COCH}_2\text{NCH}_2$), 167.75 ($\text{CH}_3\text{CH}_2\text{C OCH}_2\text{NCH}_2$), 65.20 ($\text{CH}_3\text{C H}_2\text{COCH}_2\text{NCH}_2$), 61.79 ($\text{CH}_3\text{CH}_2\text{COCH}_2\text{NCH}_2$). FTIR: $\nu_{\text{C}=\text{O}} (\text{ester}) = 1736 \text{ cm}^{-1}$, disappearance of $\nu_{\text{C}=\text{O}} = 1721 \text{ cm}^{-1}$.

Second step. LiAlH_4 in an ether solution (10 mL, 10 mmol) was diluted in dried ether (15 mL) in a three-necked, round-bottom flask with magnetic stirring under argon. Oligomer **4** (0.70 g, 0.18 mmol) in ether (0.01 mol/L) was added dropwise to the diluted LiAlH_4 solution at RT. After 6 h of stirring at RT, the mixture was hydrolyzed to break the LiAlH_4 excess by the dropwise addition of water (H_2O) until no clearing of hydrogen gas. The product was extracted by CH_2Cl_2 and dried by MgSO_4 . The solvent was removed *in vacuo* to give oligomer **6** (yield = 56%).

¹H-NMR (CDCl_3 , δ): 3.63 (t, 2H, $\text{NCH}_2\text{CH}_2\text{OH}$), 2.69 (t, 2H, $\text{NCH}_2\text{CH}_2\text{OH}$), 2.54 (m, 2H, $\text{CH}_2\text{NCH}_2\text{CH}_2\text{OH}$), 1.04 (s, 3H, $\text{CH}_3\text{CH}(\text{NH})\text{CH}_2$), 2.74 (m, 1H, $\text{CH}_3\text{CHNHCH}_2$), 2.61 (m, 2H, $\text{CH}_3\text{CHNHCH}_2$). ¹³C-NMR (CDCl_3 , δ): 59.61 ($\text{NCH}_2\text{CH}_2\text{OH}$), 56.13 ($\text{NCH}_2\text{CH}_2\text{OH}$), 54.9 ($\text{CH}_2\text{NCH}_2\text{CH}_2\text{OH}$). FTIR: $\nu_{\text{OH}} = 3370 \text{ cm}^{-1}$, disappearance of $\nu_{\text{C}=\text{O}} (\text{ester}) = 1736 \text{ cm}^{-1}$.

Preparation of oligomer **8** (Fig. 1)

LiAlH_4 in an ether solution (2.7 mL, 2.7 mmol) was diluted in dried ether (5 mL) in a three-necked, round-bottom flask with magnetic stirring under

argon. Oligomer 7 (0.28 g for 10% of epoxidation and 0.86 g for 20% of epoxidation) in ether (0.036 mol/L) was added dropwise to the diluted LiAlH_4 solution at RT. After 6 h of stirring at RT, the mixture was hydrolyzed to break the LiAlH_4 excess by the dropwise addition of H_2O until no clearing of hydrogen gas. The product was extracted by CH_2Cl_2 and dried by MgSO_4 . The solvent was removed *in vacuo* to give oligomer 8 (yields = 83 and 76%, respectively).

$^1\text{H-NMR}$ (CDCl_3 , δ): 1.42 [t, 2X H, $\text{CH}_3\text{C}(\text{OH})\text{—CH}_2$], 3.80 (m, 1H, CH_3CHOH), 3.63 (t, 2H, CH_2OH), 1.15 [s, 3X H, $\text{CH}_3\text{C}(\text{OH})\text{CH}$], 1.18 (d, 3H, CH_3CHOH). $^{13}\text{C-NMR}$ (CDCl_3 , δ): 71.63 [$\text{CH}_3\text{C}(\text{OH})\text{—CH}$], 40.92 [$\text{CH}_3\text{C}(\text{OH})\text{CH}_2$], 67.36 (CH_3CHOH), 62.36 (CH_2OH), 39.02 [$\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$], 30.51 ($\text{CH}_2\text{CH}_2\text{OH}$), 23.79 (CH_3CHOH), 28.69 [$\text{CH}_3\text{C}(\text{OH})\text{CH}_2$]. FTIR: intensity increase of $\nu_{\text{OH}} = 3440\text{ cm}^{-1}$, intensity decrease of $\nu_{\text{C—O}}(\text{epoxide}) = 755\text{ cm}^{-1}$.

Preparation of oligomer 9 (Fig. 1)

Oligomer 7 (0.24 g for 10% of epoxidation and 0.23 g for 20% of epoxidation) was dissolved in 95/5 v/v (0.03 mol/L) THF/ H_2O in a three-necked, round-bottom flask with magnetic stirring. Then, ACN was added to the solution in a molar ratio of $[\text{ACN}]/[\text{epoxidized units}] = 0.4$. After stirring for 24 h at 40°C , the mixture was dried by MgSO_4 and filtered

to remove the catalyst (ACN). The solvent was removed *in vacuo* to give oligomer 9 (yields = 85 and 81%, respectively).

$^1\text{H-NMR}$ (CDCl_3 , δ): 1.59 [s, 3X H, $\text{CH}=\text{C}(\text{CH}_3)\text{CHOH}$], 4.03 [m, 1X H, $\text{CH}=\text{C}(\text{CH}_3)\text{CHOH}$], 3.80 (m, 1H, CHOH), 3.63 (t, 2H, CH_2OH), 1.18 (d, 3H, CH_3CHOH). $^{13}\text{C-NMR}$ (CDCl_3 , δ): 74.85 [$\text{CH}=\text{C}(\text{CH}_3)\text{CHOH}$], 15.48 [$\text{CH}=\text{C}(\text{CH}_3)\text{CHOH}$], 134.72 [$\text{CH}=\text{C}(\text{CH}_3)\text{CHOH}$], 124.54 [$\text{CH}=\text{C}(\text{CH}_3)\text{CHOH}$], 67.36 (CH_3CHOH), 62.36 (CH_2OH), 39.02 [$\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$], 30.51 ($\text{CH}_2\text{CH}_2\text{OH}$), 23.79 (CH_3CHOH). FTIR: intensity increase of $\nu_{\text{OH}} = 3350\text{ cm}^{-1}$, intensity decrease of $\nu_{\text{C—O}}(\text{epoxide}) = 755\text{ cm}^{-1}$.

Test of the hydroxyl reactivity of oligomers 5 and 8 through a reaction with phenyl isocyanate

Phenyl isocyanate (1.3 mmol for oligomer 5; 0.42 mmol for oligomer 8) was added to solutions of 5 and 8 in 5 mL of THF (0.014 mol/L) and was heated at 30°C in a three-necked, round-bottom flask under argon. The catalyst (DBTL) was added to the solutions in a ratio of $[\text{DBTL}]/[\text{OH}] = 0.045$. The mixture was stirred for 6 h. The solvent and the nonreacted phenyl isocyanate were removed *in vacuo* to give oligomers 10 and 11, respectively (Figs. 2 and 3).

Characterization of oligomer 10. $^1\text{H-NMR}$ (CDCl_3 , δ ; Fig. 2): 7.05, 7.29, 7.36 (m, 15H, $\text{HC}=\text{CH}$ of aryl groups); 4.90 (m, 1H, CHOCONH—Ar); 2.56 [t, 2H,

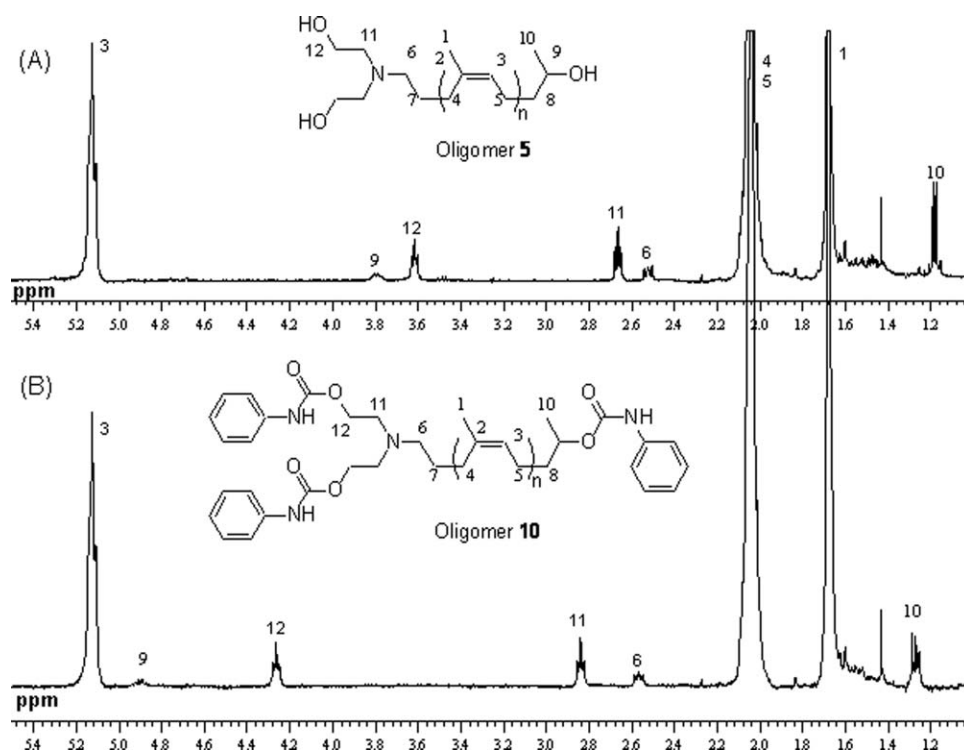


Figure 2 $^1\text{H-NMR}$ spectra of (A) oligomer 5 and (B) oligomer 10.

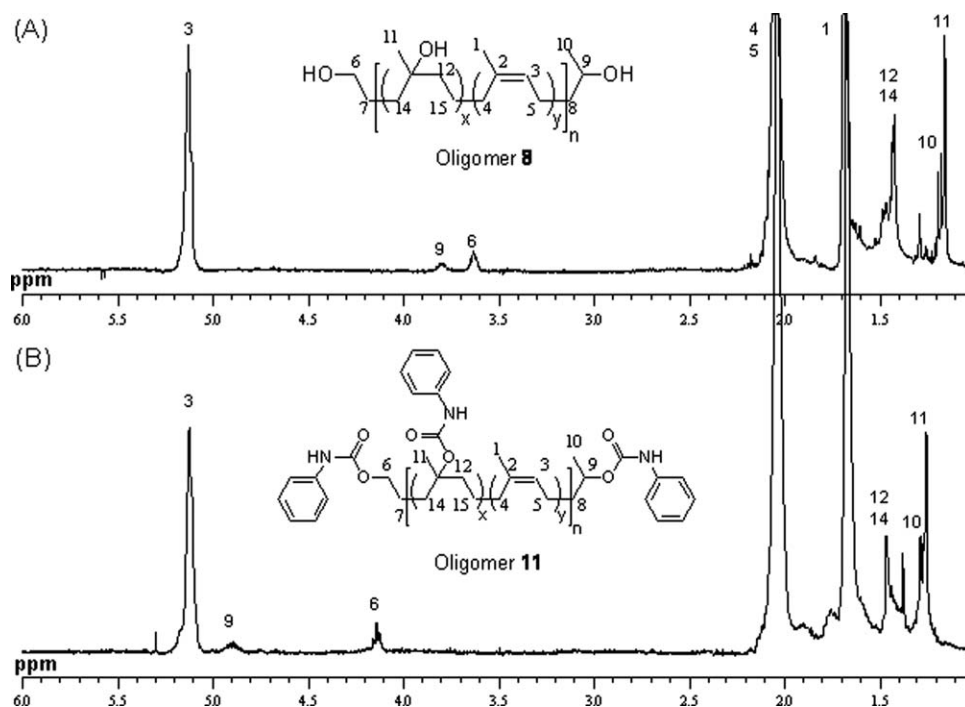


Figure 3 $^1\text{H-NMR}$ spectra of (A) oligomer 8 and (B) oligomer 11.

$\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OCONH-Ar})_2$; 2.84 [t, 2H, $\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OCONH-Ar})_2$]; 4.27 [t, 2H, $\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OCONH-Ar})_2$]; 1.28 (d, 3H, $\text{CH}_3\text{CHOCONH-Ar}$). $^{13}\text{C-NMR}$ (CDCl_3 , δ): 122.75–137.64 (HC=CH of phenyl groups), 71.36 ($\text{CH}_3\text{CHOCONH-Ar}$), 35.99 [$\text{CH}_2\text{CH}(\text{OCONH-Ar})\text{CH}_3$], 19.76 ($\text{CH}_3\text{CHOCONH-Ar}$). FTIR: ν_{NH} carbamate = 3330 cm^{-1} , $\nu_{\text{C=O}}$ carbamate = 1735 cm^{-1} , $\nu_{\text{C=O}}$ carbamate = 1710 cm^{-1} , $\nu_{\text{C=C}}$ aromatic = $1601, 1538, 1313, 1234\text{ cm}^{-1}$.

Characterization of oligomer 11. $^1\text{H-NMR}$ (CDCl_3 , δ ; Fig. 3): 7.05, 7.29, 7.36 (m, 15H, HC=CH of aryl groups); 1.46 [t, 2H, $\text{CH}_3\text{C}(\text{OCONHAr})\text{CH}_2$]; 4.90 (m, 1H, $\text{CH}_3\text{CHOCONHAr}$); 4.14 (t, 2H, $\text{CH}_2\text{OCONHAr}$); 1.25 [s, 3H, $\text{CH}_3\text{C}(\text{OCONHAr})\text{CH}$]; 1.28 (d, 3H, $\text{CH}_3\text{CHOCONHAr}$). $^{13}\text{C-NMR}$ (CDCl_3 , δ): 122.75–137.64 (HC=CH of phenyl groups), 71.36 ($\text{CH}_3\text{CHOCONHAr}$), 64.57 ($\text{CH}_2\text{OCONHAr}$), ($\text{CH}_3\text{CHOCONHAr}$), 19.76 ($\text{CH}_3\text{CHOCONHAr}$). FTIR: ν_{NH} carbamate = 3330 cm^{-1} , $\nu_{\text{C=O}}$ carbamate = 1735 cm^{-1} , $\nu_{\text{C=O}}$ carbamate = 1710 cm^{-1} , $\nu_{\text{C=C}}$ aromatic = $1601, 1538, 1313, 1234\text{ cm}^{-1}$.

Preparation of the polyurethane films

Hydroxytelechelic oligomers were dissolved in THF (1 g/mL) after they were dried at 60°C *in vacuo*. The catalyst (DBTL) was added to the solutions in a ratio of $[\text{DBTL}]/[\text{OH}] = 0.045$. TDI was added last with an effective ratio of $[\text{NCO}]/[\text{OH}] = 1.05$. The different solutions were cast in PTFE molds under a dry argon atmosphere for 2 h. The films formed

($50 \times 50 \times 1.5\text{ mm}^3$) after solvent evaporation were cured for 12 h at 60°C .

RESULTS AND DISCUSSION

Comparative study of the hydroxytelechelic oligomers

Preparation

Two families of hydroxytelechelic oligomers possessing hydroxyl functionalities higher than 2 were synthesized from oligomer 1 (i.e., CTPI) and oligomer 2 (i.e., HTPI). The hydroxyl groups were exclusively located at the chain ends (first family: oligomers 5 and 6) or both along and at the end of the chains (second family: oligomers 8 and 9; Fig. 1).

CTPI (oligomer 1) was obtained by the controlled degradation of high-molecular-weight *cis*-1,4-PI, as described elsewhere.^{20,21} This degradation was performed in two steps: partial epoxidation by *m*CPBA followed by the oxidative scission of epoxides with periodic acid. HTPI (oligomer 2) was synthesized by reduction of the carbonyl groups of the CTPI by NaBH_4 (Fig. 1).²¹

Oligomer 3 was prepared by the selective reductive amination of the aldehyde group of CTPI with $(\text{EtOCOCH}_2)_2\text{NH}$ in the presence of $\text{NaBH}(\text{OAc})_3$. The reduction of the ester groups of oligomer 3 by LiAlH_4 led to oligomer 5, as previously described.²⁵ The reductive amination of the ketone end group of oligomer 3 with a 0.5 equivalent ratio of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ in the presence of $\text{NaBH}(\text{OAc})_3$

led to oligomer 4. The reduction of ester end groups of oligomer 4 by an excess of LiAlH_4 led to new polyols, namely, oligomer 6 (Fig. 1).

Oligomer 7 was obtained by the reaction of different amounts of *m*CPBA with the HTPI.²¹ Only 10 and 20% epoxidized HTPI were used for this work as precursors of the second family of oligomers. On the other hand, the epoxidation of CTPI led to a total conversion of the aldehyde groups (NMR) and the SEC analysis showed an increase of the molecular weight (twofold), which suggested a coupling reaction between aldehydes. This aldolization reaction was catalyzed by the acetic acid released after epoxidation. Therefore, epoxidized CTPI was not used as a precursor of oligomers 8 and 9.

The reduction of oxirane units of 10 and 20% epoxidized HTPI (oligomer 7) by LiAlH_4 led to a new hydroxytelechelic *cis*-1,4-PI (oligomer 8; Fig. 1) bearing primary and secondary alcohols at the end of the chains and bearing tertiary alcohols along the chains. The reaction of the oxirane units of the 10 and 20% epoxidized HTPI with H_2O at 45°C in the presence of ACN as a catalyst led to a new hydroxytelechelic *cis*-1,4-PI (oligomer 9; Fig. 1) bearing primary and secondary alcohols at the end of the chains and bearing secondary ethylenic alcohol along the chains. Actually, the oxirane opening by H_2O led to vicinal secondary and tertiary alcohols; at 45°C, the tertiary alcohol was eliminated to give in majority the most substitute allylic alcohol (Fig. 1). $^1\text{H-NMR}$ analysis showed the quasi-total disappearance of signals of the epoxidized moi-

eties. The residual epoxidation amount was about 2%. The moieties corresponding to minor allylic secondary alcohols were observed in a negligible percentage corresponding to very weak intensities and resolutions of their $^1\text{H-NMR}$ signals. SEC analysis of the 20% modified oligomer (oligomer 9_20%) showed an increase of the average molecular weights and of polydispersity. This suggests reactions between the alcohol formed and the residual oxirane rings; therefore, this oligomer was not of interest for this work.

The prepared oligomers possessed several kinds of hydroxyl groups, that is, alcohols, with different reactivities. It is well known that tertiary alcohols are less nucleophilic than secondary and primary ones. In addition, the reactivity of two neighboring similar groups was different because when one of them reacts, the second is encumbered. Therefore, to check the quantitative reactivity toward isocyanate of these alcohols, oligomers 5 and 8 (oligomer 8_10%) were reacted with phenylisocyanate in the presence of DBTL as a catalyst. Then, after 6 h of reaction in THF in dilute conditions, $^1\text{H-NMR}$ (Figs. 2 and 3) and FTIR spectra revealed 100% of conversion of alcohol and isocyanate groups into urethane ones.

Characterization

The average molecular weights and molecular weight distributions of the different oligomers were determined by SEC with polystyrene calibration standards. The values are reported in Table I

TABLE I
Characteristics of the Prepared Hydroxytelechelic Oligomers

Oligomer		M_n by SEC (g/mol)	Polydispersity	M_n by $^1\text{H-NMR}$ (g/mol)	\bar{f}_n^b	Composition of repeating units	T_g (°C)	$T_{\text{liq-liq}}$ (°C)
No.	Code							
2	HTPI ^a	2400	1.80	1600	2.0	100% <i>cis</i> -1,4-PI	-54	-49
5	Oligomer 5	2680	2.08	1929	3.0	100% <i>cis</i> -1,4-PI	-49	-38
6	Oligomer 6	2400	1.99	3670	4.0	100% <i>cis</i> -1,4-PI	-44	-32
8	Oligomer 8_10%	2570	1.87	1650	4.7	90% <i>cis</i> -1,4-PI and 10% polyisoprene units with tertiary alcohol	-28	-19
8	Oligomer 8_20%	2500	2.07	1750	7.0	80% <i>cis</i> -1,4-PI and 20% polyisoprene units with tertiary alcohol	-19	-10
9	Oligomer 9_10%	3150	1.95	2150	4.0	90% <i>cis</i> -1,4-PI, 8% polyisoprene units with ethyl- enic alcohols, and 2% epoxi- dized <i>cis</i> -1,4-PI	-27	-19

^a The data were obtained from Kébir et al.²²

^b Average number of OH's per oligomer chain calculated by $^1\text{H-NMR}$.

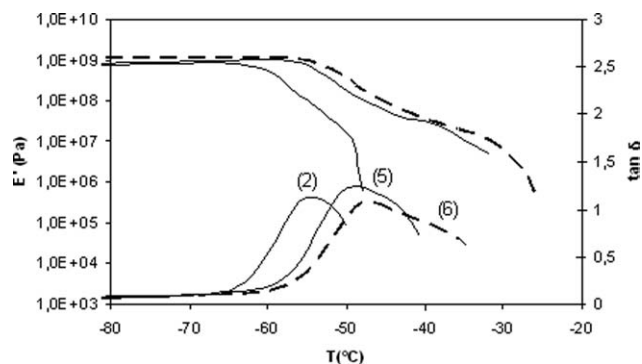


Figure 4 Thermomechanical behavior at 1 Hz of (2) HTPI, (5) oligomer 5, and (6) oligomer 6 (T = temperature).

and are compared with those calculated by $^1\text{H-NMR}$. The $M_n(\text{NMR})/M_n(\text{SEC})$ average ratio varied between 0.64 and 0.72, except for oligomer 4, for which this ratio was higher than 1. This last result was in disagreement with the Benoît factor ($B = 0.67$).^{16,17}

$$M_{\text{PI}} = BM_{\text{PS}}$$

where M_{PS} is the standardized molecular weight of polystyrene and M_{PI} is the corresponding molecular weight of *cis*-1,4-PI. This suggests a variation of the hydrodynamic volume of the oligomers after chemical modification.

Typical DMTA traces showing the temperature dependence of E' and $\tan \delta$ of some of the prepared oligomers are shown in Figures 4 and 5. The curves are compared to the HTPI one. All T_α and liquid-liquid transition temperature ($T_{\text{liq-liq}}$) values are given in Table I. The samples appeared to be homogeneous, as indicated by a narrow damping ($\tan \delta$) peak (Figs. 4 and 5). Because of a slightly higher molecular weight and/or to presence of hydrogen interactions between amine and alcohols, oligomers 5 and 6 exhibited higher values of T_α and of the rubbery plateau ($T_{\text{liq-liq}} - T_\alpha$) in comparison with HTPI. The second family (oligomer 8_10%, oligomer 8_20%, and oligomer 9_10%) exhibited higher values of T_α than the first family. Furthermore, their T_α values increased with the percentage of modification of the oligomer moieties. This was due to decrease of chain flexibility and increase of interactions between the chains.

TGA curves of the prepared hydroxytelechelic oligomers showed generally two steps of degradation. The first one corresponded to the chain-backbone degradation. During the second one, the oligomer residues decomposed slowly by oxidation, which justified the disappearance of this step under a nitrogen atmosphere. The main TGA parameters are shown in Table II.

Oligomer 9 showed a first additional degradation step at 230°C. Thus, it exhibited a lower thermal stability in comparison with the other prepared oligomers. This result was consistent with previous investigations performed on epoxidized HTPI²² and suggests the degradation of neighboring functionalized moieties (with epoxide or ethylenic alcohol) and/or of the moieties located near the chain ends; this led to evaporation of small molecules.

Comparative study of the polyurethanes

Preparation

The prepared hydroxytelechelic oligomers were reacted with TDI in an effective $[\text{NCO}]/[\text{OH}]$ ratio of 1.05 to give newly crosslinked polyurethanes. The presence of secondary amine functions in the chemical structure of oligomer 6 was not taken into account in the calculation of the required quantity of TDI. Therefore, the hydroxyl groups of oligomer 6 were not totally consumed because amines are more reactive than alcohols toward isocyanates. Actually, urea linkages would be formed within materials based on oligomer 6. Characteristics of the different polyurethanes prepared are shown in Table III.

Characterization

The FTIR spectra of all of the polyurethanes exhibited absorptions at approximately 3300 and 1700 cm^{-1} , which could be assigned to the stretching vibrations of N-H and hydrogen-bonded C=O of urethane groups, respectively. The absorption at 1730 cm^{-1} , corresponding to free C=O, were not observed or were masked by the hydrogen-bonded one; this suggests a strong interaction and aggregation of the hard segments, leading to phase separation or domain formation. Furthermore, other interactions among the polymeric chains were responsible for the shift of the wave number of the

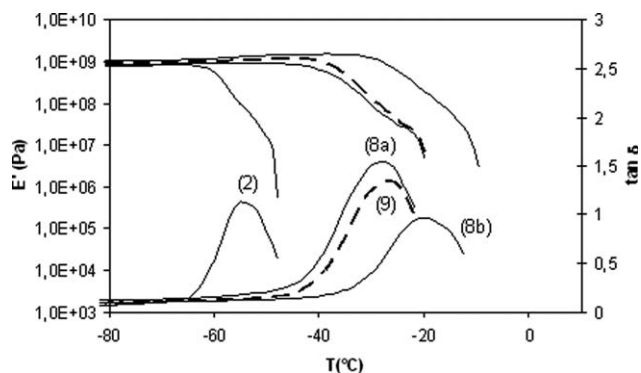


Figure 5 Thermomechanical behavior at 1 Hz of (2) HTPI, (8a) oligomer 8_10%, (8b) oligomer 8_20%, and (9) oligomer 9_10% (T = temperature).

TABLE II
 T_{\max} Values and Weight Losses of the Different Synthesized Polyurethanes and Their Oligomer Precursors

Product code	Thermal degradation step					
	First		Second		Third	
	T_{\max} (°C)	Weight loss (%)	T_{\max} (°C)	Weight loss (%)	T_{\max} (°C)	Weight loss (%)
HTPI ^a	380	93.1	539	6.7	—	—
Oligomer 5	413	82.0	526	16.7	—	—
Oligomer 6	410	89.7	562	6.5	—	—
Oligomer	409	88.8	532	8.7	—	—
8_10%	406	81.3	518	10.9	—	—
Oligomer 8_20%	230	4.9	412	84.3	590	9.7
Oligomer 9_10%						
PU2 ^a	323	15.8	399	75.8	560	6.6
PU5	320	19.5	417	64.3	552	13.6
PU6	285	14.0	420	66.4	580	13.4
PU8_10%	322	26.2	410	58.4	549	12.3
PU8_20%	321	34.4	413	48.1	520	12.5
PU9	302	25.7	441	51.4	574	18.7

^a The data were obtained from Kébir et al.²²

free urethane C=O within the hard segments: (1) dipole–dipole interaction between carbonyls and (2) induced dipole–dipole interaction between aromatic rings.^{12,26–29} After polymerization, the NCO absorption at 2270 cm⁻¹ disappeared totally; this showed that the reaction was completed and that the material possessed its ultimate properties. As expected, the highest was the hydroxyl functionality of the oligomer precursor, and the highest was the intensity of the urethane bands of the final material.

DMTA helps in evaluating the viscoelastic properties of polymer materials such as polyurethanes. In a previous work, thermoplastic polyurethanes based on dihydroxytelechelic polyisoprenes exhibited a very high segregation between soft and hard segments.^{22–24} The same results were obtained with the prepared crosslinked polyurethanes. Generally, T_{α} of hard segments is difficult to observe because of their low concentration within the material and/or their very weak damping efficiency. Examples of DMTA curves showing the temperature dependence of E' and $\tan \delta$ of the polyurethanes are reported in Fig-

ures 6 and 7. The $\tan \delta$ curves are presented below the E' curves. The curve of thermoplastic PU2 was considered the reference and control. The sharpness and height of the damping peak ($\tan \delta_{\max}$) can give information about the degree of order and the freedom of motion of molecules in the soft domains, and the shift of T_{α} is related to the degree of the interaction between the components.²⁶ The values of T_{α} , $\tan \delta_{\max}$, and E' at the rubbery plateau (at 25°C), which is linearly related to the Young's modulus, are depicted in Table III.

A comparison of the $\tan \delta$ behavior of the samples in Figure 6 shows that the polyurethanes PU5 and PU6 based on chain-end-functionalized oligomers (oligomers 5 and 6) exhibited similar values of soft segment T_{α} 's and of the damping efficiency compared to PU2 based on HTPI. This result suggests an absence of interactions between the soft and hard domains and that the average molecular weight between physical and/or chemical knots was similar for these three materials. This result shows also that the difference observed between the values of T_{α} of

TABLE III
 Compositions and Physical Properties of the Prepared Polyurethanes

Polymer code	Precursor code	Hard segment (%) ^a	Appearance ^b	T_{α} (°C)	E' at 25°C by DMTA (MPa)	Soft-segment $\tan \delta_{\max}$	T_g (°C)	Density
PU2 ^c	HTPI	12.6	Y, S, T	-40	13	0.67	-58	0.994
PU5	Oligomer 5	14.1	Y, S, T	-42	157	0.65	-58	1.006
PU6	Oligomer 6	10.5	B, S, O	-42	424	0.63	-58	1.004
PU8_10%	Oligomer 8_10%	23.4	Y, H, O	-28	545	0.36	-42	1.030
PU8_20%	Oligomer 8_20%	30.0	Y, H, O	5	1220	0.25	-25	1.139
PU9	Oligomer 9_10%	16.4	B, H, O	-27	1220	0.36	-41	1.059

^a Hard segment (%) = 100 × Weight of isocyanate/Total weight.

^b B, brownish; H, hard; O, opaque; S, soft; T, transparent; Y, yellowish.

^c The data were obtained from Kébir et al.²²

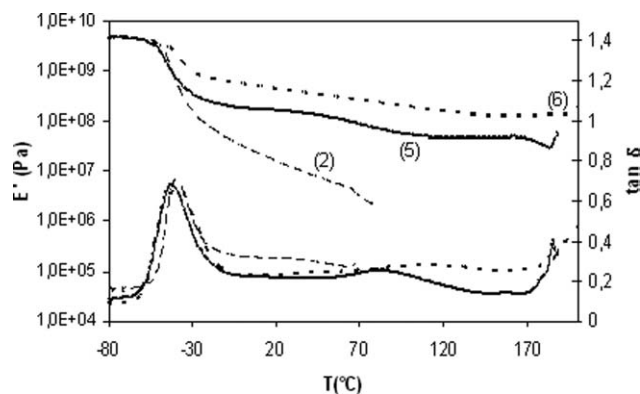


Figure 6 Thermomechanical behavior at 1 Hz of (2) PU2, (5) PU5, and (6) PU6 (T = temperature).

oligomer 5 and HTPI was probably due to physical interactions between chain ends and not to the slight difference of their molecular weights. Typically, T_{α} of the soft segments decreased as their molecular weight increased within polyurethanes.²² However, PU6 and PU2 exhibited approximately the same T_{α} of soft segments, although the molecular weights of their oligomer precursors were different. This result suggests the formation of urea linkages in the middle of the oligomer 6 structure, which was due to the higher reactivity toward isocyanates of the secondary amines, in comparison with the terminal hydroxyl groups. On the other hand, for approximately the same hard segment content, the elastic modulus at 25°C of PU5 and PU6 were 12 and 33 times greater, respectively, than the thermoplastic PU2 one (Table III). In addition, the piercing of the materials by the DMTA probe occurred at about 70°C for PU2 because of thermoplastic softness and above 170°C for PU5 and PU6 because of urethane degradation. Consequently, PU5 and PU6 exhibited a longer rubbery plateau than PU2. The $\tan \delta$ curves of Figure 6 show an additional transition (increasing with hydroxyl functionality) at approximately 85°C for PU5 and about 115°C for PU6, with very weak damping efficiency. This could be assigned to the hard-segment T_{α} value. These results suggest the occurring of chemical crosslinking at the ends of the *cis*-1,4-PI chains, that is, at the hard segments. Nevertheless, the PU6 exhibited a higher elastic modulus than PU5, even when its hard segment content was slightly lower. This suggests that the presence of urea led to an increase in the Young's modulus, which was consistent with previous investigations concerning thermoplastic analogues.²¹

The presence of hydroxyl groups both along the chains and at the end of the chains of oligomer 8_10%, oligomer 8_20%, and oligomer 9_10% led to the obtaining of polyurethanes (PU8_10%, PU8_20%, and PU9, respectively) with high crosslinking

density, that is, with low molecular weight between knots. Indeed, a comparison of the $\tan \delta$ behavior of the samples in Figure 7 reveals an increasing T_{α} of soft segments with \bar{f}_n of the precursors; this led as well to a decrease of the damping efficiency. The increase of the sharpness of the $\tan \delta$ peak with hydroxyl functionality suggests heterogeneous soft domains, which were due to the polydispersity of hydroxyl group distribution within the precursors and/or to the lack of chemical conversion after the gel point. In addition, because of high material rigidity and hardness,²⁷ the elastic moduli of PU8_10%, PU8_20%, and PU9 were 94, 94, and 42 times greater than the thermoplastic PU2 one, respectively.

The DSC analysis of all of the polyurethanes showed only the glass-transition temperatures (T_g) of the *cis*-1,4-PI soft chains. The obtained values of T_g are given in Table III. They were consistent with the T_{α} values obtained by DMTA, with an average standard deviation of 14°C. For oligomer 8_20%, the deviation was 30°C because of its uncertain value of T_{α} related to a large $\tan \delta_{\max}$ value.

The TGA traces under an air atmosphere of all of the prepared polyurethanes showed a three-step degradation. They indicated that the polyurethanes remained stable up to 260°C; after that, the first step of degradation occurred. In the base of a previous TGA study performed on thermoplastic analogues,^{22,33} the first step corresponded mainly to the urethane degradation. The second and the third steps corresponded to the soft segment degradations. Table II shows the weight losses and T_{\max} values for each polyurethane and for each step. Generally, we observed that weight losses observed at the urethane degradation step were consistent with the percentage in weight of hard segments. Indeed, the thermal stability decreased linearly with hard segment content. However, in the case of PU9, the weight loss during the urethane degradation was higher than expected. This could be explained by the lack of thermal stability of oligomer 9.

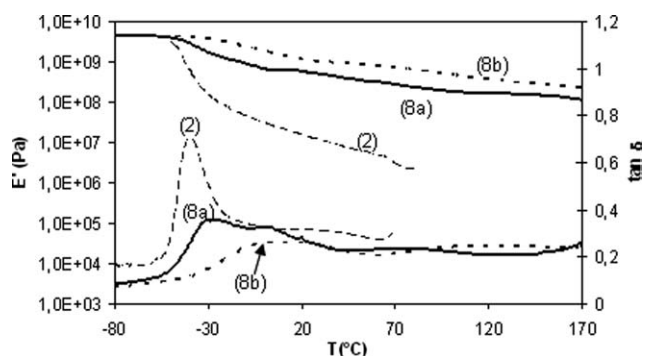


Figure 7 Thermomechanical behavior at 1 Hz of (2) PU2, (8a) PU8_10%, and (8b) PU8_20% (T = temperature).

CONCLUSIONS

In this work, hydroxytelechelic *cis*-1,4-PIs with different chemical structures and functionalities were prepared and characterized. The hydroxyl groups were either located exclusively at the chain ends (oligomer **5** and **6**) or located both along and at the end of the chains (oligomers **8_10%**, **8_20%**, and **9_10%**). They were then reacted with TDI to elaborate new crosslinked polyurethanes. The DMTA and DSC studies allowed distinction between two families of networks. For the first family (based on oligomers **5** and **6**), the average value and distribution of molecular weight between knots were similar to those of the corresponding precursors; the T_α and the damping efficiency were independent of \bar{f}_n . The elastic modulus increased with \bar{f}_n and with the presence of urea groups. For the second family (based on oligomers **8_10%**, **8_20%**, and **9_10%**), the crosslinking density was very high, and the distribution of molecular weight of soft segments was very large. The increase of \bar{f}_n led to an increase of T_α and elastic modulus and led to a decrease of damping efficiency. The TGA results mainly showed a linear loss of thermal stability in terms of weight with hard segment content. In summary, the control of the chemical structures and the functionalities of the precursors allowed us to obtain crosslinked polyurethanes with various and controlled properties. Finally, this work shows the possibility of elaborating a new class of versatile polymer materials from natural rubber, a potential petroleum substitute.

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