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"Grafting From" Polymerization of Vinylidene Fluoride (VDF) from Silica to Achieve Original Silica−PVDF Core−Shells

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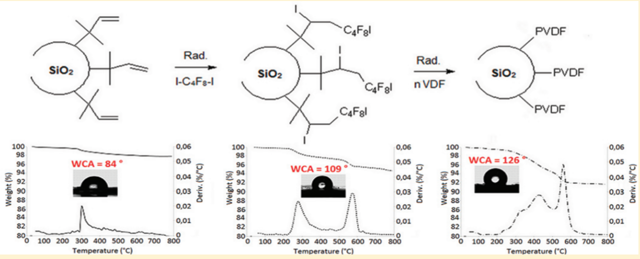
S *Supporting Information*

ABSTRACT: A new method of surface modification based on the "grafting from" polymerization process enabled to prepare original silica nanoparticles covered with PDVF "hair". This strategy involved two steps: (i) the radical addition of 1,4-diiodoperfluorobutane initiated by *tert*-butylperoxypivalate onto the double bonds of silica nanoparticles (specific area of 150 m^2 g^{-1}) led to silica that bore C_4F_8I end-groups on its surface, and (ii) its use as original macrochain transfer agent in the "grafting from" polymerization of vinylidene fluoride (VDF) initiated by bis(4-*tert*-butylcyclohexyl) peroxydicarbonate. The characterizations of both modified silica were achieved by elemental analysis, ^{1}H and ^{19}F magic angle spinning solid state rotational-echo double resonance NMR spectroscopy, thermogravimetry, and water contact angle (WCA) assessments. The grafting efficiency was confirmed by three features: (i) the increase of weight percentage of fluorine atom (that ranged from 0 for the starting unsaturated silica to 2.50% for silica-bearing $-C_4F_8I$ end-group and to 3.32% for original silica−PVDF core−shells), (ii) a high thermostability (that reached more than 400 °C under air), and (iii) a good hydrophobicity: the WCA values were ranging from 84° to 109° and to 126° for vinyl silica, for silica coated with $-C_4F_8I$, and for PVDF-covered silica nanoparticles, respectively.



■ INTRODUCTION

Nanohybrids composed of an inorganic core and a polymeric shell have been of great interest to improve the properties of nanostructured polymeric materials.[1,2] In the specific case of nanocomposites, the quantity and the dispersion of nanoparticles in the polymer matrix have a real input on the properties of the final materials.[3,4] Dispersion improvement generally requires a physical[5] or chemical modification of nanoparticles surfaces.[1] Physical methods improved the physisorption of polymer chains onto particles surfaces with van der Waals interactions or hydrogen bonds.[1] Chemical modifications[6−8] or "chemisorptions" created a covalent bond between macromolecules and particles surface. Such strategies usually consider three pathways: (i) the "grafting through"[9] which allows a copolymerization between growing polymeric chains and polymerizable groups on the surface, (ii) the "grafting from"[10−18] where initiation and propagation steps of polymeric chains are achieved from the surface, even in a controlled radical polymerization of styrene[19] or styrene sodium sulfonate,[20] and (iii) the "grafting onto"[2,21−31] that enables a covalent reaction between the end-groups of polymeric chains and the surface.

The synthesis of nanocomposites combining high polarity of fillers with oleo- and hydrophobicity of coating (typically fluoropolymers) is a great challenge. Additionally, it is known that these nanohybrids can be used for scratch-resistant coatings thanks to their low surface tension and high temperature.

Generally, various routes lead to a fluorinated silica: by sol−gel process between a perfluoroalkyl di- or trialkoxysilane,[32,33] by condensation of perfluoroalkyl alkoxysilanes[34−36] (or chlorosilanes[37]) onto silica surface, from a fluorinated functional copolymer with tetraethoxysilane and nanosilica,[38] or by radical addition of ω-iodofluorinated telomers.[39] In cases of coating, polymeric matrix could be in solvent or aqueous dispersion and limited the dispersion of nanoparticles. Though PVDF/nanofiller composites have already led to extensive studies,[40] to the best of our knowledge, the radical polymerization of vinylidene fluoride (VDF) with silica activated with α,ω-diiodoperfluoroalkane has never been reported in the literature. Our present approach is based on dispersion polymerization of fluooralkenes, especially tetrafluoroethylene (TFE) which involves several parameters: (i) various initiators such as persulfates ($K_2S_2O_8$ and $(NH_4)_2S_2O_8$),[41−63] peroxide (hydrogen peroxide, dialkyl peroxide, or benzoyl peroxide[7]) or azoic ($C_8H_{12}N_4$ or AIBN),[41,43,49,64−70] and (ii) the nature of transfer agents such as alkanes (C_2H_6, C_3H_8,

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etc.),[41,42,46,50,58,62,63,67,69] halogenated derivatives (CCl_4, CH_2Cl_2, $C_4F_8I_2$, etc.),[42,44,54,59,61−63,65,69,70] alcohols (including methanol),[42,46,58,62,63,69,70] or ethers (CH_3OCH_3 and $CH_3OC(CH_3)_3$).[46] However, as TFE is highly explosive, it was worth replacing it by VDF. Hence, silica first was modified by I-C_4F_8-I used as a transfer agent via its radical addition onto double bonds of silica, followed by the polymerization of VDF initiated by bis(4-*tert*-butylcyclohexyl)peroxydicarbonate.

EXPERIMENTAL PART

Materials. Activated silica bearing vinyl groups (named S_{150}) with a specific area of 150 m^2 g^{-1} was given from Sébastien LIVI (IMP/LMM-INSA de Lyon). The particle size of S-150 is 14 nm. 1,4-Diiodoperfluorobutane ($C_4F_8I_2$) (purity 99%) was kindly supplied by Dupont Performance Elastomers (Experimental Station, Wilmington, DE). This 1,4-diiodoperfluorobutane was worked up with sodium thiosulfate and then distilled prior to use to remove impurities and molecular iodine. 1,1-Difluoroethylene (vinylidene fluoride, $CH_2{=}CF_2$, VDF) was kindly supplied by Solvay S.A. (Tavaux, France). Bis(4-*tert*-butylcyclohexyl) peroxydicarbonate (BBCHPDC, Perkadox 16S) (purity 99%) and *tert*-butyl peroxypivalate (TBPPi) dissolved in isodecane (Trigonox25-C75, purity 75%) were gifts from Akzo Nobel (Chalons sur Marne, France). Sodium thiosulfate and acetonitrile (purity 99%) were purchased from Sigma-Aldrich (Saint Quentin-Fallavier, France).

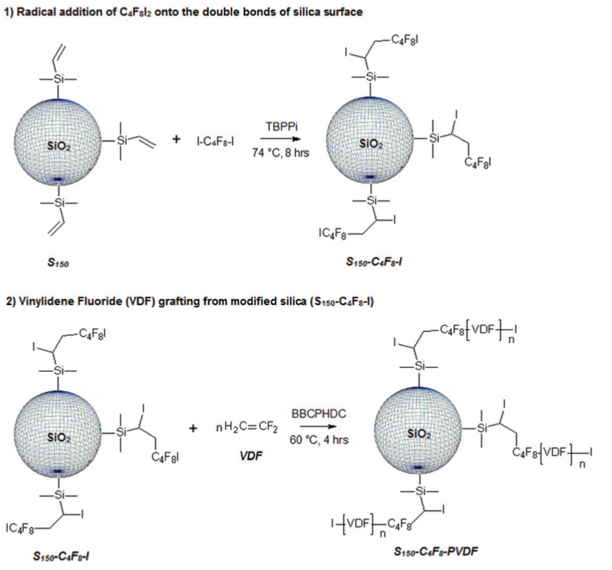
VDF telomers were synthesized by radical telomerization of vinylidene fluoride (VDF) with a chain transfer agent (silica modified by radical addition of $C_4F_8I_2$) and a radical initiator, bis(4-*tert*-butylcyclohexyl) peroxydicarbonate[45] (BBCHPDC, Perkadox 16S). The radical addition of these fluorinated telomers onto silica nanoparticles was achieved in acetonitrile and initiated by *tert*-butyl peroxypivalate (TBPPi).

Radical Addition of TFE Telomers onto Silica Containing Vinyl Groups. Silica activated with vinyl groups (4.00 g, referred as S_{150} in this paper) was homogeneously dispersed into a dry acetonitrile solution (100 mL) under vigorous stirring and warmed to 74 °C. 1,4-Diiodoperfluorobutane (24.63 g, 54.2 mmol) and *tert*-butyl peroxypivalate (0.06 g, 3.9 mmol) were added, and the mixture was refluxed under stirring for 48 h. After reaction, the total product mixture was filtered and washed several times with acetone and led to a powder. Finally, the resulting fluorosilica was dried under vacuum (10^{-1} mmHg) at 80 °C for 8 h until constant weight.

"Grafting From" Polymerization of Vinylidene Fluoride (VDF) from Fluorinated Silica by Radical Polymerization of VDF. The radical polymerizations of vinylidene fluoride (VDF) were performed in a 160 mL Hastelloy HC 276 Parr autoclave system (HC 276) equipped with a manometer, a mechanical Hastelloy anchor, a rupture disk (3000 psi), and inlet and outlet valves. An electronic device regulated and controlled both the stirring and heating of the autoclave. Prior to reaction, the autoclave was pressurized with 30 bar of nitrogen to check for leaks. The autoclave was then conditioned for the reaction with several nitrogen/vacuum cycles (10^{-2} mbar) to remove any trace of oxygen. The liquid and dissolved solid phases (bis(4-*tert*-butylcyclohexyl) peroxydicarbonate) (0.31 g, 0.78 mmol), SiO_2-R_F-I (2.00 g), and acetonitrile (50 mL) were introduced via a funnel, and then VDF (5.0 g, 0.078 mol) was introduced by double weighing (i.e., the difference of weight before and after filling the autoclave with the gas). The autoclave was then progressively heated to 60 °C for 4 h, whereupon a decrease of pressure from 6 to 1 bar up was noted. After cooling to 35 °C, the autoclave was placed in an ice bath for about 60 min and was opened, and the total product mixture was recovered, washed with acetone, filtered, and dried under vacuum at 60 °C until constant weight. This procedure yielded 3.65 g of a white powder.

Characterization. The weight percentages of X (where X represents the carbon or fluorine atoms) were assessed by elemental analysis on different silica samples at the CNRS-Service Central d'Analyze (Solaize, France).

Scheme 1. Silica Surface Modified by Radical Addition of 1,4-Diiodoperfluorobutane Followed by the "VDF Grafting From" Polymerization of Vinylidene Fluoride (VDF)[a]



[a] TBPPi and BBCPHDC stand for *tert*-butyl peroxypivalate and bis(4-*tert*-butylcyclohexyl) peroxydicarbonate, respectively.

Solid-state nuclear magnetic resonance spectra were recorded on Varian VNMRS 400 and 600 spectrometers with magnetic fields strength of 9.4 and 14.1 T, respectively. T3 triple and quadruple resonance magic angle spinning (MAS) probes with Vespel stators and Zirconia pencil MAS rotors were used at room temperature. A HXY probe with 1.6 mm o.d. rotors was used for ^1H and ^{19}F MAS up to 35 kHz spinning rates. A HFXY probe with 2.5 mm o.d. rotors was used for $^1H\{^{19}F\}$ and $^{19}F\{^1H\}$ REDOR experiments with a spinning rate of 25 kHz. The REDOR pulse sequence used in this study is similar to that described by Matsuoka and Inoue[71] using direct polarization instead of cross-polarization for the detected nucleus. The echo delay is the duration between the π pulse and the beginning of acquisition on the detected channel. Typically, $\pi/2$ pulse durations were 4 μs and the recycle delay was set to 3 s (64 transients) for ^1H and to 10 s (128 transients) for ^{19}F. The ^1H chemical shifts reported herein are relative to tetramethylsilane, and the ^{19}F chemical shifts are relative to $CFCl_3$, referenced via the $CF_2{-}CF_2{-}CF_2$ signal of PTFE at −122 ppm.

Thermogravimetric analyses were carried out on a TA Instruments Q50 apparatus. Samples were heated under a mixed atmosphere of nitrogen and oxygen (60 and 40 mL min^{-1}, respectively) with a ramp temperature of 20 °C min^{-1} from room temperature to 800 °C.

The sessile drop method was used for static contact angle measurements at ambient temperature with an automatic video water contact angle (WCA) testing apparatus (Contact Angle System OCA-Data Physics). The average WCA values were determined by measuring five different positions of the same sample with 0.8 μL water volume and used to assess water repellency of modified silica.

RESULTS AND DISCUSSION

The structure of vinyl groups grafted onto silica S_{150} surface and the efficiency of radical addition of TFE telomers were characterized in a previous study.[39] Results are subsequently used to assign the grafting steps. Indeed, the modification method used was composed in two steps (Scheme 1): (i) the radical

Table 1. Carbon and Fluorine Contents, Water Contact Angles (WCAs), and Thermal Properties of (i) Vinylsilica (Specific Area = 150 $m^2 g^{-1}$), (ii) Vinylsilica Modified by Radical Addition (S_{150}-C_4F_8I), and (iii) Silica−PVDF Core−Shell Achieved by "Grafting From" Polymerization of VDF (S_{150}-C_4F_8-PVDF)

samples	wt % C	wt % F	WCA (deg)	$T_d^{1\,a}$ (°C)	$T_d^{2\,a}$ (°C)	$T_d^{3\,a}$ (°C)	wt % loss at 800 °C
S_{150}	2.50	0.00	84 ± 2	300			2
S_{150}-C_4F_8-I	1.87	2.50	109 ± 2	280		570	5
S_{150}-C_4F_8-PVDF	3.78	3.32	126 ± 2	300	430	570	8

[a] Maximum of the derivative peaks in the TGA thermograms.

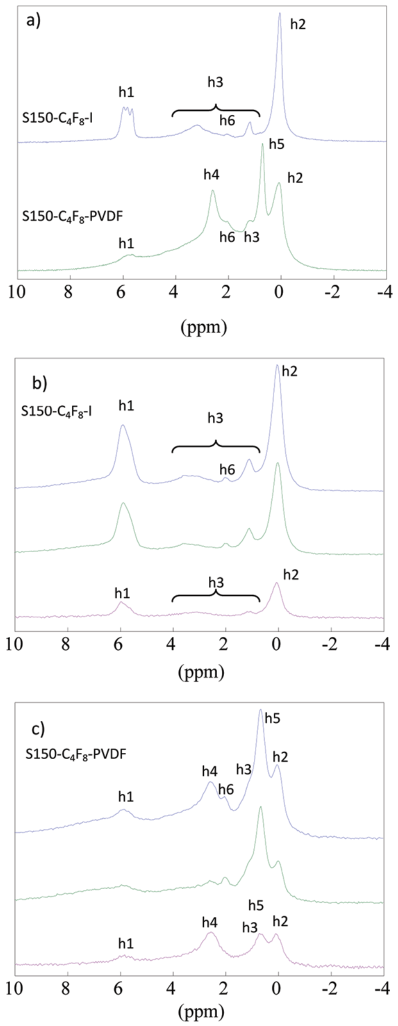


Figure 1. 35 kHz ^1H magic angle spinning NMR spectra of S150-C_4F_8-I and S150-C_4F_8-PVDF samples (a); rotational-echo double-resonance magnetic nuclear (REDOR NMR) S_0 rotor synchronized spin−echo experiment (top), S rotor synchronized spin−echo with reintroduction of the $^1H/^{19}F$ dipolar interaction (middle), and (S_0 − S) difference (bottom) for S150-C_4F_8-I (b), and S150-C_4F_8-PVDF (c). Spinning frequency is 25 kHz, and echo delay is 0.76 ms for REDOR. Lines are labeled according to Table 2.

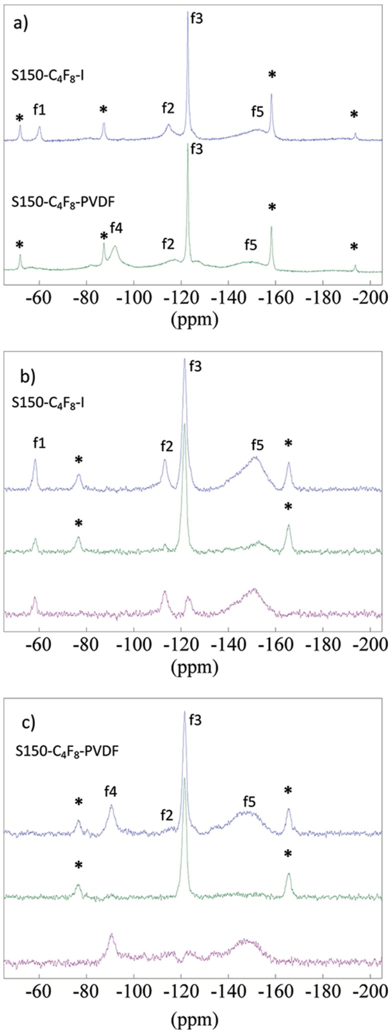


Figure 2. 20 kHz ^{19}F magic angle spinning NMR spectra of S150-C_4F_8-I and S150-C_4F_8-PVDF samples (a); rotational-echo double-resonance magnetic nuclear (REDOR NMR) S_0 rotor synchronized spin−echo experiment (top), S rotor synchronized spin−echo with reintroduction of the $^{19}F/^1H$ dipolar interaction (middle), and (S_0 − S) difference (bottom) for S150-C_4F_8-I (b), and S150-C_4F_8-PVDF (c). Spinning frequency is 25 kHz, and REDOR echo delay is 0.76 ms. Lines are labeled according to Table 2.

addition of α,ω-diidoperfluoroalkane ($C_nF_{2n}I_2$) initiated by *tert*-butylperoxypivalate at 74 °C onto double bonds of silica nanoparticles bearing vinyl groups (S_{150}) and (ii) the use as that resulting chain transfer agent during the radical polymerization of fluoride vinylidene (VDF) initiated by bis(4-*tert*-butylcyclohexyl) peroxydicarbonate at 60 °C.

Modified silica was characterized by elemental analysis (EA), water contact angle measurements (WCA) achieved by sessile drop method, and thermogravimetric analysis (TGA). Results obtained are reported in Table 1. Results obtained for silica modified by radical addition of TFE and VDF telomers[39] were compared to them.

The increasing weight percentage of carbon and fluorine atoms onto modified nanoparticles was determined with elemental analysis (Table 1) and confirmed the grafting of $C_4F_8I_2$ and PVDF chains.

To deeper evidence these results, these modified nanoparticles were characterized by ^1H (Figure 1) and ^{19}F (Figure 2) solid-state NMR spectroscopy. Isotropic chemical shift values for ^1H and ^{19}F in both samples are gathered in Table 2.

Table 2. Main ^{1}H and ^{19}F Isotropic Chemical Shift Values Observed in the Present Work Together with Their Attributed Groups and Labels

groups	^{1}H δ_{iso} (ppm) ± 0.5 ppm	^{19}F δ_{iso} (ppm) ± 1 ppm	label[c]
$Si-CH=CH_2$	6		h1
$Si-CH_3$	0		h2
$Si-OH$	1−4		h3
$-(CF_2-CH_2)-$	2.6		h4
	0.7[a]		h5
CH_3COCH_3	2		h6
$-CF_2-CF_2I$		−59	f1
$-CH_2-CF_2-CF_2-$		−113	f2
$-CF_2-CF_2-CF_2-$		−122	f3
$-(CH_2-CF_2)_n-$		−90	f4
$-CH_2-CF-$[a]		−150[b]	f5

[a] Close to silica surface. [b] Broad line. [c] Figures 1−3.

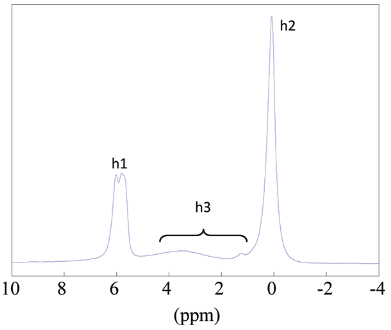


Figure 3. 20 kHz ^{1}H magic angle spinning NMR spectrum of starting silica S150 recorded at 400 MHz (B_0 = 9.4 T).

Indeed, the ^{1}H NMR spectrum of silica S_{150} used in this present study exhibits one multiplet and one singlet centered at 6 and 0 ppm (Figure 3) assigned to $Si-CH=CH_2$ and $Si-CH_3$ groups,[39,72] respectively, and this confirms a previous study based on S_{50} silica.[39] The small signal located at 1.2 ppm and the broad one at 3.2 ppm may be attributed to silanol groups already present in the starting material.

After modification of vinyl silica by radical addition with I-C_4F_8-I, almost no difference was observed by standard ^{1}H MAS NMR between S_{150} (Figure 3) and S_{150}-C_4F_8-I spectra (Figure 1). Traces of acetone used during washing process of the sample led to a small line at 2 ppm (line labeled h6). The intensity of the multiplet at 6 ppm remained high, indicating that the radical addition was partial. This arises from (i) the slow reaction previously mentioned[39] and (ii) the smaller excess of 1,4-diiodooctafluorobutane compound which prevents a total conversion of the vinyl groups. However, the ^{1}H{^{19}F} difference rotational-echo double resonance magnetic nuclear (REDOR NMR) spectrum presented in Figure 1b evidence that all the ^{1}H nuclei except the acetone line have fluorine atoms in their neighborhood. This means that vinyl groups modified by radical addition are close enough to unmodified groups so that dipolar interaction between ^{1}H and ^{19}F NMR spectra is present. Such an additional feature brings further evidence of the successful fluorination.

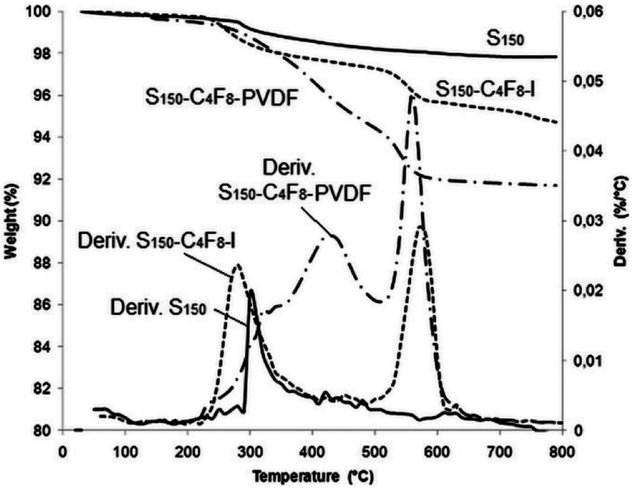


Figure 4. TGA and DTGA thermograms of silica activated with vinyl groups (full curves, S_{150}), modified with $C_4F_8I_2$ (dotted curves, S_{150}-C_4F_8-I), and VDF grafting from (dashed curves) S_{150}-C_4F_8-PVDF.

Strong differences were observed with ^{1}H NMR between S_{150}-C_4F_8-I and S_{150}-C_4F_8-PVDF. Signals observed in the NMR spectrum of S150-C_4F_8-I sample were still observed. Unmodified vinyl groups ^{1}H lines at 6 and 0 ppm present increasing ^{1}H line width for singlet and multiplet led to a lower resolution. This may be due to interactions with PVDF chains that create local disorder and/or reduce motional narrowing. Extra lines were observed at 2.6 and 0.7 ppm. The first one can unambiguously be attributed to methylenes in $-(CF_2-CH_2)-$ groups of PVDF grafts which is the main polymeric constituent added during the process. The second one is then expected to correspond to the similar groups in interaction with the silica surface. As for S_{150}-C_4F_8-I, every ^{1}H line except acetone evidences ^{1}H{^{19}F} REDOR effect (Figure 1c).

^{19}F solid-state NMR spectra were also examined and characteristic signals of PVDF chains[73] were detected. Various teams[74−81] observed crystalline forms of VDF telomers and (co)polymers by ^{19}F solid-state NMR spectroscopy. Figure 2 displays the ^{19}F echo solid-state NMR spectra of telomers (synthesized by radical telomerization of VDF[73]) and silica modified by the "grafting from" polymerization of VDF from S_{150}-C_4F_8-I (S_{150}-C_4F_8-PVDF).

Figure 2a indicates that the MAS ^{19}F spectrum of S_{150}-C_4F_8-I contains three main entities directly related to the radical addition: the signal at −59 ppm is assigned to $-CF_2-CF_2I$ terminal groups (as shown in ^{19}F liquid NMR spectra[73,82]), and the one at −113 ppm is characteristic of the reversed $-CH_2-CF_2-CF_2-$ groups in VDF−VDF dyads.[73,82] The signal centered at −122 ppm is obviously attributed to $-CF_2-CF_2-CF_2-$ sites. However, the intensity of this line is higher than expected from the formulation. A possible explanation is that recombination of S_{150}-$C_4F_8^\bullet$ radicals may occur. This step leads to S_{150}-C_8F_{16}-S_{150} which enables to yield a central oligo(TFE). In such C_8F_{16} group, most difluoromethylenes are adjacent to other CF_2 groups and thus cannot be spatially close to protons. These attributions are supported by the ^{19}F{^{1}H} REDOR difference spectrum in Figure 2b (bottom) which indicates that the line at −122 ppm contains a main contribution with no dipolar interaction with protons in opposition to lines at −59 and −113 ppm. It can be noted at −123 ppm that the small right shoulder of the −122 ppm line

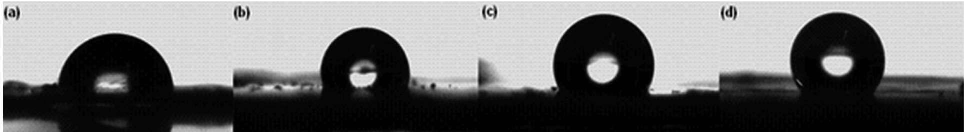


Figure 5. Water droplets on silica that bears vinyl groups (a), modified with $C_4F_8I_2$ (b), silica−PVDF core−shell achieved by "grafting from" polymerization of vinylidene fluoride (VDF) (c), and modified by radical addition of VDF telomer, $C_4F_9(VDF)_{23}I$[39] (d).

corresponds to fluorine atoms spatially closer to protons as for instance in $-CH_2-CF_2-CF_2-$ groups. The last broad line at −150 ppm is not unambiguously attributed, but the slope of the REDOR curves (Figure S1 in the Supporting Information) which are similar for $-(CH_2-CF_2)-$ in S_{150}-C_4F_8-I and S_{150}-C_4F_8-PVDF suggests that it could correspond to fluorine atoms in $-CH_2-CF-$ groups. Such a line position has never been observed in the fluoropolymers that our group have studied, and we were unable to found any attribution in the literature. The more probable hypothesis may arise from the line position closely related to the presence of silica in the materials, and we tentatively assign it to $-CH_2-CF-$ groups close or in interaction with the silica surface.

The ^{19}F MAS spectrum of S_{150}-C_4F_8-PVDF (Figure 2a) enables to confirm that the "grafting from" process was successful. The chemical shift at −59 ppm is not present anymore, which indicates that all $-CF_2I$ terminations available for the polymerization of VDF were consumed. The reactivity of such end-group confirms previous studies.[73,82] In addition, a new signal appears at −91 ppm that is characteristic to normal VDF-VDF normal additions (or $-(CH_2-CF_2)_n-$ alternations) in PVDF.[82,83] The other groups previously observed in S_{150}-C_4F_8-I are still present but as in ^1H spectra, and for the same reasons (local disorder, lower motion) the line widths are broader. The difference REDOR spectrum (Figure 2c) evidences that all fluorine atoms are in dipolar interaction with protons, except for the highest contributions at −122 ppm.

Silica nanoparticles activated with vinyl groups (S_{150}) show an onset decomposition temperature around 300 °C (Figure 4). However, silica modified with I-C_4F_8-I exhibits two weight losses (at 280 and 570 °C) assigned to vinyl groups and those reacted (S_{150}-C_4F_8-I, Scheme 1), respectively. In the case of the "grafting from" polymerization of VDF from S_{150}-C_4F_8-I (S_{150}-C_4F_8-PVDF, Scheme 1), a third temperature was observed around 430 °C and attributed to PVDF grafted chains.[39]

Figure 5 displays the water contact angles (WCA) of drops of water deposited onto vinyl silica that exhibit a great increase ranging from WCA = 84 ± 2° for S_{150} silica to WCA = 109 ± 2° or 126 ± 2° for silica modified by I-C_4F_8-I and VDF grafting, respectively. This is interesting since WCA value of PVDF is lower (ca. 120°)[84] showing that a possible organization should occur in that core−shell. We have tried to characterize these three different silica by transmission electronic microscopy to assess the averaged size such silicas. In fact, Hasegawa et al.[85] reported that for satisfactory grafting density attractive interactions between grafted chains dominate and induce aggregation of particles. Thus, the grafting of fluorinated telomers onto silica nanoparticles thus clearly favors an increase in the hydrophobicity of such silica (Table 1).

CONCLUSIONS

The modification of vinyl silica (S_{150}) by radical addition of 1,4-diiodoperfluorobutane was successfully initiated by *tert*-butylperoxypivalate. Then, the "grafting from" polymerization of VDF from such fluorinated silica (S_{150}-C_4F_8-I) led to original silica−PVDF core−shell polymeric nanoparticles achieved for the first time. The reactivity of vinyl groups with 1,4-diiodoperfluorobutane was evidenced by ^1H MAS NMR spectroscopy while the grafting of PVDF chains onto the silica's surface was monitored by ^{19}F MAS NMR spectroscopy, especially from REDOR. Thermogravimetric analysis as well as elemental analysis confirmed the grafting of $C_4F_8I_2$ and VDF chains on silica nanoparticles. Finally, the contact angle measurements indicated the sharp evolution of hydrophobicity of these original fluorosilica. Initial vinyl silica exhibited a water contact angle of 84° which is clearly lower than that assessed after the modification with $C_4F_8I_2$ (109°) and even lower than that of silica−PVDF core−shell (126°). So far, no evidence has been supplied on the possible controlled radical polymerization of VDF from such original fluorinated macrotransfer agents (i.e., iodine transfer polymerization of VDF[86]) and is presently investigated. In addition, such nanosilica that bear PVDF have been blended with various fluoropolymers to lead to original nanocomposites, under study.

ASSOCIATED CONTENT

Supporting Information. Assessment of the chain length of PVDF grafted onto the silica and $^{19}F\{^1H\}$ REDOR curves $(S_0 - S)/S_0$ for S150-C_4F_8-I and S150-C_4F_8-PVDF silica nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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