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Use of Original Fluorinated Telomers in the Synthesis of Hybrid Silicones

BRUNO AMEDURI, BERNARD BOUTEVIN, GERARDO CAPORICCIO, FRANCINE GUIDA-PIETRASANTA, ABDELLATIF MANSERI, and AMÉDÉE RATSIMIHETY

5.1. INTRODUCTION

Fluorosilicone polymers have become of great interest for specific applications owing to their outstanding performances.[1,2] They exhibit not only good thermal stability and a high degree of chemical inertness, but also remarkable mechanical and rheological properties. They can be used as lubricants or heat-carrying fluids, as rubbers and resins, and as elastomers in O-rings and gaskets. When dissolved in solvents, fluorosiloxanes can be utilized as stain-resistant coatings on textile fibers, both natural and synthetic. In particular, their surfactant properties (mainly attributable to their fluorine content) allow low-molecular-weight fluorosiloxanes to be used as defoaming agents and as surfactants.

Actually, both Si—O—Si and C—F linkages are efficient for providing rather good thermostability and also confer excellent chemical inertness and low surface energy. On the other hand, while the —$Si(CH_3)_2O$— group offers good properties at low temperatures it usually leads to elastomers that exhibit poor resistance to

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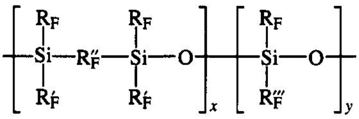
BRUNO AMEDURI and BERNARD BOUTEVIN • Ecole Nationale Supérieure de Chimie de Montpellier, F-34296 Montpellier Cédex 5, France • GERARDO CAPORICCIO • Via Filiberto 13, Milan 20149, Italy • FRANCINE GUIDA-PIETRASANTA, ABDELLATIF MANSERI, and AMÉDÉE RATSIMMETY • Ecole Nationale Supérieure de Chimie de Montpellier, F-34296 Montpellier Cédex 5, France

Fluoropolymers 1: Synthesis, edited by Hougham *et al.,* Plenum Press, New York, 1999.

swelling. As a matter of fact, fluorinated elastomers[3-7] are known to preserve good properties even at high temperatures and to exhibit a high resistance to solvent, oil, UV and aging, but they have poor properties at low temperatures.

For these reasons, the fluorosilicone elastomers appear to be very promising products as that proposed by the Dow-Corning Company, which commercializes poly(trifluoropropyl methyl siloxane) (PTFPMS) containing $—(CH_3)Si(C_2H_4CF_3)O—$ base units. Such a polymer is presently the best compromise for elastomers used in connectics. However, such a product may lead to reversion at high temperatures by undergoing a depolymerization that produces low-molecular-weight cyclic oligomers.

We investigated the synthesis of hybrid fluorinated silicones with high fluorine content, building up fluorinated blocks and grafts via a controlled structure shown in Scheme 1, (where R_F represents a fluorinated group). Actually, since polydimethyl siloxanes still have good properties in the –123 to + 320°C range, and Won elastomers preserve good properties between –30 and + 420°C, our objective was to obtain a hybrid fluorosilicone that would be stable in the –100 to +400°C range.



Scheme 1

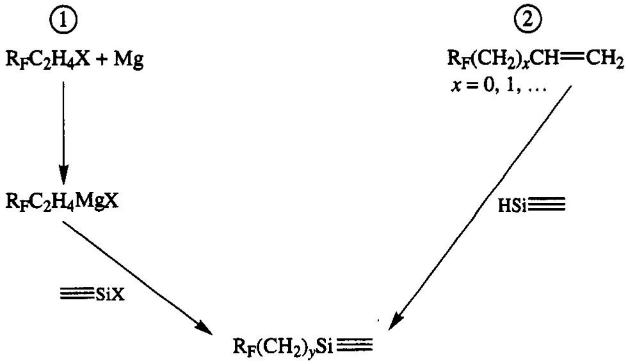
5.2. RESULTS AND DISCUSSION

Tho main routes for the insertion of fluorinated alkyl groups in the silicones are suggested: either by organometallic ① or by hydrosilylation ② methods as shown in Scheme 2. Consequently, research can be pursued in two directions: (a) synthesis of fluorohalides and alkenes, and (b) introduction in siliconated groups and polymerization.

5.2.1. Synthesis of Fluorinated Precursors

Perfluoroalkyl iodides $CF_3(CF_2)_xI$ are commercially available reactants useful for interesting chemistry, offering various functional products such as $CF_3(CF_2)_xC_2H_4I$, $CF_3(CF_2)_xC_2H_4—G$, where G represents hydroxyl, amine, thio, thiocyanate, isocyanate, nitrile, carboxy, or $CF_3(CF_2)_x CH{=}CH_2$, $CF_3(CF_2)_x CH_2CH{=}CH_2$.

However, crystallization occurs when $x > 7$ and such behavior is not required in the elastomers. Consequently, it is necessary to synthesize co-oligomers from various fluorinated monomers such as vinylidene fluoride (VDF), trifluoroethylene



Scheme 2

(VF_3), chlorotrifluoroethylene (CTFE), and hexafluoropropene (HFP), in order to avoid crystallization as described below.

One of the most interesting strategies is telomerization. Such a reaction, introduced for the first time by Hanford in 1942, unlike polymerization, usually leads to low-molecular-weight polymers, called telomers, or even to monoadducts with well-defined end groups. Such products A are obtained from the reaction between a telogen or a transfer agent (X-Y), and one or more (n) molecules of a polymerizable compound M (called a taxogen or a monomer) having ethylenic unsaturation under radical polymerization conditions, as follows:

$$\text{X-Y} + n\text{M} \longrightarrow \underset{\mathbf{A}}{\text{X(M)}_n\text{Y}}$$

Telogen X-Y can be easily cleavable by free radicals (formed according to the conditions of initiation) leading to an X radical that will be able to react further with the monomer. After the propagation of the monomer, the final step consists of the transfer of the telogen to the growing telomeric chain. Telomers **A** are intermediate products between organic compounds (e.g., n = 1) and macromolecular species (n = 100). Hence, in certain cases, end groups exhibit a chemical importance that can provide useful opportunities for further functionalizations.

The scope of telomerization was outlined by Starks in 1974,[8] and further developed by Gordon and Loftus.[9] We recently reviewed such a reaction[10,11] in which mechanisms and kinetics of radical and redox telomerizations were described.

5.2.1.1. Monofunctional Telomers

(a) Telomerization of Fluorinated Monomers with CF_3CFClI. The addition of [IF] (formed *in situ* from I_2 and IF_5) to CTFE leads to CF_3CFClI (90%)

and $ClCF_2CF_2I$ (10%) in 75% yield.[12,13] CF_3CFClI has been shown to behave as an efficient telogen in the telomerization of CTFE, in contrast to $CF_3(CF_2)_x I$[11] as well as in that of HFP.[13]

(b) Synthesis of Viton Cotelomers. Viton-type cotelomers were synthesized in two ways. $C_4F_9(HFP)_x(VDF)_yI$ was produced in 86% overall yield by stepwise cotelomerization of HFP and VDF with C_4F_9I, unlike the results starting from iC_3F_7I.[14,15] $CF_3(CF_2)_x(VDF)_z(HFP)_tI$ was also produced in a two-step process leading to ca. 83–85% overall yield.[15,16] A wide variety of different cotelomers containing VDF, VF_3, CTFE, and HFP base units have been synthesized through such a succession of reactions, as shown in Figure 5.1.

Interestingly, the (co)telomers used behave as further potential telogens for subsequent telomerizations, and all of them can be end-capped with ethylene (E).

These ω-iodinated cotelomers were functionalized into vinyl or allyl type olefins by two different two-step processes as follow[17,18]:

$$R_FI \xrightarrow[\mathrm{CuI}]{CH_2=CH_2} R_FC_2H_4I \xrightarrow{\mathrm{KOH}} R_FCH = CH_2$$

$$R_FI + H_2C = CHCH_2OAc \xrightarrow{\mathrm{Peroxide}} R_FCH_2CHICH_2OAc \xrightarrow{\mathrm{Zn}} R_FCH_2CH = CH_2$$

The yields obtained were higher for allyl-type alkenes, and the nature of R_F (e.g., the presence of a CF_3 side chain) does not affect the yield.

5.2.1.2. Telechelic Oligomers

The strategy utilized for the synthesis of monofunctional telomers was also successfully adapted to telechelic oligomers. α,ω-Diiodoperfluoroalkanes, which are generally produced by telomerization of tetrafluoroethylene with iodine (see Tortelli and Tortelli[19] and the references therein) are efficient telogens in the thermal telomerization of vinylidene fluoride[20] leading to novel α,ω-diiodofluoroalkanes with various $\overline{\mathrm{Dp}}_n$ depending on the chain length of the telogen:

$$I(C_2F_4)_nI + H_2C = CF_2 \xrightarrow[\Delta]{} I(VDF)_x\,(C_2F_4)_n\,(vDF)_y\,I$$

$$n = 1, 2, 3 \qquad\qquad x+y = 1\text{–}10$$

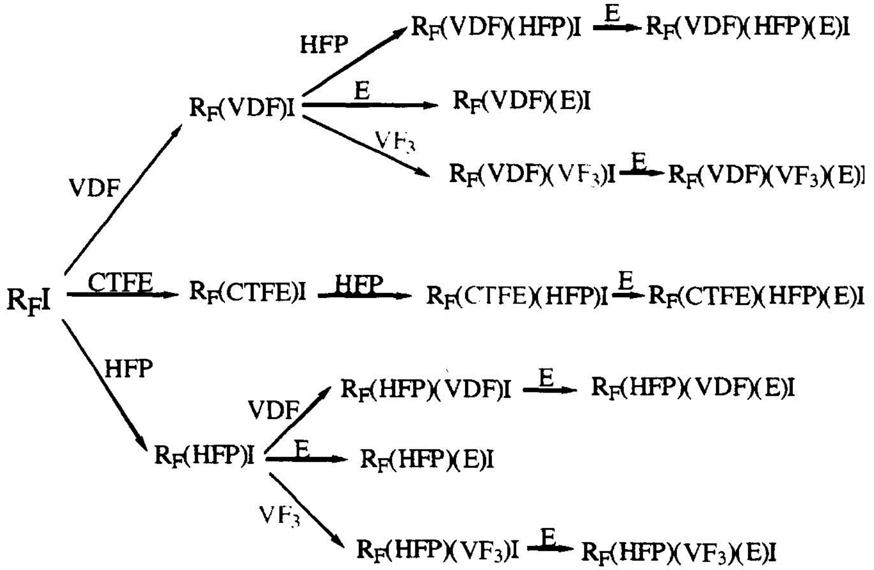


Figure 5.1. Basic strategy of well-architectured cotelomers of vinylidene fluoride (VDF), trifluoroethylene (VF_3), chlorotrifluoroethylene (CTFE), hexafluoropropene (HFP), and ethylene (E).

Apart from IC_2F_4I, which undergoes a β-scission, they also behave nicely with regard to HFP[19]:

$$\mathrm{I(C_2F_4)_pI + C_3F_6} \xrightarrow[\Delta]{} \left\{ \begin{array}{l} \mathrm{I(C_2F_4)_pC_3F_6I} \\ \mathrm{I(HFP)(C_2F_4)_p(HFP)I} \\ \mathrm{I(HFP)(C_2F_4)_p(C_3F_6)_2I} \end{array} \right.$$

$$p = 2, 3$$

New α,β-diiodofluoroalkanes containing Viton structure were prepared by stepwise telomerization of VDF and HFP (or HPF and VDF) with IR_FI as follows[20,21]:

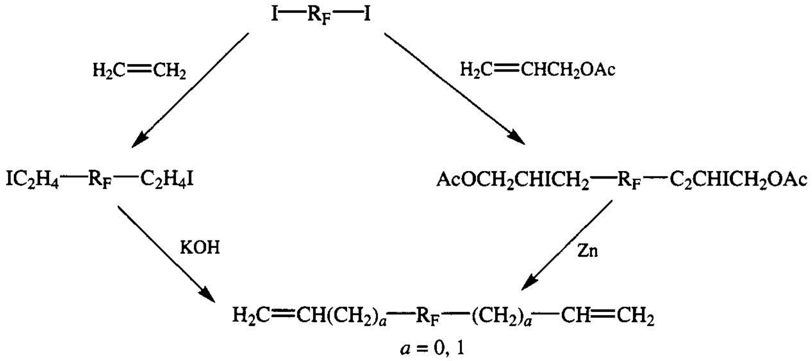
$$\mathrm{I(C_2F_4)_n(VDF)I + C_3F_6 \longrightarrow 1(C_2F_4)_n(VDF)(C_3F_6)I + 1(C_3F_6)(C_2F_4)_n(VDF)(C_3F_6)I}$$

$$\mathrm{I(VDF)(C_2F_4)_n(VDF)I + C_3F_6} \xrightarrow[\Delta]{} \mathrm{1(C_3F_6)(VDF)(C_2F_4)_n(VDF)(C_3F_6)I}$$

$$\mathrm{I(HFP)(C_2F_4)_p(HFP)I + H_2C = CF_2} \xrightarrow[\Delta]{} \mathrm{I(VDF)_a(HFP)(C_2F_4)_p(HFP)(VDF)_bI}$$

$$p = 2,3 \qquad a + b = 3\text{–}20$$

As above, these α, ω-diiodinated cotelomers were fuctionalized into vinyl or allyl types of nonconjugated dienes as follows[22]:



Scheme 3

Diallyis were obtained in higher yields (70–40%) than divinyls (40–55%).

5.2.2. Introduction of Fluorinated Groups in Silanes and Silicones

There are two possible ways to introduce fluorinated groups into silanes and silicones: through the use of fluorinated organometallic reactants (mainly organomagnesians and organolithians) or by hydrosilylation of fluorinated alkenes.

5.2.1.1. Organometallic Derivatives

(a) Organomagnesians. Several fluorinated alkyl halides were used for the synthesis of these organometallic compounds as follows:

$$R_FX + Mg \longrightarrow \underset{(\mathbf{1})}{R_FMgX} + R_F{-}R_F$$

where R_FX represents $CF_3C_2H_4Cl$, $C_6F_{13}C_2H_4Y$ (with Y = Cl, Br, I), $iC_3F_7C_2H_4I$, and $C_5F_{11}CF(CF_3)C_2H_4I$.

The reactivity series of R_F depends on the nature of X and is I > Br > Cl. In addition, the longer the R_F group and the higher the steric hindrance, the lower the yield of **1**.[23] Further, the more hindered R_F, the more dimer produced. In order to prepare tetrafluoroalkyl silanes, such fluorinated magnesians must react with alkyl silane halides as follows:

$$R_FMgX + R_xSiX_{4-x} \longrightarrow (R_F)_YR_xSiX_{4-x-y}$$

The reactivity of these fluorinated magnesian reactants depends on: (a) the chain length and the steric hindrance of the R_F group; (b) the nature of the silane: $HSiCl_3 > SiCl_4 > \,>\!SiCl_2 > \equiv SiCl$; and (c) the nature of the halogen: SiF > SiCl > SiOR. However, it is not possible to synthesize tetrafluoroalkyl silanes as the maximum number of substitutions when X = Cl or F is three.

Moreover, by-products coming from Wurtz reactions have been observed in nonnegligible amounts. Thus, a better alternative involves the use of organolithian intermediates.

(b) Lithian Reactants. In the same way as organomagnesians, organolithian compounds were produced from fluoroalkyl halides as follows:

$$R_F C_2 H_4 + {}_2Li \longrightarrow R_F C_2H_4Li + LIX + \text{dimer}$$

and again, the longer the chain length of R_F and the higher the steric hindrance, the lower the yield of the reaction.

Such fluorinated organolithians have also been shown to be precursors of tetraalkyl silanes:

$$R_F C_2 H_4 Li + R_1 R_2 R_3 SiX \longrightarrow R_1 R_2 R_3 SiC_2 H_4 R_F$$

However, the reactivity of such compounds is still low; e.g., when $R_1 = R_2 = R_3 = CH_3$ and X = Cl, the silanes produced from $CF_3C_2H_4Li$ and $C_6F_{13}C_2H_4Li$ were obtained in 40 and 20% yields, respectively. As a result of this poor reactivity, this method was abandoned and efforts now center around hydrosilylation reactions involving fluorinated olefins.

5.2.1.2. Hydrosilylation

Various hydrosilylation reactions of hydrogenosilanes were carried out in the presence of Speirs' catalyst for the preparation of fluorinated silanes:

$$R_F(CH_2)_xCH = CH_2 + HSiClR_1R_2 \xrightarrow[100^\circ C/18h]{H_2PtCl_6} R_F(CH_2)_2SiClR_1R_2 \qquad x = 0, 1$$

The yield of the silane produced depends on: (a) the nature of the olefin ($R_FCH_2CH{=}CH_2 > R_FCH = CH_2$); (b) the nature of the fluorinated group (e.g., linear olefins are more reactive than branched ones); (c) the nature of the silane ($HSiCl_3 \sim HSiCl_2R_1 > HSiR_1R_2Cl$).[24]

Nevertheless it was possible to synthesize tetrafluoroalkyl silanes by combining the use of organometallic reactants and the hydrosilylation reaction. A few examples follow:

1. When $R_1 = R_2 = R_3 = R_4 = C_6F_{13}C_2H_4$,

$$C_6F_{13}C_2H_4MgI + HSiCl_3 \longrightarrow HSi(C_2H_4C_6F_{13})_3 \xrightarrow[H_2PtCl_6]{H_2C{=}CHC_6F_{13}} \underset{(\mathbf{2})}{Si(C_2H_4C_6F_{13})_4}$$

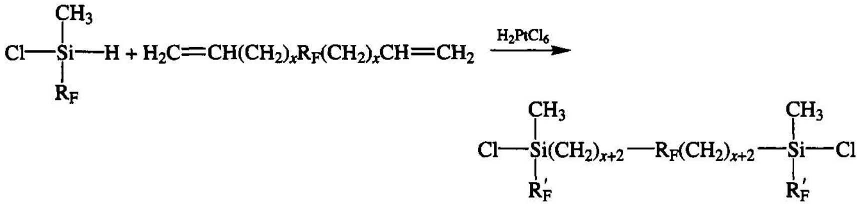
2. For $R_1 = R_2 \neq R_3 = R_4$,

$$C_6F_{13}C_2H_4MgI + CF_3C_2H_4SiF_3 \longrightarrow CF_3C_2H_4SiF(C_2H_4C_6F_{13})_2$$

$$\xrightarrow{CF_3C_2H_4Li} (CF_3C_2H_4)_2Si(C_2H_4C_6F_{13})_2$$

Thus, a large variety of tetrafluoroalkyl silanes were prepared with a wide range of thermal properties. The lowest T_g was obtained for **2** (T_g =–75°C) or for $(C_6F_{13}C_2H_4)Si\ (C_2H_4CF_3)[C_2H_4CF(CF_3)_2]$ T_g = –67°C) or for **3** (T_g = –66°C), whereas for $Si(C_2H_4CF_3)_4$, T_m = 131°C but no T_g was observed.

Similarly, fluorinated nonconjugated dienes could undergo hydrosilylation with hydrogenochloromethyl silanes:



$$Cl{-}\underset{R_F}{\overset{CH_3}{Si}}{-}H + H_2C{=}CH(CH_2)_xR_F(CH_2)_xCH{=}CH_2 \xrightarrow{H_2PtCl_6} Cl{-}\underset{R_F'}{\overset{CH_3}{Si}}(CH_2)_{x+2}{-}R_F(CH_2)_{x+2}{-}\underset{R_F'}{\overset{CH_3}{Si}}{-}Cl$$

Scheme 4

Indeed, allyl-type dienes were more efficient than divinyl olefins, even for the branched R_F group. Various heptafluoroalkyl disilanes were thus obtained with T_g varying from –42 to –59°C.[25]

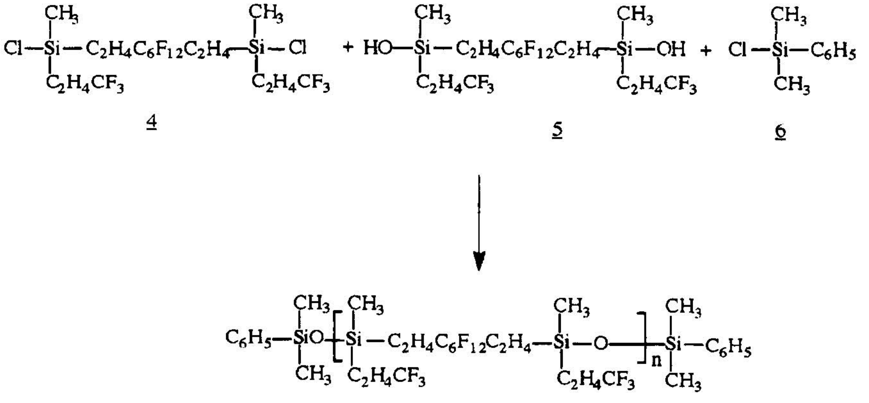
5.2.1.3. Synthesis of Fluorosilicones

It is well known that silicones can be prepared from dihalogenosilanes that undergo hydrolysis to generate disilanol. These latter intermediates produce cyclic or linear dialkylsiloxanes. The cyclic dialkylsiloxanes can be separated and ring-opening polymerized whereas the linear ones can be condensed to yield silicones. However, it is still difficult to purify cyclic and linear precursors. Thus, in order to avoid cyclization, our objective concerned the polycondensation of fluorohybrid silanes.

(a) Fluorosilicones without Fluorocotelomers. Two homopolymers **7a** and **7b,** in Figure 5.2, having different molecular weights, were prepared by copolycondensation of bis-chlorosilane **(4)** (provided by Dow-Corning) and the monomer bis-hydroxysilane **(5)** in the presence of a chain-stopper $(C_6H_5)Si(CH_3)_2Cl$ (**6**).[26]

The monomer silane diol **(5)** was prepared by hydrolysis of the bis-chlorosilane **(4)** in the presence of sodium hydrogenocarbonate $NaHCO^3$ at reflux of diethyl ether for 24 h. The hydrolysis was quantitative. The silane diol **(5)** was characterized by IR, where a narrow band at 3690 cm^{-1} and a wide band between 3650 and 3050 cm^{-1} were observed, respectively, for free $\upsilon_{\equiv SiOH}$ and bonded $\upsilon_{\equiv SiOH}$. Its ^{1}H- and ^{19}F-NMR spectra exhibited the expected signals and its ^{29}Si-NMR spectrum showed a singlet at +16.4ppm characteristic for a $\delta_{\equiv SiOH}$ and no trace of the starting chlorosilane at +31 ppm.[26]

A small amount (5%) of oligomeric homopolymer was observed using size-exclusion chromatography (SEC) of silane diol **5,** showing that some polycondensation had already occurred. The copolymerization of **4** and **5** was performed in toluene at 90°C for 19 h. Homopolymers **7a** and **7b,** obtained as oils, were characterized by IR, where no more $\upsilon_{\equiv SiOH}$ band was present, and in ^{1}H-, ^{19}F-, and ^{29}Si-NMR. Their ^{1}H-NMR spectra allow us to calculate the value of n by comparing the integration of the aromatic protons to that of the methylene protons linked to the silicon atoms, and thus to determine the average molecular weight $\overline{M}_n$. It is possible to use this NMR method as the values of n that were found, 16.5 and 25.5 for **7a** and **7b** respectively, are not too high. Thus the integrations of the aromatic protons are still accurate. However, for higher values of *n,* these



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a) n = 16.5

b) n = 25.5

Figure 5.2. Synthesis of fluorosilicones by condensation of bis-chlorosilane **(4)** and disilanol **(5).**

integrations will be more difficult to measure and the values found will become less reliable. $\overline{M}_n$ was also evaluated by SEC using polystyrene standards, and the values found are in good agreement with those obtained from NMR. The results are given in Table 5.1. The ^{29}Si-NMR spectra of the homopolymers exhibited a signal at +8.90ppm for $\delta_{\equiv SiOSi\equiv}$ but not for $\delta_{\equiv SiOH}$ at +16.4 ppm.

The homopolymers were also studied by differential scanning calorimetry (DSC), where a glass transition temperature (T_g) was measured, and by thermogravimetric analysis (TGA). The results are summarized in Table 5.1, together with those of a similar hybrid homopolymer prepared by Riley *et al* .,[1] of the dimethyl disubstituted homopolymer previously synthesized,[27] and of the classic commercially available polytrifluoropropylmethylsiloxane (PTFPMS). It is interesting to note that homopolymers having the same lateral groups have a nearly identical T_g whatever the length of the linear internal fluorinated chain and that the hybrid homopolymers are much more stable at high temperatures than PTFPMS (cf. the values for 50% weight loss, $T_{-50\%}$). It is also worth noting the influence of the nature of the side chains; e.g., when a methyl group is replaced

Table 5.1. ^{1}H-NMR, SEC, DSC and TGA Data for Homopolymers

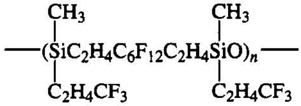
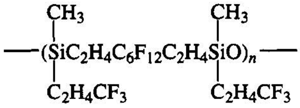
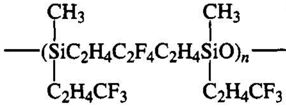
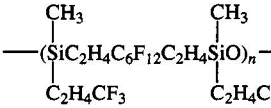
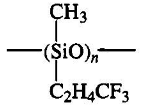
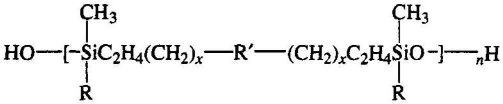
Homopolymer	^{1}H-NMR		SEC	DSC 10°C/min	TGA (in N_2) 5°C/min
	n	M_n	M_n	T_g, °C	$T_{50\%}$
 $-(\overset{CH_3}{\underset{C_2H_4CF_3}{Si}}C_2H_4C_6F_{12}C_2H_4\overset{CH_3}{\underset{C_2H_4CF_3}{Si}}O)_n-$ **7a**	16.5	11,000	12,500	–29	490
 $-(\overset{CH_3}{\underset{C_2H_4CF_3}{Si}}C_2H_4C_6F_{12}C_2H_4\overset{CH_3}{\underset{C_2H_4CF_3}{Si}}O)_n-$ **7b**	25.5	17,500	16,800	–28	490
 $-(\overset{CH_3}{\underset{C_2H_4CF_3}{Si}}C_2H_4C_2F_4C_2H_4\overset{CH_3}{\underset{C_2H_4CF_3}{Si}}O)_n-$ **1**				–27	493
 $-(\overset{CH_3}{\underset{C_2H_4CF_3}{Si}}C_2H_4C_6F_{12}C_2H_4\overset{CH_3}{\underset{C_2H_4CF_3}{Si}}O)_n-$ **27**				–53	470
PTFPMS  $-(\overset{CH_3}{\underset{C_2H_4CF_3}{Si}}O)_n-$				–67	245

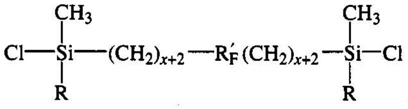
Table 5.2. Molecular Weights and Thermal Properties of Fluorinated Hybrid Homopolymers

 $HO{-}[-\underset{R}{\overset{CH_3}{Si}}C_2H_4(CH_2)_x{-}R'{-}(CH_2)_xC_2H_4\underset{R}{\overset{CH_3}{Si}}O-]_n{-}H$			SEC	DSC (10°C/mn)			TGA (5C/mn)		State
			M_n	T_g	T_m	T_c	$T_{50\%}$ (N_2)	$T_{50\%}$ (Air)	
R = CH_3	R′ = C_6F_{12}	$x = 0$	10,000	–53	26	–11	470	380	Solid
		$x = 1$	10,000	–40	25	–27	465	330	Solid
R = $CF_3C_2H_4$	R′ = C_65F_{12}	$x = 0$	40,000	–28			480	410	Oil
		$x = 1$	14,000	–18			465	360	Oil
R = $C_4F_9C_2H_4$	R′ = C_6F_{12}	$x = 0$	30,000	–42			490	360	Oil
		$x = 1$	12,000	–29			470	310	Oil
R = CH_3	R′ = HFP/C_4F_8HFP	$x = 1$	10,000	–49			425	300	Oil
R=$CF_3C_2H_4$	R=HFP/C_4F_8/HFP	$x = 1$	30,000	–34			445	310	Oil
R = $C_4F_9C_2H_4$	R′ = HFP/C_4F_8/HFP	$x = 1$	50,000	–38			450	320	Oil
	R′ = C_2F_4/VF_2/HFP	$x = 1$	9,000	–47			420	315	Oil

by a trifluoropropyl group the T_g increases from –53 to –29°C, this loss in T_g being compensated for by an almost equivalent gain of 20°C in thermal stability at high temperatures. The influence of the side chains is also seen in the fact that the homopolymers **7a** and **7b** exhibit only a T_g and neither a crystallization (T_c) nor a melting (T_m) temperature as was observed for the dimethyl disubstituted homopolymer.[27]

So, if these hybrid homopolymers exhibit interesting properties at high temperatures, their properties at low temperatures are poorer than those of the classical polysiloxanes, which is why we decided to study fluorinated hybrid polysiloxanes containing the telomers prepared above.

(b) Fluorosilicones Containing Fluorinated (Co)Telomers. We prepared α,ω-dichlorofluorinated disilanes **8** using the same reaction described in Section 5.2.1.2:



$$Cl-\underset{R}{\overset{CH_3}{Si}}-(CH_2)_{x+2}-R'_F(CH_2)_{x+2}-\underset{R}{\overset{CH_3}{Si}}-Cl$$

(8)

with R=CH_3 or $C_2H_4CF_3$ and R'_F=C_6F_{12} or HFP—C_4F_8—HFP or C_2F_4—VDF—HFP. Table 5.2 gives the molecular weights and thermal properties of the fluorosilicones we obtained. The influence of the key group in terms of these properties is as follows:

1. The longer the spacer between the fluorinated central group and the silicon atom, the higher the T_g and the less thermostable the fluorosilicon is in air, which confirms a previous investigation performed on model fluorosilicones.[27]
2. Substituting CH_3 by $CF_3C_2H_4$ as the fluorinated side group on the polymeric backbone increases the T_g but a $C_4F_9C_2H_4$ lateral group lowers the T_g of the fluorosilicone containing a $CF_3C_2H_4$ group, and slightly decreases its thermostability in air.
3. The fluorinated central group in the polymeric backbone has a drastic effect on both the T_g and T_{dec}. The introduction of CF, side groups coming from HFP base units lowers the T_g (e.g., from –18°C for fluorosilicones where R = $CF_3C_2H_4$, R′ = C_6F_{12} and x = 1 to –34°C for R = $CF_3C_2H_4$, R′ = HFP/CuF_8/HFP and x = 1), but does not contribute to a higher thermostability.

5.3. CONCLUSIONS

The wide use of fluorosilicones is the result of their combination of excellent properties: good resistance to heat, solvents, acids, alkalies, and oxidizing media. Gaskets for connectics, hydraulic fluids, and heat-carrier fluids still account for the largest number of applications. After a first generation proposed by Dow-Corning, fluorinated hybrid silicones based on well-architectured fluorooligomers built by controlled stepwise telomerization of various fluoroolefins are presented. Such cotelomers are very interesting precursors of functional or telechelic derivatives (containing hydroxy, carboxy, amine or unsaturated groups).

We also described various strategies for the synthesis of tetrafluoroalkyl silanes or fluorinated disilanes or silicones. Such a series of hybrid polymers compete with those of Dow-Corning. These fluorosilicones are prepared in three steps from original nonconjugated dienes in high yields. Their thermal characteristics depend upon the spacer between the central fluorinated group and the silicon atom, the nature of lateral groups linked to silicon atoms, and the nature of the central fluorinated group (e.g., the presence of the branched CF_3 group).

In spite of their price, fluorinated silicones seem to be high-value-added materials, which should challenge both industrial and academic researchers.

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