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Reactions of fluoroalkanoyl peroxides with organosilicon compounds

Hideo Sawada, Yoshihiro Minoshima, Takeo Matsumoto,
Masaharu Nakayama,
Tsukuba Research Laboratory, Nippon Oil & Fats Co. Ltd., Tokodai, Tsukuba, Ibaraki 300-26 (Japan)

Yue-Fa Gong, Masanori Kosugi and Toshihiko Migita
Department of Applied Chemistry, Faculty of Engineering, Gunma University, Tenjin-cyo, Kiryu, Gunma 376 (Japan)

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Abstract

The reactions of 3-methacryloxypropyltrimethoxysilane (MMA-Si) and 3-acryloxypropyltrimethoxysilane (AC-Si) with fluoroalkanoylperoxides [$(R_fCO_2)_2$, $R_f = C_3F_7$, $CF(CF_3)\{OCF_2CF(CF_3)\}_mOC_3F_7$, ($m = 0$, 1)] gave new fluorine-containing silicon oligomers [$R_f-\{CH_2-CRCO_2(CH_2)_3Si(OMe)_3\}_n-R_f$, $R_f = Me$, H] in good yields under mild conditions. These fluorine-containing silicon oligomers were found to be useful as new silane-coupling agents and to confer good water- and oil-repellency.

Introduction

Considerable interest has been devoted in recent years to organosilicon compounds, due to their synthetic utilities and unique physical properties [1]. In particular, much effort has been focused on the synthesis of new functional organosilicon materials possessing excellent properties imparted by fluorine. In the synthesis of organosilicon compounds containing fluoroalkyl groups, Steward and Pierce reported the novel hydrosilylation of fluorine-containing olefins promoted by a platinum catalyst [2]. This procedure has been developed commercially for the production of 'fluorosilicone'. Ojima *et al.* reported that rhodium, ruthenium and palladium complexes are also useful catalysts for the hydrosilylation of these olefins [3]. However, preparative methods for these compounds had been limited hitherto.

We have studied the reaction behaviour of a series of fluoroalkanoyl peroxides, $R_fCO_2O_2CR_f$, $R_f = CF_3$, C_2F_5, C_3F_7, C_6F_{13}, C_7F_{15}, $CF(CF_3)\{OCF_2CF(CF_3)\}_mOC_3F_7$, $m = 0$, 1, 2), which are useful reagents for the introduction of fluoroalkyl groups into arenes or alkenes [4]. Very recently, we have developed this fluoroalkylation with the peroxides to synthesize fluorine-containing organosilicon compounds by the use of vinylsilanes [5] or allylsilanes [6], respectively. However, the reaction mechanisms in the novel syntheses of these fluorosilicon compounds have not yet been clarified. In

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continuation of our studies on the synthesis of fluorine-containing organosilicon compounds with fluoroalkanoyl peroxides, we now report on the reactions of 3-methacryloxy- and 3-acryloxy-propyltrimethoxysilanes with fluoroakanoyl peroxides and on the surface nature of these reaction products. In addition, we discuss these reaction mechanisms and those of fluoroalkanoyl peroxides with vinylsilanes or allylsilanes for comparison with the MNDO-PM3 MO method [7a].

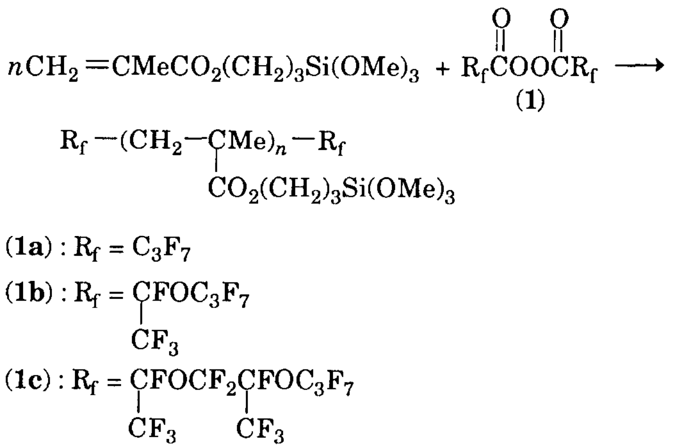
Results and discussion

The reactions of 3-methacryloxypropyltrimethoxysilane (MMA-Si) with fluoroalkanoyl peroxides (**1**) in 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) were carried out by heating the reaction mixtures at 30 °C for 5 h under nitrogen. The process is outlined in Scheme 1. MMA-Si was found to react smoothly with **1** under mild conditions to give fluorine-containing silicon oligomers in good yield as shown in Table 1.

In general, these reactions went smoothly and gave high yields. The similar reactivity of all the fluoroalkanoyl peroxides **1a, 1b** and **1c** suggests that the ether group bound to fluorine has little effect on this oligomerization. The molecular weights of the fluorine-containing silicon oligomers obtained were found to be markedly dependent upon the molar ratio of MMA-Si and the peroxide, and to be greater ($M_n = \sim 5600$) with an increase in the molar ratio (from 1 to 10) of MMA-Si in MMA-Si/**1**.

In the reaction of 3-acryloxypropyltrimethoxysilane (AC-Si) with **1** in Freon 113, fluorine-containing silicon oligomers were obtained in good yield as in the case of MMA-Si.

However, the results in Table 2 reveal that AC-Si is more capable of polymerization than MMA-Si in the oligomerization initiated by **1**, the molecular



$$n\mathrm{CH_2{=}CMeCO_2(CH_2)_3Si(OMe)_3} + \underset{(1)}{\mathrm{R_f\overset{\displaystyle O}{\overset{\|}{C}}O O\overset{\displaystyle O}{\overset{\|}{C}}R_f}} \longrightarrow$$

$$\mathrm{R_f{-}(CH_2{-}\underset{\displaystyle CO_2(CH_2)_3Si(OMe)_3}{\underset{|}{C}}Me)_{\mathit{n}}{-}R_f}$$

(**1a**) : $\mathrm{R_f = C_3F_7}$

(**1b**) : $\mathrm{R_f = \underset{\displaystyle CF_3}{\underset{|}{C}}FOC_3F_7}$

(**1c**) : $\mathrm{R_f = \underset{\displaystyle CF_3}{\underset{|}{C}}FOCF_2\underset{\displaystyle CF_3}{\underset{|}{C}}FOC_3F_7}$

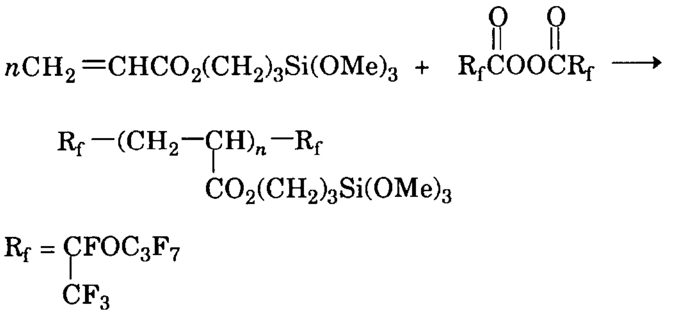
Scheme 1.

TABLE 1

Reactions of MMA-Si with fluoroalkanoyl peroxides [$(R_fCO_2)_2$]

R_f in $(R_fCO_2)_2$ (mmol)	Molar ratio MMA-Si/$(R_fCO_2)_2$	Product	
		Isolated yield (%)[a]	$M_n/M_w/M_n)^b$
C_3F_7 (117 mmol)	1	75	820 (1.02)
$\underset{CF_3}{\underset{\vert}{C}}FOC_3F_7$ (70 mmol)	1	65	1200 (1.03)
$\underset{CF_3}{\underset{\vert}{C}}FOCF_2\underset{CF_3}{\underset{\vert}{C}}FOC_3F_7$ (56 mmol)	1	78	1300 (1.03)
$\underset{CF_3}{\underset{\vert}{C}}FOC_3F_7$ (5 mmol)	2	95	1200 (1.02)
$\underset{CF_3}{\underset{\vert}{C}}FOC_3F_7$ (5 mmol)	3	91	4000 (1.82)
$\underset{CF_3}{\underset{\vert}{C}}FOC_3F_7$ (3 mmol)	5	88	4700 (1.87)
$\underset{CF_3}{\underset{\vert}{C}}FOC_3F_7$ (2 mmol)	10	98	5600 (2.30)

[a] Yields based on the starting materials {MMA-Si and the decarboxylated peroxide unit (R_f–R_f)}.
[b] Average molecular weight determined by GPC methods.



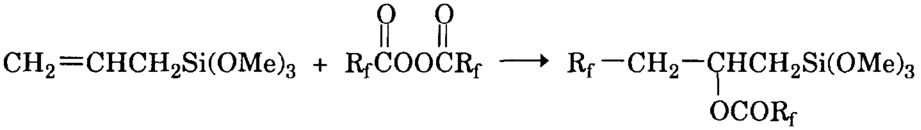
$$nCH_2{=}CHCO_2(CH_2)_3Si(OMe)_3 + R_f\overset{O}{\overset{\Vert}{C}}O\text{-}O\overset{O}{\overset{\Vert}{C}}R_f \longrightarrow R_f{-}(CH_2{-}\underset{CO_2(CH_2)_3Si(OMe)_3}{\underset{\vert}{C}H})_n{-}R_f$$

$$R_f = \underset{CF_3}{\underset{\vert}{C}}FOC_3F_7$$

weights of the fluorine-containing silicon oligomers becoming greater even at similar molar ratios of the silicon compound and **1**.

The new fluorine-containing silicon oligomers obtained by the reactions of MMA-Si or AC-Si with fluoroalkanoyl peroxides are considered to be useful as surface-active substances. For this reason, these compounds have been tested for surface activity as new types of fluorine-containing silane coupling agents. As Table 3 shows, the contact angles for water and dodecane of the treated glass showed a significant increase, indicating that the silicon oligomers studied possess good water- and oil-repellency. For the MMA-Si type fluorine-containing silicon oligomers, the contact angles for both water and dodecane diminished slightly with an increase in the molecular weight of these oligomers.

We have already reported that allyltrimethoxysilane (AL-Si) reacts with **1** to give 1:1 adducts [$R_f-CH_2-CH(OCOR_f)CH_2Si(OMe)_3$] in good yield without any formation of oligomer [6].



$$CH_2{=}CHCH_2Si(OMe)_3 + R_f\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}R_f \longrightarrow R_f-CH_2-\underset{\underset{OCOR_f}{|}}{C}HCH_2Si(OMe)_3$$

TABLE 2

Reactions of AC-Si with fluoroalkanoyl peroxide (**1b**)

AC-Si (mmol)	Molar ratio AC-Si/**1b**	Product	
		Isolated yield (%)[a]	M_n (M_w/M_n)[b]
5	1	62	820 (1.02)
5	2	68	8500 (1.21)
5	10	91	89000 (2.16)

[a]Yields based on the starting materials {AC-Si and the decarboxylated peroxide unit (R_f–R_f)}.
[b]Average molecular weight determined by GPC methods.

TABLE 3

Contact angle for water and dodecane on glass treated with new fluorine-containing silicon oligomers [$R_f-\{CH_2-CRCO_2(CH_2)_3Si(OMe)_3\}_n-R_f$, $R_f=CF(CF_3)OC_3F_7$]

R	M_n (M_w/M_n) for oligomer	Contact angle (°)	
		Water	Dodecane
Me	1200 (1.03)	107	61
Me	1200 (1.02)	106	59
Me	4000 (1.82)	100	48
Me	4700 (1.87)	97	46
Me	5600 (2.30)	96	42
H	820 (1.02	107	45
Untreated glass		49	0

Thus, reaction of fluoroakanoyl peroxides with MMA-Si (AC-Si) and AL-Si leads to quite different products. It is suggested that the different reactivities with MMA-Si (AC-Si) and AL-Si depend upon the different HOMO energy levels and HOMO electron densities possessed by these silicon compounds. In fact, both the HOMO electron densities and HOMO energy levels for these substrates and styrene have been calculated by the MNDO-PM3 semiempirical MO method using the MOPAC 5.0 program [7a]. The results are as shown in Fig. 1.

We have also reported that styrene reacts with perfluorobutyryl peroxide to give a 1:1 adduct [$PhCH(OCOC_3F_7)CH_2C_3F_7$] via single-electron transfer from styrene to peroxide [8]. These results show that AL-Si has a similar HOMO energy level to styrene, and strong interaction between HOMO and LUMO (peroxide) should determine the electron transfer from AL-Si to the peroxide as depicted in Scheme 2.

As shown in Fig. 2, the site where the higher electron density in the HOMO orbital of AL-Si is located would be fluoroalkylated preferentially via electron transfer in the same manner as with styrene. Furthermore, the carbonium ion **2** situated at the β position from a silicon atom in Scheme 2 should be stabilized by σ–π conjugation, which leads to a very large resonance effect [9] so that the electron-transfer reaction between AL-Si and peroxide would proceed more smoothly.

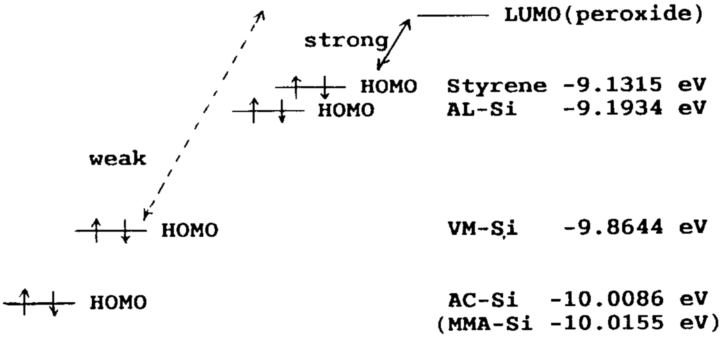
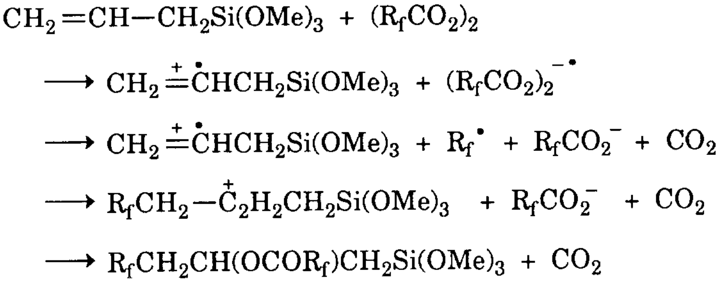


Fig. 1. HOMO energy levels of styrene, AL-Si, VM-Si, AC-Si and MMA-Si, together with the HOMO–LUMO (peroxide) interaction.



$$
\begin{aligned}
&CH_2{=}CH{-}CH_2Si(OMe)_3 + (R_fCO_2)_2\\
&\longrightarrow CH_2\overset{+\ \bullet}{=}CHCH_2Si(OMe)_3 + (R_fCO_2)_2^{-\bullet}\\
&\longrightarrow CH_2\overset{+\ \bullet}{=}CHCH_2Si(OMe)_3 + R_f^{\bullet} + R_fCO_2^{-} + CO_2\\
&\longrightarrow R_fCH_2{-}\overset{+}{C}_2H_2CH_2Si(OMe)_3 + R_fCO_2^{-} + CO_2\\
&\longrightarrow R_fCH_2CH(OCOR_f)CH_2Si(OMe)_3 + CO_2
\end{aligned}
$$

Scheme 2.

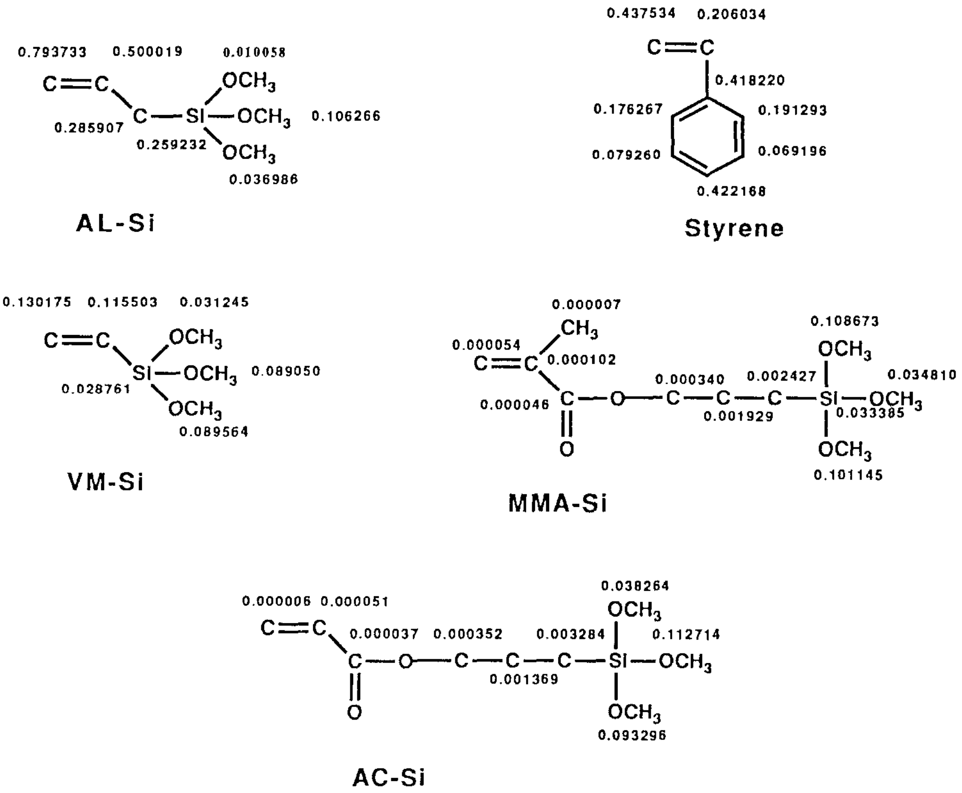
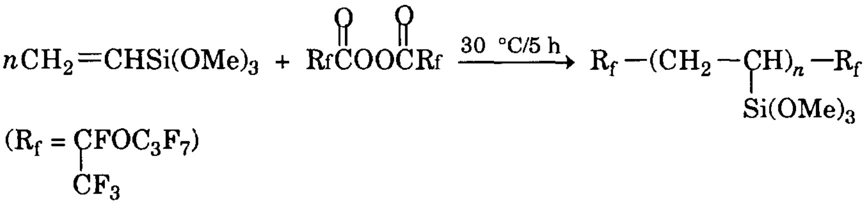


Fig. 2. HOMO electron densities of AL-Si, VM-Si, styrene, MMA-Si and AC-Si calculated by the MNDO-PM3 semiempirical MO method using the MOPAC 5.0 program.

In contrast, vinyltrimethoxysilane (VM-Si), MMA-Si or AC-Si have considerably lower HOMO energy levels than AL-Si as depicted in Fig. 1. Fluoroalkyl radicals are electrophilic, in general, owing to the high electronegativity of the fluorine atom [10]. Hence, interaction between a SOMO (fluoroalkyl radical) and a HOMO (VM-Si, MMA-Si, or AC-Si) should determine radical addition of the fluoroalkyl radicals ($R_f\cdot$), which is produced by the thermal decomposition of the peroxide, to VM-Si, MMA-Si or AC-Si to afford the corresponding oligomeric products in good yield. It has been shown for the reaction of VM-Si with the peroxide that the molecular weight of each oligomer obtained is not influenced by the molar ratio of VM-Si and peroxide, in contrast to the situation with MMA-Si or AC-Si as depicted in Scheme 3.

As shown in Figs. 1 and 2, both the HOMO energy level and the electron densities in the HOMO at vinyl positions in VM-Si are increased substantially in comparison with the situation in MMA-Si or AC-Si. This suggests that oligomer formation (mainly as the dimer and trimer) as depicted in Scheme would depend in part upon a strong interaction of between the SOMO of $R_f\cdot$ and the HOMO of VM-Si.



$$n\mathrm{CH_2{=}CHSi(OMe)_3} + \mathrm{Rf\overset{O}{\overset{\|}{C}}OO\overset{O}{\overset{\|}{C}}Rf} \xrightarrow{30\ ^\circ\mathrm{C}/5\ \mathrm{h}} \mathrm{R_f{-}(CH_2{-}\underset{Si(OMe)_3}{\underset{|}{C}H})_{\mathit{n}}{-}R_f}$$

$$(\mathrm{R_f} = \mathrm{\underset{CF_3}{\underset{|}{C}}FOC_3F_7})$$

Vinylsilane (mmol)	Peroxide (mmol)	M_n (M_w/M_n)
128	64	870 (1.02)
20	2	1000 (1.03)

Scheme 3.

Experimental

Measurements

NMR spectra were measured with a JEOL JNM FX 90Q FT-NMR (90 MHz) spectrometer while IR spectra were recorded on a JASCO IR-810 spectrophotometer. Gas chromatography was performed using a Shimadzu GC-8A gas chromatograph filled with a 2 m glass column (SE-30, 2%). Molecular weights were calculated by using a Toyo Soda HLC-802A gel permeation chromatograph (calibration being based on polystyrene standards). Contact angles were measured by using a Kyowa Kagaku CA-A Gonio-type apparatus.

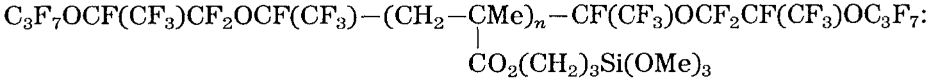
Materials

Fluoroalkanoyl peroxides [$(\mathrm{R_fCO_2})_2$; $\mathrm{R_f} = \mathrm{C_3F_7}$, $\mathrm{CF(CF_3)\{OCF_2CF(CF_3)\}_{\mathit{m}}OC_3F_7}$, $m = 0, 1$] were prepared from the corresponding acyl halides and hydrogen peroxide in the presence of aqueous sodium hydroxide in 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113) according to our previously reported method [4c, 4p].

General procedure for the synthesis of fluorine-containing silicon oligomers

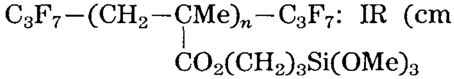
Perfluoro-2-methyl-3-oxahexanoyl peroxide (5 mmol) in Freon 113 (54 g) was added to a mixture of 3-methacryloxypropyltrimethoxysilane (15 mmol) and Freon 113 (10 g). The solution was stirred at 30 °C for 5 h under nitrogen. The solution was then concentrated by evaporating the solvent under reduced pressure. The liquid product obtained was dried *in vacuo* to yield a colorless fluorine-containing silicon oligomer (6.0 g). This oligomer exhibited the following spectral data. IR(cm^{-1}): 1740 (CO); 1335 ($\mathrm{CF_3}$); 1240 ($\mathrm{CF_2}$). ^{19}F NMR ($\mathrm{CDCl_3}$, ext. $\mathrm{CF_3CO_2H}$) δ: -2.81–-9.91 (16F); -53.09 (4F); -54.96 (2F) ppm. ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 0.50–0.95 ($-C\mathit{H}_2-\mathrm{Si}\equiv$); 1.10–1.40 ($-C\mathit{H}_2-\mathrm{CH_2Si}\equiv$); 1.50–1.90 ($-\mathrm{Me}$); 2.50–3.22 ($-C\mathit{H}_2-\mathrm{CMe}-$); 3.46–3.60 [$-\mathrm{Si(OMe)_3}$]; 3.85–4.25 ($-\mathrm{CO_2CH_2}-$) ppm.

The following spectral data were obtained for the other products studied:



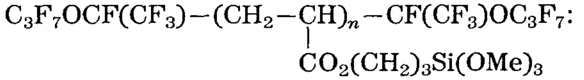
$$\mathrm{C_3F_7OCF(CF_3)CF_2OCF(CF_3)-(CH_2-\underset{\displaystyle CO_2(CH_2)_3Si(OMe)_3}{\underset{|}{C}}Me)_{\mathit{n}}-CF(CF_3)OCF_2CF(CF_3)OC_3F_7}:$$

IR(cm^{-1}): 1740 (CO); 1335 ($\mathrm{CF_3}$); 1240 ($\mathrm{CF_2}$). ^{19}F NMR ($\mathrm{CDCl_3}$, ext. $\mathrm{CF_3CO_2H}$) δ: -3.20–-9.25 (26F); -56.20 (6F) ppm. ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 0.65–1.10 ($\mathrm{-CH_2-Si}\equiv$); 1.15–1.50 ($\mathrm{-C}H_2\mathrm{-CH_2Si}\equiv$); 1.60–2.10 ($\mathrm{-Me}$); 2.61–3.21 ($\mathrm{-C}H_2\mathrm{-CMe-}$); 3.93–3.99 [$\mathrm{-Si(OMe)_3}$]; 4.00–4.32 ($\mathrm{-CO_2CH_2-}$) ppm.



$$\mathrm{C_3F_7-(CH_2-\underset{\displaystyle CO_2(CH_2)_3Si(OMe)_3}{\underset{|}{C}}Me)_{\mathit{n}}-C_3F_7}:$$

IR (cm^{-1}): 1740 (CO); 1350 ($\mathrm{CF_3}$); 1235 ($\mathrm{CF_2}$); ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 0.52–1.09 ($\mathrm{-CH_2-Si}\equiv$); 1.12–1.49 ($\mathrm{-C}H_2\mathrm{-CH_2Si}\equiv$); 1.55–2.01 ($\mathrm{-Me}$); 2.52–3.28 ($\mathrm{-C}H_2\mathrm{-CMe-}$); 3.48–3.72 [$\mathrm{-Si(OMe)_3}$]; 3.80–4.29 ($\mathrm{-CO_2CH_2-}$) ppm.



$$\mathrm{C_3F_7OCF(CF_3)-(CH_2-\underset{\displaystyle CO_2(CH_2)_3Si(OMe)_3}{\underset{|}{C}}H)_{\mathit{n}}-CF(CF_3)OC_3F_7}:$$

IR(cm^{-1}): 1740 (CO); 1340 ($\mathrm{CF_3}$); 1240 ($\mathrm{CF_2}$); ^{19}F (NMR $\mathrm{CDCl_3}$, ext. $\mathrm{CF_3CO_2H}$) δ: -3.11–-9.10 (16F); -54.53 (4F); -56.51 (2F) ppm. ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 0.55–0.90 ($\mathrm{-C}H_2\mathrm{-Si}\equiv$); 1.55–2.00 ($\mathrm{-C}H_2\mathrm{-CH-CO_2-}$, $\mathrm{-C}H_2\mathrm{-CH_2Si}\equiv$); 2.10–2.50 ($\mathrm{-CH-CO_2-}$); 3.59 [$\mathrm{-Si(OMe)_3}$]; 3.86–4.20 ($\mathrm{-CO_2CH_2-}$) ppm.

Measurement of contact angles

Contact angles for water and dodecane on glass treated with fluorine-containing silicon oligomers were measured according to our previously reported method [6].

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