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"Hybrid" silicones — an overview on polysilalkylene or polysilarylene siloxanes fluorinated or not

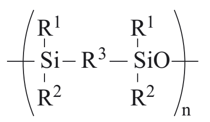
Summary — This overview on polysilalkylene or polysilarylene siloxanes fluorinated or not, so-called "hybrid" silicones reports the main synthetic routes to obtain these polymers together with the properties of the different polymers. Two routes are presented in more detail:
— synthesis of α,ω-bis silanol monomers (prepared either *via* an organometallic route or *via* hydrosilylation of α,ω-dienes) followed by polycondensation of these bis silanols;
— polyhydrosilylation of α,ω-dienes by α,ω-dihydrooligosiloxanes.
This new class of polysiloxanes has been developed, mainly since the 1970s, to avoid the possible depolymerization observed under certain conditions (acid or base, medium or high temperature) for classical polysiloxanes.
The elastomers prepared by crosslinking of these inorganic-organic hybrid polymers exhibit very high thermal stability and rather low temperature flexibility, and depending on the nature of their backbones or of their side chains, they may be resistant to solvents or fuels. They may thus find applications in advanced technological areas (aerospace, defense, computer applications).
Keywords: polysilalkylene siloxanes, polysilarylene siloxanes, polycarbosiloxanes, fluorinated polysiloxanes, hydrosilylation, polycondensation.

SILIKONY „HYBRYDOWE" — PRZEGLĄD FLUOROWANYCH I NIEFLUOROWANYCH SILOKSANÓW POLISILALKILENOWYCH LUB POLISILARYLENOWYCH

Streszczenie — W artykule przeglądowym przedstawiono główne metody syntezy siloksanów polisilalkilenowych lub polisilarylenowych zwanych silikonami "hybrydowymi". Szczegółowo opisano dwie drogi syntezy: polikondensację zsyntetyzowanych α,ω-bissilanoli (schematy A, C—P) i polihydrosililowanie α,ω-dienów przez α,ω-dihydrooligosiloksany (schematy B, Q—V). Omówiona nowa klasa polisiloksanów była zaprojektowana by zapobiegać depolimeryzacji, której ulegają klasyczne polisiloksany w średniej lub wysokiej temperaturze i w środowisku kwaśnym i zasadowym. Elastomery otrzymane w reakcji sieciowania tych nieorganiczno-organicznych polimerów hybrydowych charakteryzują się wysoką stabilnością termiczną pozwalającą na ich stosowanie w szerokim zakresie temperatur. Właściwy dobór łańcucha głównego i łańcuchów bocznych polimeru umożliwia uzyskanie materiałów o specyficznych właściwościach kwalifikujących je do używania w obszarze zaawansowanych technologii (kosmicznej, wojskowej, komputerowej, itp.).
Słowa kluczowe: siloksany polisilalkilenowe, siloksany polisilarylenowe, polikarbosiloksany, fluorowane polisiloksany, hydrosililowanie, polikondensacja.

Because of the increasing need for high performance materials and especially high-temperature resistant materials for application in advanced technological areas (aerospace, defense, computer applications), a vast amount of research was developed in the field of inorganic-organic hybrid polymers. Organosiloxane polymers form one of the most important classes of such materials due to their outstanding properties (thermal stability, low glass transition temperature, unusual surface properties, excellent gas permeability). But the classical polysiloxanes — $[(R)(R')SiO]_n$ — which have been extensively studied and already commercialized as early as the 1940s present the drawback of depolymerization under certain conditions (high temperature) and give rise to cycles and shorter linear chains *via* an intramolecular cycloreversion through a six center mechanism [1, 2].

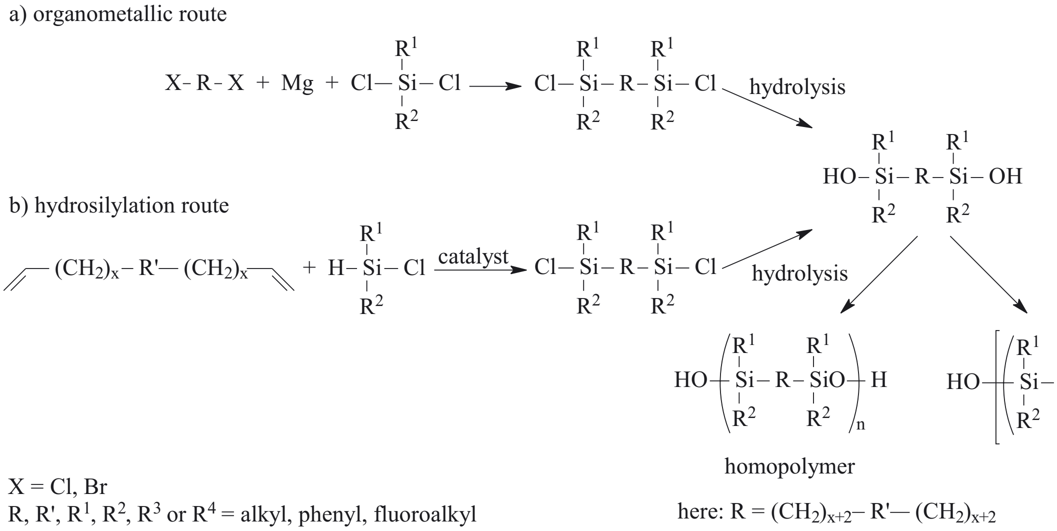
So, in an attempt to avoid this possible depolymerization, a new class of polysiloxanes has been developed, mainly since the 1970s: the so-called "hybrid silicones", which are polysilalkylene siloxanes, fluorinated or not, and polysilarylene siloxanes also fluorinated or not, alternating SiO and SiC bonds in their backbones and having the following general formula where R^1, R^2 and R^3 = alkyl, aryl, fluoroalkyl, fluoroaryl (Formula 1):



$$\left(\overset{R^1}{\underset{R^2}{\mathrm{Si}}} - R^3 - \overset{R^1}{\underset{R^2}{\mathrm{SiO}}} \right)_n \qquad \text{(I)}$$

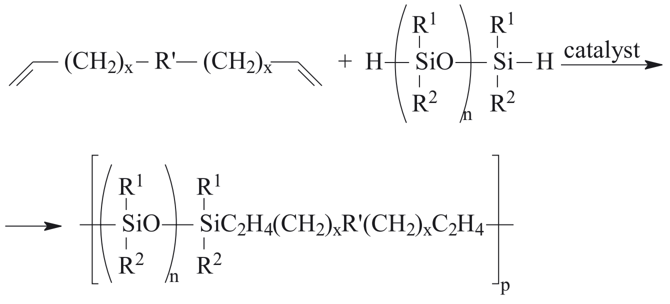
The elastomers prepared by crosslinking of these polymers are materials of very high thermal stability and rather high flexibility at low temperature. Depending on the nature of their backbones or of their side chains, they may exhibit an excellent resistance to solvents or fuels. Main synthetic routes leading to polysilalkylene or silarylene siloxanes fluorinated or not, so-called "hydrid" silicones, are presented hereafter together with properties of different polymers.

During the years 1960—1970 many examples of "hybrid" silicones were described, particularly silphenylene-siloxanes ("hybrid" silicones containing phenyl groups in the backbone) and also fluorinated "hybrid" silicones with or without aromatic groups in the backbone or as side chains. These silicones are generally obtained through two main pathways:



Scheme A

— polycondensation of bis-silanol monomers, themselves prepared either *via* an organometallic route or *via* hydrosilylation of α,ω-dienes. The bis-silanol monomers are then polycondensed to give hybrid homopolymers or condensed with difunctional silanes to give copolymers (Scheme A).



Scheme B

— polyhydrosilylation, *i.e.* polyaddition of α,ω-dienes with α,ω-dihydro — or oligo siloxanes (Scheme B).

Very recently, another method was reported for the synthesis of "hybrid silicones" through ring opening polymerization [3]. It will not be presented here as there are very few examples.

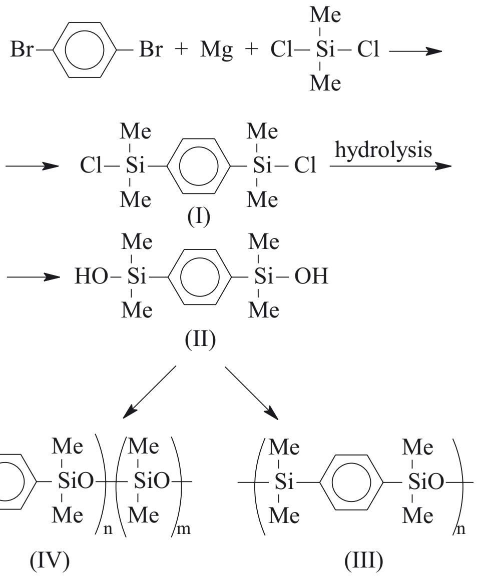
SYNTESIS OF "HYBRID" SILICONES STARTING FROM BIS-SILANOL MONOMERS

From bis-silanol monomers obtained *via* an organometallic route

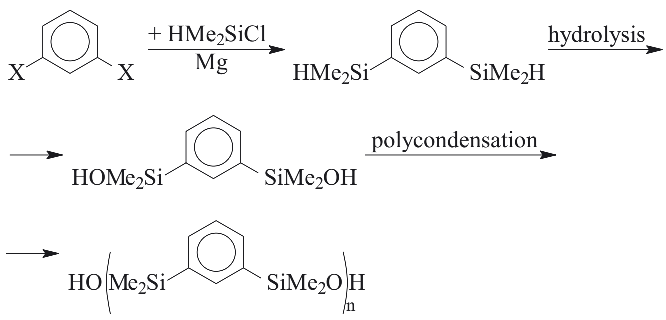
Aryl and/or alkyl backbone

One of the first bis-silanols that was used in the synthesis of "hybrid" silicones, and reported by Merker and Scott in 1964 [4], was bishydroxy(tetramethyl-*p*-silphenylene siloxane) [formula (II) in Scheme C]. It was obtained *via* a magnesium route according to Scheme C.

And, after polycondensation, it led to the corresponding homopolysilphenylene siloxane [formula (III) in



Scheme C



Scheme D

Scheme C] or to random, alternated or block copolymers [formula (IV) in Scheme C]. Similarly, the synthesis of poly(tetramethyl-*m*-silphenylene siloxane) was reported later by Mark *et al.* [5] (scheme D).

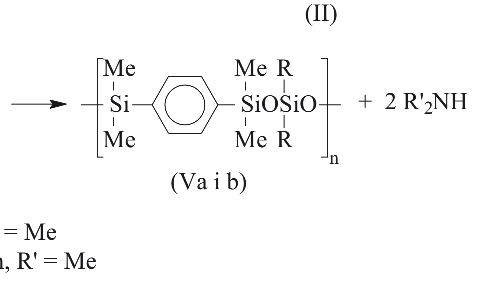
Its glass transition temperature (T_g) was evaluated as -52 °C and no melting was detected, contrary to the equivalent *p*-silphenylene polymer which exhibits T_g = -18 °C. TGA analyses showed very good high temperature properties (onset degradation temperature at 415 °C in nitrogen and 495 °C in air).

Bishydroxy(tetramethyl-*p*-silphenylene siloxane) [formula (II)] has been used in different syntheses of random, alternated or block copolymers [6, 7]. Its condensation with dimethyldichlorosilane [6] led to random and block copolymers, while the condensation with diaminosilanes [7, 8] led to alternating copolymers (Scheme E).

The thermal properties of the copolymers were evaluated. Copolymer (Va) or poly[1,4-bis(oxydimethylsilyl)benzene dimethylsilane] exhibited glass transition temperature T_g = -63 °C and very good stability at high temperature. Copolymer (Vb) or poly[1,4-bis(oxydimethylsilyl)benzene diphenylsilane] exhibited T_g = 0 °C and higher stability at high temperature.

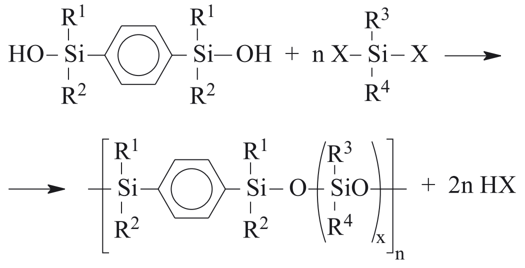
They were crosslinked at room temperature with $Si(OEt)_4$ and dibutyltin diacetate to give thermostable elastomers with applications for the aeronautic industry.

During the 1980s, Dvornic and Lenz and their co-workers have published numerous articles on the synthesis of silarylene siloxanes (Cf. Scheme F) and the study of their thermal properties that are summarized in a chapter of a monograph on silicon polymers [9].



a) R = R' = Me
b) R = Ph, R' = Me

Scheme E



Scheme F

During the 1990s, they compared four different ways [X = Cl, X = $OCOCH_3$, X = N Me_2 and X = N(Ph)CON< or ureido group] to obtain these hybrid silarylene-siloxane copolymers [10] and showed that the copolymers of higher molecular weights were obtained with ureidosilanes, while those of the lower molecular weights were obtained with chloro- and acetoxy silanes, because in both these cases, degradation side reactions occured with the acids formed (HCl and CH_3COOH). The average molecular weights of the polymers were ranging from 70 000 to 340 000 Da. Different groups R^1 to R^4 were studied: methyl, ethyl, vinyl alkyl, phenyl, cyanoethyl, cyanopropyl, hydrogen [9—11] and fluoroalkyl one [12].

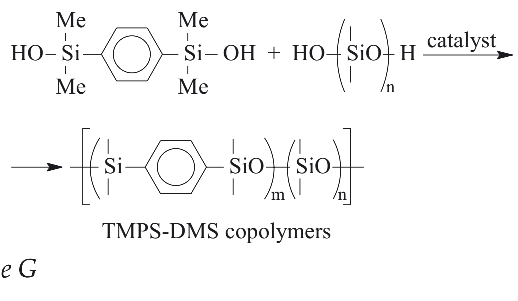
The relations between the nature of the polymers and the glass transition temperatures have been studied, as well as their thermal stability: the presence of an aromatic unit in the main chain increases T_g, as well as the presence of bulky side groups (phenyl, cyanoalkyl, fluoroalkyl one). On the contrary, the presence of vinyl or allyl side groups decreases T_g.

Concerning the thermal stability which is very high (decomposition generally above 480 °C in TGA), the best resistance to thermal degradation is obtained with exactly alternating copolymers. In nitrogen, resistance to pure thermal degradation decreases depending on the type of the side groups R^3 and R^4 (when $R^1 = R^2 = CH_3$) in the following order:

$CH{=}CH_2 > C_6H_5 > CH_3 > H > C_2H_4CF_3 > C_2H_4C_6F_{13}$

So, the highest stability is observed for the vinyl group.

The structural analyses of poly(tetramethyl-*p*-silphenylene siloxane)-poly(dimethylsiloxane) copolymers (TMPS-DMS copolymers) were performed by ^{29}Si NMR

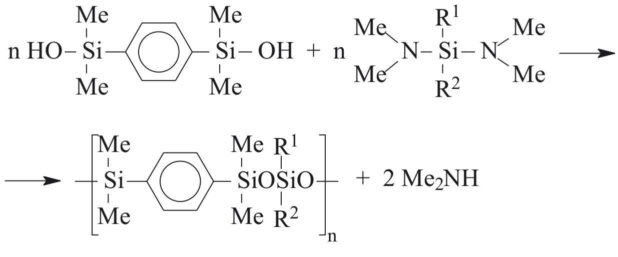


Scheme G

[13]. These copolymers were obtained by the condensation of bis-hydroxy(tetramethyl-*p*-silphenylene siloxane) [formula (II) i Scheme C] with α,ω-dihydroxy polydimethyl oligosiloxanes, in the presence of a guanidinium catalyst (Cf. Scheme G).

This NMR analysis was particularly useful as the block TMPS-DMS copolymers exhibit a wide range of properties depending upon the composition and average sequence lengths of the soft dimethylsiloxane segments and the hard crystalline silphenylene blocks.

More recently, in 1998—1999 McKnight *et al.* [14—16] reported some vinyl-substituted silphenylene siloxane copolymers with exactly alternating structures and varying vinyl content that were synthesized as follows (Scheme H):

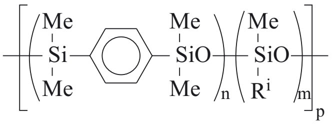


$R^1 = R^2 = CH_3$, $CH{=}CH_2$, mixt. $CH_3/CH{=}CH_2$

Scheme H

The copolymers were described as thermally stable, high-temperature elastomers ("highest degree of thermal and oxidation stability that has been observed so far for any elastomers"). Additionally they were supposed to be promising candidates for potential applications as flame-retardant elastomers, one of the critical needs in many industrial branches such as the aircraft and automotive industries.

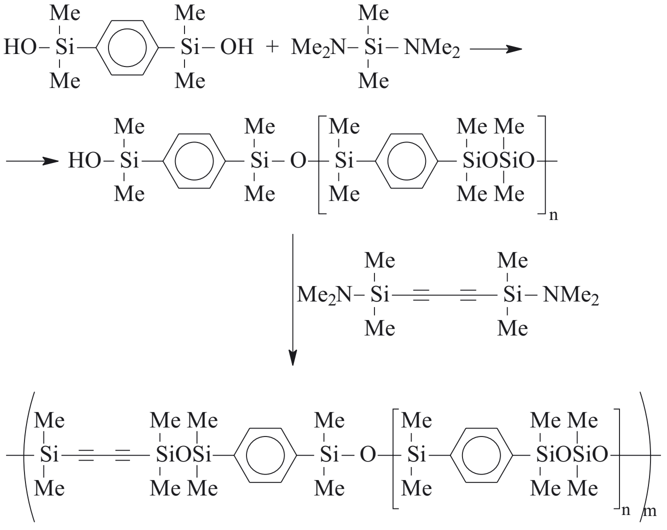
In the years 1988 and 1989 in our laboratory [17, 18] the same bishydroxy(tetramethyl-*p*-silphenylene siloxane) [formula (II) in Scheme C] had been used in polycondensation with chlorosilanes fluorinated or non fluorinated, type $Cl_2Si(Me)R^i$ with R^i = H, $CH=CH_2$ or R_F, where R_F = $C_3H_6OC_2H_4C_nF_{2n+1}$, $C_2H_4C_6F_5$, $C_3H_6OCF_2CFHCF_3$, $C_2H_4SC_2H_4C_nF_{2n+1}$, $C_3H_6SC_3H_6OC_2H_4C_nF_{2n+1}$ and silicones with the following general formula were obtained [formula (VI)].



(VI)

Silicones containing at the same time $R^i = R_F$, R^i = H and R^i = vinyl are fluorinated silicones of low viscosities, easy to crosslink (with Pt catalyst) and they give access to "pumpable" silicones.

Later, in 1997, we also described polysiloxane with (C_6H_{12}) silalkylene backbone obtained by polycondensation of the corresponding hybrid bisilanol bearing methyl and phenyl pendant groups and showed that it also exhibited a good thermal stability [19]. Its T_g = -52 °C was higher than that of PDMS, but its degradation temperature in nitrogen was about 100 °C higher than for PDMS and was also higher in air.



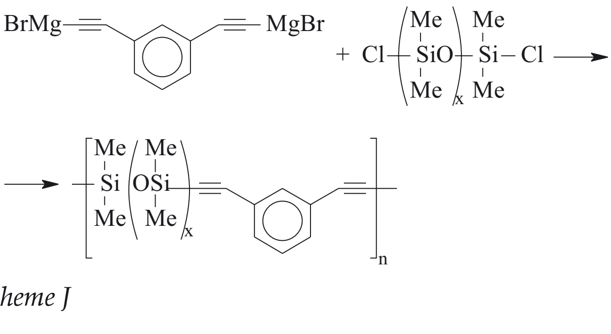
Scheme I

Finally, silarylene-siloxane-diacetylene polymers were reported by Homrighausen in 2000 [20], as precursors to high temperature elastomers. They were obtained as in Scheme I.

Depending upon diacetylene content, the linear polymers can be transformed (*via* thermolysis) to either highly crosslinked plastics or slightly crosslinked elastomers. The crosslinked polymers degrade thermally above 425 °C under inert conditions.

As a variant of this first method using Grignard reagents to prepare hybrid silicones, it may be cited a very recently published synthesis of poly(sil-oxylene-ethylene-phenylene-ethylene)s by reactions of bischlorosiloxane with bismagnesium derivative of diethynyl compound [21] according to the following scheme (Scheme J).

These compounds are said to be useful for composites showing good heat resistance.

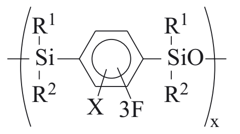


Scheme J

Fluorinated backbone

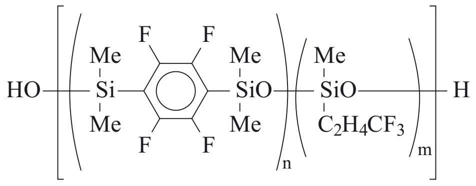
Concerning hybrid silicones having a fluorinated backbone, that are prepared from fluorinated hybrid bis-silanols obtained *via* Grignard route, several examples may be cited:

— A patent deposited in 1970 by Dow Corning Corp. [22] described the synthesis of bis-silylfluoro-aromatic compounds and derivated polymers. The monomer diols, synthesized through Grignard reactions, were polymerized by autocondensation in the presence of catalysts such as the complex tetramethylguanidine/trifluoroacetic acid (TMG/CF_3CO_2H) or tertiobutyl hydroxyamine/trifluoroacetic acid to give hybrid homopolymers [Formula (VII) where X = F, CF_3 and R^1, R^2 = CH_3, $C_2H_4CF_3$].

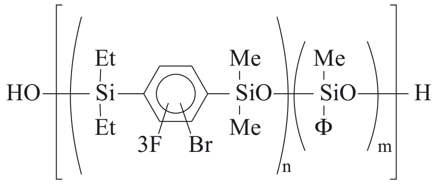


(VII)

These polymers, after addition of charges, led to elastomers that were stable at high temperature and had applications as sealant materials. The diol monomers had also been *co*-hydrolysed with other siloxanes to give copolymers such as, for example Formulas (VIII) and (IX).

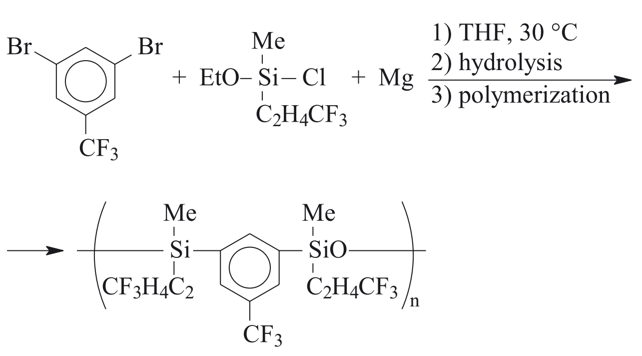


(VIII)

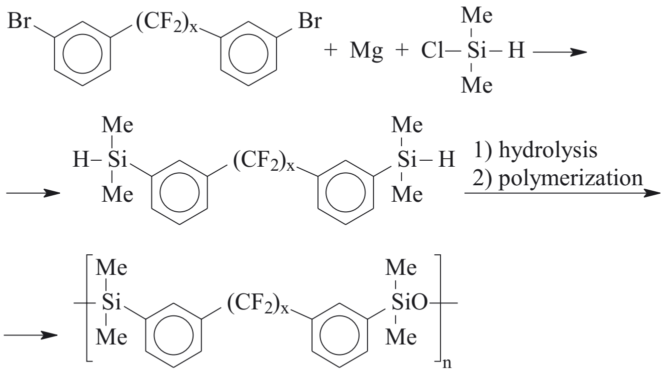


(IX)

— In parallel, another patent also deposited by Dow Corning Corp. [23] described the synthesis of silylfluoro-aromatic homopolymers (Scheme K).



Scheme K



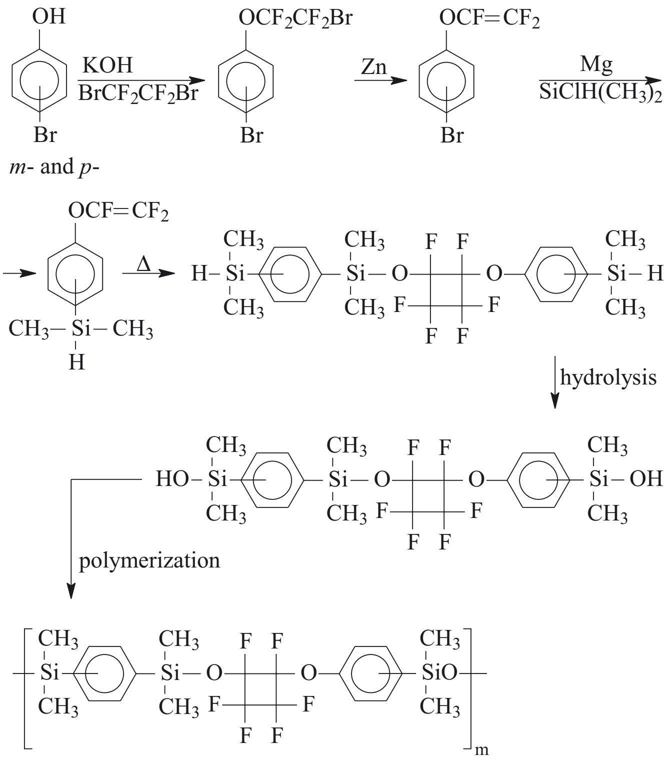
x = 2 or 3

Scheme L

— At the same time, Critchley *et al.* [24] published the synthesis of perfluoroalkylene organopolysiloxanes obtained from monomer diol prepared *via* Grignard route (Scheme L).

The study of the thermal degradation of these "hybrid" silicones [25] was achieved in comparison to the classical polydimethyl and polytrifluoropropylmethyl siloxanes, and the authors showed that the introduction of perfluoroalkylene segments -C_6H_4-$(CF_2)_x$-C_6H_4- into the main chain of the polysiloxane increased the thermal stability both under inert and oxidative atmosphere.

The same type of fluorinated silphenylene siloxane polymers (with *para*—silphenylene groups instead of *meta*), was described by Patterson *et al.* [26, 27] starting



Scheme M

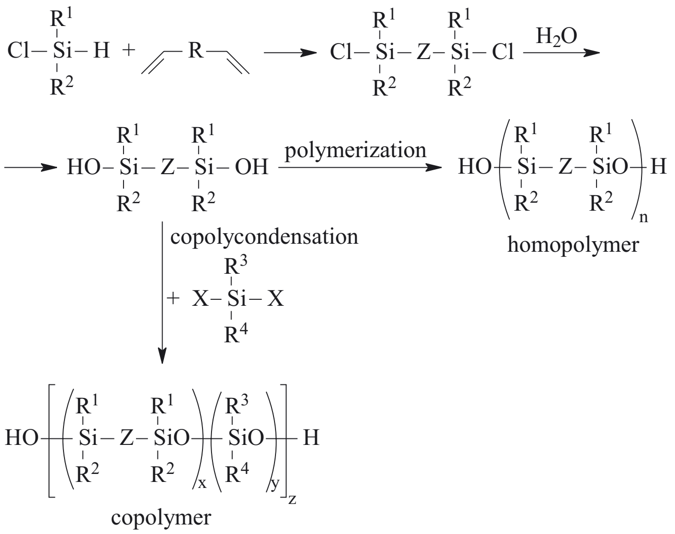
from diol monomers also obtained *via* Grignard route. The hybrid silicon homopolymers gave thermostable elastomers, after crosslinking.

Recently, Rizzo and Harris reported the syntheses and thermal properties of fluorosilicones containing perfluorocyclobutane rings [28] that can be considered as a particular kind of hybrid fluorinated silicones. Their work was directed towards "developing elastomers that could lead to high temperature fuel tank sealants that can be used at higher temperatures than the commercially available fluorosilicones". Actually, after base (KOH or NaOH)-catalyzed self-condensation of the sililanol monomer, they obtained high molecular weight homopolymers (M_n ranging from 19 000 to 300 000 Da) exhibiting very good thermal properties. The synthesis of the homopolymers was performed as above (Scheme M).

They also prepared copolymers by addition of α,ω-bishydroxy homopolymers with an α,ω-silanol terminated 3,3,3-trifluoropropyl methyl siloxane oligomer (classical fluorosilicone). T_g of the copolymers (ranging from -60 to -1 °C depending on the composition) increased when the amount of perfluorocyclobutane-containing silphenylene repeated units increased. TGA analysis showed that when the copolymers contained more than 20 % of this repeated unit, they displayed less weight loss at elevated temperature than a classical fluorosilicone homopolymer. The crosslinking (using a peroxide) of a copolymer containing about 30 wt. % of the perfluorocyclobutane-containing repeating unit lead to a network that displayed a volume swell of under 40 % in isooctane, similar to a crosslinked fluorosilicone.

From bis-silanol monomers obtained through hydrosilylation

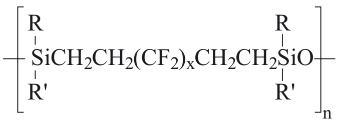
During the years 1970, several articles have been published by Kim *at al.* [29—33] on the synthesis and the properties of fluorinated hybrid silicone homopolymers and copolymers. These polymers were obtained by hydrosilylation of α,ω-dienes with chlorohydrogenosilanes, and the obtained bis-chlorosilanes were then hydrolyzed into bis-silanols and polycondensed or copolycondensed (Scheme N, where $R^i = R^1$ or R^2 or R^3 or R^4, Z = alkyl, alkyl ether, fluoroalkyl, fluoroether... etc.).



Scheme N

In a general article about fluorosilicone elastomers [29], Kim analyzed the properties of classical fluorosilicones -[(R) (R_F) SiO]$_n$- and concluded that they were superior to fluorocarbon elastomers, but they were not very good at high temperatures (above 450 °C) because of a possible depolymerization that deteriorates the physical properties like for conventional polidimethylsiloxanes.

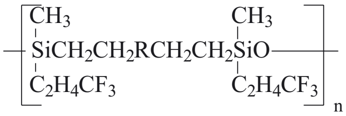
So, in order to obtain polymers that are resistant to reversion (or depolymerization) at high temperature, Kim decided to consider the synthesis of polymers of the type of Formula (X).



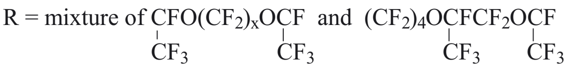
$$\left[-\underset{R'}{\overset{R}{Si}}CH_2CH_2(CF_2)_xCH_2CH_2\underset{R'}{\overset{R}{Si}}O-\right]_n$$ (X)

$R = CH_3$, $R' = C_2H_4CF_3$, x = 1—10

He recognized, then, that this type of compounds would be less flexible than classical silicones, at low temperature and thus would exhibit a higher T_g. Later, Kim *et al.* introduced a fluoroether segment Z into the homopolymers (Cf. Scheme N) and they showed that the thermal and oxidative stabilities of these new homopolymers were comparable to those of the previous polymers, while their flexibility at low temperature was better, *i.e.* their T_g was lower [30]. They have synthesized numerous hybrid fluorosilicon homopolymers with fluoroalkyl or fluoroether backbones [Formula (XI)].



$$\left[-\underset{C_2H_4CF_3}{\overset{CH_3}{Si}}CH_2CH_2RCH_2CH_2\underset{C_2H_4CF_3}{\overset{CH_3}{Si}}O-\right]_n$$ (XI)



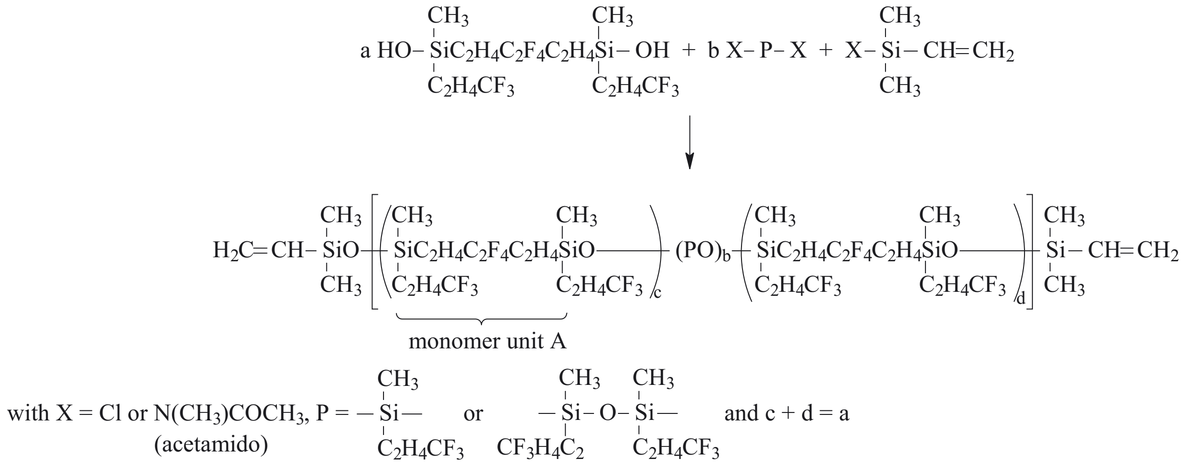
R = mixture of $\underset{CF_3}{CF}O(CF_2)_xO\underset{CF_3}{CF}$ and $(CF_2)_4O\underset{CF_3}{CF}CF_2O\underset{CF_3}{CF}$

or

$R = (CF_2)_l[O(CF_2)_m]_nO(CF_2)_2$ where l = 2 or 3, m = 2 or 5, n = 0 or 1

Then, they prepared fluorinated hybrid copolymers by condensation of hybrid bis-silanol monomers and dichloro- or diacetamidosilanes, in the presence of a monofunctional silane as chain stopper, according to the Scheme O.

For X = Cl, they obtained random copolymers and for X = acetamido group, they obtained alternated copoly-

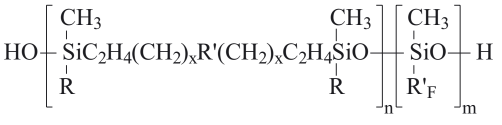


Scheme O

mers $(AB)_n$ or $(ABA)_n$ depending on the nature of P [33], the monomer unit B being — $(CH_3)(C_2H_4CF_3)SiO$-.

A comparative study on the thermal properties and glass transition temperature of $(A)_n$ and $(B)_n$ homopolymers, $(AB)_n$ random and alternated copolymers and $(BAB)_n$ alternated copolymers has been achieved and showed the influence of the polymer structure. Random copolymers may lead to depolymerization like $(B)_n$ homopolymers do. On the contrary, alternated copolymers present much better resistance to reversion. Copolymers exhibit lower T_g (of 10 to 20 °C) than that of the hybrid homopolymer $(A)_n$. Thermogravimetric analyses of random and alternated copolymers show that they are more stable than each of homopolymers $(A)_n$ or $(B)_n$.

Different homopolymers and copolymers similar to those of Kim's were synthesized in our laboratory [34—39] [Formula XII]:



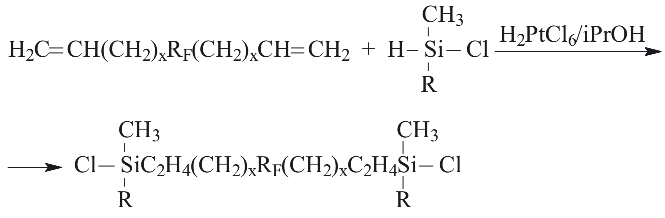
$$HO\left[\begin{matrix}CH_3 & & CH_3\\ Si & C_2H_4(CH_2)_xR'(CH_2)_xC_2H_4 & SiO\\ R & & R\end{matrix}\right]_n\left[\begin{matrix}CH_3\\ SiO\\ R'_F\end{matrix}\right]_m H \qquad (XII)$$

$R = CH_3, C_2H_4CF_3, C_2H_4C_4F_9$
$R' = C_6F_{12}, CF(CF_3)CF_2C_4F_8CF_2CF(CF_3)$
$R'_F = C_2H_4C_6F_{13}$
$x = 0$ or 1, $m = 0$ or n

It was shown that when the side chain R is fluorinated, the longer the fluorinated chain, the better thermal resistance was observed. T_g was lower for $R = C_2H_4C_4F_9$ than for $R = C_2H_4CF_3$, whereas the thermal resistance at high temperature was comparable.

The influence of the length of the spacer between R_F chain and Si atom was studied. Already in the first step of hydrosilylation, big differences in the reactivities of α,ω-dienes were observed when x = 0 (vinyl type) and x = 1 (allyl type) (Scheme P).

The hydrosilylation, with Speier catalyst (H_2PtCl_6/iPrOH), was quantitative with allyl type α,ω-dienes, whereas with vinyl type α,ω-dienes it led to a great amount of by-products. It was thus necessary to achieve the hydrosilylation in the presence of a peroxide.



x = 0 or 1

Scheme P

Hydrolysis of α,ω-bischlorosilanes issued from the hydrosilylation was quantitative, and an important amount of oligomers was already present in the compound issued from the vinyl type α,ω-diene (silicone with x = 0). Then, the polymerization, or polycondensation was faster when x = 0 and it led to a polymer of higher molecular weight.

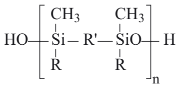
Concerning the thermal properties of these hybrid homopolymers, T_g was higher and the thermal stability at high temperature was lower when x = 1 than when x = 0 [35] (Table 1).

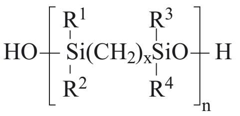
Copolymers were obtained by copolycondensation of hybrid bis-silanols and dichlorosilanes to give random copolymers or by copolycondensation of hybrid bis-silanols and diacetamidosilanes to give alternated copolymers. The thermal properties of these two kinds of copolymers were not much different and were slightly better than those of the parent hybrid homopolymers [37].

Some of these polymeric hybrid fluorosilicones were crosslinked to obtain fluorosiloxane elastomers that combine a good flexibility at low temperature, lower than -40 °C, and a good thermooxidative stability over 250 °C [38, 29]. They may be proposed as alternative materials with respect to polyfluoroolefin elastomers.

Finally, various Japanese patents [40—42] should be cited as they describe the syntheses of homopolymers and copolymers with non fluorinated backbone, issued

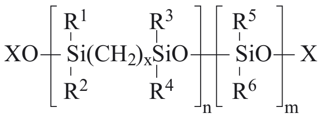
T a b l e 1. Thermal properties of hybrid fluorosilicone homopolymers; denotations: T_m — melting temperature, T_c — crystallization temperature, $T_{50\%}$ (N_2) — temperature at 50 % decompositon in N_2 atmosphere, $T_{50\%}$ — temperature at 50 % decomposition in an air atmosphere

Rand R′ in  $\mathrm{HO}\left[\begin{array}{c}\mathrm{CH_3}\\ \mathrm{Si}\\ \mathrm{R}\end{array}-\mathrm{R'}-\begin{array}{c}\mathrm{CH_3}\\ \mathrm{SiO}\\ \mathrm{R}\end{array}\right]_n\mathrm{H}$		DSC (10 °C/min)			TGA	
		T_g, °C	T_m, °C	T_c, °C	$T_{50\%}$ (N_2), °C	$T_{50\%}$, °C
R = CH_3	R′ = $C_2H_4C_6F_{12}C_2H_4$	-53	26	-11	470	380
	R′ = $C_3H_6C_6F_{12}C_3H_6$	-40	25	-27	465	330
R = $C_2H_4CF_3$	R′ = $C_2H_4C_6F_{12}C_2H_4$	-28			490	410
	R′ = $C_3H_6C_6F_{12}C_3H_6$	-18			465	360
R = $C_2H_4C_4F_9$	R′ = $C_2H_4C_6F_{12}C_2H_4$	-42			490	360
	R′ = $C_3H_6C_6F_{12}C_3H_6$	-29			470	310
R = CH_3	R′ = C_3H_6/HFP/C_4F_8/HFP/C_3H_6	-49			425	300
R = $C_2H_4CF_3$	R′ = C_3H_6/HFP/C_4F_8/HFP/C_3H_6	-34			445	310
R = $C_2H_4C_4F_9$	R′ = C_3H_6/C_2F_4/VDF/HFP/C_3H_6	-47			420	315


$$\mathrm{HO}\left[\begin{array}{c}\mathrm{R^1}\\ \mathrm{Si}\\ \mathrm{R^2}\end{array}(\mathrm{CH_2})_x\begin{array}{c}\mathrm{R^3}\\ \mathrm{SiO}\\ \mathrm{R^4}\end{array}\right]_n\mathrm{H}$$

(XIII)

$R^{1-4} = C_1$ to C_8
x = 4—16


$$\mathrm{XO}\left[\begin{array}{c}\mathrm{R^1}\\ \mathrm{Si}\\ \mathrm{R^2}\end{array}(\mathrm{CH_2})_x\begin{array}{c}\mathrm{R^3}\\ \mathrm{SiO}\\ \mathrm{R^4}\end{array}\right]_n\left[\begin{array}{c}\mathrm{R^5}\\ \mathrm{SiO}\\ \mathrm{R^6}\end{array}\right]_m\mathrm{X}$$

(XIV)

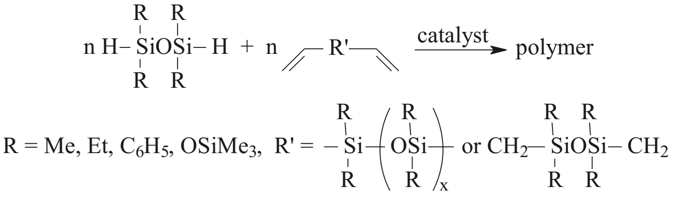
from the corresponding bis-silanol monomers (themselves issued from α,ω-dienes) and having the following formulas (XIII) and (XIV) where R^{1-5} = monovalent substituted (or not) aliphatic hydrocarbon, R^6 = unsaturated monovalent hydrocarbon, X = H or $SiR^7R^8R^9$ and R^{7-9} = monovalent substituted (or not) hydrocarbon.

These products have been used in silicone compositions that have been crosslinked and the elastomers obtained showed very good mechanical properties (high tension and tear strength).

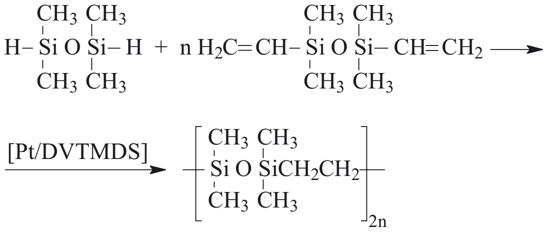
SYNTHESIS OF "HYBRID" SILICONES THROUGH POLYHYDROSILYLATION OF α,ω-DIENES

The principle of this method is the addition of α,ω-dienes onto α,ω-dihydrosiloxanes or oligosiloxanes according to scheme B (previously given).

The first works performed by this method were published by Russian researchers [43—45] who had studied the reaction described in Scheme Q.


$$n\,\mathrm{H}-\begin{array}{c}\mathrm{R}\\ \mathrm{Si}\\ \mathrm{R}\end{array}\mathrm{O}\begin{array}{c}\mathrm{R}\\ \mathrm{Si}\\ \mathrm{R}\end{array}-\mathrm{H} + n\ \diagup\!\!=\!\!\diagdown\mathrm{R'}\diagup\!\!=\!\!\diagdown \xrightarrow{\text{catalyst}} \text{polymer}$$
$$\mathrm{R = Me, Et, C_6H_5, OSiMe_3},\ \mathrm{R'} = -\begin{array}{c}\mathrm{R}\\ \mathrm{Si}\\ \mathrm{R}\end{array}\left(\mathrm{O}\begin{array}{c}\mathrm{R}\\ \mathrm{Si}\\ \mathrm{R}\end{array}\right)_x \text{ or } \mathrm{CH_2}-\begin{array}{c}\mathrm{R}\\ \mathrm{Si}\\ \mathrm{R}\end{array}\mathrm{O}\begin{array}{c}\mathrm{R}\\ \mathrm{Si}\\ \mathrm{R}\end{array}-\mathrm{CH_2}$$

Scheme Q


$$\mathrm{H}-\begin{array}{c}\mathrm{CH_3}\\ \mathrm{Si}\\ \mathrm{CH_3}\end{array}\mathrm{O}\begin{array}{c}\mathrm{CH_3}\\ \mathrm{Si}\\ \mathrm{CH_3}\end{array}-\mathrm{H} + n\,\mathrm{H_2C{=}CH}-\begin{array}{c}\mathrm{CH_3}\\ \mathrm{Si}\\ \mathrm{CH_3}\end{array}\mathrm{O}\begin{array}{c}\mathrm{CH_3}\\ \mathrm{Si}\\ \mathrm{CH_3}\end{array}-\mathrm{CH{=}CH_2} \longrightarrow$$
$$\xrightarrow{[\mathrm{Pt/DVTMDS}]} \left[\begin{array}{c}\mathrm{CH_3}\\ \mathrm{Si}\\ \mathrm{CH_3}\end{array}\mathrm{O}\begin{array}{c}\mathrm{CH_3}\\ \mathrm{Si}\\ \mathrm{CH_3}\end{array}\mathrm{CH_2CH_2}\right]_{2n}$$

Scheme R

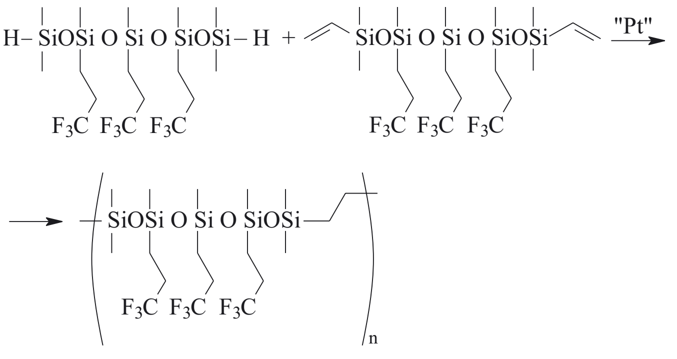
The authors had used Speier catalyst, H_2PtCl_6/i-PrOH and obtained products of low molecular weights (1000—2000 Da).

More recently, Dvornic *et al.* [46, 47] used the hydrosilylation polymerization method for 1,1,3,3-tetramethyl disiloxane and 1,3-divinyl-1,1,3,3-tetramethyl disiloxane and succeeded in obtaining the first hybrid silicones, called here "polycarbosiloxanes" of high molecular weight (up to 76 000 Da), according to the reaction (Scheme R).

The hydrosilylation was, then, catalyzed by the complex of platinum-divinyl-1,3-tetramethyldisiloxane (Pt-DVTMDS) or Karstedt catalyst. It was studied in different conditions: in bulk, with a diluted or with concentrated toluene solution. The higher molecular weight was obtained when the polymerization was carried out without any solvent. According to Dvornic, the selection of Karstedt catalyst seems to be the key factor for the preparation of high molecular weight products, in contrast to hexachloroplatinic acid used by the previous Russian workers, which may generate HCl after reduction.

Rheological studies and thermogravimetric analyses of the polymers obtained showed that the flexibility and thermal and oxidative stabilities were lower than for polysiloxanes showing a close structure. This is due to the stiffening and destabilizing effect of C-C groups introduced between the main Si-O-Si units in the chain.

However, these authors strongly insisted on the fact that hydrosilylation was a good method for the preparation of linear carbosiloxanes of high molecular weights.



Scheme S

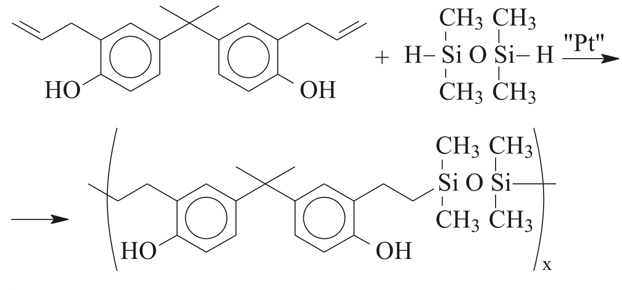
Very recently, another example of Pt-DVTMDS catalyzed hydrosilylation copolymerization leading to fluorinated copoly(carbosiloxane)s has been described [48]. It concerned the addition of α,ω-divinyl fluorooligosiloxanes onto α,ω-dihydrofluorooligosiloxanes as in Scheme S.

The structures of the copoly(carbosiloxane)s have been determined by IR as well as by ^{1}H, ^{13}C, ^{19}F and ^{29}Si NMR spectroscopy. Gel permeation chromatography (GPC) analysis showed that high molecular weights were obtained (20 000 — 40 000 Da) and DSC and TGA analyses showed very low T_g in the range -77 to -80 °C and good thermal stability both in nitrogen (stability to approximately 380 °C) and in air (stability to approximately 270 °C).

Another example of polyhydrosilylation is the addition of diallylbisphenol A to tetramethyldisiloxane which was reported by Lewis in 1993 [49, 50] (Cf. Scheme T).

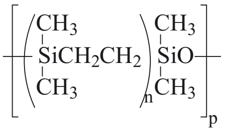
The reaction is strongly exothermic and must be performed in a solvent as the *co*-reagents are not miscible. But, even if the reaction is performed at 0 °C, the molecular weights are here limited by the non stoichiometry due to the volatility of disiloxane. Some years later, almost the same reaction was performed with hexafluoro derivative of bisphenol A [51, 52] and the resulting polymers proved to be excellent sorbents for basic vapors due to their strong hydrogen bond acidity.

Recently, Boileau *et al.* [53, 54] performed the polyhydrosilylation of diallylbisphenol A with hydride terminated polydimethylsiloxanes to prepare "tailor-made polysiloxanes with anchoring groups" composed of dimethylsiloxane segments (DMS) of different lengths, regularly separated by one bisphenol A (BPA) unit. They studied the influence of the control of [Si-H]/[double bond] ratio and the protection of -OH groups on the molecular weight distribution of the polymers. A strong influence of DMS segment length and of the presence of H-bonding interactions on the thermal properties of the resulting polymers was observed. T_g decreased (from +32 to -114 °C) with increasing siloxane segment length and TGA analysis under nitrogen showed a quite good thermal stability.



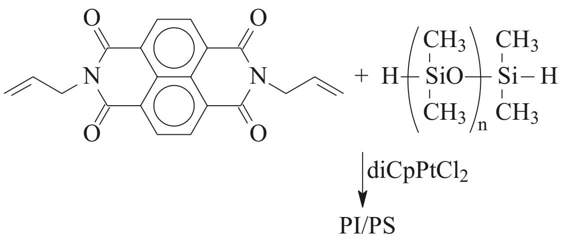
Scheme T

The polyhydrosilylation method had also been applied earlier by Boileau *et al.* [55] to synthesize well-defined polymers containing silylethylene siloxy units [Formula (XV)].



$$\left[\left(\mathrm{Si(CH_3)_2CH_2CH_2}\right)_n \mathrm{Si(CH_3)_2O}\right]_p \qquad \text{(XV)}$$

Additionally the method has been used in a patent to prepare poly(imidesiloxanes) (PI/PS) "in a relatively simple manner, without undesirable side reactions and high conversions achieved in short reaction time" [56]. *N,N'*-dialkenyldiimide was reacted with an organosilicon compound containing two Si-H, in the presence of $DiCpPtCl_2$ as catalyst (Scheme U).

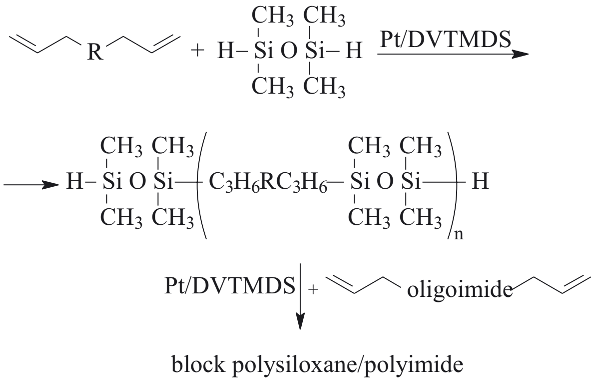


Scheme U

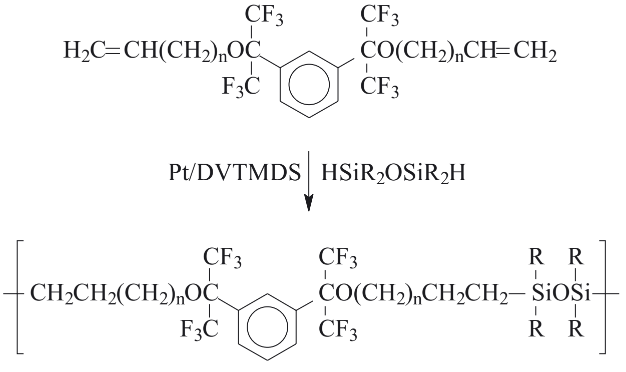
The prepared poly(imidesiloxanes) showed higher heat stability and their T_g was lower when the proportion of siloxane was higher. These products may find applications as coatings, adhesives or membranes for gas separation.

More recently, we have also reported the synthesis of hybrid polysiloxane/polyimide block copolymers (the hybrid polysiloxane being fluorinated or not) that were obtained through polyhydrosilylation of dienes with α,ω-dihydrooligosiloxanes [57—62], as in Scheme W.

These block copolymers exhibited both good thermomechanical properties and low surface tension and some of them exhibited also thermoplastic elastomer properties depending on the length and the amount of soft polysiloxane and hard polyimide segments.



Scheme W



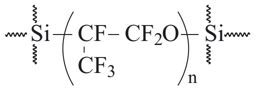
Scheme V

Finally, the platinum-catalyzed hydrosilylation polymerization was also used very recently by Cassidy *et al.* [63, 64] to prepare fluorine containing silicon-organic hybrid polymers in supercritical carbon dioxide (Sc CO_2) (Scheme V).

They showed that, in Sc CO_2, the reaction provided higher percent conversion in shorter time and that the molecular weights of polymers obtained were notably greater than those obtained in benzene.

Before ending this review, it is worth citing a product that may be seen as a particular hybrid silicone: SIFEL perfluoro elastomer from Shin-Etsu. Actually, it consists of perfluoroether polymer backbone combined with an addition-curing silicone crosslinking agent. The perfluoroether polymer was capped with vinyl silicone functions and the crosslinking was achieved with a special crosslinking agent containing several Si-H end groups [general type as in Formula (XVI)], in the presence of a platinum catalyst [65, 66].

The product is described as a liquid perfluoroelastomer and it is becoming popular in the industry as an universal material for O-rings, diaphragms and other mold parts due to its unique properties issued from its special chemical formula [Formula (XVII)].



$$-Si-\left(\underset{CF_3}{CF}-CF_2O\right)_n-Si- \qquad \text{(XVII)}$$

The compound is specially interesting for aerospace industries as it can perform well with different media: jet fuel, hydraulic oil, engine oil and hydraulic fluid, under severe environmental conditions.

This new type of elastomer, with its wide range of applications, constitutes a solution to some of the increasingly complex demands of the different industries.

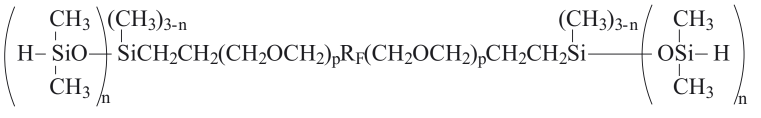
CONCLUSIONS

This review on "hybrid" silicones or polysilalkylene and polysilarylene siloxanes, fluorinated or not, also called "polycarbosiloxanes", gives the different ways of syntheses of these special polysiloxanes that have been developed to avoid the drawback of depolymerization of classical polysiloxanes in certain conditions of temperature or of acid or base medium.

The first method that was mainly used from the 1960s was based on polycondensation of α,ω-dihydroxysiloxanes (generally leading to not very high molecular weights), while the second method which has been developed during the three last decades is based on polyhydrosilylation of α,ω-diolefines with α,ω-dihydro terminated siloxanes (better to obtain high molecular weights products).

All the homopolymers or copolymers that have been obtained show very interesting properties in terms of thermal stability. They generally present rather low T_g and good stability at high temperature and may thus be used in a wide range of temperature. In the search for new materials with new applications, the preparation of polymers showing specific properties is required, and depending on the nature of their main chain (alkyl, fluoroalkyl, aryl, fluoroaryl, alkyl ether...) and on the nature of their side chains, these "hybrid" silicones may be directed to exhibit these specific properties.

Actually, a few years ago, Hergenrother [67] precised the requirements of the technology for high speed civil transports (HSCTs): the sealants must exhibit a combination of properties such as elongation, moderate peel strength, fuel resistance and performance for 60 000 h at 177 °C. He said that the most popular commercially available fuel tank sealant that can be used at a tempera-



$$\left(H-\underset{CH_3}{\overset{CH_3}{Si}}O-\right)_n\overset{(CH_3)_{3-n}}{Si}CH_2CH_2(CH_2OCH_2)_pR_F(CH_2OCH_2)_pCH_2CH_2\overset{(CH_3)_{3-n}}{Si}\left(-O\underset{CH_3}{\overset{CH_3}{Si}}-H\right)_n \qquad \text{(XVI)}$$

R_F = perfluoropolyether or perfluoroalkylene group
n = 1, 2 or 3
p = 0 or 1

ture of around 177 °C is based upon poly(3,3,3-trifluoropropylmethylsiloxane), but this product may degrade after continued exposure to high temperature.

Since then, the Sifel from Shin-Etsu has emerged, but it is a very expensive material. So, finding a good combination of "hybrid" or silalkylene siloxanes, classical siloxanes, silarylene siloxanes, preferably fluorinated, remains a challenge to obtain the best elastomer. It seems that there is still a promising future for these "hybrid" silicone materials.

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