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Journal of Fluorine Chemistry 104 (2000) 185–194

JOURNAL OF FLUORINE CHEMISTRY

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Hybrid organic–inorganic gels containing perfluoro-alkyl moieties

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Received 25 October 1999; accepted 21 December 1999

Abstract

Perfluoroalkyltrialkoxysilanes were prepared by hydrosilylation of the allylic or vinylic derivatives with trialkoxysilane or with trichlorosilane (followed by a quantitative methanolysis). The hydrolysis and polycondensation of these precursors were performed in the presence of tetrabutylammoniumfluoride (TBAF) as the catalyst, leading to a series of new polysilsesquioxanes, which were characterized by solid state ^{13}C and ^{29}Si CPMAS NMR. The porosity and surface area of these materials were determined by N_2 absorption experiments. Thermogravimetric analyses (TGA) were also performed. The surface properties of films prepared from these silsesquioxanes were studied by contact angle measurements. The hybrids having fluoroalkyl groups at the surface of the material showed a better thermostability and a higher hydrophobic and oleophobic character than their hydrocarbon analogues. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Sol–gel; Perfluoroalkyl silsesquioxanes; Hybrid organic–inorganics; Silica based materials

1. Introduction

Fluorinated polymers offer unique high-performance properties rendering them particularly attractive for surface modification and protection [1–3]. In this field many investigations have been developed for the protection of stone [4], optical fibers [5], leather [6], metals [7], paper [8], for the waterproofing of textiles [9,10] or the protection of electronic devices [11], and also for antifouling properties of paints for boats [12,51]. The synthesis of fluorinated polymers containing silicon atoms has already attracted the interest of several authors. Particularly, fluorosilicones are valuable materials since they combine excellent solvent resistance [13], good thermal stability [14] [15] and low surface energy [16–18]. The synthesis of fluorosilicones can be achieved either by adding the fluorocarbon side-chain moieties to a preformed siloxane [19,20] or by the polymerization of suitable monomers [14,21–25].

Hybrid organic–inorganics constitute a unique class of materials which can combine the properties associated to the two components [26–30]. Our current interest in hybrid silsesquioxanes [31–36], which are solids consisting of a well defined hybrid network, led us to study the preparation of fluorinated polysilsesquioxanes. Related materials possessing perfluoroalkyl alkyl silyl groups are of interest as novel UV and hydrophobic resistant coatings [15,37–39]. Water-repellent properties can be easily obtained upon surface treatment of solid materials [39]. However, the hydrolysis and polycondensation of organotrialkoxysilanes can provide an easy preparation of materials with covalently retained fluorinated moieties, owing to the presence of a non-hydrolysable C–Si bond.

In this paper, the syntheses of fluoroalkylmono- and bis-trialkoxysilanes are described. These precursors led to new hybrid silica gels, containing fluoroalkyl chains the properties of which were investigated and compared to those of related materials containing analogous hydrocarbon chains.

2. Results and discussion

The synthesis of hybrid gels was performed by the hydrolysis/condensation of trialkoxysilanes containing perfluoroalkyl or alkyl chains.

2.1. Synthesis of the silylated precursors

Two types of trialkoxysilanes were prepared: mono-silylated (Scheme 1) and bis-silylated compounds (Schemes 2 and 3).

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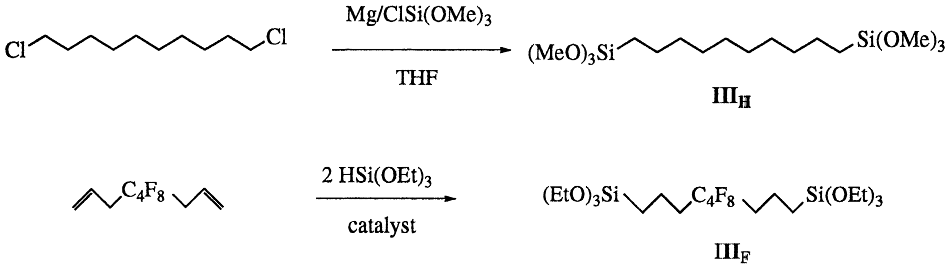
PII: S0022-1139(00)00211-6

$$R(CH_2)_xCH{=}CH_2 \xrightarrow[H_2PtCl_6]{HSiCl_3} R(CH_2)_{x+2}SiCl_3 \xrightarrow{MeOH} R(CH_2)_{x+2}Si(OMe)_3$$

$R{=}C_8F_{17}$; x=0	$\mathbf{I_F0}$	$\mathbf{II_F0}$
$R{=}C_8F_{17}$; x=1	$\mathbf{I_F1}$	$\mathbf{II_F1}$
$R{=}C_8H_{17}$; x=0	$\mathbf{I_H0}$	$\mathbf{II_H0}$
$R{=}C_8H_{17}$; x=1	$\mathbf{I_H1}$	$\mathbf{II_H1}$

Scheme 1. Synthesis of pendant group monomers.



Scheme 2. Synthesis of spacer group containing monomers.

The mono-silylated precursors (**II**) were obtained in a two-step reaction: hydrosilylation of the corresponding vinylic or allylic alkyl and fluoroalkyl derivatives with $HSiCl_3$, in the presence of hexachloroplatinic acid, followed by methanolysis (Scheme 1).

The fluorinated monomers were obtained quantitatively by performing the hydrosilylation in a stainless steel autoclave or in sealed Carius tubes. The hydrosilylation of the hydrocarbon monomers was successfully achieved in sealed tubes. The methanolysis step was quantitative and was performed either with or without triethylamine (NEt_3).

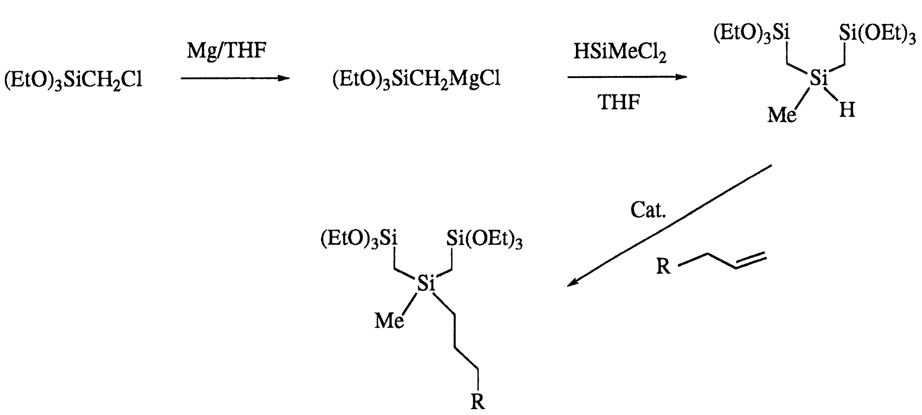
Two kinds of bis trialkoxysilyl monomers were considered: the alkyl or perfluorinated group being located either in the chain as a spacer group between the two silicon atoms or in a side-chain as a pendant group.

The monomers with a spacer group were obtained according to two different methods as illustrated in Scheme 2.

1,10-Bis(trimethoxysilyl)decane ($\mathbf{III_H}$) was prepared from 1,10-dichlorodecane by reacting an in situ formed Grignard reagent with chlorotrimethoxysilane in THF as solvent.

The fluorocarbon analogue ($\mathbf{III_F}$) was prepared by hydrosilylation of the corresponding α,ω-diene with $HSi(OEt)_3$ using a platinum catalyst in the absence of solvent [25,40]. In this case, ethoxy substituents at silicon were preferred to methoxy groups. Owing to the higher thermal stability of the former it allows an easy purification of the silylated product by distillation. Attempts to distil the monomer bearing methoxy groups at silicon led to decomposition.

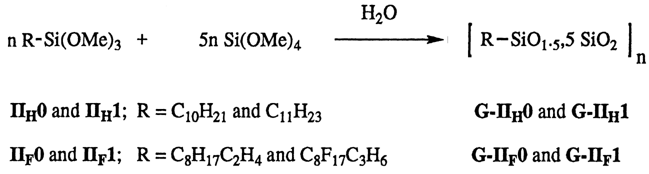
The synthesis of the precursors $\mathbf{IV_F}$ and $\mathbf{IV_H}$ with pendant groups (Scheme 3) required the preparation of a triethoxysilylmethyl Grignard reagent [41] which reacted with dichloromethylsilane to give the corresponding hydrogenosilane. Hydrosilylation with the unsaturated derivatives:



$\mathbf{IV_H}$; $R = C_8H_{17}$

$\mathbf{IV_F}$; $R = C_8F_{17}$

Scheme 3. Synthesis of monofunctional silanes.



Scheme 4. Synthesis of gels from monosilylated precursors.

undec-1-ene or allyl perfluoro octane led to compounds **IV**$_H$ and **IV**$_F$, respectively.

2.2. Preparation and NMR characterisation of gels

2.2.1. Gels from monosilylated precursors

The monosilylated precursors **II**$_H$ and **H**$_F$ and five mole equivalent of tetramethoxysilane, $Si(OMe)_4$ were hydrolysed in the presence of TBAF as catalyst (Scheme 4).

In the case of the hydrocarbon precursors (**II**$_H$**0** and **II**$_H$**1**), only methanol was used as solvent. For the perfluorinated ones (**II**$_F$**0** and **II**$_F$**1**), owing to their insolubility in usual organic solvents, a mixture of solvents (methanol/ $C_6F_{13}C_2H_4OH$ — v/v: 1/5) was necessary for obtaining homogeneous solutions before gelation. These cogels are called **G-II**$_H$**0**, **G-II**$_H$**1**, respectively, for those derived from the hydrocarbon precursors, and **G-II**$_F$**0**, **G-II**$_F$**1** for those prepared from the fluorinated precursors. These materials were analysed and characterized by ^{13}C and ^{29}Si solid state NMR spectroscopies and by nitrogen adsorption measurements according to BET [42].

The solid state ^{13}C CP-MAS NMR spectra clearly shows that the organic moieties are retained in the materials. In the first case (gel **G-II**$_H$**1**), five sharp and distinct peaks at 13.9, 22.9, 29.9, 32.4 ppm (corresponding to the hydrocarbon chain) and at 50.5 ppm (residual methoxy groups at silicon) are observed. For gel **G-II**$_F$**1**, the spectrum was more complex owing to coupling between the carbon and the fluorine atoms. The signals centered at 10.6 and 29.7 ppm are attributed to the two carbon atoms of the hydrocarbon segment and the broad signal with low intensity, in the 110–115 ppm range, corresponds to the carbon atoms in the fluorocarbon part. A peak at 50.3 ppm was assigned to non-hydrolyzed residual methoxy groups at the silicon atoms.

The ^{29}Si CP-MAS NMR spectra of **G-II**$_H$**1** and of **G-II**$_F$**1**, gels are shown in Fig. 1a and b, respectively.

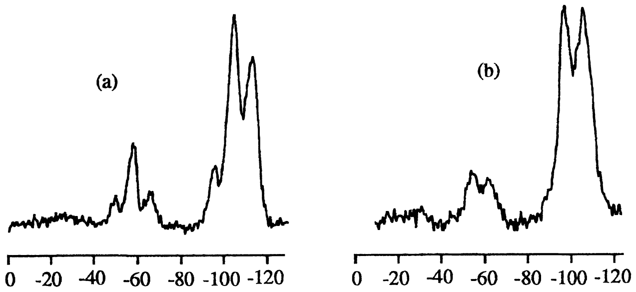


Fig. 1. Solid state ^{29}Si CP-MAS NMR of **G-II**$_H$**1** (a) and **G-II**$_F$**1** (b).

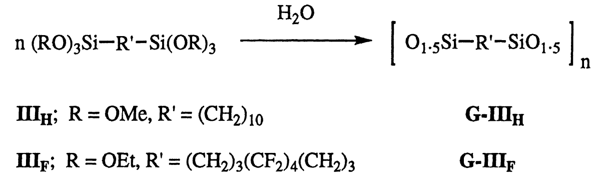
The first set of resonances at −49, −57 and −64 ppm corresponds to the T ($:CO_3Si$) units originating from the hydrolysis of the organotrialkoxysilanes. A second set of signals at −94, −102 and −110 ppm is attributed to the Q ($:SiO_4$) units produced by the hydrolysis of $Si(OMe)_4$ (TMOS). It seems that gel **G-II**$_F$**1** presents a higher degree of condensation than gel **G-II**$_H$**1**. Although, the ^{29}Si NMR spectra were recorded using cross-polarisation techniques [43], since the silicon atoms in gels **G-II**$_H$**1** and **G-II**$_F$**1** have identical environments, the observed intensities of the signals are related to the ratios of the various T^1, T^2, T^3 substructures. This was previously observed in the case of related silsesquioxane materials [31,34]. The spectra in the T sites region show in the case of gel **G-II**$_H$**1** the presence of T^1 [$:SiC(OSi)(OH)_2$] substructures, at −50.6 ppm, whereas this is not observed in the spectrum of gel **G-II**$_F$**1**. Additionally, the relative intensities of the signals corresponding to T^2 [$:SiC(OSi)_2(OH)$] units at −58 ppm and T^3 [$:Si\,C(OSi)_3$] substructures at −65 ppm, with higher intensity of the T^3 signal in the case of gel **G-II**$_F$**1**, are indicative of a higher degree of condensation around silicon in gel **G-II**$_F$**1**.

2.2.2. Gels prepared from bis-silylated precursors with a spacer group

In this case, methanol was used as solvent for the hydrolysis of the hydrogenated precursor (**III**$_H$) whereas the fluorinated compound (**III**$_F$) was hydrolysed in THF (Scheme 5).

Transparent gels formed rapidly, these were dried to give the xerogels **G-III**$_H$ and **G-III**$_F$, respectively. The ^{13}C CP-MAS solid state NMR spectrum of the hydrocarbon gel, **G-III**$_H$ showed four peaks (12.5, 23.0, 29.8 and 33.1 ppm) corresponding to the carbon atoms of the chain and another peak at 49.8 ppm (residual methoxy groups at silicon), in agreement with the molecular structure of the precursor. In the case of gel **G-III**$_F$, the signals centered at 17.6 and 34.6 ppm were assigned to the hydrocarbon part of the chain and the broad signal (100–125 ppm) centered at 115 ppm was attributed to fluorinated carbons.

Fig. 2a and b show the ^{29}Si CP-MAS solid state NMR spectra of **G-III**$_H$ and **G-III**$_F$, respectively. Only resonances corresponding to T ($:CO_3Si$) substructures are present. The absence of Q units in both spectra clearly demonstrates that there is no C–Si bond cleavage occurring during the hydrolysis/condensation process.



Scheme 5. Synthesis of gels bearing spacer group.

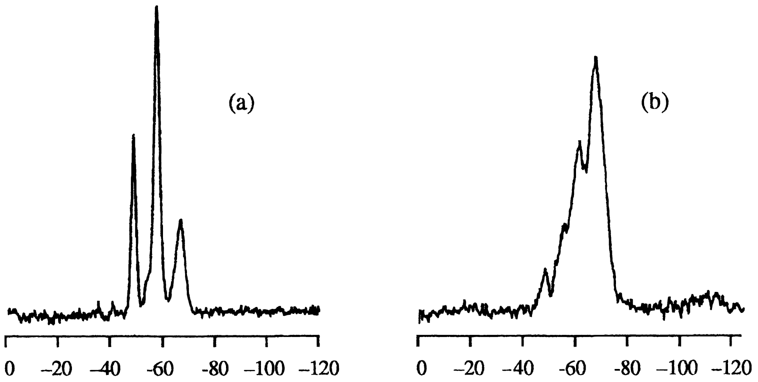


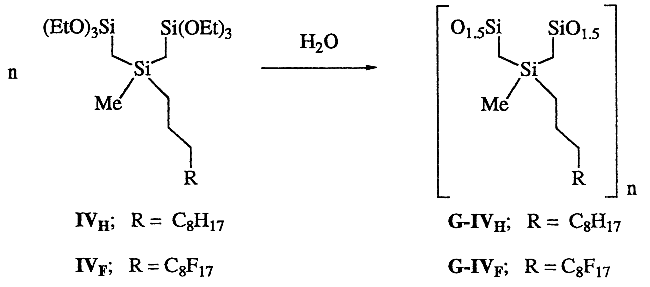
Fig. 2. Solid state ^{29}Si CP-MAS NMR of **G-III$_H$** (a) and **GIII$_F$** (b).

Whereas the spectrum of **G-III$_H$** exhibits three distinct sharp peaks, owing to the flexibility of the hydrocarbon chain, at −50, −59 and −68 ppm, that of **G-III$_F$** presents broader overlapping peaks in the region −47, −67 ppm. The broadness of the signal in Fig. 2b, is probably related to the more rigid nature of the perfluoroalkyl spacer, compared to that of the hydrocarbon spacer. Moreover, **G-III$_F$** seems a more condensed material than **G-III$_H$** since the T^3 signal [: C Si (OSi)$_3$] (−67 ppm) exhibits the highest intensity. The hybrid network in **G-III$_F$** has a higher degree of condensation than in **G-III$_H$** and is also probably more rigid than the hybrid network in **G-III$_H$**.

2.2.3. Gels prepared from bis-silylated precursors with pendant group

The hydrolysis of the hydrogenated derivative **IV$_H$** did not lead to gel formation in ethanol but was successful in THF to give gel **G-IV$_H$**. The hydrolysis polycondensation of **IV$_F$** was performed in a 1/5 mixture of methanol/ $C_6F_{13}C_2H_4OH$ and led to gel **G-IV$_F$** (Scheme 6).

The gels **G-IV$_H$** and **G-IV$_F$** were characterised by ^{13}C CP-MAS NMR. The spectrum of **G-IV$_H$** exhibits sharp signals consistent with the molecular structure of **IV$_H$**. The signals centered at −3.5 and −0.5 ppm are assigned to the carbon atoms bonded to the central silicon atom. The sharp peaks at 14.3, 23.0, 24.0, 29.9, 32.3 and 34.0 ppm are attributed to the carbon chain and the remaining two sharp peaks at 18.5 and 58.1 ppm correspond to the carbon atoms of residual uncondensed ethoxy groups at silicon. For **G-IV$_F$**, an intense broad signal assigned to the carbon atoms bonded to the central silicon atom is observed at −0.7 ppm. A broad signal at 36.5 accounts for the hydrocarbon part of the chain, and another broad signal (100–125 ppm) was attributed to the fluorocarbon atoms.



Scheme 6. Synthesis of gels bearing pendant groups.

The ^{29}Si CP-MAS solid state NMR spectra of both gels **G-IV$_H$** and **G-IV$_F$** are similar. Both spectra exhibit a sharp resonance at 3 ppm, assigned to the central silicon (Si–Me) atom and a broad signal centered at −63 ppm corresponding to the T (:CSiO$_3$) units. No signal is observed in the Q (:SiO$_4$) units region meaning that no carbon–silicon bond cleavage occurred during gel formation.

2.3. Properties of gels 1

The surface areas were determined by nitrogen absorption experiments according to BET [42]. The calculated surface area from the adsorption–desorption isotherms are given in Table 1. Most gels were non-porous materials and showed very low surface areas ranging from 0.6 to 21.0 m^2 g^{-1}. Only the gel **G-III$_F$** was a porous material with a quite high surface area (300 m^2 g^{-1}).

For **G-III$_F$** the adsorption/desorption isotherm plot exhibits a hysteresis loop at high relative pressure, P/P_0, consistent with a mesoporous material. The BJH desorption dV/d log (D) pore volume plot [44] showed a bimodal distribution of pores with average diameter in the region 30–35 Å and with larger mesopores over a wide range 100–400 Å.

The pore structure of sol–gel prepared hybrid materials has been shown to be strongly dependent on the reaction conditions during gel formation and on the structure of the precursor [31,43]. Bis-silylated precursors having a rigid bridging spacer were, for example, shown to give highly porous materials, whereas those with a flexible bridging unit led to hybrid materials with low porosity. The high porosity

Table 1
BET surface areas (m^2 g^{-1}) of gels measured using N_2 as sorption gas

G-II$_H$0	**G-II$_F$0**	**G-II$_H$1**	**G-H$_F$1**	**G-III$_H$**	**G-III$_F$**	**G-IV$_H$**	**G-IV$_F$**
2.3	0.6	1.9	21.0	5.9	300.6	0.8	1.1

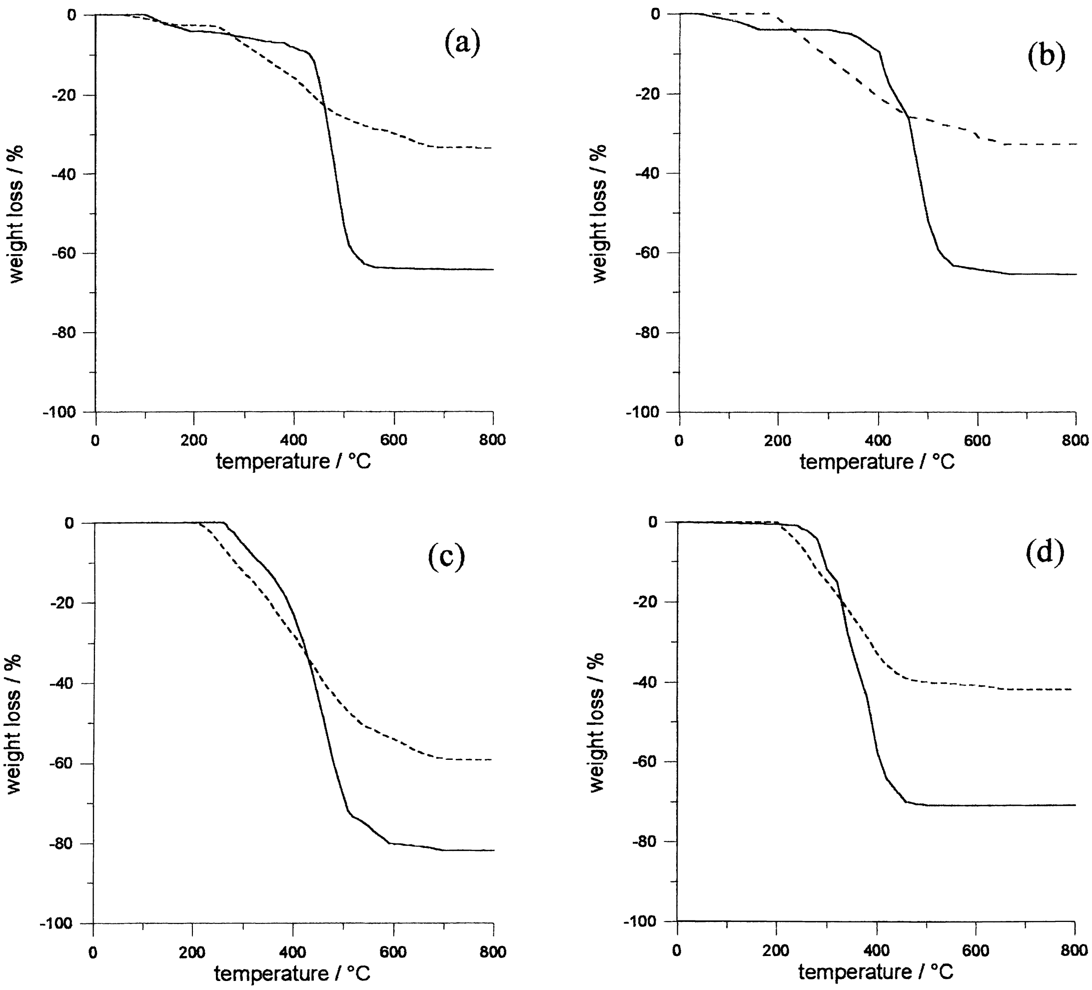


Fig. 3. TGA-thermograms of: (a) **G-II$_H$0** (- - -) and **G-II$_F$0** (—); (b) **G-II$_H$1** (- - -) and **G-II$_F$1** (—); (c) **G-III$_H$** (- - -) and **G-III$_F$** (—); (d) **G-IV$_H$** (- - -) and **G-IV$_F$** (—).

in gel **G-III$_F$** probably results from the more rigid nature of the perfluoro-alkyl bridging spacer in precursor **III$_F$**. Long chain hydrocarbon spacers which are flexible, like in precursor **III$_H$**, have been shown to yield a hybrid with low porosity [43].

2.3.1. *Pyrolysis of hybrid gels in air*

It is well-known that fluorinated polymers can withstand severe temperature conditions without being degraded [2,3]. For example, polyfluoroalkylsilanes used as coating agents proved to bring higher thermal stability to silicas [15]. This led us to examine the thermogravimetric behaviour (TGA) of the fluorocarbon gels and to compare them with the hydrocarbon gels analogues. These analyses were performed in an air flow and the samples were heated at a rate of 10°C min^{-1} from 20 to 1200°C.

The thermograms of gels from **G-II** to **G-IV** are shown in Fig. 3.

In most cases, the hybrid gels containing fluorocarbon fragments exhibit a thermal stability significantly higher than that of the related gels containing hydrocarbon fragments. The gels **G-II$_F$0** and **G-II$_F$1** showed a marked thermostability. The thermal decomposition of **G-II$_F$1** is significant above 400°C (versus 200°C for **G-II$_H$1**) and ends at 550°C. The weight loss (65%) corresponds to the elimination of the organic fluorocarbon moieties in the hybrid material. The gel **G-II$_F$0** behaves similarly. The gels **G-II$_H$0** and **G-II$_H$1** decomposed above 200°C up to 600°C to give a 33–38% weight loss associated with the elimination of the hydrocarbon moieties. The thermal decomposition of the fluorinated gels starts at higher temperature and the weight loss appeared more abrupt than for the hydrocarbon gels. A different behavior was observed for the gels **G-III$_F$** and **G-IV$_F$** (Fig. 3c and d).

The similar thermal stability was found for gels **G-III$_F$** and **G-IV$_F$** for which decomposition started at a temperature of 230°C, only slightly higher than the decomposition temperature (200°C) for the analogous hydrocarbon hybrid gel **G-III$_H$** and **G-IV$_H$**. At about 500–600°C respective weight losses of 82 and 72% for fluorinated gels, and 56 and 43% for hydrocarbon gels corresponded to the elimination of the organic spacers. The behaviour of these hybrid materials may be related to the structure of the bis-silylated precursors $\mathbf{III_H}$, $\mathbf{III_F}$, $\mathbf{IV_H}$ and $\mathbf{IV_F}$ and to the structure of the resulting hybrid network in gel $\mathbf{G\text{-}III_H}$, $\mathbf{G\text{-}III_F}$, $\mathbf{G\text{-}IV_H}$ and $\mathbf{G\text{-}IV_F}$. Compared to hybrid gels $\mathbf{G\text{-}II_H}$ and $\mathbf{G\text{-}II_F}$, having pendant organic or fluoro-organic moieties, the structure of the hybrid network is quite different. In gels **G-II** the pendant group is more likely to be located at the surface of the silica-based material [31,43], in some way coating the material, and, therefore, a large influence of the nature of the organic fragment may be expected on the thermal stability. In the case of gels **G-III**, owing to the structure of the bis-silyl precursor the organic or fluoro-organic bridging spacer is more likely to be embedded in the silica matrix [31,42]. Therefore, it may have a lower influence on the thermal stability and little difference can be seen in decomposition temperatures between the hydrocarbon or fluorocarbon hybrid gels. The fluorocarbon gel $\mathbf{G\text{-}IV_F}$, behaves similarly to hybrid gel $\mathbf{G\text{-}III_F}$. This may be indicative of a similar structure for the two gels, both arising from the hydrolysis of bis-silylated precursors.

In summary, it appears that the presence of fluorocarbon chains in the gels, no matter how they are introduced, affords to these materials a higher thermal stability than that of gels prepared from hydrocarbon precursors. The highest gain in stability is observed in the case of the gels prepared from the monosilylated precursors. The presence of the fluorocarbon moieties at the surface of the material may account for the behaviour of these materials, which present a similar stability to that observed for fluorosilicones [14,45].

2.3.2. Hydrophobic properties

Thin films of hybrid gels were prepared on glass slides by spin coating of the solutions containing the hydrolysed precursor. The contact angles of a drop of water (polar fluid) and diiodomethane (apolar fluid) on the films were determined and listed in Table 2.

As expected, the contact angles observed for coatings with fluorocarbon hybrid gels (98–112° for water and 70–103° for CH_2I_2,) are higher than those determined for coatings obtained with hydrocarbon hybrid gels (85° for water and 60° for CH_2I_2,). In addition, Table 2 shows that in all cases the values of the contact angles from water are always higher than those obtained from diiodomethane. These results are consistent with water and oil repellancy brought by the fluorinated groups orientated on the surface of the film. The silica fragments, $SiO_{1.5}$, probably have a much better affinity with the glassy substrate. It is worth noting, that two behaviours were observed: the coatings prepared from precursors $C_8F_{17}(CH_2)_nSi(OMe)_3$ $\mathbf{II_F}$ or from difunctional bis(trialkoxy)silanes $\mathbf{IV_F}$ having a pendant fluorinated chain exhibit the highest contact angle values, 112 and 108° for water, respectively. By contrast, a lower contact angle (98° for water) was observed for the coating obtained from the bis-silylated precursors $\mathbf{III_F}$ having a perfluoroalkyl group as spacer between the two silicon atoms.

Table 2
Contact angles (degree) of poly(fluoroalkylsilsesquioxanes) and poly (hydrogenoalkylsilsesquioxanes) in water and diiodomethane

Sample	θ_{H_2O} (○)	$\theta_{CH_2I_2}$ (○)
$\mathbf{G\text{-}II_F0}$	112±5	89±4
$\mathbf{G\text{-}II_H0}$	85±6	58±8
$\mathbf{G\text{-}II_F1}$	109±10	103±7
$\mathbf{G\text{-}III_F}$	98±5	70±6
$\mathbf{G\text{-}III_H}$	90±5	60±10
$\mathbf{G\text{-}IV_F}$	108±4	90±3
$\mathbf{G\text{-}IV_H}$	91±5	66±4

The results are consistent with the observations concerning differences in thermal stability as a function of the structure of the precursors. The hybrid gel $\mathbf{G\text{-}II_F}$ which shows the highest thermal stability also corresponds to the one which shows the highest value for contact angles. These observations are consistent with the assumption that fluorocarbon moieties in the hybrid gel are likely to be at the surface of the material. By contrast, the precursor $\mathbf{III_F}$ yielded the gel $\mathbf{G\text{-}III_F}$, in which the fluorocarbon spacer is less likely to be at the surface as it shows the lowest thermal stability and lowest contact angles.

This observation is in good agreement with a recent investigation performed on the preparation of poly(fluoroacrylates)deposited on glass [45]. Also it is consistent with the usually enhanced surface properties of materials which also contain fluorinated side chains: polyurethanes [12], silicones [46,47] or poly[methylfluoroalkyl]-siloxanes [48–50].

3. Experimental section

3.1. General comments

Fluorinated vinylic or allylic monomers were prepared as previously described [40], the former being produced by ethylenation of perfluoroalkyl iodides (n-$C_6F_{13}I$ or n-$C_8F_{17}I$) followed by dehydroiodination, while the latter were obtained by radical addition of perfluoroalkyl iodides to allyl acetate, followed by deiodoacetalization. TBAF (1.0 M solution in THF) was purchased from Aldrich. $C_6F_{13}C_2H_4OH$ was kindly provided by Elf Atochem.

After reaction, the products were worked up and analyzed by gas chromatography (GC) using a Delsi apparatus (Model 330) equipped with an SE 30 column, 1 m×1/8 in. (i.d.). The nitrogen pressure at the entrance of the column was maintained at 0.6 bar and the detector and injector temperatures were 260 and 255°C, respectively. The temperature programme was from 50 to 250°C at a heating rate of 15°C min^{-1}. The GC apparatus was connected to a Hewlett–Packard integrator (Model 3390) which automatically calculated the area of each peak on the chromatogram.

The products were characterized by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy all undertaken at room temperature. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 200, 250 or MW 360 instruments, using deuterated chloroform as solvent and with TMS as internal reference. The letters s, d, t, q, and m designate singlet, doublet, triplet, quartet and multiplet, respectively. ^{19}FNMR spectra were also recorded on Bruker AC 200 or 250 instruments using deuterated chloroform with $CFCl_3$ as internal reference. Coupling constants and chemical shifts are given in Hertz and ppm, respectively. Solid state NMR spectra of ^{13}C and ^{29}Si were obtained with a Bruker FT-AM200 or FT-AM400 apparatus with cross polarization and magic angle spinning techniques (CP-MAS) and TMS as reference for the chemical shifts.

Nitrogen surface area measurements were performed according to the BET method, at 77 K with a Micromeritics Gemini 2375 equipment.

Thermogravimetry (TG) experiments were performed on a STA 409TH Netszch apparatus. Approximately, 50 mg of the powdered samples was used for each run with an air flow of 50 $cm^3\ min^{-1}$ and a heating rate of 10°C min^{-1}.

Surface properties measurements were determined from samples prepared by spin coating on microscope slides from a liquid sol–gel solution, on a Karl Suss Technique SA apparatus (CT60 model) with an acceleration of 2000 rpm, a spinning speed of 200–500 rpm for 10–20 s. The contact angle of a drop of polar (water) or nonpolar (diiodomethane) liquid on the film was measured with a Kruss G1 instrument, at room temperature (23°C) by means of the sessile drop technique by micrometer drive G23. On each sample, at least five measurements were performed: the difference from the average values was not more than 7°. The measuring liquids were doubly distilled water whose surface tension at 23°C was 72.0 mN m^{-1} and methylene iodide was 67.0 mN m^{-1}.

Elemental analyses were performed at the Service Central d'Analyse (CNRS, Lyon).

3.2. Synthesis of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyltrichlorosilane, I_F-0

In a Carius tube (CT) were introduced 44.6 g (0.1 mol) of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecene, 16.3 g (0.12 mol) of trichlorosilane and 100 ml of a solution of 10% H_2PtCl_6 in isopropanol. The CT was frozen in an acetone/liquid nitrogen bath ($T=-80$°C) and sealed. It was placed in the cavity of an aluminum block put in a shaking oven ($T=100$–115°C for $t=19$ h). After reaction, the CT was cooled to room temperature and then immersed in liquid nitrogen and opened. The black liquid was passed over alumina, the solvent evaporated and the fluoroalkyltrichlorosilane distilled giving 56.4 g (97%) of $\mathbf{I_F}$**-0** as a colorless liquid. bp=115–118°C/23 mmHg. ^{1}H NMR ($CDCl_3$): δ, 1.7 (m, 2H, CH_2SiCl_3); 2.4 (m, 2H, CF_2CH_2). ^{19}F NMR ($CDCl_3$) δ, −81.8 (CF_3, 3F); −115.5 (2F, CF_2CH_2); −122.5 (2F, $CH_2CF_2CF_2$); −123.0 (2F, $CH_2C_2F_4CF_2$); −123.7 (2F, $CH_2C_3F_6CF_2$); −124.0 (2F, $CH_2C_4F_8CF_2$); −124.5 (2F, $CH_2C_5F_{10}CF_2$); −127.2 (2F, CF_3CF_2). ^{29}Si NMR ($CDCl_3$) δ, 11.6 (s).

3.3. Synthesis of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyltrimethoxy-silane, II_F-0

In a two-necked round bottom flask containing 50 g (86 mmol) of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyltrichlorosilane cooled in an ice bath and equipped with a condensor and a dropping funnel was added dropwise 8.3 g (259 mmol) of methanol. After complete addition, the mixture was kept stirring at room temperature. Afterwards the lower organic phase was collected by means of a separating funnel and distilled yielding 48.9 g (85.3 mmol) of $\mathbf{II_F}$**-0** as a colorless liquid. bp=75–80°C/ 0.5 mmHg. Yield=99%. ^{1}H NMR ($CDCl_3$): δ, 0.9 (m, 2H, $SiCH_2$); 2.3 (m, 2H, CF_2CH_2); 3.5 (s, 9H, OCH_3). ^{19}F NMR ($CDCl_3$) δ, −81.8 (CF_3, 3F); −115.5 (2F,CF_2CH_2); −122.5 (2F, $CH_2CF_2CF_2$); −123.0 (2F, $CH_2CF_2CF_2$); −123.7 (2F, $CH_2C_3F_6CF_2$); −124.0 (2F, $CH_2C_4F_8CF_2$); −124.5 (2F, $CH_2C_5F_{10}CF_2$); −127.2 (2F, CF_3CF_2). ^{29}Si NMR ($CDCl_3$) δ, −44.6 (s).

3.4. Synthesis of 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyltrichloro-silane, I_F-1

In a similar experiment as above, 46.0 g (100 mmol) of 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecene, 16.3 g (120 mmol) of trichlorosilane and 100 ml of the H_2PtCl_6 catalyst were shaken at 110°C for 19 h. After the same work-up, the expected fluoroalkylsilane was distilled as a colorless liquid. bp=143–146°C/23 mmHg (yield=98%). ^{1}H NMR ($CDCl_3$): δ, 1.5 (m, 2H, $SiCH_2$); 1.9 (m, 2H, $\underline{CH_2}CH_2Si$), 2.2 (m, 2H, CF_2CH_2). ^{19}F NMR ($CDCl_3$): same as that of $\mathbf{I_F}$**-1**. ^{29}Si NMR ($CDCl_3$) δ, 11.4 (s).

3.5. Synthesis of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluoroundecyltrimethoxysilane II_F-1

As above, the methanolysis of the fluoroalkyltrichlorosilane was performed with a three-fold excess of methanol leading to expected $\mathbf{II_F}$**-1** in 99% yield. bp=108–112°C/ 0.5 mmHg ^{1}H NMR ($CDCl_3$): δ, 0.8 (t, $^3J_{HH}=8.0$ Hz, 2H, $SiCH_2$); 1.7 (m, 2H, $\underline{CH_2}CH_2Si$); 2.1 (m, 2H, CF_2CH_2); 3.5 (s, 9H, OCH_3). ^{19}F NMR ($CDCl_3$) similar to that of $\mathbf{II_F}$**-0**. ^{29}Si NMR ($CDCl_3$) δ, −42.0 (s).

3.6. Synthesis of decyltrimethoxysilane, II_H-0

In a three-necked flask, 7.1 g (50 mmol) of 1-decene, 7.32 g (60 mmol) of trimethoxysilane and 92.3 mg (0.1 mmol, 0.5 mol%) of $ClRh(PPh_3)_3$ were dissolved in 20 ml of toluene and the mixture was heated to 120°C with an oil bath. The reaction was monitored by ^{1}H NMR and was complete after 4 h. The solvent was removed in vacuo and the crude mixture was distilled to give 8.1 g (61%) of **II_H-0**. bp=102–106°C/3.5 mmHg. ^{1}H NMR ($CDCl_3$): δ, 0.6 (m, 2H, $SiCH_2$); 0.8 (t, 3H, CH_3); 1.1–1.4 (m, 16H, 8 CH_2); 3.6 (s, 9H, O–CH_3). ^{13}C NMR ($CDCl_3$) δ, 9.1 (CH_2Si); 14.0 (CH_3); 22.5, 22.6, 29.2, 29.3, 29.5, 29.6, 31.9, 33.1 (8 CH_2); 50.4 (OCH_3). ^{29}Si NMR ($CDCl_3$) δ, −41.3 (s).

3.7. Synthesis of undecyltrimethoxysilane, ***II_H-1***

The same procedure as above was applied with 6.16 g (40 mmol) of 1-undecene, 6.1 g (50 mmol) of trimethoxysilane and 73.8 mg (0.08 mmol, 0.5 mol%) of $ClRh(PPh_3)_3$. After distillation, 8.3 g (75%) of **II_H-1** was obtained as a colorless liquid. bp=92–94°C/0.7 mmHg. ^{1}H NMR ($CDCl_3$): δ, 0.6 (m, 2H, $SiCH_2$); 0.9 (t, 3H, CH_3); 1.1–1.4 (m, 18H, 9 CH_2); 3.6 (s, 9H, O–CH_3). ^{13}C NMR ($CDCl_3$) δ, 9.1 (CH_2Si); 14.1 (CH_3); 22.6, 22.7, 29.2, 29.3, 29.5, 29.6, 29.7, 31.9, 33.1 (9 CH_2); 50.4 (OCH_3). ^{29}Si NMR ($CDCl_3$) δ, −41.1 (s).

3.8. Synthesis of 1,10-bis(trimethoxysilyl)decane, ***III_H***

To a solution of $ClSi(OMe)_3$ (34.4 g, 0.22 mol) and magnesium chips (6 g, 0.25 mol) in 100 cm^3 of THF cooled in an ice bath was added 1,10-dibromo-octane (30 g, 0.1 mol) diluted in 100 cm^3 of THF. After the addition was complete, the reacting mixture was stirred at room temperature for 12 h. The solvent was removed in vacuo and the remaining sticky solid was extracted with hexane. The mixture was filtered in order to eliminate the magnesium salt. Hexane was pumped off and the liquid was distilled to afford 26.7 g (70%) of **III_H** as a colorless liquid. bp=143–144°C/0.02 mmHg. ^{1}H NMR ($CDCl_3$): δ, 0.55–0.65 (m, 4H, $SiCH_2$); 1.1–1.4 (m, 16H, 8 CH_2); 3.5 (s, 18H, OCH_3). ^{13}C NMR ($CDCl_3$) δ, 9.1 (CH_2Si); 22.6, 29.2, 29.5,33.1 (4 CH_2); 50.4 (OCH_3). ^{29}Si NMR ($CDCl_3$) δ, −41.3 (s).

3.9. Synthesis of 1,10-bis(triethoxysilyl)-4,4,5,5,6,6,7,7-octafluorodecane, ***III_F***

4,4,5,5,6,6,7,7-octafluoro-1,9-decadiene (4 g, 14.2 mmol), $HSi(OEt)_3$ (4.92 g, 30 mmol) and H_2PtCl_6 (0.3 mol%) were mixed in a Schlenk (v.c) tube. The stirred mixture was heated for 6 h at 120°C and was monitored by ^{1}H NMR. The crude product was distilled yielding **III_F** in 65%. bp=120–122°C/0.015 mmHg. ^{1}H NMR ($CDCl_3$): δ, 0.7 (t, 4H, $SiCH_2$); 1.2 (t, 18H, CH_3); 1.6–1.8 (m, 4H, CH_2); 1.9–2.3 (m, 4H, CH_2CF_2); 3.8 (q, 12H, O–CH_2). ^{13}C NMR ($CDCl_3$) δ=10.1 (CH_2Si); 14.1 (CH_2); 18.1 (CH_3); 33.8 (t, $^2J_{CF}$=22.6 Hz, CH_2CF_2); 58.4 (OCH_2); 105–125 (m, CF_2). ^{29}Si NMR ($CDCl_3$) δ=−46.6 (s).

3.10. Synthesis of bis(triethoxysilylmethyl)methylsilane

To a stirred solution of dichloromethylsilane (3.45 g, 30 mmol) in THF (10 cm^3) cooled in an ice bath was added dropwise a molar THF solution (70 cm^3, 70 mmol) of $(EtO)_3SiCH_2MgCl$ [41]. After complete addition of the Grignard reagent, the reaction mixture was left stirring overnight at room temperature. The volatiles were pumped off and hexane was added to the oily residue. The mixture was filtered and hexane was evaporated in vacuo. The remaining liquid was then distilled at reduced pressure leading to a colorless liquid corresponding to bis(triethoxysilylmethyl)methylsilane (7.8 g, yield=65%). bp=95°C/0.5 mmHg. ^{1}H NMR ($CDCl_3$): δ, 0.0 (m, 4H, $SiCH_2$); 0.2 (d, 3H, $SiCH_3$); 1.2 (t, 18H, CH_3); 3.8 (q, 12H, O−CH_2); 4.1 (m, ^{1}H, Si−H). ^{13}C NMR ($CDCl_3$) δ=−4.5 (CH_2Si); −3.5 (CH_3Si); 18.2 (CH_3CH_2); 58.2 (OCH_2). ^{29}Si NMR ($CDCl_3$) δ=−16.0 (Si−H); −44.3 (Si−O). Mass spectrometry (EI): M^+=398 (7%), $M-1^+$=397 (24%), $M-Me^+$=383 (3%), $M-(EtO)_3SiCH_2^+$=221 (100%). Elemental analysis calcd for $C_{14}H_{38}O_6Si_3$: C, 45.18; H, 9.61. Found: C, 45.04; H, 9.89%.

3.10.1. Synthesis of bis(triethoxysilylmethyl)undecylmethylsilane, ***IV_H***

In a glass tube were introduced bis(triethoxysilylmethyl)-methylsilane (3.98 g, 10 mmol), undecene-1 (1.68 g, 10 mmol) and H_2PtCl_6 (0.3 mol% from a solution of 10.7% Pt in isopropanol). The tube was sealed and was heated in an oil bath at 100°C for 4 h. The black liquid was filtered and distilled. A colorless liquid was obtained (4.7, 83%). bp=110°C/0.1 mmHg. ^{1}H NMR ($CDCl_3$): δ, −0.1 (s, 4H, $SiCH_2$); 0.1 (s, 3H, $SiCH_3$); 0.6 (m, 2H, $SiCH_2$); 0.9 (m, 3H, CH_3); 1.2 (t, 18H, CH_3); 1.2 (m, 18H, CH_2); 3.8 (q, 12H, O−CH_2). ^{13}C NMR ($CDCl_3$) δ=−3.4 ($SiCH_2Si$); 0.8 (CH_3Si); 14.1 (CH_3CH_2C); 17.5 ($SiCH_2$); 18.2 (CH_3CH_2O); 22.7, 23.8, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9, 33.8 (9CH_2); 58.1 (OCH_2). ^{29}Si NMR ($CDCl_3$) δ=−43.5 (Si−O); 1.9 (Si−C). Elemental analysis calcd for $C_{26}H_{60}O_6Si_3$: C, 56.47; H, 10.93. Found: C, 56.04; H, 10.81%.

3.11. Synthesis of bis(triethoxysilylmethyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-(heptadecafluoroundecyl)methylsilane, ***IV_F***

The same procedure as above was used. The dark brown solution was filtered on celite to yield a viscous colorless liquid (7.7 g, 90%). Attempt to distil the product resulted in decomposition. ^{1}H NMR ($CDCl_3$): δ, −0.1 (s, 4H, $SiCH_2Si$); 0.1 (s, 3H, $SiCH_3$); 0.7 (m, 2H, $SiCH_2$); 1.2 (t, 18H, CH_3); 1.64 (m, 12H, CH_2); 2.0 (m, 12H, CH_2); 3.8 (q, 12H, O−CH_2). ^{13}C NMR ($CDCl_3$) δ=−3.4 ($SiCH_2Si$); −0.9 (CH_3Si); 14.8 (CH_3CH_2C); 17.2 ($SiCH_2$); 18.2 (CH_3CH_2O); 34.7 (CH_2CF_2); 58.1 (OCH_2); 102–125 (8C–F). ^{29}Si NMR ($CDCl_3$) δ=−44.1 (Si–O); 2.1 (Si−C). Mass spectrometry (EI): $M-Me^+$=843 (10%), $M-(EtO)_3SiCH_2^+$=681 (40%), $M-C_8F_{17}C_3H_6^+$=397 (71%). Elemental analysis calcd for $C_{26}H_{43}O_6F_{17}Si_3$: C, 36.39; H, 5.05; F, 37.64. Found: C, 36.62; H, 5.06; F, 37.46%.

3.12. Preparation of gels

3.12.1. Typical procedure for the hydrolysis of R–Si(OMe)3 and Si(OMe)$_4$ (R=$C_{10}H_{21}$, $C_{11}H_{23}$, $C_8F_{17}C_2H_4$, $C_8F_{17}C_3H_6$): formation of gels **G-II$_H$0**, **G-II$_H$1**, **G-II$_F$0**, **G-II$_F$1**

R-Si(OMe)$_3$ (1 mmol) and Si(OMe)$_4$ (5 mmol) were mixed in 6 cm^3 of methanol (R=$C_{10}H_{21}$ and $C_{11}H_{23}$) or a mixture of methanol and $C_6F_{13}C_2H_4OH$ (R=$C_8F_{17}C_2H_4$, $C_8F_{17}C_3H_6$) as solvents (v/v: 1/10). Water (11.5 mmol) and a catalytic amount of TBAF (0.1% mol with respect to silicon) were added and the mixture was mixed for a while and left to stand at room temperature until gelation took place. After 2 days, the gel was washed with acetone and ether, powdered and the remaining material was dried by means of a vacuum pump.

3.12.1.1. Characteristics of **G-II$_H$0**. 426 mg of white powder was obtained. ^{13}C CP-MAS NMR (δ, ppm) 12.8, 23.0, 29.7, 32.4 and 50.5. ^{29}Si CP-MAS NMR (δ, ppm) −51, −58, −65 (T units), −94, −103, −110 (Q units). N_2 BET surface area: 2.3 m^2 g^{-1}.

3.12.1.2. Characteristics of **G-II$_H$1**. 551 mg of white powder was obtained.^{13}C CP-MAS NMR (δ, ppm) 13.9, 22.9, 29.9, 32.4 and 50.5. ^{29}Si CP-MAS NMR (δ, ppm) −49, −57, −64 (T units), −94, −102, −110 (Q units). N_2 BET surface area: 1.9 m^2 g^{-1}.

3.12.1.3. Characteristics of **G-II$_F$0**. 396 mg of white powder was obtained. ^{13}C CP-MAS NMR (δ, ppm) 0.7, 20–35, 50.4, 110–125. ^{29}Si CP-MAS NMR (δ, ppm) −59, −67 (T units), −102, −110 (Q units). N_2 BET surface area: 0.6 m^2 g^{-1}.

3.12.1.4. Characteristics of **G-II$_F$1**. 413 mg of white powder was obtained. ^{13}C CP-MAS NMR (δ, ppm) 5–20, 25–35, 50.3 and 100–125. ^{29}Si CP-MAS NMR (δ, ppm) −58, −65 (T units), −102, −110 (Q units). N_2 BET surface area: 21 m^2 g^{-1}.

3.12.1.5. Hydrolysis of (MeO)$_3$Si- $C_{10}H_{20}$-Si(OMe)$_3$: preparation of **G-III$_H$**. To a solution of (MeO)$_3$Si–$C_{10}H_{20}$–Si(OMe)$_3$ (3 mmol) in methanol (3 cm^3), water (9 mmol) and TBAF (0.1% mol) were added. The mixture was stirred and left to stand at room temperature until gelation occurred. After 2 days the gel was washed with acetone and ether, then powdered. The obtained material was dried at 100°C, overnight, using a vacuum pump. 876 mg of white powder was obtained. ^{13}C CP-MAS NMR (δ, ppm) 12.5, 23.0, 29.8, 33.1 and 49.8. ^{29}Si CP-MAS NMR (δ, ppm) −49.9, −58.8 and −67.9. N_2 BET surface area: 5.9 m^2 g^{-1}.

3.12.1.6. Hydrolysis of (EtO)$_3$Si-(CH$_2$)$_3$C$_4$F$_8$(CH$_2$)$_3$-Si(OEt)$_3$: preparation of **G-III$_F$**. The same procedure as above was applied with ethanol as solvent. 1.12 g of white powder was obtained.^{13}C CP-MAS NMR (δ, ppm) 17.6, 34.6, 58 and 115.0. ^{29}Si CP-MAS NMR (δ, ppm) −47.2, −54.1, −60.8,and −67.1. N_2 BET surface area: 300.6 m^2 g^{-1}.

3.12.1.7. Hydrolysis of ($C_{11}H_{23}$)SiMe[CH$_2$Si(OEt)$_3$]$_2$: formation of gel **G-IV$_H$**. ($C_{11}H_{23}$)SiMe[CH$_2$Si(OEt)$_3$]$_2$ (2 mmol) was diluted in 2 cm^3 of THF. Water (6 mmol) and a catalytic amount of TBAF (0.1% mol) were added and the same procedure as above was performed. 318 mg of white powder was obtained after drying. ^{13}C CP-MAS NMR (δ, ppm) −3.5, −0.5, 14.3, 23, 29.9, 32.3 and 58.1. ^{29}Si CP-MAS NMR (δ, ppm) 2.7 and −62.8. N_2 BET surface area: 0.8 m^2 g^{-1}.

3.12.1.8. Hydrolysis of ($C_8F_{17}C_3H_6$)SiMe[CH$_2$Si(OEt)$_3$]$_2$: formation of gel **G-IV$_H$**. This gel was prepared as above using a mixture of ethanol and $C_6F_{13}C_2H_4OH$ as solvents (v/v: 1/5). 587 mg of white powder was obtained after drying.^{13}C CP-MAS NMR (δ, ppm) −0.7, 17.7, 36.5, 58.2 and 117.0. ^{29}Si CP-MAS NMR (δ, ppm) 2.7 and −62.8. N_2 BET surface area: 1.1 m^2 g^{-1}.

4. Conclusions

Fluorocarbon-containing hybrid gels as well as their hydrocarbon analogues were prepared from monosilylated and linear or branched disilylated precursors via sol–gel hydrolysis condensation in the presence of TBAF as the catalyst. The properties of these gels were investigated. The surface area and the porosity of almost all gels were very low (0.6–5.9 m^2 g^{-1}). Only the hybrid gel produced from the bis-silyl precursor containing a more rigid fluorocarbon spacer yielded a mesoporous material with high surface area (300 m^2 g^{-1}). Thermogravimetric analysis in air showed a higher thermal stability for fluorocarbon hybrid gels. The surface properties were also enhanced for fluorocarbon hybrid gels, exhibiting higher hydrophobicity and oleophobicity than those of hydrocarbon homologue gels. The best results in terms of thermal stability and hydrophobicity were observed for materials produced by sol–gel hydrolysis of perfluoroalkyl monofunctional trimethoxysilanes. The results support the hypothesis that in this case the fluorocarbon moieties are more likely to be segregated at the surface of the material than in the case of hybrids containing a more rigid perfluoroalkyl spacer.

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