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Synthesis of Fluorinated Polysiloxanes. 8. Properties at Low and High Temperatures of Polysiloxanes with Fluorinated Grafts

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ABSTRACT: The copolycondensation of commercial diols $HO[SiCH_3)_2O]_nH$ with fluorinated dichlorosilanes as $CH_3SiCl_2(CH_2)_3O(CH_2)_2C_6F_{13}$ and blocking agent $H_2C{=}CHSi(CH_3)_2Cl$ led to fluorinated polysiloxanes having vinyl end groups. The chemical (^1H, ^{13}C, and ^{29}Si NMR) and physicochemical [viscosities, glass transition temperatures (T_g's) by DSC, and degradation temperatures (T_d's) by TGA] characteristics were determined. The properties of these polymers were compared with those of poly(dimethylsiloxane) (PDMS) and poly[methyl(trifluoropropyl)siloxane] at low and high temperatures, and it was shown that it was possible to prepare elastomers with T_g's lower than −100 °C that do not exhibit a better high-temperature resistance. At temperatures above 300 °C, the network has a behavior close to that of PDMS and much better than that of commercial fluorosilicones.

Introduction

Recently, we studied the copolycondensation of 1,4-bis(hydroxydimethylsilyl)benzene[1] with dichlorosilanes possessing a fluorinated lateral chain as well as SiH and $SiCH{=}CH_2$ groups. We obtained two series of liquid fluorinated polysiloxanes, called "pumpable" polysiloxanes.

These polymers and their derivatives exhibit a glass transition temperature (T_g) close to that of commercial poly[methyl(trifluoropropyl)siloxane] from Dow Corning.[2] However, it is well-known that the introduction of an aromatic nucleus increases the T_g,[3] but adding a fluorinated lateral chain such as $C_6F_{13}(CH_2)_2O(CH_2)_3$ into the polymer decreases the T_g[4] about the $CF_3(CH_2)_2$ group.

For this reason, we carried out the synthesis of fluorinated polysiloxanes as previously, but commercial α,ω-dihydroxypoly(dimethylsiloxane) was used in order to obtain a polymer that does not have any aromatic ring in order to improve the T_g.

Experimental Section

IR spectra were recorded with a Perkin-Elmer 398 spectrophotometer. The band positions are given in cm^{-1} with an accuracy of 2.5 cm^{-1}.

^1H NMR spectra were obtained on a Bruker WH apparatus (250 MHz), and TMS was used as a reference.

^{13}C and ^{29}Si NMR spectra were recorded on a Bruker SWV apparatus (80 MHz). Deuterated chloroform was used as solvent. For ^{29}Si NMR, TMS was the reference.

Molecular weights were determined by GPC with a Waters Associates Model 5900 chromatograph equipped with three μ-Styrogel columns, the maximum permeabilities of which were 1000, 500, and 100 Å, respectively. The detector was a Waters Associates R401 differential refractometer, and THF was used as eluant.

Glass transition temperatures (T_g's) were determined by differential scanning calorimetry using a Perkin-Elmer apparatus, and the heating rate was 20 °C/min.

Thermogravimetric analyses (TGA) were performed with a homemade JCG-LM apparatus with reference to 1 Meler AE 100. The heating rate was 5 °C/min.

Viscosimetric analyses were carried out at 25.00 ● 0.01 °C with an Amtec 52 automatic Ubbelohde viscosimeter equipped with a 0.5-mm capillary, whereas the viscosimetric analyses by rheometry were executed on a Rotovisco RV 100 rotometer, linked to an HP 85 microcomputer. An ME 31 mobile phase was used, and the temperature was 10.0 ± 0.1 °C.

1. **Synthesis of $H_2C{=}CHSi(CH_3)_2[O(Si(CH_3)_2O)_n$-$Si(CH_3)(R_F)]_pO(Si(CH_3)_2O)_nSi(CH_3)_2CH{=}CH_2$ ($R_F = C_6F_{13}$-$(CH_2)_2O(CH_2)_3$, $n = 3.75$, $p = 9$) (Compound IV-1).** In a two-neck, round-bottom flask equipped with a condenser 180.0 g of α,ω-dihydroxypoly(dimethylsiloxane) (I) (0.608 mol), 283.9 g of $C_6F_{13}(CH_2)_2O(CH_2)_3Si(CH_3)Cl_2$ (II) (0.547 mol), 14.6 g of $CH_2{=}CHSi(CH_3)_2Cl$ (III) (0.121 mol), 300 mL of toluene, and 8 g of amine salt were introduced. The mixture was heated to 85 °C for 24 h. After cooling, the white precipitate (amine hydrochloride) was filtered off, and the toluene and the unreacted compounds were evaporated. Then the residue was diluted in ethyl ether and was washed several times with water in order to eliminate any residual catalyst (yield = 89%).

2. **Synthesis of Compound IV-2.** A mixture composed of 100.0 g (10 parts) of compound I, 315.4 g (9 parts) of compound II, 16.3 g (2 parts) of compound III, 400 mL of toluene, and 10 mL of pyridine was stirred at 85 °C for 24 h. The workup was as previously described (yield = 90%).

3. **Analysis of $[CH_2{=}CHSi(CH_3)_2O(Si(CH_3)_2O)_n$-$Si(CH_3)(R_F)]_{p/2}$ ($R_F = C_6F_{13}(CH_2)_2O(CH_2)_3$).** Anal. Calcd: F, 31.16; C, 32.13; H, 5.05. Found: F, 30.66; C, 31.90; H, 5.17.

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Figure 1. ^1H NMR spectrum of compound IV.

Table I
Intrinsic Viscosity [η] and Average Molecular Weight $\bar{M}_v$

product	viscosity, 10^{-3} mL·g^{-1}	$\bar{M}_v$
IV-1	3.73	9970
IV-2	3.22	8075

^1H NMR: δ 6.90 (m) ($h/N = 0.24$); 0.10 (s) ($h/N = 0.38$); 0.50 (m) ($h/N = 0.35$), 1.60 (m) ($h/N = 0.36$), 3.35 (m) ($h/N = 0.36$); 3.70 (m) ($h/N = 0.34$), 2.37 (m) ($h/N = 0.34$). (h/N = integration/H atom number ratio.)

^{13}C NMR: δ 131.40 (s), 139.50 (s); 1.03 (s); 13.60 (s), 23.30 (s), 62.50 (s); 73.00 (s), 31.80 (t) ($^2J_{C-F}$ = 22 Hz).

The IR spectrum does not show any band at 3690 cm^{-1} (vibration of $Si(CH_3)_2OH$) but it exhibits $Si(CH_3)_2O$ bands at 1260 and 800 cm^{-1} and $Si(CH_3)_2OSi(CH_3)_2$ bands at 1220, 1090, and 1020 cm^{-1}.

Results and Discussion

The polymerization of silanes is usually performed according to the following scheme:[5]

$$ClSi(CH_3)(R)Cl \xrightarrow{H_2O} \overline{(Si(CH_3)(R)O)}_4 \xrightarrow{\text{cat.}} (Si(CH_3)(R)O)_x$$

Catalysts such as $C_6H_5CH_2N(CH_3)_3{}^+OH^-$ [6] or n-butyllithium[7] are often used for ring opening. With this latter catalyst, Lee[7] obtained, in 2 min from cyclic $[(CF_3C_2H_4)(C_6H_5)SiO]_3$, a polymer with $\overline{DP}_n$ = 270 which exhibited a narrow polydispersity.

Other series of reactions have been developed, e.g., in the case of fluorinated silicones[8]:

$$ClSi(CH_3)((CH_2)_2C_6F_{13})Cl \xrightarrow[2\text{ h}]{NaOH}$$

$$\text{“hydrolysate”} \xrightarrow[\text{cat.}]{HO(Si(CH_3)_2O)_nH} \text{fluorinated silicone}$$

Dow Corning also uses a similar reaction to prepare foams that may or may not contain fluorinated chains by condensation of a dihydropolysiloxane with several reactive cross-linking agents, e.g., $CH_3Si(ON{=}C(Et)(Me))_3$,[9] to form styrene–acrylate graft polymers in the presence of silica-p-(DMS-g-styrene/acrylate) and an expansion agent. In the same way, Lim et al.[10] used fluorinated silanes to improve the surface properties of fluorosilicones.

Table II
Dynamic Viscosity of α,ω-Dihydroxypoly(dimethylsiloxane) and Compound IV-2

product	n	viscosity, cP
$HO(Si(CH_3)_2O)_nH$	3.75	31.4
	56.00	107.8
IV-2		188.7

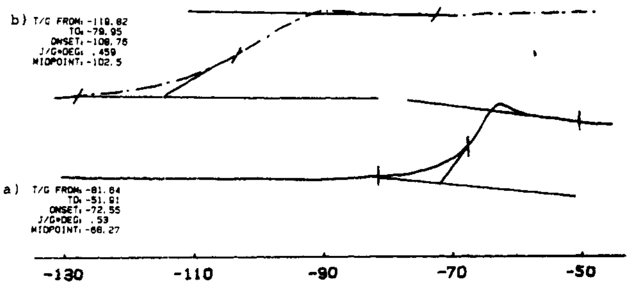

Figure 2. DSC endotherms of compound IV and poly[methyl(trifluoropropyl)siloxane].

Various condensation catalysts have been used, e.g., salts of tin,[11] alkali metals, or alkaline-earth complexes of tertiary amines or cryptands.[12] However, introduction of long groups into the silane leads to important changes of the silane's reactivity and also favors the formation of stable cycles over the linear polymers.

Finally, we note that the processing of nonfluorinated silicones has been improved and that General Electric has optimized a formulation with two components that perform well in that they are cross-linked in several seconds from low-viscosity blends. For that, SiH groups must be a part of the formulation and $SiCH{=}CH_2$ another one (with platinum catalysts), but it is important to control the molecular weight in order to predetermine the viscosities of the formulations filled in silica. Other companies supply “pumpable silicones”: Dow Corning,[13,14] Toray Silicone,[15] and Shin Etsu.[16]

In this field, we have directed our research to prepare liquid fluorinated silicones that have vinyl end groups so

Table III
T_g's (DSC) of Standard and Commercial or Synthesized Polymers

compd	T_g, °C	$\bar{M}_n$	ref
$R_FSi(CH_3)_2OSi(CH_3)_2R_F$			
$R_F = C_6F_{13}(CH_2)_2O(CH_2)_3$ (L_2)	−93	942	18
$R_F = CF_3CHFCF_2O(CH_2)_3$	−99	526	18
$R_F = C_6F_5(CH_2)_2$	−89	522	18
$R_FSi(CH_3)_2OSi(CH_3)_2C_6H_4Si(CH_3)_2OSi(CH_3)_2R_F$	−81	1150	21
$R_FSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2OSi(CH_3)_2R_F$ (L_4)	−102	1090	21
$R_F = C_6F_{13}(CH_2)_2O(CH_2)_3$			
$(R_F\overline{Si(CH_3)O})_4$ (D_4)			
$R_F = C_6F_{13}(CH_2)_2O(CH_2)_3$	−69	1856	1
$R_F = C_6F_{13}(CH_2)_2S(CH_2)_2$	−53	1920	22
commercial $Si(CH_3)_2(OSi(CH_3)_2)_nO$	−122		Dow Corning
obtained in the laboratory	−124	6200	
$R_FSi(CH_3)_2O[Si(CH_3)_2C_6H_4Si(CH_3)_2OSi(CH_3)(R_F)O]_n$			
$R_F = C_6F_{13}(CH_2)_2O(CH_2)_3$	−71	4360	1
$R_F = CF_3CHFCF_2O(CH_2)_3$	−74	5800	1
$Si(CH_3)_2O(Si(CH_3)R_FO)_nSi(CH_3)_2$ ($R_F = CF_3(CH_2)_2$)	−68		Dow Corning
$CH_2{=}CHSi(CH_3)_2[(OSi(CH_3)_2)_nOSi(CH_3)(R_F)]_pOSi(CH_3)_2CH{=}CH_2$	−103	6300	
$R_F = C_6F_{13}(CH_2)_2O(CH_2)_3$; $n = 3.7$			

Table IV
Weight Loss of Commercial and Synthesized Siloxanes versus Temperature (from TGA Curves)

	loss % at T (°C)			
compd	200	300	400	500
$R_FSi(CH_3)_2OSi(CH_3)_2C_6H_4Si(CH_3)_2OSi(CH_3)_2R_F$				
$R_F = C_6F_{13}(CH_2)_2O(CH_2)_3$	2	73	97	
$(R_F\overline{Si(CH_3)O})_4$ (D_4)	2	40	82	
$R_F = C_6F_{13}(CH_2)_2O(CH_2)_3$				
$R_F = C_6F_{13}(CH_2)_2S(CH_2)_3$	6	32	100	
$[Si(CH_3)_2C_6H_4Si(CH_3)_2OSi(CH_3)(R_F)O]_n$	4	26	55	84
$R_F = C_6F_{13}(CH_2)_2O(CH_2)_3$				
$Si(CH_3)_2(OSi(CH_3)_2)_n$	0	0	6.4	29
$Si(CH_3)_2O(Si(CH_3)((CH_2)_2CF_3)O)_n$		9	96	
$Si(CH_3)_2[(OSi(CH_3)_2)_nOSi(CH_3)(R_F)]_p$		25	40	75
$R_F = C_6F_{13}(CH_2)_2O(CH_2)_3$				

that when they react with poly(dimethylsiloxanes) that contain several SiH groups, the polymers cross-link in 20 s at 150 °C.

Thus, we carried out the copolycondensation between an α,ω-dihydroxy[poly(dimethylsiloxane)], $HO(Si(CH_3)_2O)_nH$ (I) ($\bar{n} = 3.75$, % OH = 11.5, $\bar{M}_n = 296$), and the fluorinated dichloromethylsilane $C_6F_{13}(CH_2)_2O(CH_2)_3Si(CH_3)Cl_2$ (II).[17] We used dimethylvinylchlorosilane (III) to limit the chain length.

$$\begin{array}{ll} 2CH_2{=}CHSi(CH_3)_2Cl + & HO(Si(CH_3)_2O)_nH + \\ \quad 0.121\ \text{mol} & \quad 0.608\ \text{mol} \\ \quad (2\ \text{parts}) & \quad (10\ \text{parts}) \end{array}$$

$$\begin{array}{l} pClSi(CH_3)(R_F)Cl \\ \quad 0.547\ \text{mol} \\ \quad (9\ \text{parts}) \end{array} \xrightarrow[C_6H_5CH_3,\ 85\ °C]{\text{cat., 24 h}}$$

$$CH_2{=}CHSi(CH_3)_2O[(Si(CH_3)_2O)_n\text{-}Si(CH_3)(R_F)O]_pSi(CH_3)_2CH{=}CH_2 \quad \text{IV-1}$$

with $R_F = C_6F_{13}(CH_2)_2O(CH_2)_3$, $n = 3.75$, and the expected $p = 9$.

Two polymers were prepared with an expected $\overline{DP}_n$ of 19 (according to Flory's theory) by using two catalysts: the first one is a salt of an amine (IV-1) (2-ethylhexanoic acid and tetramethylguanidine) and the second one, the pyridine (IV-2). The reactions were performed with either several grams or quantities close to 400 g. The yields were ca. 90%.

The products obtained from the two catalytic systems were analyzed by ^{1}H, ^{13}C, and ^{29}Si NMR.

In the ^{1}H NMR spectrum (Figure 1),the classic multiplet of the $SiCH{=}CH_2$ group can be seen at $\delta = 6.9$ and also the two peaks of the methyl groups attached to silicon: $OSi(CH_3)_2O$ at $\delta = 0.1$ and $OSi((CH_2)_3CH_3)O$ at $\delta = 0.5$. We also found the signal of the $(CH_2)_3OCH_2CH_2CF_2$ group, as we described previously.[18] The heights of integration fit to what we expected from the given formula.

In the ^{29}Si NMR spectrum, we note the disappearances of the peaks at $\delta = +31$ and $\delta = -11$, which, respectively, correspond to the silicon that has two chlorine atoms and to the silicon of the $OSi(CH_3)_2OH$ groups. However, such a spectrum exhibits a signal at $\delta = -21.9$ that we attributed to the $OSi(CH_3)_2O$ chain.

It is interesting to note the peak at $\delta = -5$: this peak represents the silicon atoms that have vinyl groups; actually, there is <5% of these sequences, and the sensitivity of the apparatus (Bruker 80-MHz spectrometer) is not high enough to detect the end groups.

In our previous work,[1] we determined a GPC calibration curve for fluorinated polysiloxanes from cyclic or linear monodispersed model molecules in the range of 500–2000 molecular weight ($\bar{M}_n$). Thus the GPC spectra of these novel polymers allowed us to calculate $\bar{M}_n = 6300$ for IV-1 and $\bar{M}_n = 6200$ for IV-2. These values correspond to the formula $CH_2{=}CHSi(CH_3)_2O[(Si(CH_3)_2O)_{3.75}(Si(CH_3)(R_F)O)]_{8.5}Si(CH_3)_2CH{=}CH_2$.

This corresponds to $\overline{DP}_n = 18$ for an expected value of 19.

We also calculated the average molecular weight $\bar{M}_v$ from a viscosimetric survey in ethyl acetate at 25 °C. Actually, $\bar{M}_v$ is related to the intrinsic viscosity by the Mark–Houwink–Sakurada law: $[\eta] = K\bar{M}_v^{\alpha}$, where K and α are characteristic constants of the polymer, of the solvent, and of the temperature, respectively. These values were obtained from ref 19: for poly[methyl(trifluoropropyl)siloxane] at 25 °C in ethyl acetate, we found $K = 5.92 \times$

10^{-3} mL g^{-1} and $\alpha = 0.7$. The results are listed in Table I.

The dynamic viscosity was also determined (Table II).

Differential scanning calorimetry (DSC) was used to determine the glass transition temperatures (T_g's) of the polymers (Figure 2a), which we compared to those of the commercial products: PDMS and synthesized poly[methyl(trifluoropropyl)siloxane] (PMTFPS) (Figure 2b).

We also prepared models L_2, L_4, and D_4, which were previously obtained in our laboratory. The results are listed in Table III.

First, we note that the T_g of the polymers is −103 °C (which is 35 °C lower than that of the fluorinated silicone for a fluorine amount of 30%). Furthermore, there is also a difference of 20 °C compared to the case for traditional silicones (PDMS).

Also, we determined the contribution of the fluorinated base unit of the copolymer from Fox's law[20] for the T_g's of blends:

$$T_g^{-1} = \omega_1/T_{g_1} + \omega_2/T_{g_2}$$

There are 8.4 fluorinated base units and 33 (8.4 × 3.75 + 2) dimethylsiloxane units ($\bar{M}_n = 6300$), and that corresponds to $\omega_1 = 62.5$ wt % of fluorinated units. For $T_{g_2} = 151$ K, we found $T_{g_1} = 184$ K (−89 °C). Thus, we calculate −93.0 °C for L_2 and −94.5 °C for L_4. This shows a good similarity of results except for D_4, for which the value is −69 °C. However, we can imagine that the stress of the cycle influences the T_g value.

Thus, from our method it is possible to prepare a fluorinated silicone that exhibits both a low T_g and a high fluorine content.

We performed thermogravimetric analysis (TGA) of the same molecules and macromolecules and the results are gathered in Table IV. Figure 3 compares the thermograms of our fluorinated polymer (Figure 3-1), the poly[methyl(trifluoropropyl)silicone] (Figure 3-2), and a PDMS (Figure 3-3), and this leads to the following comments:

(i) From 230 °C, all the structures that contain the $R_F(CH_2)_2Z(CH_2)_3$ group start to decompose, and this is worse when Z = S than Z = O.

(ii) We note that there is a plateau that corresponds to about the loss of the $R_F(CH_2)_2Z$ unit in every case for model and polymer.

(iii) The basic structure remains the same up to a temperature higher than 400 °C, as the referenced PDMS.

(iv) The silicone that exhibits the $(CH_2)_2CF_3$ group is stable up to 300 °C, but from that temperature, it quickly decomposes and at 400 °C, there is 100% loss.

It seems that fragile fragments were introduced but when they decomposed, they did not lead to the decomposition of the overall structure.

Conclusion

The polycondensation of siliconated diols $HO[Si(CH_3)_2O]_nH$ and dichlorosilanes with the fluorinated lateral chain $(CH_2)_3O(CH_2)_2C_6F_{13}$ and chain-blocking agent $H_2C{=}CHSi(CH_3)_2Cl$ led to oligomers with molecular weights in the range 8000–10000, as shown in the GPC and viscosimetry measurements.

The chemical ^{29}Si and ^1H NMR characteristics are in good agreement with the proposed structures.

Moreover, we studied the behavior of such products at high and low temperatures by TGA and DSC analysis in order to compare them to dimethylsilicone and methyl(trifluoropropyl)silicone. The introduction of a long fluorinated chain in the polymers allows one to easily obtain elastomers with $T_g = -100$ °C, lower by ca. 30 °C than the T_g's of available fluorosilicones. At high temperatures, we can conclude that a long chain branched silicone with an ether group exhibits a stability lower than that of (trifluoropropyl)silicone but we showed that after elimination of fluorinated group, the resin is stable and exhibits a behavior close to that of poly(dimethylsiloxane).

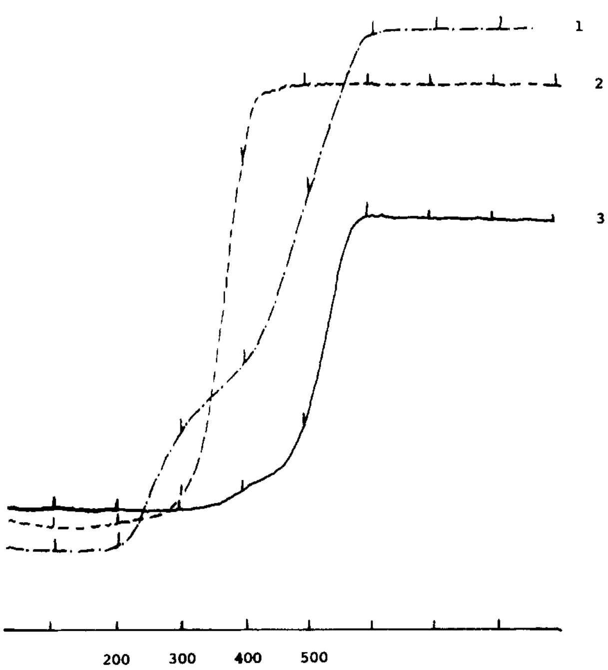

Figure 3. TGA curves of siliconated compounds: (1) graft fluorinated silicone; (2) poly[methyl(trifluoropropyl)silicone; (3) PDMS.

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