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Poly-silafluoroalkyleneoligosiloxanes: a class of fluoroelastomers with low glass transition temperature

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Abstract

This work reports some results about the synthesis of unsaturated poly-silafluoroalkyleneoligosiloxanes—derived from TFE telomers—which, after crosslinking, gave elastomeric materials characterized by good flexibility at low temperature, glass transitions below −45 °C and good thermooxidative stability over 250 °C. They are proposed as alternative materials with respect to polyfluoroolefin elastomers.

Keywords: Fluorinated polysiloxanes; Fluoroelastomers; Crosslinking; Thermal stability

1. Introduction

The simplest prototype of the fluorinated silicones (1) is the poly-methyl-3,3,3-trifluoropropyl-siloxane that was pioneered in the 1950s [1] and commercially developed by Dow Corning in the 1960s [2,3].

The major drawback of the polysiloxanes (1) was their tendency to depolymerize at high temperature, or in the presence of acid or basic agents, by unzipping to give thermodynamically stable cyclosiloxanes, mainly formed by 3-4 siloxy units (D_3, D_4); the heavier the dialkylsiloxy units are, the easier the unzipping process is (cf.; Table 1, entries 9, 10 versus 6).

Such a depolymerization process was prevented by inserting an alkylene (or phenylene) spacer between two silicon atoms, leading to the poly-silafluoroalkylenesiloxanes, named "hybrid" silicones (2), which showed higher reversion strength [4,5]. Random copolymers containing both type (1) and (2) units showed intermediate properties depending on their composition. No hybrid fluorosilicone was ever commercialized.

$$-[R(R')SiO]_X- \quad R = -CH_3; R' = -C_2H_4CF_3, -C_2H_4C_4F_9$$

$$-[R(R')SiC_nH_{2n}R_FC_nH_{2n}SiR(R')O]_y- \quad R_F = -(CF_2)_m-,$$

$$-(CF_2)_mO(CF_2)_m-; n = 2, 3; m = 1 - 10$$

Later, the present authors developed monoiodo-telomers and telechelic diiodo-cotelomers of fluorinated olefins that have been converted to polysiloxanes type (1) and polysilafluoroalkylenesiloxanes type (2) carrying heavier and branched substituents, first by following the general early Scheme 1 [6b], then through the Scheme 2 [7].

In particular, several hybrid fluorosilicones, their silane precursors and their copolymers have been widely described elsewhere by the authors [8–12]; their properties of high thermostability and low glass transition temperatures (Table 1) appeared attractive for applications in the areas where high flexibility at low temperature was required while it was not well satisfied by commercial polyfluoroolefins.

However, the interesting thermophysical properties of the hybrid fluorosilicones were counterbalanced by the evident complexity of the cotelomerization process. Consequently there was a need to look for alternative structures of fluoroelastomers, easily synthesizable at competitive costs, and showing good elastomeric properties in a wide range of temperatures, from about −50 to +250 °C.

2. Results and discussion

2.1. Synthesis of new hybrid fluoro silicone elastomers apt to be applied in a wide range of temperature (WTFSE)

TFE is the most convenient source to build a fluoroelastomer backbone; however, the perfluorinated segment

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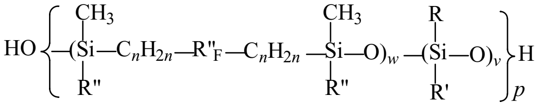
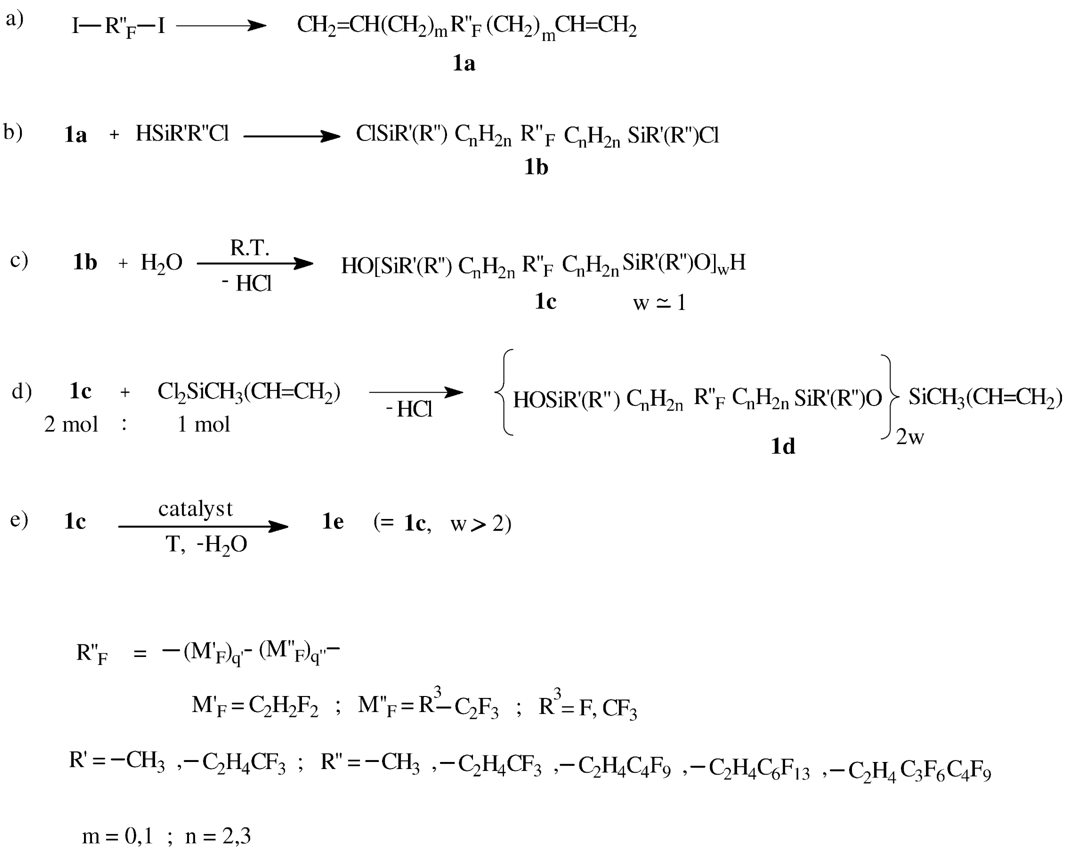
Table 1
Thermophysical properties of hybrid fluorosilicones and copoly-dialkylsiloxanes



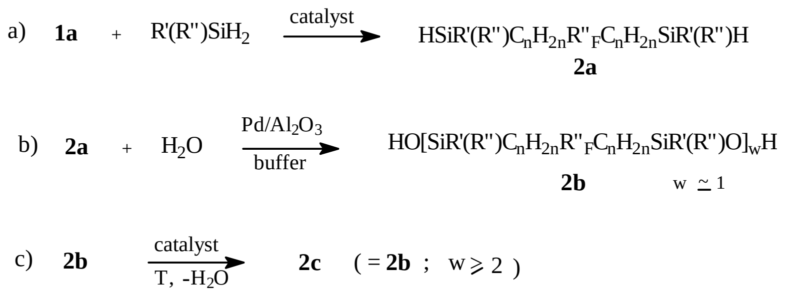
$$HO\left\{-(\underset{R''}{\overset{CH_3}{Si}}-C_nH_{2n}-R''_F-C_nH_{2n}-\underset{R''}{\overset{CH_3}{Si}}-O)_w-(\underset{R'}{\overset{R}{Si}}-O)_v\right\}_p H$$

	R''	R''_F	n	w	R	R'	v	p	DSC (10 °C min^{-1})		TGA, loss wt.% (5 °C min^{-1})					
									T_g	T_m	N_2			Air		
											T_2	T_{10}	T_{50}	T_2	T_{10}	T_{50}
1	CH_3	C_6F_{12}	2	1	–	–		20	−53	+26	315	410	470	255	300	380
2	CH_3	C_6F_{12}	3	1	–	–		19	−40	+25	315	410	465	250	270	330
3	$C_2H_4CF_3$	C_6F_{12}	2	1	–	–		61	−28	Abs	320	450	480	340	365	410
4	$C_2H_4C_4F_9$	C_6F_{12}	2	1	–	–		40	−42	Abs	330	460	490	295	325	360
5	$C_2H_4C_4F_9$	C_6F_{12}	3	1	–	–		12	−29	Abs	310	410	470	275	285	310
6	$C_2H_4CF_3$	C_6F_{12}	3	1	CH_3	CH_3	1	14	−34.5	Abs	290	430	480	280	360	400
7	$C_2H_4CF_3$	HFP/C_4F_8/HFP	3	1	–	–		10	−34	Abs	245	320	445	200	290	310
8	$C_2H_4C_4F_9$	C_2F_4/VF_2/HFP	3	1	–	–		12	−47	Abs	295	400	420	290	295	315
9	$C_2H_4CF_3$	C_6F_{12}	2	1	CH_3	$C_2H_4C_6F_{13}$	0.63	10.5	−40	Abs	245	400	475	–	–	–
10	$C_2H_4CF_3$	C_6F_{12}	2	1	CH_3	C_2H_4–C_3F_6–C_4F_9	1*	15.3	−44	Abs	220	310	470	–	–	–
11	$C_2H_4CF_3$	C_6F_{12}	2	1*	CH_3	$C_2H_4C_6F_{13}$	2**	21	−35	Abs	400	450	475	–	–	–
12	$C_2H_4C_4F_9$	C_6F_{12}	2	1**	CH_3	$C_2H_4C_4F_9$	20	7	−59	Abs	230	260	330	–	–	–

HFP = $-CF_2CF(CF_3)-$; VF_2 = $-CH_2CF_2-$.
* Block copolym. $(wv)_p$.
** Block copolym. $(vwv)_p$.



Scheme 1.



Scheme 2.

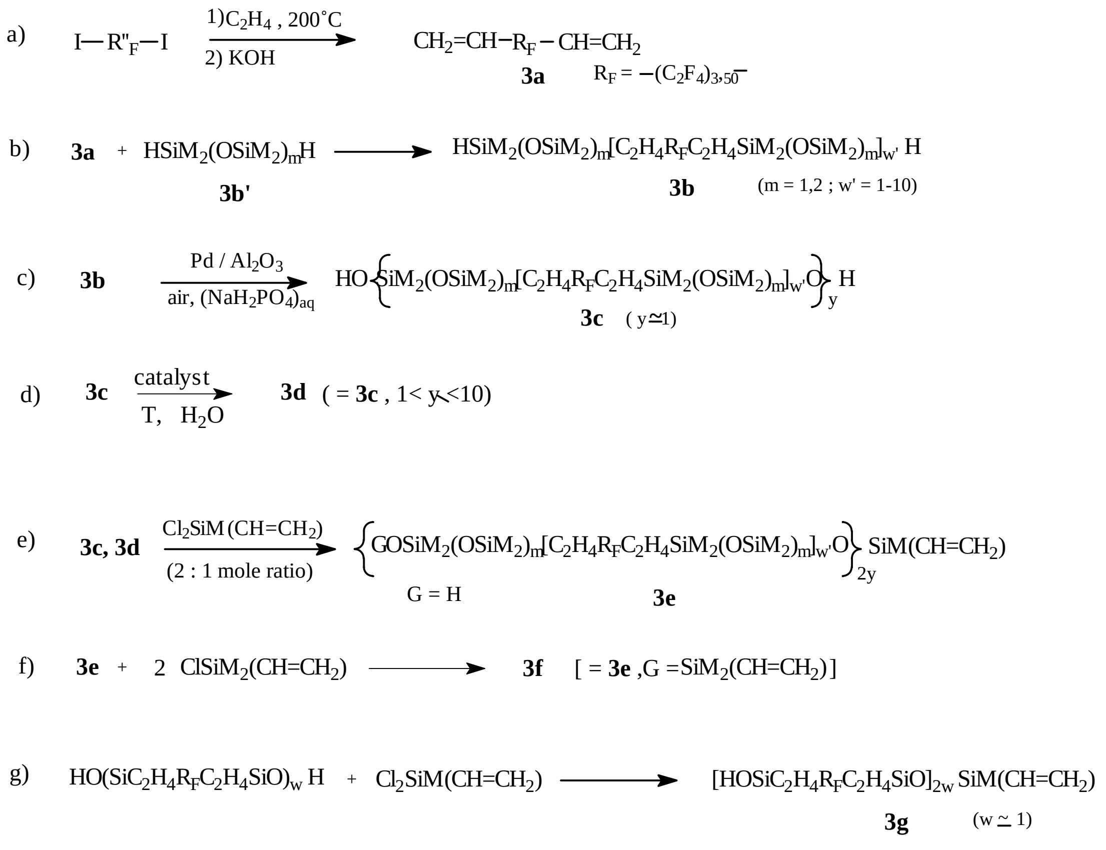
derived, being rigid, needs to be not very long and to be alternated by a flexible joint. A convenient flexible joint may be a siloxy unit, but a single siloxy unit, interposed between two subsequent perfluorocarbon segments, does not leave enough free rotation to prevent the interchain aggregation and cristaline organization (Table 1, entries 1, 2); a sequence of siloxy groups is a good option provided that it is shorter than three –SiO– units inserted between two silacarbon groups in order to avoid any intramolecular unzipping of volatile cyclopolysiloxanes under thermal stress.

A procedure has been set up to obtain polysilafluoroalkylene oligosiloxane elastomers from discrete linear perfluorinated segments alternated with flexible discrete oligosiloxane joints and able to cover a range of thermophysical and chemical properties complementary to the existing commercial fluoroelastomers [13].

2.2. Preliminary preparation of the intermediates

The objective was pursued by the following steps according to Scheme 3 and to the previous Schemes 1 and 2:

(a) A mixture of TFE telomers, trimers and tetramers (possibly with a negligible percentage of pentamers),



Scheme 3.

Table 2
Macrointermediates for novel hybrid fluorosilicone elastomers

	Scheme intermediates	Intermediate conventional label	M_W (typical value)
$ClSi(CH_3)_2–C_2H_4–R_F–C_2H_4–Si(CH_3)_2Cl$	**1b**	Cl–I–Cl	593
$HOSi(CH_3)_2-[OSi(CH_3)_2]_m\{C_2H_4R_FC_2H_4Si(CH_3)_2[OSi(CH_3)_2]_m-\}_{w'}OH$	**3c**	HO–II–OH	2380
$[HO–Si(CH_3)_2–C_2H_4–R_F–C_2H_4Si(CH_3)_2O]_{2w}SiCH_3(CH=CH_2)$	**3g**	HO–III–OH	1180

$R_F = –(C_2F_4)_{3.5}–$; $m = 2$; $w' = 3.5$; $w \sim 1$.

was considered a convenient intermediate from both the standpoints of the producer, with available TFE and telomerization process from a telogen diiodide, and that of the reactive versatility of the telechelic telomers. The telechelic diiodotelomers were converted easily to the key intermediates as the telechelic α,ω-divinyl-perfluoroalkanes (**1a**, **3a**) and the α,ω-dichlorosiladialkylethylene-perfluoroalkane (**1b**).

(b) The diene **3a** was reacted with low M_W α,ω-dihydro-(oligo)dimethylsiloxane (**3b′**), commercially available. The M_W of the adduct (**3b**) depends on the ratio of the two reagents in particular the highest M_W was first obtained with a ratio near 1:1 and the remaining unsaturated terminals of the adduct were completely converted by reaction with a further excess of dihydrooligosiloxane.

(c) The telechelic α,ω-dihydrosilane terminated adduct (**3b** or **2a**) was converted to the corresponding silanol terminated adduct (**3c** or **2b**), by oxidative hydrolysis in the presence of catalyst Pd/Al_2O_3 and aq. NaH_2PO_4 buffer at room temperature. The disilanols were maintained near 0 °C in order to quench any polycondensation, that could form possible unstable longer sequences of siloxy units.

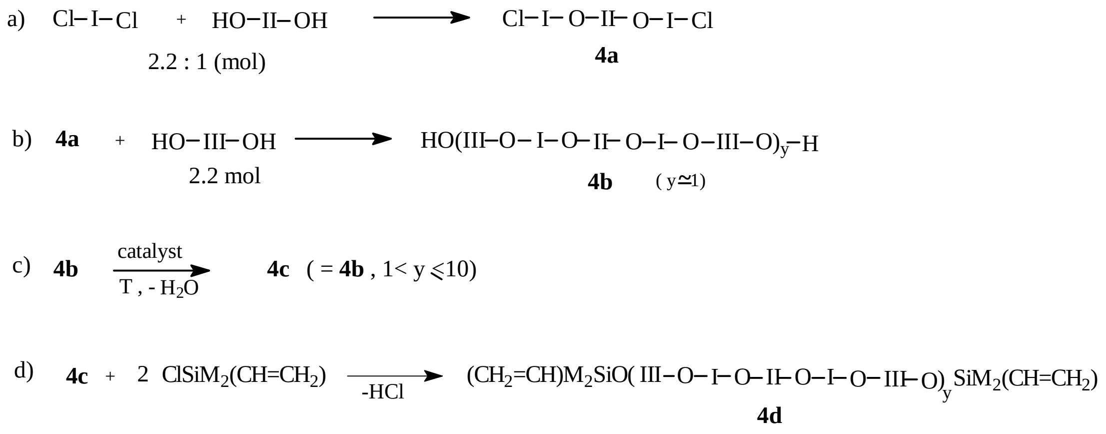
(d) The hybrid α,ω-disilanol-perfluoroalkane (**1c**, **2b**, **3c**) was reacted in a 0.5 mole ratio of dichloromethylvinylsilane to obtain an unsaturated intermediate (**1d**, **3e**).

Table 2 shows a possible system based on three key intermediates that have been properly combined to obtain a typical new hybrid fluorosilicone elastomer. The condensation of the α,ω-dichlorosilane **1b** with the α,ω-dihydroxysilane **3c** and the α,ω-dihydroxysilane **3g**, that contains pendant vinyl groups, will lead to the desired hybrid fluorosilicone and, after crosslinking, to the new hybrid fluorosilicone elastomers.

2.3. Synthesis of poly-silafluoroalkyleneoligosiloxane elastomers (WTFSE)

A concerted sequence of condensations of the three key intermediates (Table 2), dosed in proper ratios, was followed according to Scheme 4. First, the building blocks **4a** and **4b** have been obtained, then the unsaturated building block **4b** was polymerized and end capped with vinyl silane to the polyunsaturated fluorosilicone **4d** that was crosslinked to the final elastomer.

The three intermediates of Table 2 have been designed and selected in order to combine them and to avoid, or to minimize, the formation of sequences of more than two siloxy units between two silacarbon groups (Si–C) during the condensation steps. More specifically, Scheme 4 avoids the polycondensation of telechelic disilanol **3c** that would form a fluorosilicone **3d** (for $m = 2$) less thermally stable than fluorosilicone **4d**. Alternatively, a stable fluorosilicone type **3c** could be derived from tetramethyldisiloxane [14].



Scheme 4.

In the specific case detailed hereafter where the perfluoroalkane segment was derived by a quasi-equimolar mixture of TFE trimers and tetramers, the polyunsaturated hybrid fluorosilicone **4d** obtained following Scheme 4 was represented by the average structure of formula (3) as identified by NMR (^{1}H, ^{19}F, ^{29}Si) analysis and with M_W around 8500 g mol^{-1}.

$$\begin{aligned}&(CH_2{=}CH)SiM_2O\Big\{[SiM_2C_2H_4R_FC_2H_4SiM_2O]_s[SiM(CH{=}CH_2)O]_r[SiM_2C_2H_4R_FC_2H_4SiM_2O]_r\\&-SiM_2(OSiM_2)_m[C_2H_4R_FC_2H_4SiM_2(OSiM_2)_m]_{w'}O\Big\}_p SiM_2(CH{=}CH_2)\end{aligned} \tag{3}$$

$M = -CH_3, R_F = -(C_2F_4)_{\sim 3.5}-; m = 2; r = 2.2; s = 4.4; w' = 3.5; p = 1.3$

The hybrid fluorosilicone (3) was examined by DSC and showed standard behaviour for an amorphous material with glass transition temperature (T_g) around −70 °C; when charged with fumed silica (17 parts), peroxide (0.6 parts) and crosslinked at 160–180 °C by moulding under the press plates it formed flexible and elastic sheets, thin slabs and films showing T_g near −61 °C by DSC, while the tensile modulus temperature relation, determined by Dynamic Mechanical Analyser, showed a second-order transition temperature at −53 °C, between the plateau of the glassy region with modulus 2 GPa, in the range −70 to −120 °C, and the rubbery region plateau with modulus of about 6 MPa at about −40 °C and 5 MPa at +50 °C.

Samples of the crosslinked films here described were practically insoluble in organic solvents (ethylether, tetrahydrofurane, chloroform, toluene). Other samples, crosslinked with a lower peroxide content, were slightly soluble in some low dielectric constant carbonate esters such as DMC and DEC (respectively, for 4 and 8 wt.% at 20 °C, after 24 h immersion); after 7 days immersion in said solvents or their mixtures at RT, the film samples were swollen from 20 to 35 wt.% (Table 3).

The highest swelling degrees of the lightly crosslinked specimens were obtained in solvents characterized by solubility parameters near 18–20 MPa$^{1/2}$ and moderate hydrogen bonding capability as well as by low dielectric constant. Moreover, the swollen specimens appeared as consistent gels able to retain the permeated solvent without bleeding; such behaviour suggested the next investigation on their application as gel polymer membranes and polymer hybrid electrolytes for lithium ion batteries or electro-active devices. The crosslinked elastomer showed high thermostability in air as determined by TGA (Table 4).

An alternative crosslinking route was validated for the hybrid fluorosilicone (3) by the typical procedure of polyunsaturated silicones based on Pt-catalysed addition with polyhydromethylsiloxanes; at 100 °C, a crosslinked elastomer was obtained with T_g below −60 °C.

As a final consideration, the particular architecture that could be designed for the new class of hybrid fluorosilicones, where the perfluorinated segments and the sequences of the dimethylsiloxy groups, both the constituents being provided with low intermolecular forces and properly alternated, allowed chain flexibility and low glass transition temperatures; the easy feasibility to modify pendant branches, terminal groups and vinyl concentration with effects on thermal physical and mechanical properties and other chemicophysical characteristics, makes the material suitable for applications by demanding technologies of transformation (e.g. LIM and as LTV rubbers) and for application, where commercial polyfluoroolefin rubbers can be hardly applied.

Table 3
Swelling tests in organic solvents of hybrid fluorosilicone crosslinked membranes

Solvents	M_W	Density g cm^{-3} (25°C)	Dielectric constant ε_r (25°C)	Hildebrand Parameter (MPa)$^{1/2}$	Notes	Swelling (sw, wt.%), RT, 24 h	Solubility (σ, wt.%) RT, 24 h
DMC	90.08	1.07	3.1	20.3		20 ± 5	4 ± 1
DEC	118.13	0.97	2.8	18		30 ± 5	8 ± 1
EC	88.06	1.32*	89*	30*	(40°C)*	Not det.	Not det.
EC-DMC (1:1 mol)		(1.18)	(41.3)	(24.6)	(Calc.)	15 ± 3	2
EC-DEC (1:1 mol)		(1.1)	(33.6)	(22.2)	(Calc.)	22 ± 5	8 ± 2
γBL	86.09	1.13	39	25.8		4	1

Composite membrane formulation: hybrid fluorosilicone (100 parts), fumed silica (17 parts), varox peroxide (0.3 parts); 170 °C, 1 h.DMC: dimethylcarbonate; DEC: diethylcarbonate; EC: ethylenecarbonate; γBL: γ-butyrolactone.Hildebrand solubility parameters, relative dielectric constants as reported [15] or calculated (mixing volume changes were disregarded).

* Physical data referred at 40 °C, where EC is liquid.

Table 4
TGA results determined on the crosslinked hybrid fluorosilicone (iv)

Loss wt.%	Temperature (°C, program 5 °C min^{-1})	
	N_2	Air
2	280	260
5	350	310
10	410	350
50	490	420

3. Conclusion

Quasi equimolar mixtures of telechelic diiodo trimers and tetramers of TFE (convenient source of fluorinated dienes) and commercial silane derivatives (hybride terminated oligosiloxanes and chloromethylhydrosilanes) were reacted to obtain intermediates such as α,ω-dichlorosilafluoroalkanes, α,ω-dihydroxysilafluoroalkanes and α,ω-dihydroxysilafluoroalkane oligosiloxanes.

These intermediates were combined according to a concerted reaction scheme; new hybrid fluorosilicones were obtained, with perfluorocarbon segments alternated by flexible polysiloxane joints. The number of sequential siloxy units was limited in order to avoid the intramolecular unzipping of volatile cyclosiloxanes under thermal stress. Samples of these new polyunsaturated hybrid fluorosilicones have been crosslinked at high temperature with peroxides, or at lower temperature in the presence of polyhydromethyl siloxane and a Pt catalyst to obtain elastomers, flexible at low temperature, with T_g near −60 °C, and characterized by good thermal and mechanical resistance.

Finally, the particular architecture of the new hybrid fluorosilicones, easily modified in the constituents, perfluoro segments and alternated sequences of siloxy units, alkyl and vinyl pendant groups, M_W, crosslinking mechanisms, are interesting materials with properties and performances complementary to the polyfluoroolefins elastomers.

4. Experimental

4.1. General experimental procedures

FTIR spectra were recorded on a Nexus FTIR Nicolet spectrometer. The positions of the bands are given in cm^{-1} with a precision of ±2 cm^{-1}. ^1H, ^{19}F and ^{29}Si NMR spectra ($CDCl_3$ as solvent in all spectra) were recorded on a AC 200 or a WH 250 MHz Bruker apparatus with TMS as the internal reference for ^1H and ^{29}Si and $CFCl_3$ as the internal reference for ^{19}F; the letters s, d, t, q and m stand for singlet, doublet, triplet, quadruplet and multiplet, respectively. The differential scanning calorimeter was a Perkin-Elmer Pyris 1 DSC apparatus calibrated with decane and indium under N_2. All the samples were heated from −120 to +50 °C at 20 °C min^{-1} to determine a T_g.

DMA was performed with a Perkin-Elmer DMA 7e apparatus calibrated with hexane and indium. All samples were run at 5 °C min^{-1} and 1 Hz from −130 to 250 °C. TGA was performed on a TGA 51 Instruments Thermal Analyst 2000 apparatus at a heating rate of 5 °C min^{-1} from 80 to 900 °C.

Size exclusion chromatography (SEC) was performed on a Spectra Physics apparatus with two PL gel columns (5 μm particle size, 300 mm length and 50 and 100 Å pore size) and one Styragel HR2 column (7.8 mm internal diameter and 300 mm length); detection was achieved with an SP8430 differential refractometer; the eluent was tetrahydrofuran, and the flow rate was 0.8 ml min^{-1}.

Solvents were purchased from Aldrich; silanes and polyhydromethylsiloxanes from ABCR.

4.2. Preparation of the intermediates

The intermediates were prepared following Schemes 1 and 3, or in some cases the early references [1,2]; the typical intermediates listed in Table 2 have been designed in order to apply Scheme 4 and to arrive at the hybrid fluorosilicone (3).

4.2.1. Telechelic divinyl perfluoroalkane (Scheme 3, **3a**)

An aliquot of telechelic diiodo telomers of TFE (50:50 mixture of trimer and tetramer, 91 g, 0.15 mol) was converted to the α,ω-divinylperfluoroalkane (**3a**, $CH_2{=}CH–(C_2F_4)_{3,5}–CH{=}CH_2$), by reaction with ethylene under pressure and subsequently with KOH as described elsewhere [7a].

The raw product was distilled (55 °C, residual pressure 20–0.2 mm Hg, yield 92%).

4.2.2. Hydrosilylation of diene **3a** with chlorodimethylsilane (Scheme 1, **1b**)

An aliquot of the diene **3a** (48.5 g, 0.12 mol) was reacted with excess of $HSi(CH_3)_2Cl$ (91 g, 0.96 mol) in the presence of *t*-butylperoxide at 120 °C for 24 h in a sealed glass vial. The excess of dichlorosilane was distilled and the residue was identified as $ClSi(CH_3)_2–C_2H_4–(C_2F_4)_{3.5}–C_2H_4–Si(CH_3)_2Cl$ (**1b**; here labeled Cl–I–Cl; 69.7 g, 0.116 mol, yield 97%).

^1H NMR: 0.45–0.5 ppm ($\underline{CH_3}SiCl$); 1–1.15 ppm (m, $\underline{CH_2}Si$); 2–2.35 ppm (m, $\underline{CH_2}–CH_2Si$).

^{19}F NMR: −116.3 ppm ($\underline{CF_2}$-CH_2); −122 ppm ($\underline{CF_2}$–$\underline{CF_2}CH_2$); −123.85 ppm ($CF_2C_2F_4CH_2$).

^{29}Si NMR: +31.5–31.8 ppm (s, $\underline{Si}$–Cl).

4.2.3. Hydrosilylation of diene **3a** with α,ω-dihydrohexamethyltrisiloxane to α,ω-dihydro silafluoroalkaneoligosiloxane (Scheme 3, **3b**)

An aliquot of the diene **3a** (48.5 g, 0.12 mol) was reacted with excess $HSi(CH_3)_2–[OSi(CH_3)_2]_2–H$ (249.6 g, 1.2 mol) in the presence of dibutyl peroxide (2.7 g) at 120 °C for 48 h in a sealed glass vial. After cooling, the vial was opened, the excess of hexamethyl trisiloxane and the head fractions were distilled at ~100–110 °C, 0.2 mm Hg leaving a residue of 155 g, recognised as the compound **3b** (where $w' = 3.5$ as evaluated by ^{1}H NMR).

(3b) $HSi(CH_3)_2[OSi(CH_3)_2]_2-\{C_2H_4-(C_2F_4)_{3,5}-C_2H_4Si(CH_3)_2[OSi(CH_3)2]_2\}_{w'}-H$

^{1}H NMR: complex signals 0–0.3 ppm ($\underline{CH_3}$–Si), 0.7–09 ppm ($\underline{CH_2}$–Si); 1.85–2.25 ppm ($\underline{CH_2}CH_2Si$); 4.62–4.8 ppm (SiH).

^{19}F NMR: −116.6 ppm ($\underline{CF_2}$–CH_2); −122.4 to −123.9 ppm ($\underline{CF_2}$–CF_2–CH_2), ($\underline{CF_2}$–C_2F_4–CH_2).

^{29}Si NMR: +7.43 ppm (s, CH_2–$\underline{Si}$–O); −6.6 ppm (d, O$\underline{Si}$H); −18.6 ppm (s, CH_2–SiO$\underline{Si}$OSiH); −19.5 ppm (s, CH_2SiO$\underline{Si}$OSiCH_3).

IR: 2127 cm^{-1} (Si–H).

4.2.4. Oxidative hydrolysis of *3b* to α,ω-dihydroxy-silafluoroalkanesiloxane (*3c*)

The compound **3b** ($w' = 3.5$) dissolved in THF (100 ml) was hydrolysed at RT with aqueous NaH_2PO_4 buffer solution in the presence of Pd/Al_2O_3. After 3 h, the final product was separated from the water, washed twice then quenched at 0 °C to avoid any polycondensation and recognised as the product type **3c**, here labeled HO–II–OH.

(HO–II–OH)$HOSi(CH_3)_2[OSi(CH_3)_2]_2\{C_2H_4-(C_2F_4)_{3,5}-C_2H_4Si(CH_3)_2[OSi-(CH_3)_2]_2\}_{w'}OH$

^{29}Si NMR: +7.38 ppm (s, $\underline{CH_3}$SiO); −12.07 ppm (s, –OSi–OH); −19.6 ppm (s, CH_2SiO$\underline{Si}$OSiOH); −20.34 ppm (CH_2–SiO$\underline{Si}$OSCH_2–).

IR: 3333 cm^{-1} (Si–OH); absence of absorption band at 2127 cm^{-1} (Si–H).

4.2.5. Hydrolysis of α,ω-dichlorosilafluoroalkane (*1b*) to α,ω-dihydroxysilafluoroalkane (*1c*) and condensation with dichloromethylvinylsilane to unsaturated α,ω-dihydroxyhybridfluorosilicone, crosslinker comonomer (Scheme 1, *1c*, *1d*)

An aliquot of α,ω-dichlorosilafluoroalkane (**1b**), dissolved in ethylether was hydrolysed at RT with excess of 10% $NaHCO_3$ aqueous solution by stirring for 4 h. The organic layer was separated, washed twice with water, dried over Na_2SO_4 and evaporated from the solvent under vacuum, at RT; the product was recognised as α,ω-disilanol (**1c**).

(**1c**) $HOSi(CH_3)_2$–C_2H_4–$(C_2F_4)_{3,5}$–$C_2H_4Si(CH_3)_2$–OH

^{1}H NMR: 0.2 ppm (s, $\underline{CH_3}$SiOH); 0.75–0.9 ppm (m, $\underline{CH_2}$–Si); 1.6–1.75 ppm (broad, $\underline{Si}$OH); 1.9–2.3 ppm (m, $\underline{CH_2}$–CH_2Si).

^{19}F NMR: −116.65 ppm ($\underline{CF_2}$-CH); −122.3 to −122.5 ppm ($\underline{CF_2}$–CF_2–CH_2); −123.8 to −124 ppm ($\underline{CF_2}C_2F_4$–CH_2).

^{29}Si NMR: +15.2 ppm (s, CH_2–$\underline{Si}$OH).

The α,ω-disilanol (**1c**, 55.6 g, 0.1 mol) dissolved in ethylether was reacted at RT with $Cl_2SiCH_3(CH{=}CH_2)$ (7 g, 0.05 mol) in the presence of triethylamine (10 g) under stirring for 4 h. The mixture was filtered, washed twice with water, the organic layer was concentrated at RT under vacuum, quenched at 0 °C and recognised as the product **1b** (type **3g**), here labeled HO–III–OH.

(HO–III–OH) $\{HOSi(CH_3)_2$–C_2H_4–$(C_2F_4)_{3,5}$–C_2H_4–$Si(CH_3)_2O\}_2$–$SiCH_3(CH{=}CH_2)$

^{1}H NMR: 0.05–0.25 ppm (broad, $\underline{CH_3}$SiO); 0.7–0.9 ppm (m, $\underline{CH_2}$–Si); 1.9–2.25 ppm (m, $\underline{CH_2}$–CH_2–Si); 5.7–6.1 ppm (m, $CH{=}CH_2$).

4.3. Preparation of the hybrid fluorosilicone elastomer (WTFSE)

The preparation was achieved following Scheme 4:

(a) The compound labeled HO–II–OH (**3c**, 23.8 g, 0.01 mol) dissolved in THF (50 ml) was added to a solution of the compound labeled Cl–I–Cl (**1b**, 13.09 g, 0.022 mol) in THF (50 ml) in the presence of triethylamine (2.2 g). The mixture was stirred for 16 h at RT, then filtered from the salt. A solution of **4a** was thus obtained.

(b) The previous organic solution (**4a**) was added to the compound **3g**, labeled HO–III–OH (26 g, 0.022 mol) dissolved in THF (100 ml) in the presence of triethylamine (2.2 g); the mixture was stirred at RT for 16 h then filtered from the salt. A solution of **4b** was thus obtained.

(c) *Polycondensation*: the product (**4b**) was added with tetramethylguanidine trifluoroacetate adduct (0.2 g) and polycondensed by heating at 60 °C, while a nitrogen flow was bubbled through, for 4 h. A polymer type **4c** was obtained.

(d) *End-capping of polymer*: the polymer **4c** was diluted with further THF (200 ml) and added with chlorodimethylvinylsilane (12 g, 0.1 mol) under continuous nitrogen flow. The solvent and the excess of chloromethylsilane were eliminated by distillation. The analysis, IR spectroscopy and ^{1}H NMR, confirmed the absence of SiOH signals and the presence of vinyl groups on the final very viscous product (**4d**) whose average structure was corresponding to the formula (3) with average M_W near 8500 g mol^{-1} as determined by ^{1}H NMR and validated by GPC.

4.3.1. Crosslinkage of the polyunsaturated hybrid fluorosilicone (3) promoted by peroxides at high temperature (HTV): chemical and thermophysical characterisation of the elastomer

An aliquot of the title compound (3) (20 g), was blended in a mechanical mixer with fumed silica (3.4 g), 2,5-di-*t*-butylperoxy-2,5-dimethylhexane (0.12 g). The mixture was carried on a confined rectangular mould (100 mm × 100 mm × 0.5 mm) under the plates of a press that was heated at 160 °C, 1 MPa for 1 h, then at 180 °C for 1 h.

A thin sheet was obtained, that was flexible and elastic under traction. A sample was submitted to DMA in the temperature range of −100 to +50 °C and showed a T_g at

−53 °C, the elastic modulus was about 2 GPa at −100 °C and 5 MPa at 50 °C while at the DSC the T_g resulted −61 °C.

The swelling results, performed on 200 μm thick films, with 1 cm diameter, by immersion in organic solvents at 20 °C for 24 h are reported in Table 3, the solvents were characterized by moderate hydrogen bonding capability.

The results of TGA are reported in Table 4.

4.3.2. Crosslinkage of the polyunsaturated hybridfluorosilicone (iv) promoted by Pt at low temperature (LTV)

An alternative crosslinking procedure was performed on a sample of the hybrid fluorosilicone (3) by following a typical method used for polyunsaturated silicone rubbers: in a glass vial an aliquot of the elastomer (3) (10 g), swollen in THF (20 ml), was added with polyhydromethylsiloxane (M_W 900–1200, containing 50% unit –H(CH_3)SiO–, code HMS501 from GELEST Silicones ABCR, 1 g), fumed silica (1.7 g), Karsted Pt catalyst (0.01 g). The vial was sealed and heated at 80–100 °C for 1 h then opened, the solvent was evaporated and a crosslinked elastic material was obtained that, by DSC, showed a T_g near −65 °C.

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