

# Physically crosslinked fluorosilicone elastomers obtained by self-assembly and template polycondensation of tailored building blocks†

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Self-assembly and template polycondensation of two tailor-made fluorinated oligocarbosiloxanes generated physically crosslinked elastomer-like materials (denoted here as “gelastomers”). Clustering was found to arise from phase separation between strongly aggregated, polar silanol chain-ends and highly hydrophobic fluorosilicone domains. The large concentration of silanol functions promoted a template catalyst-free co-condensation to generate chains of typically 10 000 g mol<sup>-1</sup> after extended times. One of these gelastomers exhibited noteworthy mechanical properties, such an elongation as large as 1500% at a fair strain force (0.2 MPa).

## Introduction

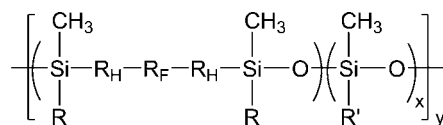
Fluorinated silicones are materials acknowledged for their low surface tension, their high solvent repellency and their remarkable mechanical resistance. The most popular polymer used in commercial applications is composed of trifluoro(propylmethyl)siloxane units.<sup>1</sup> However, this polymer reverses into small cycles in acidic or basic conditions or at high temperature, which limits its potential. Another class of alternating fluoroalkyl and silicone blocks (hybrid silicones) avoid such degradation reactions, however at the expense of the simplicity of synthesis. Hybrid fluorinated silicones have been extensively studied in our laboratory<sup>2–15</sup> in a view to generate high-tech elastomeric materials: *e.g.*, one potential application as O-rings in aeronautics requires steady mechanical properties over a large temperature range, typically from –60 to 350 °C (see a recent review<sup>16</sup>).

In previous studies, both fluorinated and silicone sequences were varied in length and in structure of peripheral groups, respectively (a generic structure is given in Scheme 1). Typically, fluoroalkyl sequences of six carbon atoms or less were chosen to avoid crystallization. Besides, less than 4 D units (–Si(CH<sub>3</sub>)<sub>2</sub>–O) were introduced between each fluorinated block to prevent backbiting reactions at high temperature. The ratio of silicone over fluorinated content over the various hybrid chains was dictated according both to the *T<sub>g</sub>* sought (typically less than –50 °C) and the level of swelling by usual solvents (ideally as low as possible). Once the building blocks were chosen, polymers were built either by polyhydrosilylation reaction between Si–H

and Si–Vi terminated oligomers, catalyzed by platinum compounds, or polycondensation of the bis-silanol oligomers using a superacid catalyst (*vide infra*).<sup>17</sup>

Silicones are soft and non-cohesive polymers, and thus the resulting materials exhibit poor mechanical properties. To improve the strength of silicone, normally one fills silicones with hydrophobically-treated silica nanoparticles, in order to improve the cohesion between the chains. Also, the (hopefully very long) silicone chains are crosslinked to harden the resulting elastomeric rubber.<sup>18</sup> In the present case of hybrid silicones, polymers were of too low molar masses (see Scheme 1, oligomers with less than 30 units), thus generating rubbers with low mechanical resistance.<sup>19</sup>

Another recent class of thermoplastic silicone elastomers, made of silicone-urethane multiblocks, were recently introduced to the market by Wacker Chemie AG under the tradename GENIOMER®. Such products were derived from Yilgor and Yilgor's numerous studies on the subject.<sup>20</sup> These materials generally exhibit very good mechanical properties, without the need for adding a filler or crosslinking the silicone chains. Here, it is the aggregation of the urea groups through hydrogen-bonding that reinforces the material.<sup>21</sup> The high silicone content in the GENIOMER films makes them particularly interesting for coatings on photovoltaic cells.



R<sub>F</sub> = C<sub>6</sub>F<sub>12</sub>, HFP/C<sub>4</sub>F<sub>8</sub>/HFP, C<sub>2</sub>F<sub>4</sub>/VDF/HFP

R<sub>H</sub> = C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>

R = CH<sub>3</sub>, C<sub>2</sub>H<sub>4</sub>CF<sub>3</sub>, C<sub>2</sub>H<sub>4</sub>C<sub>4</sub>F<sub>9</sub>

R' = CH<sub>3</sub>, C<sub>2</sub>H<sub>4</sub>C<sub>6</sub>F<sub>13</sub>, C<sub>2</sub>H<sub>4</sub>C<sub>4</sub>F<sub>9</sub>, C<sub>2</sub>H<sub>4</sub>CF(CF<sub>3</sub>)CF<sub>2</sub>C<sub>4</sub>F<sub>9</sub>

x = 0–4

y < 30 units

**Scheme 1** Main structure of hybrid fluorinated silicones prepared in past studies from our group (see also Table 1).<sup>16</sup>

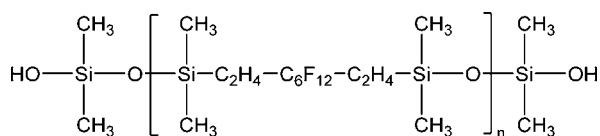
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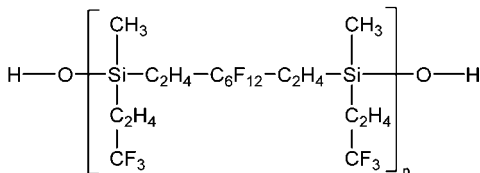
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1



2

**Scheme 2** Main structure of the two hybrid fluorinated silicone bricks studied here (see also Table 1).

In quite an old article,<sup>22</sup> Pierce and Kim from the Dow Corning company noticed that some specific building blocks of fluorinated hybrid silicones turned into “a high consistency elastomer within a few hours even though the water of condensation was not removed”. The aim of this paper is to revisit two particular fluorosilicone materials, called “gelastomers” in the following article (Scheme 2 and Table 1). Both initial building blocks contain a perfluorohexyl group in the core of the molecule, and silanol groups on their extremities. We will demonstrate the physical interactions taking place in these materials using a “top-down” analysis: first visual observation, then microscope proof of clustering and finally nanoscaled self-assembly and template polycondensation studies of these model functional oligomers.

Table 1 gives the properties of the different “naturally-gelling” materials that we observed throughout the years in the laboratory. In the following, gels analyzed after two days will be proved to be composed of original oligomers, which did not have enough time to evolve (denoted **X**). On the other hand, materials which were analyzed after a long time (typically a few months) were composed of significantly larger chains (denoted **X'**). In the case

where both a dimethylvinylchlorosilane and a chaotropic salt were needed for end-capping the materials (*vide infra*), the label **X''** was used.

## Experimental

### Synthesis of hybrid oligomers

**Sample 1<sup>3</sup>.** The hydrosilylation of 1,6-divinyl(perfluorohexane) (0.0597 mol, purity 99.9%, obtained from Tosoh F-Tech inc.) with tetramethyldisiloxane in large excess (0.597 mol, purity 98%, purchased from ABCR) was catalyzed by a radical promoter (bis(*tert*-butyl) peroxide, 9.55 mmol, purity 97%, purchased from Aldrich France) at 120 °C in a sealed tube to give 100% (relative to vinyl molecule) hybrid hydrido-oligocarbosi-loxane **I**, isolated by distillation (Scheme 3). <sup>1</sup>H NMR:  $\delta$  (ppm) 0.2 (s + d, SiCH<sub>3</sub>,  $J = 2.8$  Hz), 0.8 (m, SiCH<sub>2</sub>), 2.1 (m, R<sub>F</sub>CH<sub>2</sub>), 4.7 (m, SiH). <sup>29</sup>Si NMR:  $\delta$  (ppm) -5.4 (d, SiH,  $J = 204$  Hz), 8.4 (s, CH<sub>2</sub>SiOSiCH<sub>2</sub>), 9.3 (s, HSiOSiCH<sub>2</sub>). FT-IR:  $\nu_{\text{Si-H}} = 2125$  cm<sup>-1</sup>.

The conversion of Si-H functional groups into Si-OH groups was done by hydrolysis of **I** (0.015 mol) in tetrahydrofuran (THF, 40 mL), catalyzed by Pd/Al<sub>2</sub>O<sub>3</sub> (5%) (0.3 g, purchased from Avocado) in the presence of buffer (NaHPO<sub>4</sub>-H<sub>2</sub>O + NaOH + H<sub>2</sub>O, 2.8 mL, pH = 7.3) at 0 °C during 24 h. Yield of oligomer **1** was 100% as confirmed by complete Si-H band loss in FTIR. <sup>1</sup>H NMR:  $\delta$  (ppm) 0.15 (s + d, SiCH<sub>3</sub>), 0.8 (m, SiCH<sub>2</sub>), 2.1 (m, R<sub>F</sub>CH<sub>2</sub>). <sup>29</sup>Si NMR:  $\delta$  (ppm) -12.3 (s, SiOH), 6.8 (s, HOSiOSiCH<sub>2</sub>), 8.4 (s, CH<sub>2</sub>SiOSiCH<sub>2</sub>). FT-IR:  $\nu_{\text{Si-OH}} = 3397$  cm<sup>-1</sup>. Average DP (SEC): 2.5.

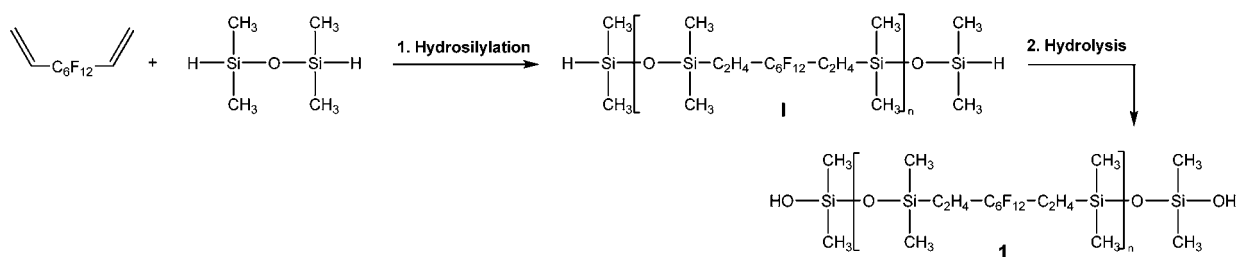
**Sample 2<sup>11</sup>.** A SiCl terminated monomer (**II** in Scheme 4, 0.21 mol), kindly provided by Dow Corning,<sup>19</sup> was reduced by LiAlH<sub>4</sub> (0.12 mol, purchased from Aldrich, France) in diethyl ether during 21 h under reflux to produce the SiH terminated monomer **III** (Scheme 4). <sup>1</sup>H NMR:  $\delta$  (ppm) 0.2 (d, SiCH<sub>3</sub>,  $J = 2.6$  Hz), 0.9 (m, SiCH<sub>2</sub>), 2.1 (m, R<sub>F</sub>CH<sub>2</sub>), 3.9 (m, SiH). <sup>29</sup>Si NMR:  $\delta$  (ppm) -6.7 (d, SiH, 186 Hz). FTIR:  $\nu_{\text{Si-H}} = 2130$  cm<sup>-1</sup>.

Monomer **III** was then hydrolyzed at room temperature using the procedure given above, to obtain the oligomer **2** in 100% yield as estimated from FTIR SiH disappearance (Scheme 4). <sup>1</sup>H

**Table 1** Main structure and some properties of various molecules cited in this study and prepared in our laboratory.<sup>a</sup>

Sample	R	$x$	$y^b$	$T_g^{c/\circ\text{C}}$	Material aspect	Ref.
<b>1</b>	CH <sub>3</sub>	1 and 2	2.5	— <sup>d</sup>		
<b>1'</b>	CH <sub>3</sub>	1 and 2	10	-65	Friable, soft elastomer	This work
<b>2</b>	(CH <sub>2</sub> ) <sub>2</sub> C <sub>4</sub> F <sub>9</sub>	1	5	-28		
<b>2'</b>	(CH <sub>2</sub> ) <sub>2</sub> C <sub>4</sub> F <sub>9</sub>	1	100	-22	Compact, shear resistant material	This work
<b>2''</b>	(CH <sub>2</sub> ) <sub>2</sub> C <sub>4</sub> F <sub>9</sub>	1	13	— <sup>d</sup>		
<b>3*</b>	CH <sub>3</sub>	0	11	-50	Viscous oil	5, 7, 9, 12
<b>4</b>	(CH <sub>2</sub> ) <sub>2</sub> C <sub>4</sub> F <sub>9</sub>	0	12	-47	Viscous oil	7-9
<b>5</b>	CH <sub>3</sub>	1	1	— <sup>d</sup>	Liquid oil	This work
<b>6'</b>	CH <sub>3</sub>	2	10	-59	Softer elastomer than <b>2'</b>	This work
<b>7'</b>	CH <sub>3</sub>	3	10	-73	Much softer elastomer than <b>2'</b>	This work
<b>8'</b>	(CH <sub>2</sub> ) <sub>2</sub> C <sub>4</sub> F <sub>9</sub>	0	11	-59	Very stiff elastomer, could not be redissolved	This work
<b>9</b>	CH <sub>3</sub>	0	1	-50	Liquid oil	5, 8-10, 16
<b>10</b>	CH <sub>3</sub>	1 and 2	51	-53 ( $T_c = -11$ , $T_f = 26$ )	Viscous oil	5, 8-10, 16

<sup>a</sup> The main components of the structures refer to Scheme 1, with R<sub>F</sub> = C<sub>6</sub>F<sub>12</sub> (\*except for sample **3**, with a core made of a VDF-HFP oligomer) and R<sub>H</sub> = C<sub>2</sub>H<sub>4</sub>. See the main text for the formalization chosen here in the sample code. <sup>b</sup> Estimated from SEC measurements on end-capped oligomers or provided from the references. <sup>c</sup> Obtained by DSC on raw materials. <sup>d</sup> Not measured.



Scheme 3 Synthesis pathway of sample 1.

NMR:  $\delta$  (ppm) 0–0.2 (m, SiCH<sub>3</sub>), 0.8 (m, SiCH<sub>2</sub>), 2.1 (m, R<sub>F</sub>CH<sub>2</sub>). <sup>29</sup>Si NMR:  $\delta$  (ppm) 8.4 (s, CH<sub>2</sub>SiOSiCH<sub>2</sub>), 16 (s, SiOH). FTIR:  $\nu_{\text{Si-OH}}$  = 3379 cm<sup>-1</sup>. Average DP (SEC): 5.

## Methods

Atomic force microscopy measurements were carried out on a commercial optical deflection microscope (stand-alone configuration for a large sample, Dimension 3100 Veeco Instruments with a Nanoscope IIIa, Digital Instrument) operating in ambient conditions. Topographic images were taken in the tapping mode (attractive). Data were acquired on 1  $\mu\text{m}$   $\times$  1  $\mu\text{m}$  frames having 512  $\times$  512 data points with a scan rate of 1.5 Hz. The phase image gives an estimate of local hardness and thus of the surface organization. Microtomed films of **1'** (Table 1) were prepared with a Reichert Ultracut E ultramicrotome equipped with a FC4D cryochamber. The cuts were deposited on a 400 mesh copper grid. The thickness of the samples thus prepared was around 80–100 nm. The samples were observed in bright-field using a JEOL 2000FX transmission electron microscope operating at 200 kV. 100 nm thickness films of sample **2'** (Table 1) were cut out with a ultracryomicrotome LEICA UTC, and were deposited on copper grids covered with a film with parlodion and carbon. Microscopic images were accumulated on a model JEOL 12EX2 transmission electron microscope at a working voltage of 120.0 kV.

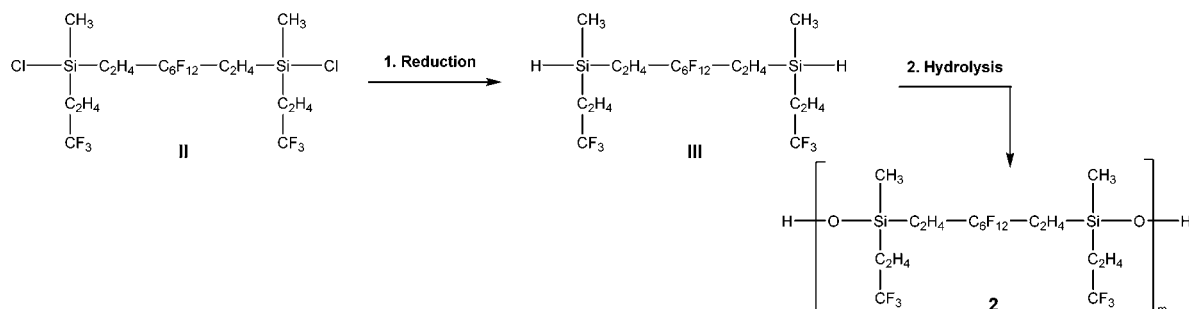
Differential scanning calorimetry (DSC) analyses were performed, under nitrogen, with a Perkin Elmer Pyris 1 DSC apparatus calibrated with indium. All the samples were analyzed in three runs from –150 to 50 °C at 20 °C min<sup>-1</sup>. The  $T_g$  values were measured during the second run and confirmed by the third one, taken at the half height of the heat capacity jump of the glass transition, whereas other transitions were recorded on the first temperature ramp.

FT-IR spectra were recorded on a Nicolet 510P FTIR spectrometer with an accuracy of  $\pm 2$  cm<sup>-1</sup>. ATR infrared spectra were recorded at room temperature on a Bruker IFS66 FTIR spectrometer (Golden Gate reflection system) to analyze the hybrid silicone after solvent evaporation. Each spectrum is an average of 32 spectra measured at a resolution of 2 cm<sup>-1</sup>. Fourier-transform infrared (FTIR) spectra were recorded between 4000 and 400 cm<sup>-1</sup>. Since the reflection system absorbs the beam between 2400 and 2000 cm<sup>-1</sup>, analysis was impossible in this zone.

NMR spectra were recorded on a BRUKER WH250 spectrometer with TMS as reference for <sup>1</sup>H and <sup>29</sup>Si NMR. Chemical shifts are reported in ppm: s = singlet, d = doublet and m = multiplet. All spectra were recorded in CDCl<sub>3</sub> solutions.

Size exclusion chromatography (SEC) was performed on a spectra Physics apparatus with two PL gel columns (5  $\mu\text{m}$  particle size, 300 mm length, one with 50 Å and one with 100 Å pore size) and one Styragel HR2 column (7.8 mm internal diameter  $\times$  300 mm length). The detection was achieved with a SP8430 differential refractometer. The eluent was THF and the flow rate was 1 mL min<sup>-1</sup> at 30 °C. Column calibration was done using polystyrene standards.

Triple detection SEC was carried out on a TDA300-EXD apparatus from Viscotek, equipped with three detectors connected in series, *i.e.* light scattering, refractometer and viscosimeter detectors. The temperature of analysis, 35 °C, was set both in columns and in the detector room to ensure better reproducibility, as well as a stable baseline throughout the characterization. Two linear ultrahydrogel GMHHR-H columns and a HHR-H Guard precolumn (both from Viscotek) were used. Toluene was chosen as eluent, at a flowrate of 1 mL min<sup>-1</sup>, without a need for a marker. Data acquisition and treatment were performed using Viscotek OmniSEC software version 4.1.



Scheme 4 Synthesis pathway of sample 2.

Intrinsic viscosity and absolute molar mass of the samples were recalculated according to the mass of sample injected.

Strain–stress curves were determined with an Instron 5544 at a draw rate of 8 mm min<sup>-1</sup> at 20 °C. Original specimens were of 7.5 mm length × 3.6 mm width × 2.4 mm height. Samples were first strained before strain–stress curves were effectively recorded (see details in text below).

Rheology measurements were performed with an AR 1000 from TA Instruments (Saint Quentin en Yvelines, France) operating in the oscillatory mode. The temperature was controlled by an environmental test chamber from 20 to 200 °C. A plate/plate rheometer, with 2.5 cm diameter cylindrical plates was used. Elastic storage modulus ( $G'$ ) and loss modulus ( $G''$ ) were measured as a function of temperature at a frequency of 1 Hz and a temperature rate of 2 °C min<sup>-1</sup>, with a strain of 0.25%.

## Results

### Preliminary (macroscopic) observations

Samples **1** and **2**, whose structures are given in Scheme 2, were prepared according to conventional silicone reactions, *i.e.* hydrosilylation, chlorosilane reduction and SiH hydrolysis in mild conditions (see Experimental section). Both samples were actually mixtures of oligomers of few repeating units, rather than single functional molecules (see an example of an SEC trace of **1** in Fig. S1, ESI†). **1** and **2** rapidly gelled into elastomers upon removal of the solvent of synthesis (THF), overnight and at room temperature (Fig. 1). These “gelastomers” thus formed could neither be resolubilized in conventional solvents for silicone and fluoroalkylated polymers nor in mixtures of these. As shown in Fig. 1, both materials **1'** and **2'** are non-tacky elastomers. Whereas material **1'** appeared very smooth and friable the material **2'** was found to be compact and shear resistant. Strain–stress curves measured on previously stretched samples‡ of materials **2'** (Fig. 2) demonstrated their elastomeric properties: remarkable elongation at break of about 1500% and moderate strain force were recorded, equivalent to those observed for a thermoplastic elastomer made of PDMS grafted with urea self-bonding functions.<sup>23</sup>

### Microscope evidence for structuration

The material **1'** was observed by different microscopic techniques, including TEM and AFM. Prior to TEM analyses, the soft material was embedded in an epoxide matrix and microtomed under cryo-conditions (below the  $T_g$  of the oligomeric material, *e.g.* -70 °C). The micrographs revealed the presence of nanoclusters randomly dispersed in the material, whose size is typically 50–100 nm (Fig. 3a). A closer approach showed clearly a phase separation inside the clusters (Fig. S4, ESI†) with electronically dense material appearing as black stains. Clustering was also observed by TEM for the cryotomed material **2'**; in this case however, clusters were larger than in **1'** (of the order of a few

microns). Inside these, again a phase separation between electron-rich and electron-poor domains is clearly seen (Fig. 3b).

We also performed AFM analysis, in tapping mode, on the surface§ of sample **1'**. Fig. 4 shows a large surface cluster accumulated using a conventional tapping mode, in phase and surface representation. The contrast (or phase) image separates soft (in black) from hard (in white) domains. The contour representation revealed an organization into lamellae.

Each lamellae exhibits widths of about 15 to 20 nm (Fig. S5, ESI†), in the same range as the patterns observed by TEM in the clusters (Fig. S4, ESI†). This lamellar path of about 15 nm is too thick to correspond to a single column of oligomer aligned through silanol–silanol interactions (a length of about 2 nm was calculated for a stretched oligomer structure). Rather, it may arise from a demixing between an amorphous water/solvent-swollen silanol-rich polar phase (soft phase) and a highly hydrophobic fluorosilicone domain (hard phase).

### Supramolecular interactions

There are numerous papers that reported the self-assembly of bis- or ter-silanol in simple organic molecules (for recent reviews, see ref. 24) and in modified polymers.<sup>25</sup> In the present study, the highly apolar oligomers **1** and **2** are likely to favour silanol–silanol interactions. Indeed, FTIR measurements on these molecules (Fig. 5) showed that Si–OH groups are mostly engaged in hydrogen bonds, by comparing the band at about 3300 cm<sup>-1</sup> against a sharp peak at 3650 cm<sup>-1</sup> for free silanol.<sup>25</sup>

We also demonstrated that these interactions are clearly (and at least partly) responsible for the gelling of the material. Indeed, one way of disrupting these interactions in organic solvent is to use a so-called chaotropic salt. For instance in the silicone industry, tetramethylguanidine (TMG)–trifluoroacetic acid (TFA) mixture in 1 : 3 proportion,<sup>26</sup> which is soluble in conventional silicone solvent, helps to disrupt hydrogen bonding between silanol groups to favor polycondensation in toluene (a slight excess of acid normally catalyzes the reaction).<sup>17</sup> Upon mixing materials **1'** and **2'** with this so-called “chaotropic agent”, both gelastomers lost their supramolecular organization and solubilized in THF (such rapid dissolution did not occur in a less polar solvent such as toluene). Another way of dissolving these materials **1'** or **2'** is through end-capping of silanol functions with a simple dimethylvinylchlorosilane.¶

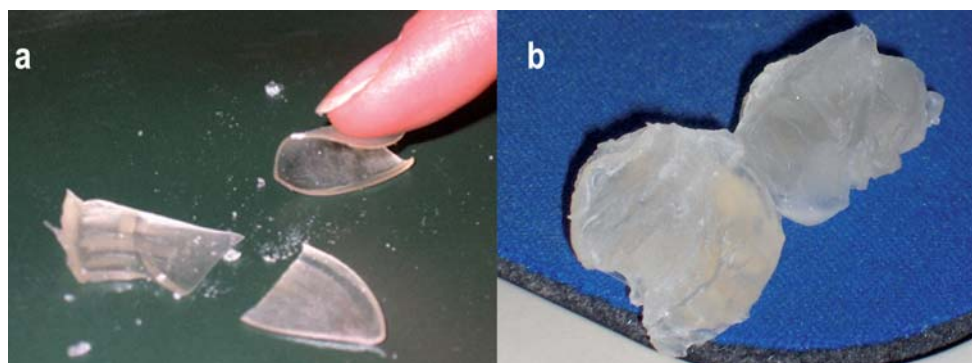
DSC measurements were also carried out on both materials (Fig. 6). Besides the  $T_g$  of **1'**, which was found naturally lower (-65 °C) than the corresponding high molar mass polymer (typically -50 °C, see ref. 16), a second transition was observed at about -30 °C, which arises from silanol–silanol interactions. Such secondary transition was not observed in a second or third ramp (Fig. S6, ESI†).

§ The surfaces generated by slicing the material under liquid nitrogen freezing were not sufficiently flat to make satisfactory observations of the core of the sample.

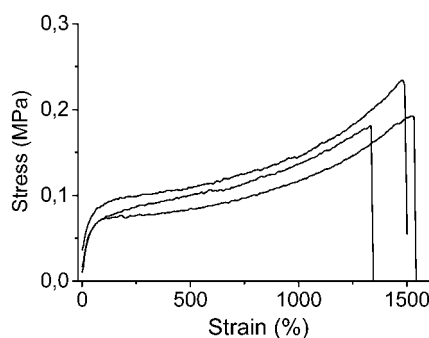
¶ For materials prepared freshly (few days), a simple mix of elastomer and the vinyl dimethylchlorosilane in THF for one night was enough to lead to a homogeneous polymer solution. For aged samples, both the chaotropic salt and vinyl dimethylchlorosilane in THF were mixed to come back to a readily homogeneous solution (sample **2'**).

‡ Stress–strain curves were originally carried out on pristine material, but we noticed a lack of reproducibility from one test sample to another (see Fig. S2, ESI†). The fact that stretched samples exhibited similar stress–strain curves can be explained by the fact that strain favors the reorganization of the polymer chains.

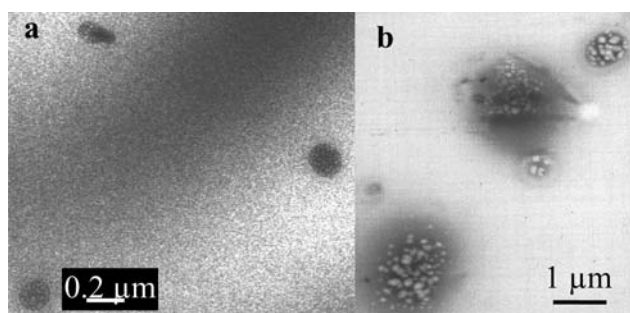




**Fig. 1** Photos of gelastomers obtained from the model fluorinated silicone oligomers described in Scheme 2: (a) material 1'; (b) material 2'.



**Fig. 2** Strain–stress curves for sampling tests of the material 2'. Speed of traction = 8 mm min<sup>-1</sup>.



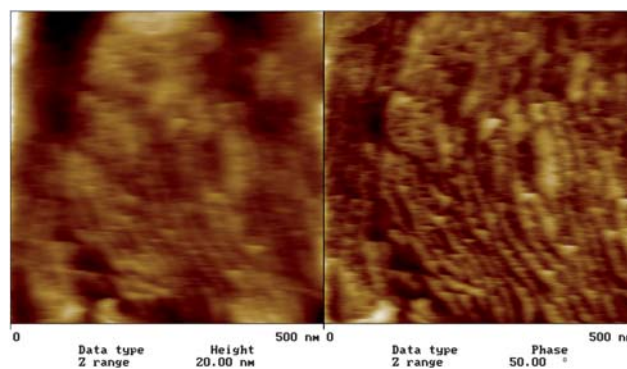
**Fig. 3** TEM microscopy of cryo-microtomed samples of 1' (a) and 2' (b). The scales are given on the photos.

For material 2' (Fig. S7, ESI<sup>†</sup>), a slightly higher glass transition ( $-21\text{ }^{\circ}\text{C}$ ) was observed by DSC, ascribed to a larger content of fluorinated groups in the oligomer. Besides, we did not observe any transition arising from silanol self-H bonding; we tentatively endorsed this absence to the larger temperature range of this transition, not observable by conventional or advanced DSC techniques.||

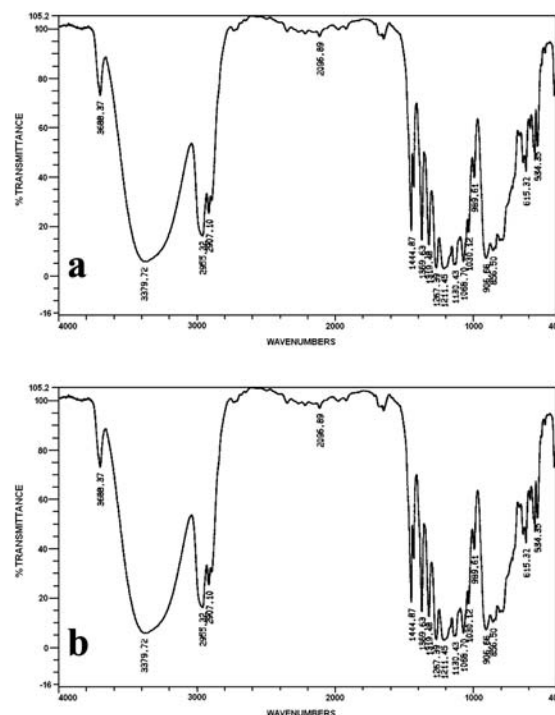
### Template polycondensation

SEC analyses of end-capped 1 and 1', revealed that the oligomer distribution has shifted towards slightly larger molar masses

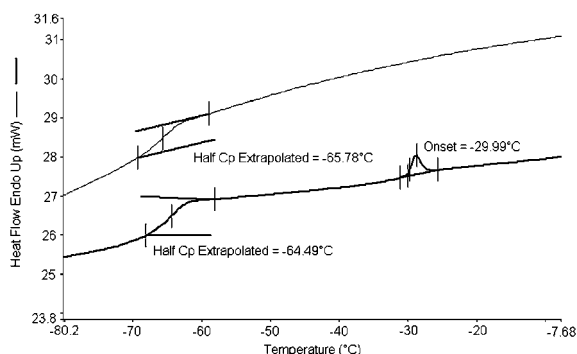
|| We carried out analyses at different temperature ramps, without success. Also, analyses were run on a modulated DSC apparatus but did not show clear transitions either (not shown).



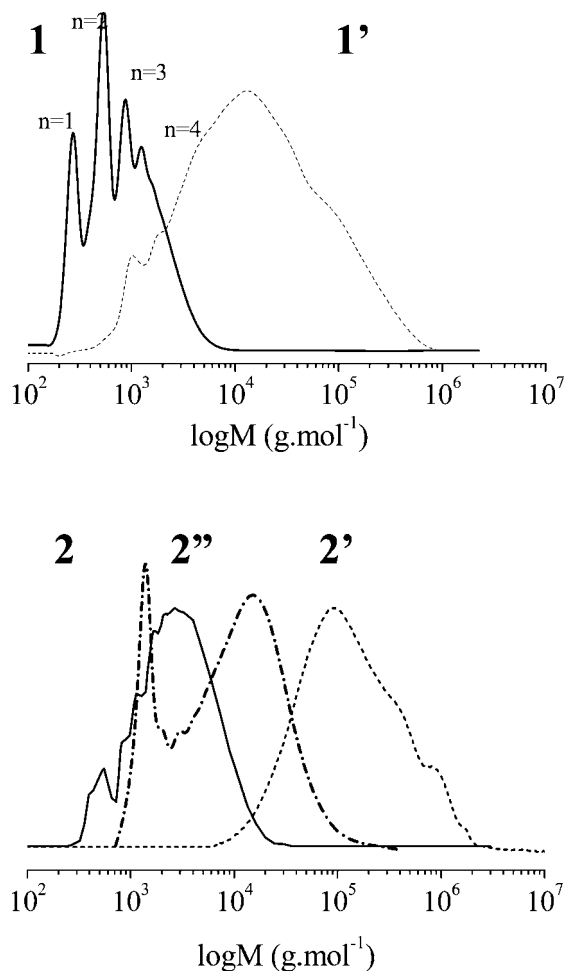
**Fig. 4** AFM micrographs on a cluster observed at the surface of the material 1. Tapping mode, with (left) surface contours (right) phase contours.



**Fig. 5** FTIR of hydrolyzed non-evaporated liquid samples 1 (a) and 2 (b).



**Fig. 6** First temperature ramp DSC analyses of the material **1'**, after two days (curve below) and after three months (top curve).



**Fig. 7** SEC curves of samples **1** and **2** (—) and **1'** and **2'** (---) end-capped by a vinyltrimethylchlorosilane. The SEC curve of **2''** (---, end-capped in the presence of TMG–TFA) presents an additional sharp low molar mass peak, assigned to the excess of chlorosilane introduced in the recipe.

through gelling (Fig. 6). Peak integration gave an average degree of polymerization of 12 for material **1'** (14.5 by  $^1\text{H}$  NMR) against 2.5 for **1** (3.6 by  $^1\text{H}$  NMR), with a broad distribution of mass (final  $M_w/M_n$  is more than 5). Such a displacement of the molar mass distribution is a sign of a template polycondensation of

silanol groups interacting in the polar phases in the clusters. The disappearing of the hydrogen bonding transition in the DSC trace after three months of stocking at room temperature (Fig. 6), as well as the vanishing of the Si–OH band in FTIR (Fig. 7) are other evidences that the materials slowly consumed the silanol groups with time.

While trying to end-cap the material **2'** SEC revealed an apparent average molar mass of about  $85\,200\text{ g mol}^{-1}$ , and again a very large polydispersity (5.6) (Fig. 7). We assumed that all silanol groups embedded in the large clusters did not react under these simple conditions, still generating supramolecular interactions. We then carried out the chlorosilane end-capping reaction *in presence of the chaotropic agent*. In these conditions, the polymer (**2''** in Table 1) totally dissolved in THF. Its average molar mass ( $M_n$  of 11 890 and 9300  $\text{g mol}^{-1}$  by conventional SEC (Fig. 7) and  $^1\text{H}$  NMR, respectively) are close to those observed for **1'**.

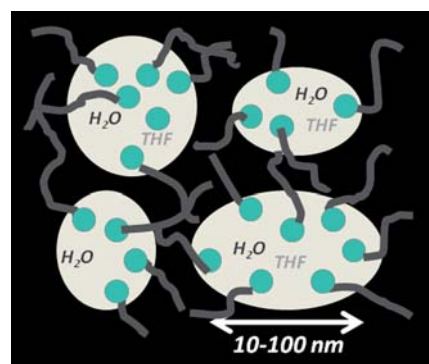
## Discussion

We have shown in the results that oligocarbosiloxanes with a sufficient (but not too large) number of repeating fluorosilicone units, where  $R_F$  is linear, and bearing silanol chain-ends, gel upon solvent removal to provide an elastomer material. We propose in this discussion complementary insights to successfully generate physically-crosslinked fluorinated silicones and enlarge the scope of this study.

Scheme 5 tentatively draws a cartoon of a typical cluster as observed by TEM in materials **1'** or **2'**. Clear zones embed silanol groups strongly interacting with each other as well as with polar solvents (THF and water liberated from Si–H hydrolysis). Around these polar zones, strongly hydrophobic fluorosilicone-rich domains form. Clusterization may first arise through an organized demixing pathway, into lamellae as observed by AFM on the *surface* of material **1'** (Fig. 4). Then, these clusters slowly evolve into “patchy” structures, as those observed by TEM *in the core* of the material.

### Chemical structures which provoke (or not) the self-assembly

In most of the syntheses carried out previously in the lab, we had rarely observed the quick setting of oligomeric building blocks



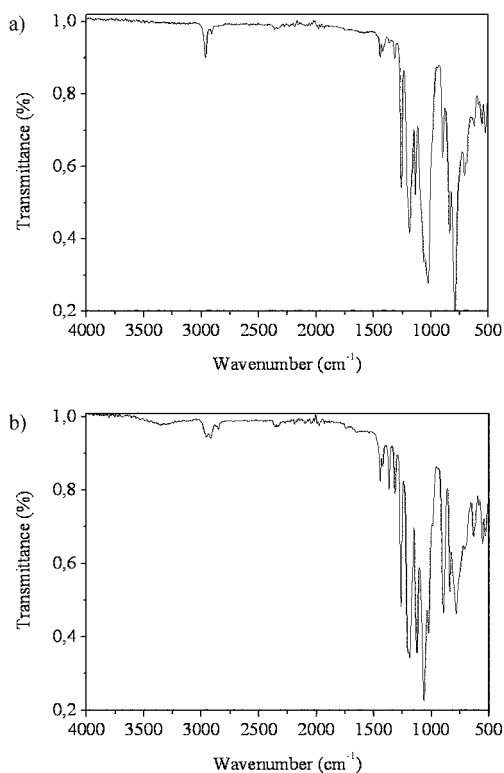
**Scheme 5** Schematic cartoon of a cluster in material **2'**. Balls represent SiOH moieties, clear areas are solvent/water swollen domains, black background + grey chains represent the fluorosilicone hard domain.

after Si–H hydrolysis and solvent removal, as those observed here. Apart from the compulsory silanol extremities, there are thus several other conditions in preparing a self-assembling material from simple oligocarbosiloxane bricks.

Adjacent fluorinated groups in the core of the fluorinated moiety (obtained from HFP monomer, samples **3** and **4** in Table 1) prevent organization of the fluorosilicone blocks, and thus gelling.<sup>5,7,9,10,16</sup> Similarly, introducing only one D unit, *i.e.* Me<sub>2</sub>SiO group (not bearing a fluorinated functional group as in oligomer **2**), on each side of the fluorinated moiety does not provoke demixing and thus gelling (sample **9**, Table 1).<sup>5,8–10,16</sup>

During the synthesis of **1**, we separated by distillation ( $T_b = 93$  °C, 0.3 mbar) the  $n = 1$  product from the mixture of Si–H functionalized oligomers **1** (see Experimental section, Scheme 3, and SEC spectrum of the residue, Fig. S1, ESI†). Once hydrolyzed, the resulting and simplest disilanol **5** (Table 1) did not gel, but remained oily. This result is consistent with the fact that perfect end-capping of a diene by other methods than Si–H hydrolysis never produced gelastomers.<sup>5,7,9,10,12,16</sup>

There are other products from our laboratory, as detailed in Table 1, that naturally transformed into gelastomers, although we did not further characterize them here. For instance, hydrosilylation between equal amounts of the diene and L<sub>3</sub>H (**6'**, Table 1) or L<sub>4</sub>H (**7'**, Table 1), rather than L<sub>2</sub>H, resulted in similar gelled materials, yet softer than **1'**. In **2**, changing the CF<sub>3</sub> side group to C<sub>4</sub>F<sub>9</sub> (sample **8'**, Table 1) produced a new gelastomer with even stronger cohesion than **2'**, since it could not be dissolved in THF by the chaotropic agent–chlorosilane system.



**Fig. 8** ATR-FTIR of materials **1'** (a) and **2'** (b).

## Silanol–silanol H bonding

We have considered here that the presence of highly polar silanol groups attached to highly hydrophobic fluorinated silicone oligomers render these latter inhomogeneous enough to perform effective phase demixing. The larger the content of silanol groups, the better the clusterization, other things being equal. FTIR spectra showed for instance that material **2'** exhibits a larger Si–OH band than material **1'** (Fig. 8), whereas the inverse tendency was observed for the original oligomers **1** and **2** (Fig. 4). The fact that the chaotropic agent alone is not able to fully disrupt the physical interactions in the polymer **2'** (Fig. 7) also suggests very strong silanol–silanol interactions.

Another evidence on the importance of silanol–silanol hydrogen bonding on the generation of gelastomers can be found from the following experiment. We carried out the polycondensation of **1** *without* proceeding to THF evaporation by using a conventional catalyst.\*\* A polymer with an average molar mass of about 10 000 g mol<sup>-1</sup> was obtained as a viscous oil, not a gelastomer (sample **10**). We already demonstrated by triple detection SEC<sup>27</sup> that in this polycondensation process, most of the polymer chains end-bite to form large contents of macrocycles, without silanol chain-ends. In the present work, however, the template polycondensation produces polymers of about the same molar masses, but keeping an important loading of silanol groups, of primary importance to maintain the integrity of the gelastomer.††

## Is crystallization required?

We wondered if crystallization would be necessary for gelling to occur: indeed, we observed previously that, all things being equal, introducing side groups in the perfluorinated core avoided the arrangement of these and did not lead to gelastomers. However, sample **10**, the polymer obtained from **1** by conventional polycondensation, has been shown by DSC to exhibit both crystallization and fusion points (Table 1), without presenting any gelling behavior. We tried to characterize the material **2'** by X-ray crystallography, but we did not observe clear diffraction peaks. Besides, DSC analyses, even under a modulated regime, did not show any transition, such as fluorinated group stacking, which would arise around 20 °C. All these data seems to evidence that the present gelastomer is amorphous but still presents important mechanical properties.

## On the template polycondensation

The template polycondensation was shown to be a very slow process, as demonstrated by DSC for sample **1/1'** (Fig. 6). In the

\*\* In a typical recipe, polycondensation of 40 mmol of product was carried out in a Dean–Stark apparatus, in 10 mL of tetrahydrofuran, using three drops of a 3.1 : 1 trifluoroacetic acid–tetramethylguanidine catalyst, at reflux of solvent (around 66 °C). Polycondensation proceeded by gradual removal of water in the trap, owing to the azeotrope formed between water and THF (65 °C at room pressure).

†† We tried in the course of this study to use triple detection SEC to generate Mark–Houwink plots and to confirm the linearity of the different chains solubilized from our materials. Unfortunately, these analyses were carried out in toluene, which is not a good solvent to fully dissolve both materials (see Fig. S8, ESI† for examples of SEC3 analyses).



course of this study, we have tried several times to follow qualitatively the kinetics of polycondensation by evaporating the THF solvent at different times (from a few hours to weeks), with no success: the apparent content of silanol groups did not decrease sufficiently to be seen by FTIR. Note also that ageing the samples in an oven at 120 °C during several days did not accelerate the process or render the material more elastic: strain–stress curves were equivalent to those obtained for pre-stretched **2'** materials.

This template polycondensation is unique *per se*, since it proceeds in absence of catalyst and in the solid state, without the need for heating the material (unlike in ref. 27, for instance). The final molar mass remains moderate however.‡‡ Coming back to the study published by Pierce *et al.* in 1971,<sup>22</sup> they proposed that their samples entailed sufficient molar masses to generate elastomeric properties. We believe that, according to the structures analyzed here, the average molar masses that they reported were apparent rather than real ones (they did not make use of the chaotropic agent).

## Conclusion

Despite the industrial potential of fluorosilicone elastomers, the synthesis of hybrid alkylated or fluorinated silicone oligomers has never led to materials with satisfactory mechanical properties to be commercially viable. The physical chemical technique described in this article, once mastered, presents a unique alternative. It consists in tailoring intelligent building blocks, made of silanol-terminated fluorinated oligomers, which naturally cluster and condense into elastic materials. These products swell, but does not dissolve, into conventional solvents and show interesting mechanical properties, even in the absence of a reinforcing filler. We are currently trying to incorporate silica into the material **2'**, prior to gelling, in a view to strengthen the Young's modulus while keeping the elasticity of the material. We are also analyzing the materials by rheometry§§ and dynamic mechanical analyses to determine a transition temperature at which the material would thermally disrupt, if it does.

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‡‡ It is not obvious whether this polymerization really provides better properties to the final elastomer. It is anticipated that the consumption of silanol functions would contribute to the disappearance of clusters and decrease the mechanical integrity of the material. Efficient and rapid aging conditions are still to be found to comment further on this point.

§§ Fig. S9 (ESI†) presents preliminary results on  $G'$  and  $G''$  data of sample **2'** acquired as a function of temperature. We did not observe any clear melting of the material in this temperature range. Besides, the materials seem to reinforce with temperature, a trend that remains to be elucidated.