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Synthesis of well defined amino telechelic *cis*-1,4-oligoisoprenes from carbonyl telechelic oligomers; first studies of their potentialities as polyurethane or polyurea materials precursors

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Abstract

Carbonyl telechelic *cis*-1,4-oligoisoprene (CTPI) obtained from high molecular weight polyisoprene through an oxidative chain cleavage reaction have been chemically modified. Thus, new well defined amino telechelic *cis*-1,4-oligoisoprenes have been obtained in a mass range of 1600–2300 g/mol according to two different pathways. The first approach involved a standard mesylate displacement by sodium azide followed by smooth reduction using triphenylphosphine. The second pathway implied a reductive amination sequence. Primary or secondary amine functions have thus been selectively obtained at both oligomer chain-ends depending on reaction conditions. Peculiar NMR experiments conducted on these functional oligomers confirmed a precise control of functionality during the chemical modification. Moreover, their abilities to react with toluene diisocyanate or bis(succinimidyl)carbonate have been investigated.

Keywords: Telechelic oligomers; *cis*-1,4-Polyisoprene; Amino-terminated oligomers

1. Introduction

The prominent role of polymers specifically bearing reactive terminated groups is now well established. More particularly, telechelic liquid polymers have proved so far to be of great interest in block copolymers [1], star polymers [2] and polyurethanes [3] synthesis. Though their increased importance as macromolecule precursors, the precise control of chain-end functionalities still remain to be improved as it can be considered as a decisive feature explaining polymers properties [4]. Among the tremendous activity devoted to this research field during the past decade [5], our laboratory suggested a promising approach which consisted in a selective cleavage of high molecular weight synthetic or natural polyisoprene [6–8]. This reaction led to liquid carbonyl telechelic *cis*-1,4-polyisoprene (CTPI) with controlled microstructure, i.e. with precise chain-ends and functionalities ($\bar{f}_n = 2$). Such oligomers can be chemically modified to give polyurethanes hydroxy functionalized precursors. Indeed, hydroxy telechelic polydienes based PUs were found to present particular interest [9–23] in regards to their physico-chemical and mechanical properties such as versatility, elasticity, transparency, chemical inertia, high hydrophobicity and thermal stability. However, synthesis of polyurethanes usually involves the use of toxic tin catalysts and/or isocyanates. Alternatively, polyurethanes can be prepared by non-isocyanate methods involving reactions of diamines with cyclic carbonates [24–29] or bischloroformates [30–32] avoiding any toxic agents. Particularly involved in synthetic polydiene recycling and in polymer synthesis from natural renewable source as well, we report in this article the obtaining from the CTPI of various well defined amino telechelic liquid polyisoprenes and investigated their first abilities to give polyurethane materials.

2. Experimental section

2.1. Materials and instrumentation

The number-averaged molecular weight ($\bar{M}_n$) and

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Table 1
Experimental conditions and results obtained for the synthesis of the carbonyl- and hydroxytelechelic *cis*-1,4-oligoisoprenes

Epoxidation						Periodic acid cleavage					Reduction				
$T=0$ °C Solvent CH_2Cl_2 (600 ml) Time = 6 h						$T=30$ °C Solvent THF (500 ml) Time = 6 h					$T=60$ °C Solvent THF (250 ml) Time = 6 h				
Run	Epoxidation : synthesis of **2**					Periodic acid cleavage : synthesis of **3**					Reduction : synthesis of **5**				
	m_{PI} (g)[a]	m_{EPI} (g)[a]	m_{mCPBA} (g)[a]	τ_{NMR} (%)[b]	Yield (%)[c]	m_{EPI} (g)[a]	m_{CTPI} (g)[a]	Yield (%)[c]	$\bar{M}_{nNMR}$ (g mol^{-1})[d]	$\bar{M}_{nSEC}$ (g mol^{-1})[e]	m_{CTPI} (g)[a]	m_{HTPI} (g)[a]	Yield (%)[c]	$\bar{M}_{nNMR}$ (g mol^{-1})[d]	$\bar{M}_{nSEC}$ (g mol^{-1})[e]
1	14.23	14.20	3.06	5.05	99	14.20	11.84	82	1600	1730	9.01	8.00	89	1900	1760
2	23.00	22.60	4.93	4.33	98	22.10	18.56	83	1660	1730	16.93	16.80	99	1530	1750
3	24.00	23.33	5.15	4.37	97	22.83	18.44	80	1660	1710	16.74	13.55	81	1460	1730
4	24.65	24.48	5.28	4.44	99	26.90	24.85	91	1730	1700	22.50	19.70	87	1600	1690
5	28.75	26.64	5.52	4.76	93	26.65	24.44	90	1660	1530	22.17	19.57	88	1530	1730
6	25.57	25.35	5.48	4.16	99	25.48	21.13	82	1660	1410	18.28	17.40	88	1530	1450
7	24.00	23.94	5.15	4.54	99	25.37	23.34	91	1660	1560	20.58	19.90	90	1600	1590
8	26.62	26.35	5.12	4.35	99	27.74	22.96	82	1800	1510	21.30	19.40	91	1670	1590

[a] m_{PI}, mass of polyisoprene; m_{EPI}, mass of recovery epoxydized polyisoprene; m_{mCPBA}, mass of *m*-chloroperbenzoic acid (about 8% molar versus PI); m_{CTPI}, mass of the recovery carbonyltelechelic polyisoprene; m_{HTPI}, mass of the recovery hydroxytelechelic polyisoprene (100% reduction of the carbonyl end-groups).

[b] τ_{NMR}, epoxidation rate estimated from ^{1}H NMR data from integrations at 2.67 ppm for epoxidized units, and 5.11 ppm for isoprene units.

[c] Yields (%) are the polymers recovery yields.

[d] $\bar{M}_{n\ NMR}$ determined according to the formula: $\bar{M}_{n\ NMR}=[I_{C=CH}/I_{CHOH}]\times 68+104$ (for HTPI); $\bar{M}_{n\ NMR}=[2I_{C=CH}/I_{CH_2CO}]\times 68+100$ (for CTPI).

[e] $\bar{M}_{n\ SEC}$ determined with polystyrene standards and corrected with Benoit factor (0.67 for polyisoprene) ($\bar{M}_{n\ SEC}PI = 0.67\times\bar{M}_{n\ SEC}PS$)

molecular weight distribution (PDI) were measured at 35 °C on a ThermoFinnigan SEC instrument (equipped with a SpectraSYSTEM AS1000 autosampler, a SpectraSYSTEM UV2000 and a SpectraSYSTEM RI150 detectors), using a polymer laboratories (PL) gel 5 μm MIXED-D columns, calibrated with a series of standard polystyrenes (580–483×10^3 g mol^{-1}). THF (1.0 ml/min) was used as eluent. Polystyrene standardized molecular weights were corrected by the Benoît factor *B* according to known formula [33]. ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER 400 Fourier transform spectrometer at 400.13 and 100.62 MHz, respectively. ^{1}H data are reported as follow: chemical shift (multiplicity: s: singlet, t: triplet, q: quadruplet and m: multiplet, integration and peak assignments). Chemical shifts are reported in ppm down-field from tetramethylsilane (TMS). ^{13}C data are reported as follow: chemical shift (peak assignments). Isoprenic moieties chemical shifts are similar for all oligomers and described as follow: ^{1}H NMR ($CDCl_3$) δ (ppm): 5.10 (t, =C*H*$_{isoprenic}$), 2.05 (m, C*H*$_{2\ isoprenic}$), 1.70 (s, C*H*$_{3\ isoprenic}$). ^{13}C NMR ($CDCl_3$) δ (ppm): 134.7 (*C*=CH$_{isoprenic}$), 124.5 (C=*C*H$_{isoprenic}$), 31.7 (*C*H$_2$-C=CH$_{isoprenic}$), 25.9 (*C*H$_2$CH=C$_{isoprenic}$), 23.0 (*C*H$_{3\ isoprenic}$). Only chain-end chemical shifts will be detailed in all NMR spectra. IR spectra were recorded on a Fourier transform Perkin–Elmer 1750 spectrometer in the 4000–500 cm^{-1} range. A diamond ATR device (attenuated total reflexion) was used for the insoluble products, though soluble samples spectra were obtained using KBr pellets. MALDI-TOF mass spectra (ms) were recorded on a Bruker Biflex III equipped with a nitrogen laser (λ=337 nm). All ms were obtained in the linear mode with an acceleration voltage of 19 kV. The irradiation targets were prepared from THF or CH_2Cl_2 solutions using dithranol as matrix and ammonium acetate as dopant. *cis*-1,4-Polyisoprene **1** (ACROS organics, 98% *cis*, $\bar{M}_w = 800,000$) was dissolved in dichloromethane (25 g in 500 ml, 0.7 M solution), and precipitated in ethanol (500 ml) prior to use. SEC analysis performed after this treatment conducted to the following results: $\bar{M}_n = 184,000$, $\bar{M}_w = 537,000$, PDI=2.9. Most reagents and solvents were commercially available reagent grade chemicals and used without further purification. All reported yields are based on oligomers recovered after reaction. Most organic reactions are performed under an inert atmosphere.

2.2. Oligomers synthesis

2.2.1. Preparation of carbonyl telechelic cis-1,4-oligoisoprene 2

High molecular weight *cis*-1,4-polyisoprene **1** was epoxidized by reaction of *m*-chloroperbenzoic acid and cleavage of oxirane units was performed with periodic acid according to the method previously described [7]. For present work, *m*-chloroperbenzoic acid (4.32 g, 176 mmol) (JANSSEN, 70% according titration) in 100 ml of CH_2Cl_2 (0.176 mol l^{-1}) were added dropwise to a solution of *cis*-1,4-polyisoprene (23.93 g, 352 mmol) in 500 ml of 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 (27.8 g, 404 mmol, 5% epoxidized) dissolved in 400 ml of THF (1.0 mol l^{-1}), periodic acid (H_5IO_6) (5.07 g, 20 mmol) (ACROS, 99%) in 50 ml of THF was added dropwise in a jacketed reaction flask at 30 °C (reaction time: 6 h) (yield=80–91%) (Table 1).

^{1}H NMR ($CDCl_3$) δ (ppm): 9.77 (s, 1H, CH_2CHO), 2.49 (m, 2H, C*H*$_2$CHO), 2.34 (m, 2H, C*H*$_2$CH$_2$CHO), 2.13 (s, 3H, C*H*$_3$COCH$_2$), 2.43 (t, 2H, CH$_3$COC*H*$_2$CH$_2$), 2.25 (m, 2H, CH$_3$COCH$_2$C*H*$_2$). ^{13}C NMR ($CDCl_3$) δ (ppm): 201.61 (CH$_2$*C*HO), 41.88 (*C*H$_2$CHO), 21.81 (*C*H$_3$COCH$_2$), 43.53 (CH$_3$CO*C*H$_2$), 208.21 (CH$_3$*C*OCH$_2$).

FTIR: $\nu_{H-C=C}$=3035 cm^{-1}; ν_{CH_2,CH_3}=2900–2730 cm^{-1}; $\nu_{C=O}$=1721 cm^{-1}; $\nu_{C=C}$=1664 cm^{-1}; $\nu_{CH_2,CH_3\ cis\text{-}1,4\text{-}isoprene}$=1448, 1376 cm^{-1}; $\delta_{C=C-H}$=834 cm^{-1}.

2.2.2. Hydroxy telechelic cis-1,4-oligoisoprene 3

In a jacketed reaction flask was introduced THF (100 ml) and sodium borohydride (4 mol equivalents). The solution was then warmed to 30 °C and a 200 ml THF solution of carbonyl telechelic *cis*-1,4-oligoisoprene **2** was added dropwise. After stirring for 6 h at 60 °C, the reaction mixture was hydrolyzed with ice, washed using saturated aqueous NaCl (250 ml) and dried ($MgSO_4$). The organic layer was finally concentrated to dryness leading to the desired hydroxy telechelic oligomer **3** (Table 1).

^{1}H NMR ($CDCl_3$) δ (ppm): 3.80 (m, 1H, C*H*OH), 3.65 (t, 2H, C*H*$_2$OH), 1.20 (d, 3H, C*H*$_3$CHOH). ^{13}C NMR ($CDCl_3$) δ (ppm): 67.5 (CH$_3$*C*HOH), 62.5 (*C*H$_2$OH), 39.0 (*C*H$_2$CH(OH)CH$_3$), 30.5 (*C*H$_2$CH$_2$OH).

FTIR: disappearance of $\nu_{C=O}$ at 1721 cm^{-1}; ν_{OH}=3350 cm^{-1}; ν_{C-C-H}=3035 cm^{-1}; ν_{CH_2,CH_3}=2900–2730 cm^{-1}; $\nu_{C=C}$=1664 cm^{-1}; $\nu_{CH_2,CH_3\ cis\text{-}1,4\text{-}isoprene}$=1448, 1376 cm^{-1}; $\delta_{C=C-H}$=834 cm^{-1}.

SEC: $\bar{M}_n = 2900$, $\bar{M}_w = 5350$, PDI=1.8.

2.2.3. Mesyl telechelic cis-1,4-oligoisoprene 4

To a solution of hydroxy telechelic *cis*-1,4-oligoisoprene **3** (1 g, 0.576 mmol) and triethylamine (241 μl, 1.728 mmol) in dichloromethane (3.5 ml) was added dropwise mesyl chloride (107 μl, 1.382 mmol) at 0 °C. After keeping the solution at 0 °C for 30 min, the mixture was allowed to stir at room temperature for 24 h. The organic solution was then cooled down, diluted with dichloromethane (4 ml), washed with water (2×5 ml) and dried over $MgSO_4$. The solution was finally concentrated to dryness yielding 80% of product **4**.

^{1}H NMR ($CDCl_3$) δ (ppm): 4.80 (m, 1H, C*H*OSO$_2$CH$_3$), 4.19 (t, 2H, C*H*$_2$OSO$_2$CH$_3$), 3.0 (s, C*H*$_3$SO$_2$OCH$_2$), 2.97 (s, C*H*$_3$SO$_2$OCH), 1.42 (d, 3H, C*H*$_3$CHOSO$_2$CH$_3$). ^{13}C NMR ($CDCl_3$) δ (ppm): 79.5 (CH$_3$*C*HOMs), 69.1 (*C*H$_2$OMs), 39.5 (*C*H$_2$CH(OMs)CH$_3$), 36.9 (*C*H$_3$SO$_2$OCH$_2$), 36.5 (*C*H$_3$SO$_2$-OCH), 29.8 (*C*H$_2$CH$_2$OMs), 20.7 (*C*H$_3$CHOMs).

FTIR: disappearance of ν_{OH} at 3350 cm^{-1}; $\nu_{C=C-H}$=

3035 cm^{-1}; ν_{CH_2,CH_3} = 2900–2730 cm^{-1}; $\nu_{C=C}$ = 1664 cm^{-1}; ν_{CH_2,CH_3} *cis*-1,4-isoprene = 1448, 1376 cm^{-1}; $\nu_{-SO2-O-}$ = 1361, 1167 cm^{-1}; $\delta_{C=C-H}$ = 834 cm^{-1}.

SEC: $\bar{M}_n$ = 2750, $\bar{M}_w$ = 5400, PDI = 2.0.

2.2.4. Azido telechelic cis-1,4-oligoisoprene **5**

A mixture of mesyltelechelic *cis*-1,4-oligoisoprene **4** (0.414 g, 0.22 mmol) and sodium azide (NaN_3, 0.035 g, 0.528 mmol) (Aldrich, 99%) in 2 ml of DMF was stirred for 24 h at 75 °C. The solution was then poured into 4.5 ml of cold water followed by an extraction with Et_2O (4×5 ml). The organic layer was finally dried ($MgSO_4$) and the solvent was removed under reduced pressure to give the oligomer **5** (yield = 70%).

^{1}H NMR ($CDCl_3$) δ (ppm): 3.40 (m, 1H, CHN_3), 3.25 (t, 2H, CH_2N_3), 1.25 (d, 3H, CH_3CHN_3). ^{13}C NMR ($CDCl_3$) δ (ppm): 66.7 (CH_3CHN_3), 60.5 (CH_2N_3), 37.5 (CH_2CHN_3-CH_3), 29.9 ($CH_2CH_2N_3$), 22.0 (CH_3CHN_3).

FTIR: $\nu_{C=C-H}$ = 3035 cm^{-1}; ν_{CH_2,CH_3} = 2900–2730 cm^{-1}; ν_{N3} = 2096 cm^{-1}; $\nu_{C=C}$ = 1664 cm^{-1}; ν_{CH_2,CH_3} *cis*-1,4-isoprene = 1448, 1376 cm^{-1}; $\delta_{C=C-H}$ = 834 cm^{-1}.

SEC: $\bar{M}_n$ = 2900, $\bar{M}_w$ = 5500, PDI = 1.9.

2.2.5. Amino telechelic cis-1,4-oligoisoprene **6**

In a round bottom flask was introduced triphenylphosphine (0.06 g, 0.224 mmol), azidotelechelic *cis*-1,4-oligoisoprene **5** (0.2 g, 0.112 mmol), water (2.5 ml) and THF (3 ml) and the reaction mixture was then vigorously stirred at room temperature. After 24 h stirring, the organic solution was washed (3 ml of water), extracted with diethylether and dried over $MgSO_4$. Solvents were finally removed under reduced pressure to give the amino derivative **6** (yield: 79%).

^{1}H NMR ($CDCl_3$) δ (ppm): 2.88 (m, 1H, $CHNH_2$), 2.68 (t, 2H, CH_2NH_2), 1.05 (d, 3H, CH_3CHNH_2). ^{13}C NMR ($CDCl_3$) δ (ppm): 37.5 (CH_3CHNH_2), 33.9 (CH_2NH_2), 32.4 ($CH_2CH(NH_2)CH_3$), 29.9 ($CH_2CH_2NH_2$), 21.5 (CH_3-$CHNH_2$).

FTIR: ν_{NH} = 3324 cm^{-1}; $\nu_{C=C-H}$ = 3035 cm^{-1}; ν_{CH_2,CH_3} = 2900–2730 cm^{-1}; $\nu_{C=C}$ = 1664 cm^{-1}; ν_{CH_2,CH_3} *cis*-1,4-isoprene = 1448, 1376 cm^{-1}; $\delta_{C=C-H}$ = 834 cm^{-1}.

SEC: $\bar{M}_n$ = 2300, $\bar{M}_w$ = 4500, PDI = 2.0.

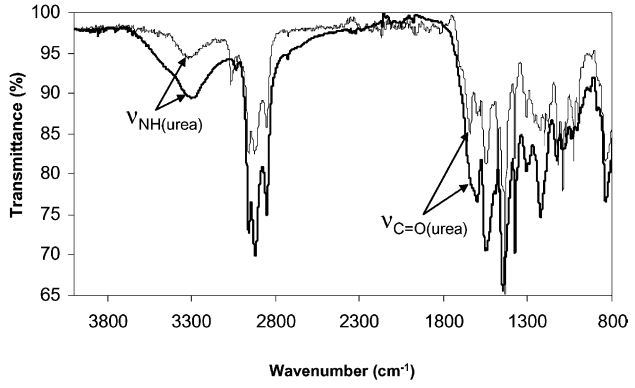


Fig. 1. FTIR spectra of the: (—) polyurea based on *n*butyl amino telechelic *cis*-1,4-polyisoprene and (- - -) polyurea based on amino telechelic *cis*-1,4-polyisoprene.

2.2.6. α-Amino, ω-carbonyl cis-1,4-oligoisoprene **7**

Carbonyltelechelic *cis*-1,4-oligoisoprene **2** (1 g, 0.60 mmol) and ammonium acetate (1.39 g, 18 mmol) (ACROS) in dichloroethane (17.5 ml) were mixed into a three-necked round bottom flask. The solution was then treated with sodium triacetoxyborohydride (0.368 g, 1.68 mmol) (ACROS, 97%) and glacial acetic acid (35 µl, 0.60 mmol) at room temperature. After 24 h stirring, the reaction mixture was washed with 1 N NaOH solution and the product was extracted with Et_2O. The organic layer was then dried ($MgSO_4$) and concentrated to dryness yielding 86% of product **7**.

^{1}H NMR ($CDCl_3$) δ (ppm): 2.68 (t, 2H, CH_2NH_2), 2.43 (t, 2H, $CH_2C(O)CH_3$), 2.13 (s, 3H, CH_3CO). ^{13}C NMR ($CDCl_3$) δ (ppm): 208.2 (CO), 43.5 (CH_2CO), 21.9 (CH_3CO), 31.7 ($CH_2C{=}CH_{isoprenic}$), 30.0 ($CH_2CH_2NH_2$).

FTIR: ν_{NH} = 3324 cm^{-1}; $\nu_{C=C-H}$ = 3035 cm^{-1}; ν_{CH_2,CH_3} = 2900–2730 cm^{-1}; $\nu_{C=O}$ = 1721 cm^{-1}; $\nu_{C=C}$ = 1664 cm^{-1}; ν_{CH_2,CH_3} *cis*-1,4-isoprene = 1448, 1376 cm^{-1}; $\delta_{C=C-H}$ = 834 cm^{-1}.

2.2.7. nButyl-amino telechelic cis-1,4-oligoisoprene **8**

Same procedure than for compound **7** but replacing ammonium acetate by *n*butylamine (0.126 ml, 1.26 mmol) (Aldrich, 99%).Yield: 86%.

^{1}H NMR ($CDCl_3$) δ (ppm): 2.60 (m, 7H, CH_2NH and $CHNH$), 1.50 (m, 4H, CH_2CHNH), 1.35 (m, 8H, $CH_{2\ butyl\ chain}$), 1.1 (s, 2H, N*H*), 1.05 (d, 3H, CH_3CHNH), 0.90 (t, 6H, $CH_{3\ butyl\ chain}$). ^{13}C NMR ($CDCl_3$) δ (ppm): 61.7 (CH_3-$CHNH$), 52.1 (CH_2NH), 39.1 (CH_2CHNH), 30.0 (CH_2CH_2-NH_2), 22.4 (CH_3CHNH), 19.5 ($CH_{2\ butyl\ chain}$), 12.9 ($CH_{3\ butyl\ chain}$).

FTIR: disappearance of $\nu_{C=O}$ at 1721 cm^{-1}; ν_{NH} is not detected, $\nu_{C=C-H}$ = 3035 cm^{-1}; ν_{CH_2,CH_3} = 2900–2730 cm^{-1}; $\nu_{C=C}$ = 1664 cm^{-1}; ν_{CH_2,CH_3} *cis*-1,4-isoprene = 1448, 1376 cm^{-1}; $\delta_{C=C-H}$ = 834 cm^{-1}.

SEC: $\bar{M}_n$ = 1600, $\bar{M}_w$ = 2870, PDI = 1.8.

2.2.8. Methylcarboxylate telechelic cis-1,4-oligoisoprene **9**

To a solution of hydroxytelechelic *cis*-1,4-oligoisoprene **3** (0.3 g, 0.17 mmol) in dry pyridine (40 ml) was added dropwise 40 ml of acetic anhydride (0.42 mol). The reaction mixture was left to stir at 70 °C. After 4 h, the organic solution was cooled down and hydrolyzed with 20 ml of cold water during 2 h. The organic layer was then concentrated under vacuum, dissolved in dichloromethane, washed with water and finally dried over $MgSO_4$. Concentration to dryness afforded pure **9** derivative (99% yield).

^{1}H NMR ($CDCl_3$) δ (ppm): 4.88 (m, 1H, $CHOAc$), 4.03 (t, 2H, CH_2Oac), 2.10 (s, 6H, CH_3CO), 1.20 (d, 3H, CH_3CHOAc). ^{13}C NMR ($CDCl_3$) δ (ppm): 170.5 (CO), 70.2

(CH_3CHOAc), 63.7 (CH_2OAc), 35.7 (CH_2CHOAc), 27.5 (CH_2CH_2OAc), 20.5 (CH_3CO), 19.5 (CH_3CHOAc).

FTIR: disappearance of ν_{OH}; $\nu_{C=C-H}=3035\ cm^{-1}$; $\nu_{CH_2,CH_3}=2900–2730\ cm^{-1}$; $\nu_{C=O}=1739\ cm^{-1}$; $\nu_{C=C}=1664\ cm^{-1}$; $\nu_{CH_2,CH_3\ cis\text{-}1,4\text{-isoprene}}=1448,\ 1376\ cm^{-1}$; $\nu_{C=O\ ester}=1212\ cm^{-1}$; $\delta_{C=C-H}=834\ cm^{-1}$.

SEC: $\bar{M}_n=2050$, $\bar{M}_w=4300$, PDI=2.1.

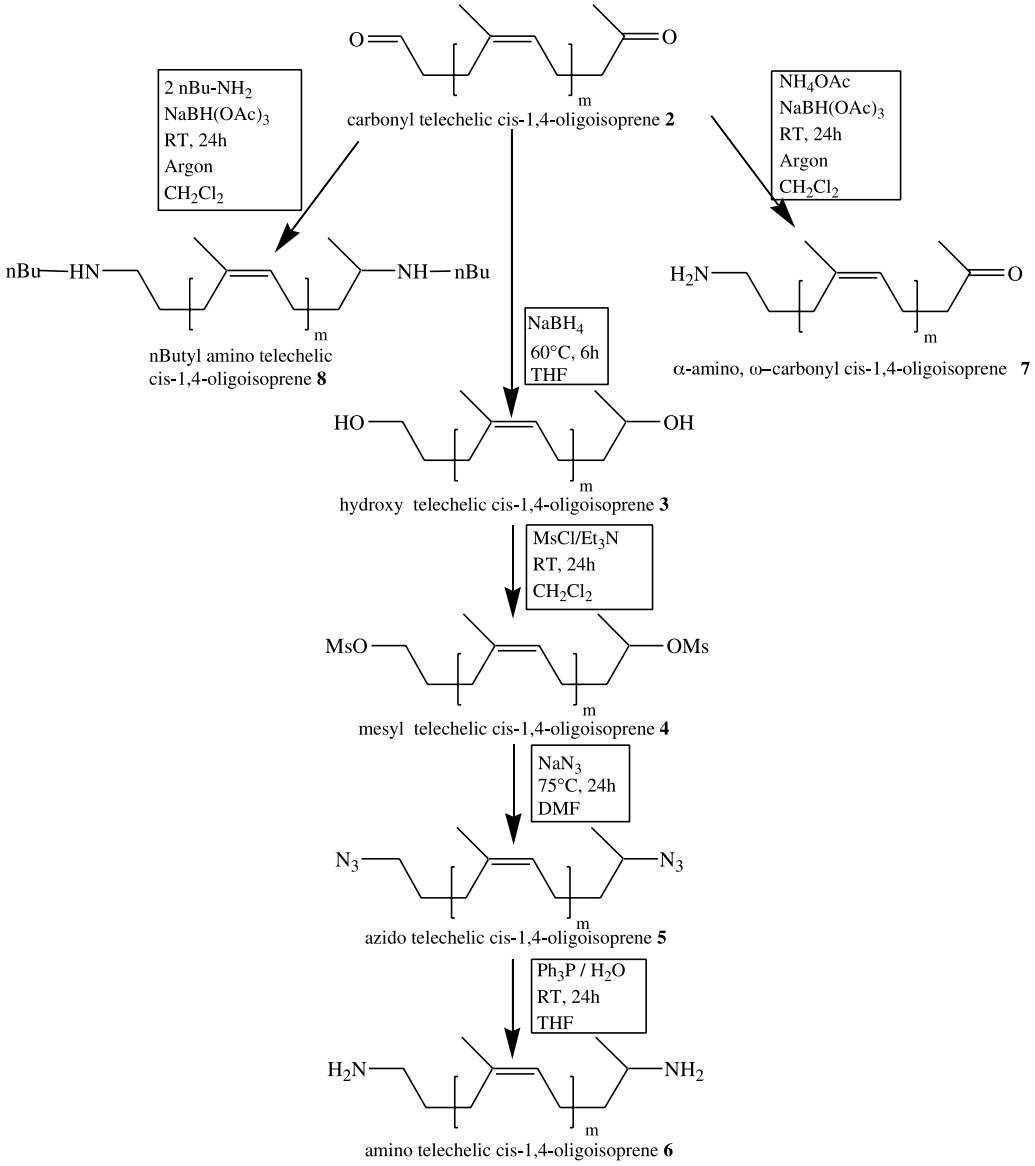
2.3. Polyurethane prepolymer synthesis

N-hydroxysuccinimide (55 mg, 0.48 mmol) was added to a solution of 1,4-butanediolbis(chloroformate) (27 μl 0.17 mmol, Aldrich, 97%) dissolved in a 10 ml mixture of toluene/dichoromethane (2/1). Freshly distilled triethylamine (44.9 μl (0,32 mmol) was then dropwise introduced. After stirring at room temperature for 3 h, aminotelechelic *cis*-1,4-oligoisoprene **6** (231 mg, 0.12 mmol) dissolved in 2 ml dichloromethane was carefully added. After 2 h reaction, the mixture was concentrated under vacuum. The crude layer was further dissolved in dichloromethane, washed with saturated aqueous sodium chloride and dried ($MgSO_4$). Finally, concentration of the organic solution afforded the expected prepolymer.

^1H NMR ($CDCl_3$) δ (ppm): 4.37 (t, 4H, CH_2O), 4.10 (t, 4H, CH_2OCONH), 3.10 (m, 1H, $CH_3CH_{carbamate}$), 2.85 (m, 2H, $CH_{2\ carbamate}$), 2.65 (m, 8H, $CH_{2\ succinimidyl}$).

FTIR: disappearance of ν_{NH}; $\nu_{C=C-H}=3035\ cm^{-1}$; $\nu_{CH_2,CH_3}=2900–2730\ cm^{-1}$; $\nu_{C=O}=1812,\ 1788,\ 1740,\ 1712\ cm^{-1}$; $\nu_{C=C}=1664\ cm^{-1}$; $\nu_{CH_2,CH_3\ cis\text{-}1,4\text{-isoprene}}=1448,\ 1376\ cm^{-1}$; $\delta_{C=C-H}=834\ cm^{-1}$.

SEC: $\bar{M}_n=5200$, $\bar{M}_w=14,800$, PDI=2.83.



Scheme 1. Synthesis of various amino telechelic *cis*-1,4-oligoisoprenes from carbonyl telechelic precursor **2**.

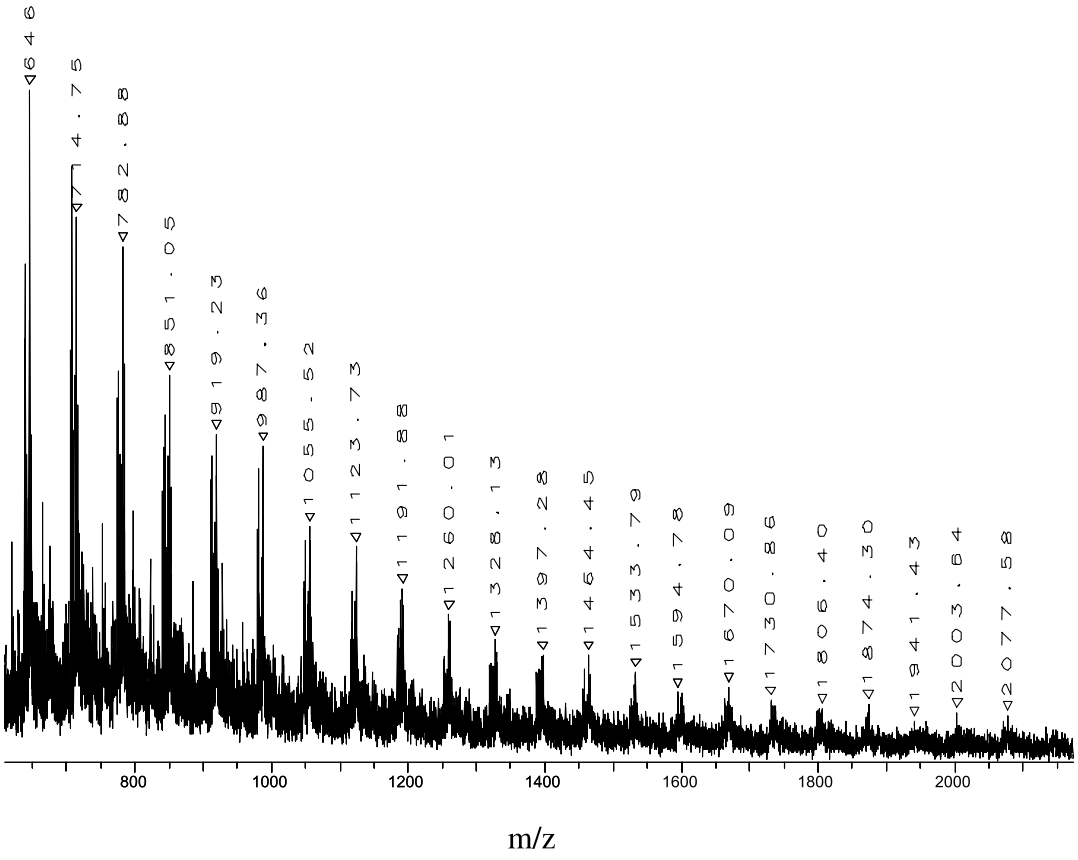


Fig. 2. MALDI-TOF mass spectrum of the amino telechelic *cis*-1,4-polyisoprene **6**.

2.4. Polyureas synthesis

To a solution of amino telechelic *cis*-1,4-oligoisoprene **6** or *n*butyl amino telechelic *cis*-1,4-oligoisoprene **8** dissolved in THF (1 g/ml) was added dibutyltin dilaurate (DBTL) (Aldrich, 95%) as catalyst ($[NH_2]/[DBTL] = 22$). Toluene diisocyanate (Aldrich, 95%) was finally introduced with a ratio of $[NCO] = 1.2 \times [NH_2]$. The solution was then casted in a PTFE mould under argon for 2 h. The film formed after usual treatment (solvent evaporated and film cured at 60 °C for 12 h) appeared insoluble in standard organic solvents. No residual isocyanate was detected after 12 h reaction time (Fig. 1).

FTIR-ATR: No isocyanate bands (complete conversion). ν_{NH}: 3321 cm^{-1}; ν_{CH_2,CH_3}: 2960–2853 cm^{-1}; $\nu_{C=C}$: 1664 cm^{-1}; $\nu_{C=O}$ (urea): 1641 cm^{-1}; $\delta_{C=C-H} = 834$ cm^{-1}.

3. Results and discussion

3.1. Amino telechelic cis-1,4-oligoisoprene synthesis

The first approach to get aminotelechelic oligoisoprene derivatives was envisaged through the sequence outlined in Scheme 1. The first step, based on a carbonyltelechelic *cis*-1,4-oligoisoprene reduction, was performed using mild agent such as sodium borohydride so that no internal unsaturations reduction occured. The reaction, conducted in THF, was found to be highly selective. In order to avoid mixtures due to partial reduction at room temperature, the reaction was warmed to 60 °C and complete carbonyl reduction was observed as confirmed by FTIR. Moreover, high reproducibility was observed on larger scale as illustrated in Table 1. The obtained hydroxytelechelic *cis*-1,4-oligoisoprene **3** was then mesylated using methanesulfonyl chloride in presence of triethylamine leading to **4** in high yield. This methylsulfonyltelechelic *cis*-1,4-oligoisoprene **4** was further converted to the azidotelechelic *cis*-1,4-oligoisoprene **5** by reaction with sodium azide in DMF. Its reduction was finally performed under mild conditions using triphenylphosphine as already described in the literature and led to the expected aminotelechelic *cis*-1,4-oligoisoprene **6**. All synthesized oligomers were fully characterized by spectroscopic and chromatographic methods (Section 2) as well as by MALDI-TOF (Fig. 2). The overall yield of this synthesis did not exceed 35% which prompted us to develop an alternative approach based on direct reductive amination starting from initial carbonyltelechelic *cis*-1,4-oligoisoprene.

Particularly, the functionality of the obtained oligomers was carefully checked either by NMR analysis or through chemical modifications. Indeed, quantitative determination

of hydroxyl units present in polymers is still a challenge owing to their low concentration in the global polymer mass [34]. Direct NMR spectroscopic analysis have been performed in the past on polymer large scales in order to get accurate microstructure determination [35]. Thus, the ^{1}H NMR analysis of hydroxytelechelic polybutadienes obtained through radical [36] or anionic [37] polymerization, in conjunction with accurate measurement of molecular weight values allowed the simultaneous determination of the number average functionality ($\bar{f}_n$) and the identification of the functional units at the chain-ends. In the present work, ^{1}H and ^{13}C NMR studies showed a good signal resolution especially of the characteristic chain-end entities due to the polymers low molecular weights. Chemical modifications performed on the hydroxytelechelic *cis*-1,4-oligoisoprene **3** were combined with NMR experiments to reach precise determination of the functionality. Thus, oligoisoprene chain-ends acetylation using acetic anhydride was conducted in dry pyridine affording product **9** which has been fully characterized (Section 2). Average hydroxytelechelic oligomer functionality was calculated by NMR analysis according to the following formula using naphtalene as internal standard:

$$\bar{f}_n = \frac{[I_{\mathbf{CH}_2\mathrm{OH}}/2 + I_{\mathbf{CH}\mathrm{OH}}]}{[I_{\mathrm{naphtalene}}/8][m_{\mathrm{naphtalene}}/m_{\mathrm{HTPI}}][\bar{M}_n/M_{\mathrm{naphtalene}}]}$$

with $I_{\mathbf{CH}_2\mathrm{OH}}$: signal integration of the CH_2 protons in α position of hydroxyl units at one chain-end of **3** (at 3.65 ppm).

$I_{\mathbf{CH}\mathrm{OH}}$: signal integration of the CH proton in α position of hydroxyl units at the other chain-end of **3** (at 3.8 ppm).

$I_{\mathrm{CH\ ethylenic}}$: signal integration of the ethylenic proton at 5.10 ppm.

$I_{\mathrm{naphtalene}}$: signal integration of the naphtalene protons at 7.45 and 7.85 ppm.

Depending on product purity, the $\bar{f}_n$ calculated values were found to vary between 1.8 and 2.0. It was possible to adjust the formula taking into account the degree of purity (dichloromethane and THF as main impurities). Thus the previous formula became:

$$\bar{f}_n = \frac{[I_{\mathbf{CH}2\mathrm{OH}}/2 + I_{\mathbf{CH}\mathrm{OH}}]}{[I_{\mathrm{naphtalene}}/8][m_{\mathrm{naphtalene}}/m_{\mathrm{HTPI}}\mathrm{dp}][\bar{M}_n/M_{\mathrm{naphtalene}}]}$$

with dp (degree of purity) $= [\bar{M}_n \times 100]/[\bar{M}_n + \bar{M}_{\mathrm{THF}}(I_{\mathrm{THF}}/4) + M_{\mathrm{CH2Cl2}}(I_{\mathrm{CH2Cl2}}/2)]$ and I_{THF}: signal integration of the two CH_2 protons corresponding to remaining THF (at 3.86 ppm).

$I_{\mathrm{CH_2Cl_2}}$: signal integration of the remaining dichloromethane protons at 5.3 ppm.

All calculations confirmed that $\bar{f}_n$ value were corresponding to 2.0 ± 0.1.

In addition, an other set of experiments were conducted using trifluoroacetic anhydride and led to trifluorinated acetoxy chain-ends oligoisoprene [38]. In this case, ^{19}F NMR analysis showed characteristic signals centered at

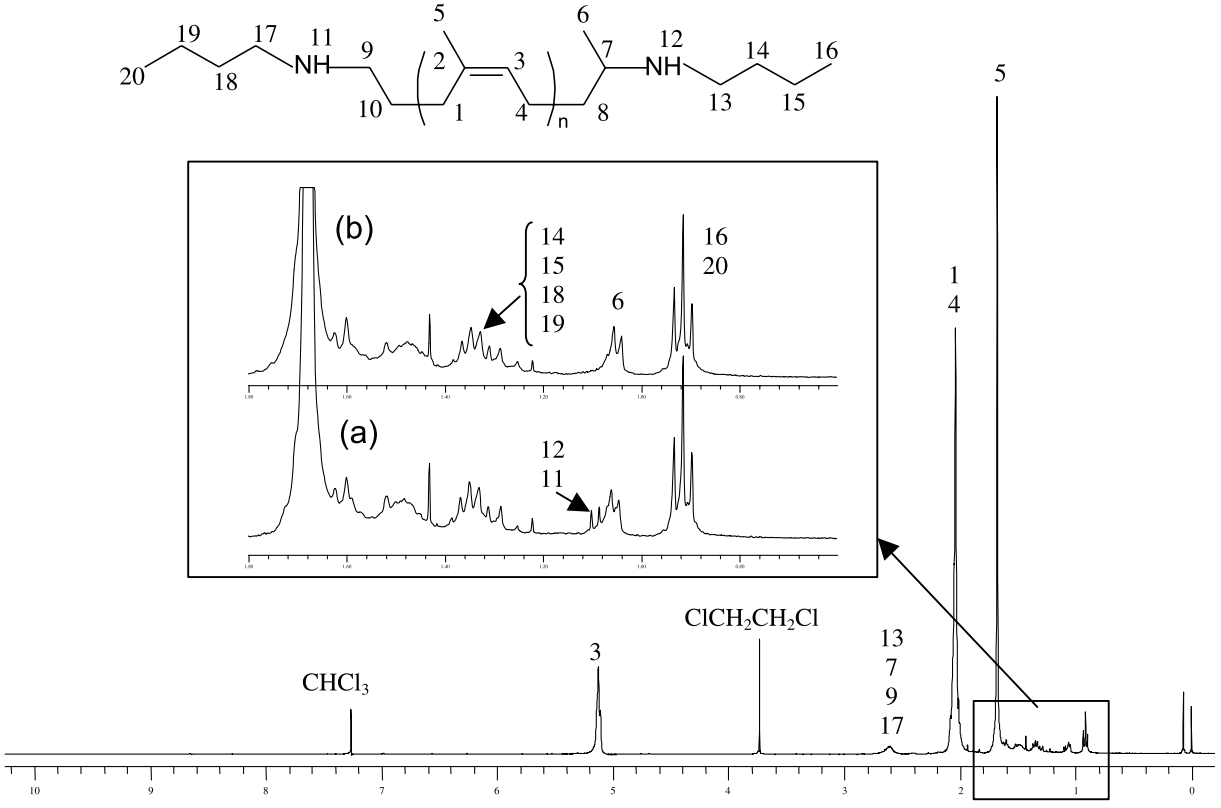


Fig. 3. ^{1}H NMR spectrum of the *n*butyl amino telechelic *cis*-1,4-polyisoprene **8** (a) before addition of D_2O; (b) after addition of D_2O.

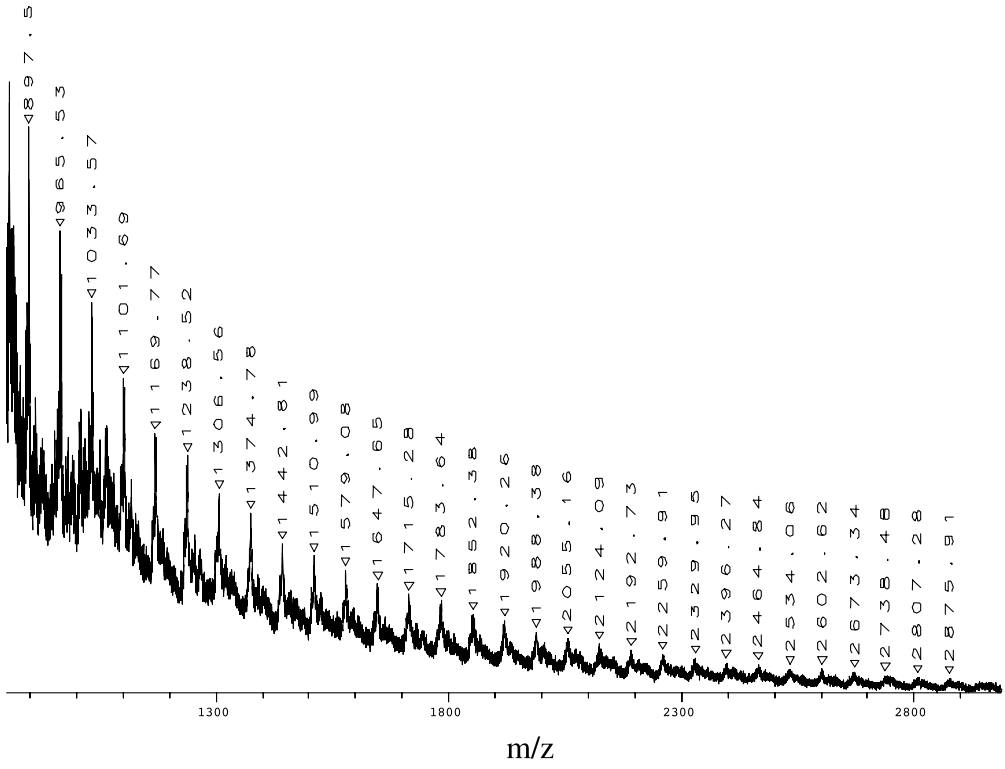
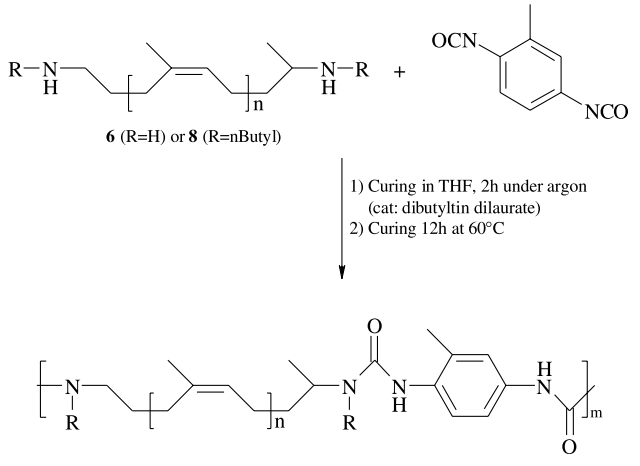


Fig. 4. MALDI-TOF mass spectrum of the *n*butyl amino telechelic *cis*-1,4-polyisoprene **8**.

−75.60 and −75.85 ppm corresponding to the two trifluoroacetyl groups localized at the oligomer both ends. From a similar calculation procedure than previously described with trifluorotoluene (TFT) as internal standard conducted to an identical result ($\bar{f}_n = 2.1 \pm 0.1$).

The second alternative approach leading to aminotelechelic *cis*-1,4-oligoisoprenes involved a reductive amination reaction starting from carbonyltelechelic precursor. This procedure was found to be a convenient methodology in order to quickly shift from carbonyl to amino end chain groups. The overall process can be described as a two steps



Scheme 2. Polymer obtaining from reaction of amino telechelic *cis*-1,4-oligoisoprene **6** or *n*butyl amino telechelic *cis*-1,4-polyisoprene **8** with toluene diisocyanate.

reaction with initial formation of imine or iminium intermediates. These highly reactive groups, obtained by condensation of amine onto carbonyl entities, can be secondly reduced in situ. A wide palette of reducing agents are described in the literature. Thus, strong reducing agents such like platinum, palladium or nickel catalysts demonstrated their high activity. Nevertheless, in order to avoid any possible reduction of the isoprenic structure unsaturations, we decided to move to smoother conditions and reagents. For this reason, we selected modified borohydride derivatives, well known to react under milder conditions [39]. Among all borohydrides developed, sodium cyanoborohydride appeared to be one of the most widespread reagent so far. Its stability combined with its high selectivity are indeed well established [40]. Unfortunately, it generates toxic by-products which forbid its use on large scales. Thus we focused on triacetoxyborohydride [$NaBH(OAc)_3$] as the best compromise between reactivity and toxicity. As already described [41,42] this reagent was found as a first rate catalyst in many reductive amination involving either aliphatic or aromatic amines and both aldehydes or ketones. First reactions were carried out from carbonytelechelic oligomers using a slight excess of *n*butylamine (5 mol%). After 24 h at room temperature, we observed, by NMR monitoring, the disappearance of the aldehydic proton signal ($\delta = 9.8$ ppm) and the methylketone signal ($\delta =$ 2.10 ppm) (Scheme 1). Concomitantly, characteristic *n*butyl end groups signals evolved at $\delta = 0.9$ ppm (CH_3), $\delta = 1.2$–1.4 ppm (CH_2) and $\delta = 2.6$ ppm (NCH_2 and CHN).

Table 2
Main characteristics of polyurea materials obtained from amino telechelic precursors

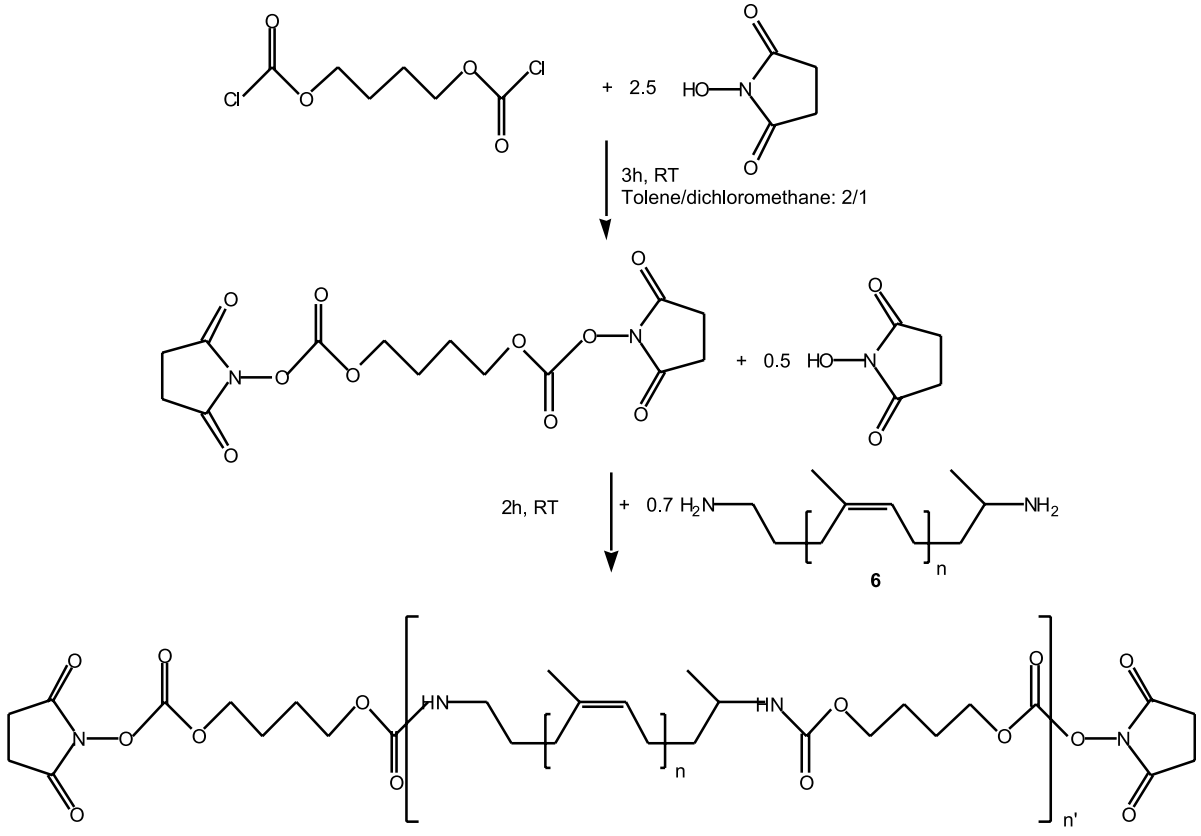
Polyurea	Appearance	T_α (°C)[a]	T_g (°C)	Young modulus (MPa)[a]	Density
Based on α,ω-diamino precursor	Brownish, soft, transparent	−38	−54	192.0	0.989
Based on α,ω-di-*n*Butyl amino precursor	Brownish, soft, transparent	−40	−54	30.3	0.879

[a] Determined by dynamic mechanic termal analysis (DMTA) at $T=25$ °C.

Moreover, a deuterium exchange experiment allowed us to precisely localize the two NH signals at $\delta=1.08$ and 1.10 ppm (Fig. 3). Further MALDI-TOF MS analysis unambiguously confirmed the expected oligoisoprene structure **8** (Fig. 4). When *n*butylamine was used in default, a mixture of oligomers was obtained indicating that no selectivity occured during the iminium formation step. This observation might be explained by the similar reactivity of both aldehyde and ketone entities toward primary amine. On the contrary, the use of excess ammonium acetate (14 mol%) in a similar manner afforded α-amino, ω-carbonyl *cis*-1,4-oligoisoprene **7** (Scheme 1). The reaction monitored by ^{1}H NMR present indeed a complete disappearance of the aldehydic proton signal whereas the methylketone moiety seemed unchanged as demonstrated by the methyl signal still present even after 24 h at room temperature. This surprising selectivity between the two carbonyl end chain groups can be related to the lowest reactivity of the ammonium salt under these conditions. Unfortunately, an increase of the reaction temperature (40 °C) led to self polycondensations. On the other hand, amino and *n*butyl amino telechelic oligomers, like hydroxy and carbonyl telechelic ones, are stable at room temperature under air. Actually, no change in these oligomers properties (molecular weights, spectroscopic analyses and physical aspect) is observed after several months.

3.2. Polyurea and polyurethane prepolymer synthesis

Two different classes of materials were focused in order to evaluate the potentialities of previous functional amino and *n*butyl amino telechelic oligomers. First, the reactivity of the amine units toward toluene diisocyanate was investigated (Scheme 2). FTIR–ATR analysis performed on the obtained material showed complete disappearance of isocyanate functions with concomitant evolvement of a



Scheme 3. Synthesis of polyurethane prepolymer.

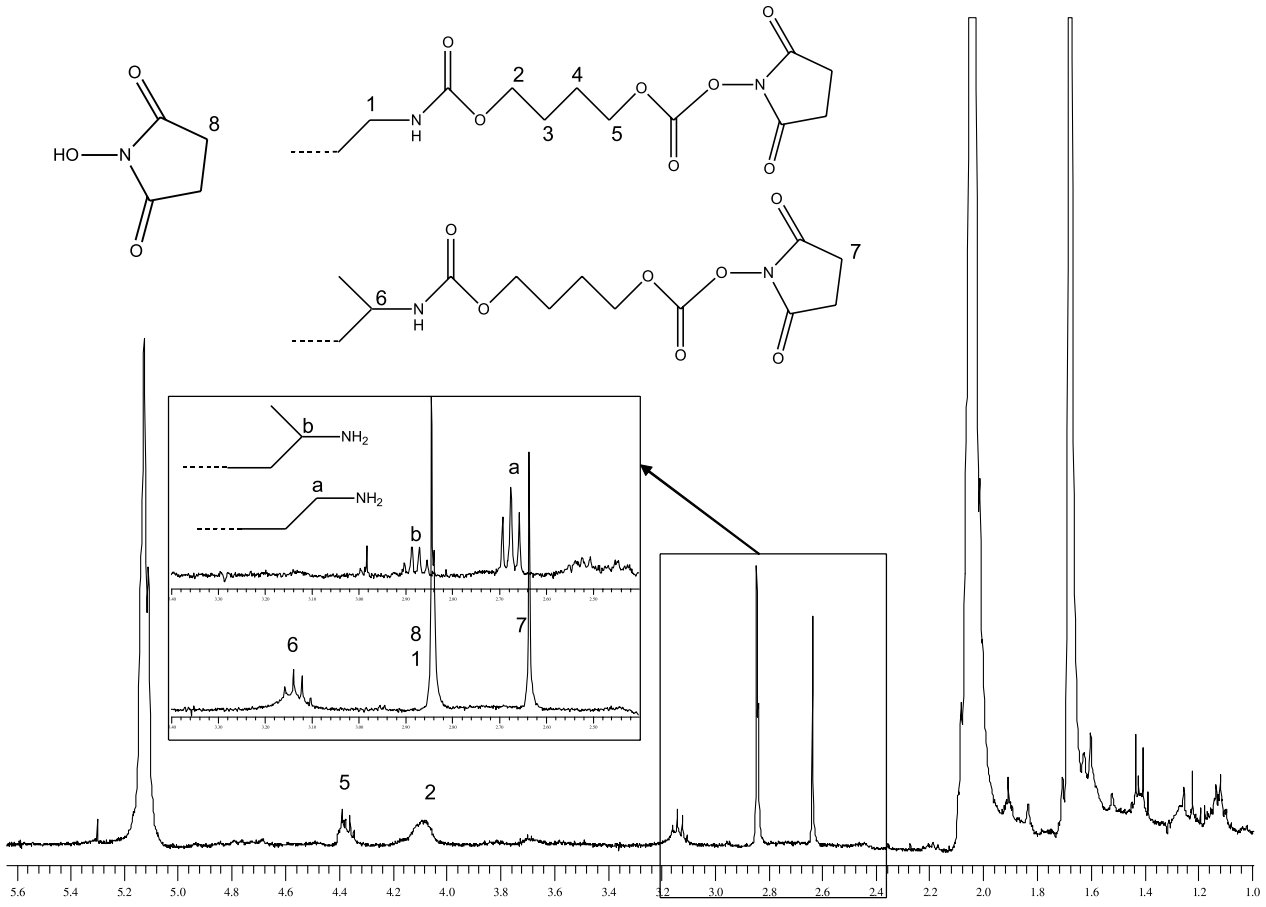


Fig. 5. ^{1}H NMR spectrum of polyurethane prepolymer.

characteristic band centered at approximately 1640 cm^{-1} corresponding to the urea C=O bond vibration (Fig. 1). The main physico-chemical properties of the obtained polyureas are reported in Table 2.

Otherwise, reactivity of amines, notably secondary amines, toward isocyanates is very high and can be performed without use of catalysts. Actually, the same polyureas were obtained without using the DBTL.

In the aim to widen the potential applications of our amino precursors, we focused in a second step on synthesis of new low molecular weight prepolymer, precursor of polyurethanes possessing elastomeric and thermoplastic properties. Our methodology involved the use of a monosuccinimidyl carbonate derived from an α,ω-diol as already described in the literature [30,31]. We targeted commercial 1,4-butanediol bis(chloroformate) as a model reagent to obtain the bis(succinimidyl)carbonate derivative by treatment with *N*-hydroxysuccinimide (Scheme 3). The ^{1}H NMR analysis (Fig. 5) showed a total disappearance of the characteristic signals at 2.68 and 2.88 ppm corresponding, respectively, to the secondary and tertiary protons of the amino end-groups. Moreover, characteristic signals were undoubtly detected corresponding to the succinimide entities at both ends. Additionally, FTIR analysis presented a characteristic band centered at 1712 cm^{-1} corresponding to the urethane C=O bond vibration. Finally, SEC analysis performed after reaction showed a molecular weight increase which confirmed the prepolymer obtaining.

4. Conclusion

Three new well defined aminotelechelic *cis*-1,4-oligoisoprene structures have been synthesized from two different methodologies. If the first approach allowed us to reach oligomers bearing primary amine functions at both ends, the overall yields appeared too low for larger scale applications. For this reason, an alternative has been developed, based on direct reductive amination onto carbonyltelechelic oligoisoprene. This last pathway present many advantages as compared with the previous one. In particular, because of the fast sequence involved, better yields are obtained leading to oligomers bearing secondary amine functions at both ends. Furthermore, an α-amino-ω-carbonyl *cis*-1,4-oligoisoprene has been obtained in high yield when ammonium acetate was used as amine source. This oligomer can be considered as a valuable intermediate because of its reactivity toward both nucleophiles an electrophiles. First investigations were conducted, on polyurea materials synthesis, from these precursors. More

particularly, a new prepolymer bearing chloroformate end-groups, activated by *N*-hydroxysuccinimide, was synthesized as precursor of segmented polyurethane according to a simple route which overcome the use of any toxic reagents (isocyanates and tin catalysts).

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