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Synthesis and thermal properties of telechelic α,ω-bis anhydride oligosiloxanes

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Abstract

Telechelic oligosiloxanes are obtained either via ring opening polymerization of polycyclodialkylsiloxane or via hydrosilylation with a α,ω-bis hydrosilane oligosiloxane or via condensation between a α,ω-bis hydroxy oligosiloxane and an appropriated chlorosilane. This study investigates the synthesis of a α,ω-bis anhydride oligosiloxane via hydrosilylation of bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride with α,ω-bis hydrosilane oligosiloxane in the presence of a Platinum catalyst. Using a Pt catalyst induced a long reaction time and especially an important increase of average molecular weight. Another method of synthesis in two steps was then set up: condensation of *exo*-5-(dimethylchlorosilyl)bicyclo-[2.2.1]heptane-*endo*-2,3-dicarboxylic anhydride with α,ω-bis hydroxy oligosiloxane which leads to the expected oligosiloxane, rapidly and quantitatively. Thermal properties have also been investigated. α,ω-bis anhydride oligosiloxane may take part in the synthesis of block copolymers. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Telechelic oligosiloxane; *exo*-5-(Dimethylchlorosilyl) bicyclo-[2.2.1]heptane-*endo*-2,3-dicarboxylic anhydride; Hydrosilylation

1. Introduction

Polysiloxanes may be considered as choice elastomers for high performance applications. They exhibit special properties such as a very good thermal behavior, stability to oxidation, a low surface tension and an excellent flame resistance [1,2]. Besides the chemistry of non-functional polysiloxanes, the synthesis of telechelic siloxane blocks was developed to prepare the block copolymers [3]. The presence of siloxane segments in the copolymer chain induces properties inherent to silicones. Moreover, the mechanical properties may be interesting like, for example, an increase in the elongation or/and a decrease of the tensile modulus with the increase of the silicone part in the copolymer [4]. Inserting siloxane blocks in a multiblock copolymer chain allows modification and improvement of the physical properties compared to the homopolymer.

The synthesis of multiblock copolymers including siloxane blocks needs to synthesize, at a first time, α,ω-functional oligosiloxanes. Three different strategies of synthesis may be considered to prepare these α,ω-functional oligosiloxanes (cf. Scheme 1):

- Ring opening polymerization of polycyclodialkylsiloxanes (D_n) by a disiloxane containing the desired functions (method 1).
- Hydrosilylation [5] of an unsaturated organic compound bearing the appropriate functional group with a α,ω-bis hydrosilane oligosiloxane (method 2).
- Condensation of a α,ω-bis hydroxy oligosiloxane with a functional chlorosilane (method 3).

The different works already published up to now about α,ω-functional oligosiloxanes are summarized in Table 1.

We have been interested in synthesizing and studying α,ω-bis anhydride oligosiloxanes (AnOSX). Some AnOSX had already been synthesized by ionic polymerization through an acido-catalyzed equilibrium of 5,5′-(1,1,3,3-tetramethyldisiloxane-1,3-diyl) bicyclo[2.2.1]heptane-2,3 dicarboxylic anhydride (**I′c**) and D_4 [15].

Our study focuses on the synthesis of AnOSX by direct hydrosilylation (method 2) of bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride (**Ia**) with a α,ω-bis hydrosilane oligosiloxane and by the condensation (method 3) of *exo*-5-(dimethylchlorosilyl) bicyclo-[2.2.1]heptane-*endo*-2,3-dicarboxylic anhydride (**Ib**) with a α,ω-bis hydroxy oligosiloxane.

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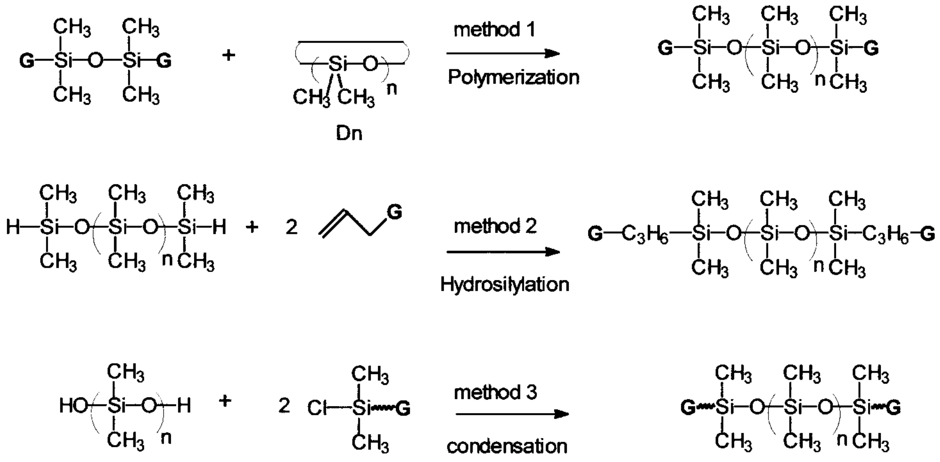


Scheme 1.

These two different synthetic routes will be discussed to determine which is the best method for the synthesis of AnOSX.

2. Results and discussion

The synthesis of AnOSX by hydrosilylation involves a α,ω-bis hydrosilane oligosiloxane which is reacted with Ia, the more stable epimer (cf. Scheme 2 for the general procedure for the synthesis of α,ω-bis anhydride oligosiloxane starting from bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride (**Ia**) and a α,ω-bis hydrosilane oligosiloxane). This synthesis had already been discussed in a US Patent [16], but the amount of Pt catalyst used was very large, about 10 000 μl of a 5% solution of Pt complexed with divinyl tetramethyl disiloxane catalyst [17] (Pt/DVTMDS or Karstedt's catalyst) by double bond mole number.

The amount of catalyst must be reduced, as it remains in the medium and accelerates the aging process of polymers made up of these AnOSX blocks, due to the presence of metal atoms in the matrix [18].

Table 1
References and methods of synthesis based on Scheme 1, for different α,ω-functional oligosiloxanes

Nature of the functional group G	Method	References
–R–OH	(1)	[6]
	(2)[a]	[7,8]
–R–SH	(1)	[9]
$-R-NO_2$	(3)	[10]
$-R-NH_2$	(1)	[12]
	(3)	[10,11]
–R-epoxide	(2)	[13]
$-R-CO_2^- N^+Et_4$	(1)	[14]

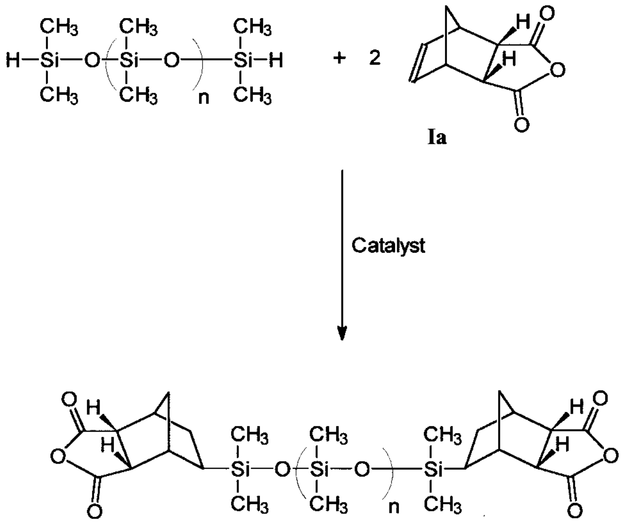
[a] Necessary presence of protecting groups during hydrosilylation.

A similar reaction was performed with α,ω-bis hydrosilane oligosiloxane of average number molecular weight ($\bar{M}_n$) of 670 g mol^{-1} and **Ia**, but with the catalyst being present just in traces. The small amount used is usually sufficient to achieve total hydrosilylation. The reaction was performed at 80°C in toluene and the amount of Karstedt catalyst was added such that the ratio, 5% catalyst volume (in μl)/double bond mole number, be equal to 400 (condition 1 in Table 2). The reaction was followed by ^{1}H NMR, which showed that on one hand, the reaction took a long time and on the other hand the conversion rate of SiH functions was not complete. After 150 h of reaction, the conversion only reached 48%. The efficiency of the reaction was improved by increasing the hydrosilylation temperature to 110°C and by adding an amount of catalyst 3 times higher than in condition 1. All the silane functions were consumed after 90 h (condition 2 in Table 2). An increase in the average number molecular weight $\bar{M}_n$ was observed by ^{1}H NMR and size exclusion chromatography (SEC); it may be explained as the oxidation of silane functions into silanols after a relatively long reaction time and then, the presence of Pt accelerated the condensation process of silanol functions.

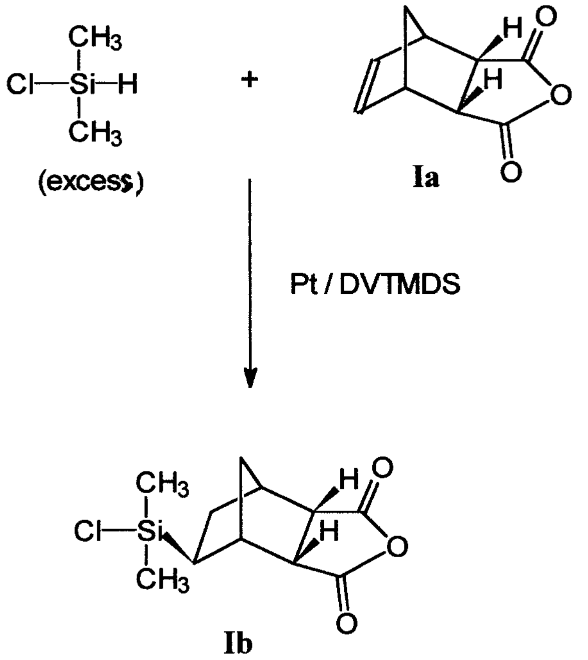
It is thus necessary to change the catalyst to avoid this increase in $\bar{M}_n$ and to improve the efficiency of the reaction [19].

One of the catalysts often used in hydrosilylation is a peroxide type compound. This type of catalyst sometimes shows a better efficiency than the Pt catalysts; whereas the hydrosilylation of a α,ω-diallyl type olefin with a Pt catalyst is quantitative, and the same addition reaction of a α,ω-divinyl type olefin is not. Thus it is necessary to use a peroxide type catalyst [20].

The catalyst used in this study is ditertiobutyl peroxide. After 3 days of reaction in a sealed tube, at 110°C (condition 3 in Table 2), the conversion is in the range of 20%. Furthermore, in ^{1}H NMR, besides the expected product and the characteristic signals at 4.7 ppm for the Si–H and at 6.3 ppm for the double bond of compound **Ia**, a signal



Scheme 2.



Scheme 3.

appears in the aromatic range between 6.9 and 7.4 ppm. A significant increase in $\bar{M}_n$ is also observed in SEC.

When compound **Ia** is reacted with ditertiobutyl peroxide (condition 4 in Table 2), the same increase in $\bar{M}_n$ is observed, and the signals between 6.9 and 7.4 ppm are also present in ^{1}H NMR. A blank reaction was also performed between the α,ω-bis hydrosilyl oligosiloxane and ditertiobutyl peroxide. NMR and SEC analyses do not show any reaction between these two compounds (condition 5 in Table 2). Up to now the mechanism of formation of products is not elucidated.

Thus, a new strategy of synthesis in two steps has been set up. It involves a hydrosilylation reaction between compound **Ia** and a powerful silylating agent, dimethylchlorosilane (synthesis of *exo*-5-(dimethylchlorosilyl)bicyclo-[2.2.1]-heptane-*endo*-2,3-dicarboxylic anhydride (**Ib**) is shown in Scheme 3). It is achieved with a minimum of Karstedt catalyst, under pressure, without the solvent and with an excess of dimethyl chlorosilane. The reaction is clear and no by-products are observed in ^{1}H, ^{29}Si NMR and IR analyses.

The *exo*-5-(dimethylchlorosilyl)bicyclo[2.2.1]heptane-*endo*-2,3-dicarboxylic anhydride (compound **Ib**) exhibits two signals in ^{1}H NMR at 0.38 and 0.43 ppm, characteristic for the methyl groups directly attached to the Si atom. Eddy and Hallgren [21] observed that the addition of a silane onto norbonene takes place exclusively on the *exo* side and no epimerisation was observed in 2, 3 positions. Actually, in our case, no epimerisation was observed and it may be stated that for compound **Ib** the conformation is blocked so that no free rotation is possible between the Si atom and the carbon atom in position 5. In ^{29}Si NMR, only one signal is observed at +30.3 ppm for Si–Cl. The anhydride function has not been affected by the hydrosilylation. Indeed, in IR, the $\nu_{C=O}$ absorption bands for the anhydride at 1780 and 1860 cm^{-1} are still present and no new carbonyl band appears.

Table 2

Experimental conditions and conversion rate for the **Ia** hydrosilylation reaction with α,ω-bis hydrosilane oligosiloxane having an average molecular weight of 670 g mol^{-1}

	Amount of **Ia** (mmol)	**Ia**/α,ω-bis hydrosilane oligosiloxane[a]	Catalyst	Catalyst amount	Solvent (g)	Temperature (°C)	Time (h)	Reaction vial	Conversion (%)
Condition 1	19.1	2.2	Pt/DVTMDS	400[b]	Toluene (35.9)	80	150	Two-necked flask	48
Condition 2	32.3	2.2	Pt/DVTMDS	1200[b]	Toluene (60.5)	110	90	Two-necked flask	100
Condition 3	17.3	2.2	Ditertiobutyl peroxide	8%[c]	Toluene (17.9)	110	72	Sealed tube	20
Condition 4	17.3	∞	Ditertiobutyl peroxide	8%[c]	Toluene (17.9)	110	72	Sealed tube	–
Condition 5	7.9[d]	0	Ditertiobutyl peroxide	8%[c]	Toluene (17.9)	110	72	Sealed tube	–

[a] Molar ratio.

[b] Volume (μl) of a xylene solution of 5 % weight of Pt catalyst complexed with divinyltetramethyldisiloxane by mole of double bond.

[c] Molar percentage in comparison with the mole number of silane functions.

[d] α,ω-bis hydrosilane oligosiloxane amount in mmol.

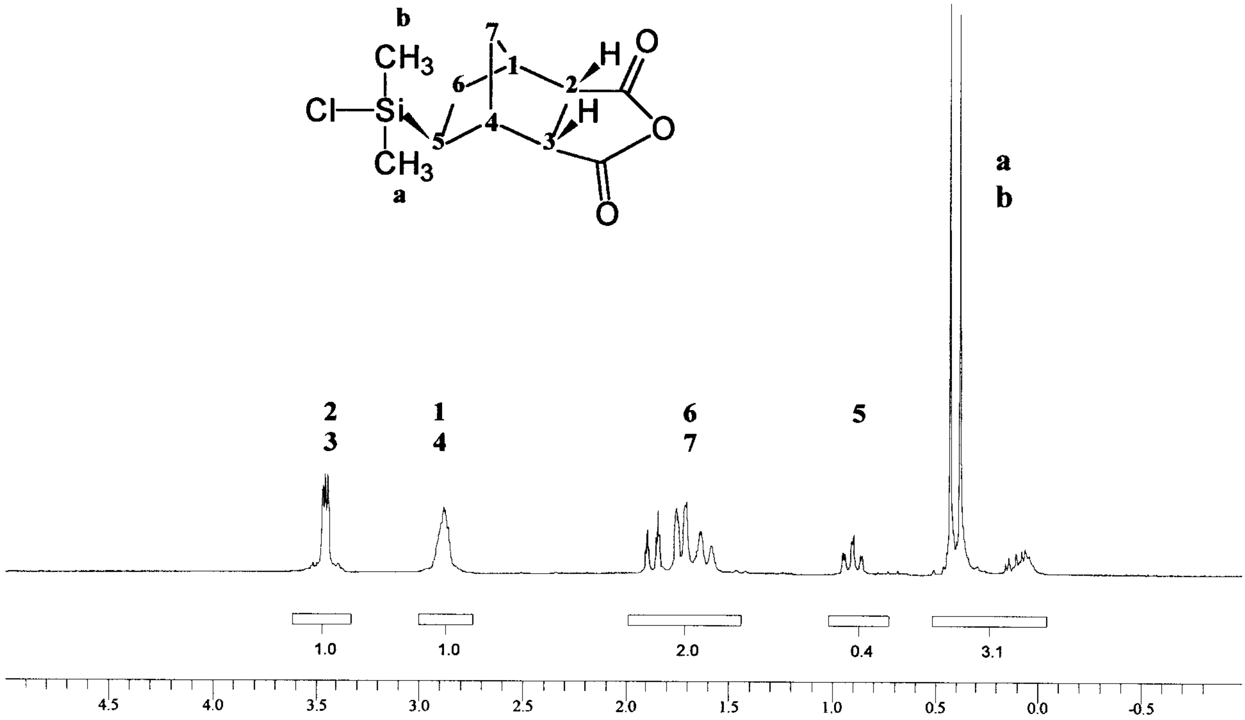


Fig. 1. ^{1}H NMR spectrum of compound **Ib** (in $CDCl_3$).

The synthesis of **Ib** was followed in kinetics. Samples were analyzed in ^{1}H NMR where the 2 protons of the double bond of **Ia** at 6.3 ppm were compared to the 2 protons on the bridgehead of **Ib** noted as 1 and 4 in Fig. 1, at 2.9 ppm. The **Ia** consumption rate (v) versus time may be expressed by the following equation:

$$v = \frac{-\mathrm{d}[\mathbf{Ia}]}{\mathrm{d}t} = k\cdot[\mathrm{Pt/DVTMDS}]\cdot[\mathrm{HSi(Me)_2Cl}]\cdot[\mathbf{Ia}]$$

where k is the kinetic constant of the hydrosilylation reaction of **Ia**, [Pt/DVTMDS] the Karstedt catalyst concentration, [$HSiMe_2Cl$] the dimethyl chlorosilane concentration and [**Ia**] is the molar concentration of **Ia**. We consider that the molar concentration of dimethylchlorosilane is rather constant and thus we can assume that:

$$k' = k\cdot[\mathrm{Pt/DVTMDS}]\cdot[\mathrm{HSi(Me)_2Cl}]$$

$$v = k'\cdot[\mathbf{Ia}]$$

Experimentally, the reaction is of order 1 versus the **Ia** concentration. If we trace the logarithm of the concentration (ln [**Ia**]) versus time, we observe a linear behavior of the conversion rate (Fig. 2), which is up to 92.4%.

$$\ln\frac{[\mathbf{Ia}]}{[\mathbf{Ia}]_0} = -k't$$

with $[\mathbf{Ia}]_0$ = Initial concentration of **Ia** (in mol l^{-1}).

k' was then found to be equal to $3.10^{-5}\ s^{-1}$. This constant k' is relatively low and the hydrosilylation reaction is complete after 40 h. The low reaction rate may be explained by the conformation of **Ia** that does not favor the catalyst approach and the activation of double bond. Another hypothesis proposed by Kuivila and Warner [22] involves another reaction intermediate with platinum being chelated on the *endo* side. Unfortunately, this assumption could not be verified experimentally by Eddy and Hallgren [21]. Their investigations clearly show a better reactivity of the double bond of the *exo* epimer compared to the *endo* one (**Ia**). The determining factor in the hydrosilylation kinetics is

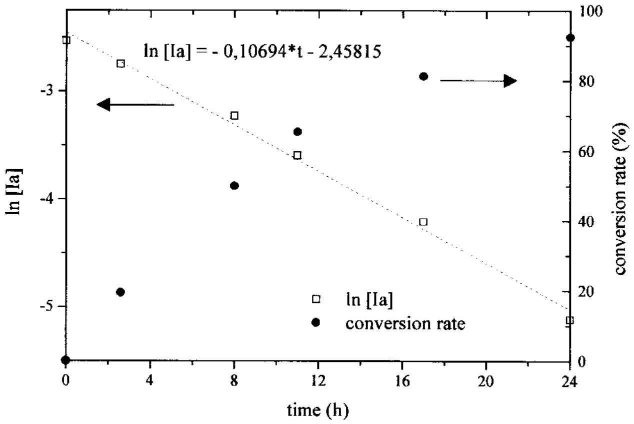
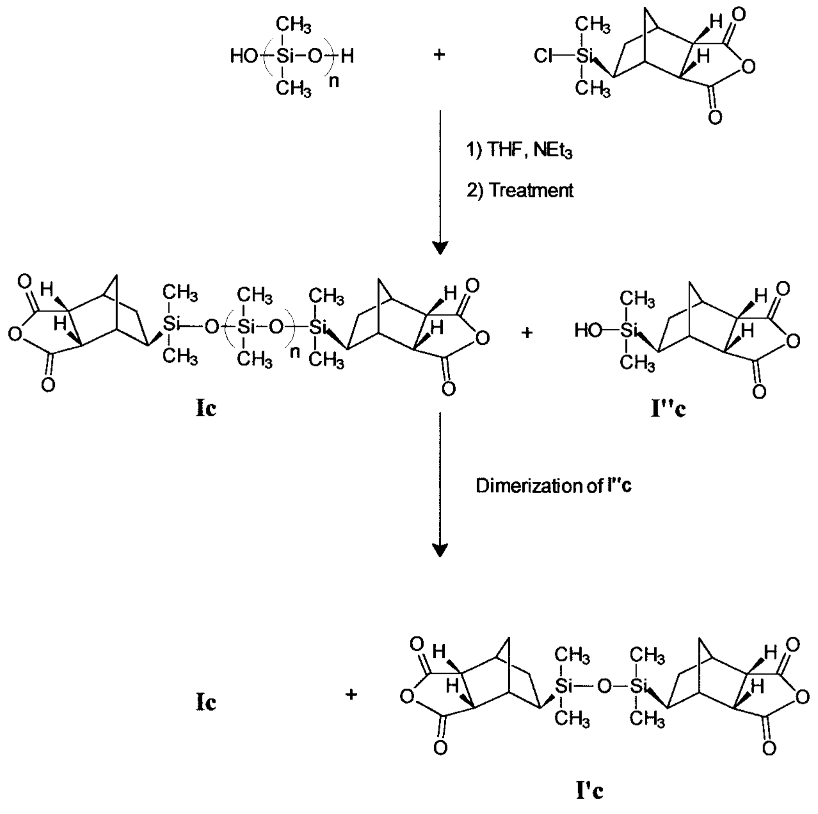


Fig. 2. Kinetics of the hydrosilylation of bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride (**Ia**) with dimethylchlorosilane in the following reaction condition: 250 ml reactor, with an initial nitrogen pressure of 5 bar, 80% weight of toluene, a molar ratio silane/double bonds equal to 4 and 800 μl of 5% xylene solution of Karstedt catalyst by mole of double bond.



Scheme 4.

the fact that the *endo* conformation does not favor the **Ia** approach.

Product **Ib** is then reacted with an α,ω-bis hydroxy oligosiloxane, in THF dried previously over sodium. The $\bar{M}_n$ of the α,ω-bis hydroxy oligosiloxane was calculated from ^{1}H NMR after end-capping of the silanol groups with vinyl dimethyl chlorosilane. The comparison of the integrate ratio of the methyl groups directly attached to the silicon atoms with the integrate ratio of the vinyl groups allows the determination of the size of the starting α,ω-bis silanol. The $\bar{M}_n$ thus found is 480 g mol^{-1} (which corresponds to $n = 6.2$). For all the ends of chain to be anhydrides, the condensation of this oligosiloxane was performed with a slight excess of **Ib**.

In IR, besides the characteristic absorption bands for anhydride groups at 1782 and 1860 cm^{-1}, a new absorption band appears at 3300 cm^{-1}. SEC shows the presence of two additional products, and the expected oligomer. The presence of these two products may be explained by the excess of **Ib** which hydrolyses into *exo*-5-(dimethylsilanol)-bicyclo[2.2.1]heptane-*endo*-2,3-dicarboxylic anhydride (noted as **I″c**) during the treatment. This silanol **I″c** may then be dimerized into 5-5′-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis-bicyclo[2.2.1]heptane-2,3-dicarboxylic anhydride (**I′c**) also present in the medium. The presence of a signal at +14.8 ppm in ^{29}Si NMR is in agreement with a silicon bearing an –OH group, and the silicon atom of compound **I′c** appears at +7.1 ppm (Scheme 4 shows the synthesis of α,ω-bis *exo*-5-(dimethylsilyl)bicyclo[2.2.1]heptane-*endo*-2,3-dicarboxylic anhydride oligosiloxane (**Ic**) and of *exo*-5,5′-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bicyclo[2.2.1]heptane-2,3-dicarboxylic anhydride (**I′c**).

As the aim was to obtain difunctional entities, the auto-condensation of **I″c** into **Ic** was performed via two routes: on one hand, by thermal treatment at 160°C (the $\nu_{\text{Si-OH}}$ elongation band in IR has completely disappeared after 6 h), and on the other hand, by chemical treatment. The latter involves a mixture of trifluoroacetic acid and tetramethylguanidine (respectively, 3 for 1 mol). After 4 h at reflux THF, the mixture exhibits the same characteristics as the product thermally treated, with the disappearance of the absorption band at 3300 cm^{-1} in IR and of the signal at +14.8 ppm in ^{29}Si NMR, together with an increase of the signal at +7.1 ppm characteristic of the Si of **I′c**. Compound **I′c** was synthesized, in parallel, to clearly define its physical and chemical characteristics. Thus, the chemical shifts in ^{1}H and ^{29}Si NMR, the characteristic absorption bands in IR and the elution time in SEC have been verified. In Fig. 3, it is possible to compare the SEC curve of the product issued from the end-capping reaction (**Ic** and **I′c**) with that of the product **I′c** which had been synthesized separately.

From ^{1}H NMR (Fig. 4), the molar percentage of **I′c** in the medium is determined to be less than 3%.

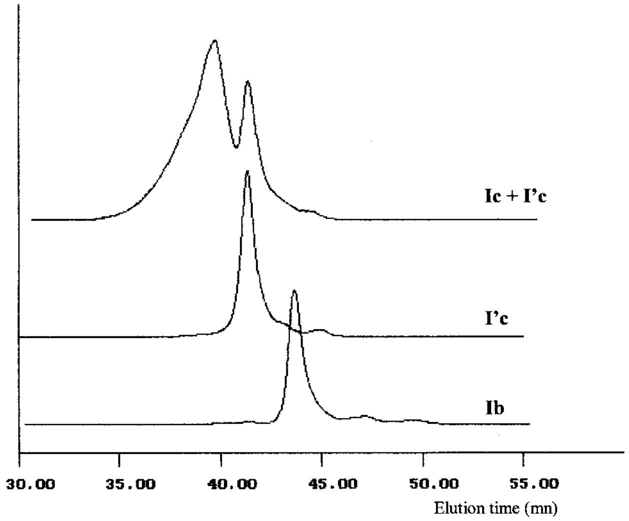


Fig. 3. Comparison of SEC curves for α,ω-bis *exo*-5-(dimethylsilyl)bicyclo[2.2.1]heptane-*endo*-2,3-dicarboxylic anhydride (**Ic**) containing the *exo*-5,5′-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bicyclo[2.2.1]heptane-2,3-dicarboxylic anhydride (**I′c**), pure *exo*-5,5′-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bicyclo[2.2.1]heptane-2,3-dicarboxylic anhydride (**I′c**) and *exo*-5-(dimethylchlorosilyl)bicyclo-[2.2.1]heptane-*endo*-2,3-dicarboxylic anhydride (**Ib**) in THF (0.8 ml min^{-1}).

This new method to obtain OSXAn is simple, as it is achieved in two steps, and secure as a slight excess of **Ib** introduced insures a complete transformation of the –SiOH ends of the chain of the α,ω-bis silanol into anhydride groups.

The thermal behavior of the α,ω-bis hydroxy oligosiloxane, and of products **Ic** and **I′c** has been studied by differential scanning calorimeter (DSC) and by thermogravimetric analysis (TGA).

Whereas the glass transition temperature (T_g) of the α,ω-bis hydroxy oligosiloxane is −120°C, the addition of norbornyl *endo* anhydride groups increases the T_g by +90°C. Indeed, the measured T_g value at −30°C reveals a certain organization induced by the presence of terminal anhydride groups, because of their steric hindrance. These terminal groups limit the mobility of the chains which are rather short ($n = 6.2$) and thus, increase the T_g. Moreover, the presence of compound **I′c** in the mixture also tends to favor the increase in T_g. Compound **I′c**, when it is pure, shows a T_g at +25°C and a melting at +159°C. The DSC analysis also reveals that **I′c** is completely miscible with **Ic** as only one T_g is observed. Unfortunately, it has not been possible to eliminate the compound **I′c** from the mixture.

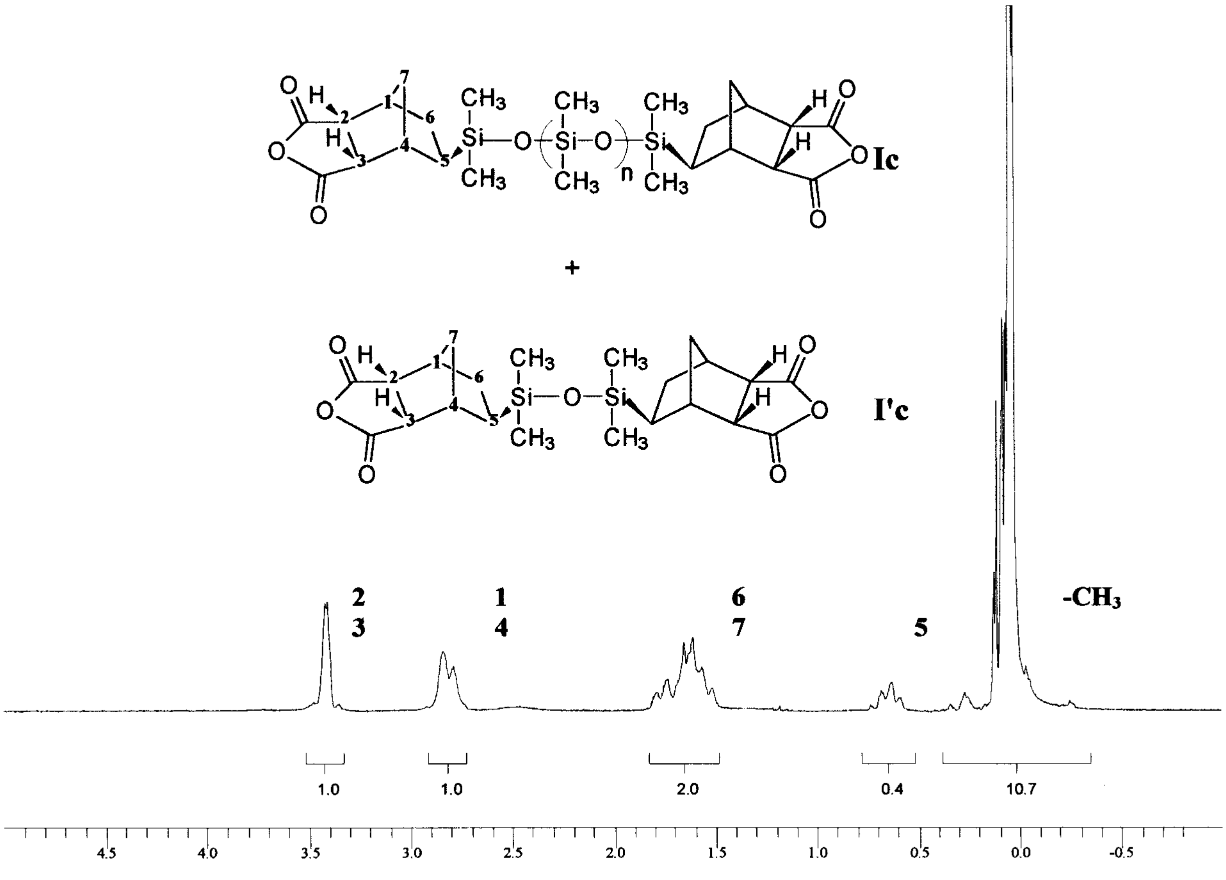


Fig. 4. ^{1}H NMR spectrum of compounds **Ic** and **I′c** (in $CDCl_3$).

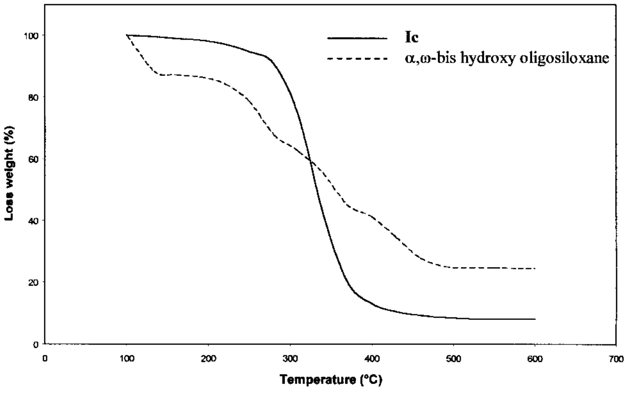


Fig. 5. Comparison of thermogravimetric curves of α,ω-bis hydroxy oligosiloxane and **Ic**, from 100 to 600°C at 5°C min^{-1} under air.

The nature of the ends of the chain greatly influences the value of T_g, and this tends to bring to light the influence of the chain ends on the molecular mobility of oligosiloxanes.

Fig. 5 represents the thermal degradation of the starting α,ω-bis hydroxy oligosiloxane and **Ic** in mass percentage versus the temperature. The presence of norbonyl *endo*-anhydride groups at the ends of chains improves the thermal stability by more than 200°C. Whereas a 10% weight loss is observed at 120°C for the α,ω-bis hydroxy oligosiloxane, **Ic**, only begins to degrade at +280°C. It is reasonable to think that the silanol chain ends play an important role in the thermal degradation process. The presence of norbornyl-*endo*-anhydride at the ends of chain reducing the mobility of the chains, as demonstrated by DSC analyses, also limits the possibility of formation of cycles with 6 or 8 $-\text{Si(Me)}_2\text{O}-$ moieties, thermodynamically more stable.

Moreover, the proportion of residue is less for **Ic** (containing a small amount of **I′c**) as the norbornyl-*endo*-anhydride groups, which represent about 35% of the mixture are completely degraded at 400°C, while the α,ω-bis hydroxy oligosiloxane may form more silica residues.

3. Experimental part

FTIR spectra were recorded on a 510P FTIR Nicolet spectrometer. The position of the bands is given in cm^{-1} with an accuracy of $\pm 2\ \text{cm}^{-1}$. ^{1}H NMR spectra were recorded on a AC 200 MHz Bruker apparatus with TMS as the internal reference. The letters s, d, t and m stand for singlet, doublet, triplet and multiplet, respectively. ^{29}Si NMR spectra were recorded on a WH 250 MHz Bruker apparatus with TMS as the internal reference. The differential scanning calorimeter is a Perkin–Elmer Pyris 1 DSC apparatus calibrated with *n*-decane and indium under N_2. All the samples were heated either from −120°C to +50°C, or from +30°C to +250°C at 20°C min^{-1} to determine a T_g and at 10°C min^{-1} to determine a melting temperature. SEC was performed with a Spectra Physics apparatus with 2 PL gel columns (300 mm length, 5 μm particle size, 50 Å average porosity for one and 100 Å for the other) and a HR 2 styragel column ($7.8 \times 300\ \text{mm}^2$). The detector was a SP 8430 differential refractometer. The eluent was THF with a 0.8 ml min^{-1} flow rate.

Bicyclo[2.2.1]hept-5-ene-*endo*-2.3 dicarboxylic anhydride (compound **Ia**), chlorodimethylsilane and ditertiobutyl peroxide were purchased from Aldrich. α,ω-bis hydrosilane and bis-hydroxy oligosiloxanes, and Karstedt catalyst were purchased from ABCR. The products were used without special purification.

3.1. Synthesis of compound **Ib**

In a 250 ml reactor were introduced 12.99 g (79 mmol) of bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride (compound **Ia**), 171 g (198 ml) of toluene dried previously over anhydrous Na_2SO_4, and 29.75 g of dimethylchlorosilane. The amount of toluene corresponds to 80% of the total mass of the reaction mixture. Then, 63 μl of Karstedt catalyst solution (800 μl by mole of double bond) were added. A nitrogen initial pressure of 5 bar was introduced, along with magnetic stirring. The mixture was heated at 110°C for 48 h.

After cooling, the excess dimethylchlorosilane and the toluene were evaporated. The product obtained was then dried under 0.4 mmHg, at 90°C for 6 h.

Compound **Ib** was obtained as a white powder and with a 100% yield.

^{1}H NMR (CDCl_3): (see Fig. 1). The signal of the double bond from compound **Ia** has disappeared.
^{29}Si NMR (CDCl_3): −30.2 ppm (s), $-Si\text{(Me)}_2\text{Cl}$.
IR: $\nu_{(\text{C=O})}$ anhydride = 1780.5 and 1860 cm^{-1}
SEC: a single peak is detected at 43.7 nm elution time.

3.2. Synthesis of compound **Ic**

In a 50 ml two necked flask, equipped with a magnetic stirrer and a condenser, were introduced 2.76 g (10.8 mmol) of compound **Ib** and 4 g (4.5 ml) of THF previously dried and distilled over sodium. A mixture of α,ω-bis hydroxy oligosiloxane (2.5 g or 5.2 mmol, $M_n = 480\ \text{g mol}^{-1}$) and triethylamine (2.2 g or 22 mmol) in 17 g (19.1 ml) of dry THF was added dropwise, at room temperature and under argon. After cooling, the mixture was filtered over a fritted glass N°4 to eliminate the ammonium salts formed, and THF was evaporated and replaced by ethyl ether in order to achieve a washing with a 10% HCl solution, followed by two washings with water. After filtration over Na_2SO_4 and evaporation of ether, a very viscous oil was obtained with a 94% yield.

3.3. Thermal treatment

In order to condense the compound **I″c** formed during the reaction, the product obtained was heated at 160°C during 6 h and under 0.6 mmHg.

3.4. Chemical treatment

The product obtained was diluted in anhydrous THF, under Argon and with magnetic stirring. A drop of freshly prepared tetramethyl guanidine/trifluoroacetic acid mixture (1/3) was added. The solution was refluxed for 3 h. After filtration, over Na_2SO_4, and evaporation of the solvent, a viscous and transparent liquid was obtained with a quantitative yield.

^{1}H NMR ($CDCl_3$): see Fig. 4
^{29}Si NMR ($CDCl_3$): +5.6 ppm (s), >CH–*Si*$(Me)_2O$, the signal at +14.8 ppm for the Si atom of **I″c** having disappeared.
IR: $\nu_{(C=O)}$ anhydride = 1782 and 1860 cm^{-1}, no Si–OH band observed at 3300 cm^{-1}.
SEC: 1 peak detected at 39.7 nm elution time for compound **Ic** and a second peak at 41.4 nm for compound **I′c** (see Fig. 3).
DSC: $T_g = -30$°C.

*3.5. Synthesis of compound **I′c***

In a 50 ml two-necked flask, equipped with a magnetic stirrer, were placed 3.23 g (12.5 mmol) of compound **Ib** in 25 ml THF; 0.26 g (14.5 mmol) of deionized water were added at 0°C. After stirring at room temperature for 2 h, the solvent was evaporated, then the product was dried at 160°C during 3 h under 0.4 mmHg.

^{1}H NMR ($CDCl_3$): 3.4 ppm (m, 4H, H_5 and H_6); 2.85 and 2.75 ppm (2s, 4H, H_1 and H_4); 1.6 ppm (m, 8H, H_2 and H_7); 0.6 ppm (t, 2H, H_3); 0.m (d, 12H, $SiCH_3$)
^{29}Si NMR ($CDCl_3$): +7.1 ppm (s), >CH–Si$(Me)_2$O–
IR: $\nu_{(C=O)}$ anhydride = 1780 and 1858 cm^{-1}; ν(SiOSi) = 1084 cm^{-1}
SEC: a single peak detected at 41.4 nm elution time for **I′c**
DSC: T_g = +25°C, T_m = +159°C.

4. Conclusions

This study has allowed the synthesis of α,ω-bis anhydride oligosiloxanes via hydrosilylation and using a reasonable amount of catalyst. During the synthesis of telechelic oligomers, the functionality must absolutely be of 2 in order to achieve good polymerization reactions. A series of reactions between bicyclo[2.2.1]hept-5-ene-*endo*-2,3-dicarboxylic anhydride (**Ia**) and a α,ω-bis hydrosilane oligosiloxane has been performed. However, using a Pt catalyst (Karstedt catalyst) induced a long reaction time and especially a significant increase in the average molecular weights. With **Ia**, the ditertiobutyl peroxide catalyst did not lead to the expected products, as a polymerization side reaction takes place.

Another method of synthesis in two steps was then set up. It involves a rapid and quantitative reaction of chlorosilane functions with silanol functions, in our case, reaction of *exo*-5-(dimethylchlorosilyl)bicyclo-[2.2.1]heptane-*endo*-2,3-dicarboxylic anhydride **Ib** with α,ω-bis hydroxy oligosiloxane. An excess of **Ib** is necessary to be sure of a complete conversion of silanol functions. At the end of the reaction, the amount of **Ib** remaining in the medium after treatment, is dimerized into 5,5′-(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bicyclo[2.2.1]-heptane-2,3-dicarboxylic anhydride (**Ic′**). The products have been well characterized by ^{1}H and ^{29}Si NMR, FTIR and SEC.

The T_g of the final product was highly increased compared to that of the starting silanol. This increase in T_g is due to the presence of the dimer *I′***c** (however, the solubility of **I′c** in **Ic** is total as only one T_g is observed), and on the other hand to the influence of the anhydride chain ends on the oligomers mobility. Moreover, the thermal resistance of oligosiloxanes improved due to the presence of terminal anhydride functions. The chain ends play a determining role in the thermal degradation process of oligomers.

The synthesis of telechelic anhydride siloxane oligosiloxanes by condensation of *exo*-5-(dimethylchlorosilyl)bicyclo-[2.2.1]heptane-*endo*-2,3-dicarboxylic anhydride with a α,ω-bis hydroxy oligosiloxane was achieved with a very good yield and in a simple way. Such products may take part in the synthesis of block copolymers, like, for example, thermoplastic elastomers including siloxane blocks and which may exhibit interesting thermal and anti-adhesive properties.

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