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Modification of Silica Nanoparticles by Grafting of Copolymers Containing Organosilane and Fluorine Moities.

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Abstract

The free-radical cotelomerization of 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) with perfluorodecylacrylate (PFDA) in the presence of 2-mercaptoethanol was performed at 80°C in acetonitrile. Hydroxy end-groups of the cotelomers were reacted with 2-isocyanatoethyl methacrylate (IME) to give macromonomers. The P(TMSPMA-*stat*-PFDA) cotelomers, containing fluoro and silane groups, were then grafted onto silica nanoparticles. Optimal grafting conditions were found with TMSPMA monomer alone in toluene at 110°C. The structure of the modified silica was analyzed by FTIR and ²⁹Si solid-state NMR. The amount of grafted TMSPMA or P(TMSPMA-*stat*-PFDA) was calculated by thermogravimetric and elemental analyses. The grafting yield increased with the copolymer/silica weight ratio until a maximum value of 2.26 μmol.m⁻².

Keywords: cotelomerization; grafting onto; hybrid nanoparticle; perfluoroacrylate; silica nanocomposite.

Introduction

Organic polymer / inorganic hybrid nanocomposites are of current research interest because of their improved mechanical, electrical and optical properties.¹ Among the inorganic nanoparticles, silica is extensively used as a filler or reinforcement agent in polymeric matrixes. The chemical modification of the silica particles by a polymer improves the solubility, the stability and the dispersion in various solvents. Processing techniques are based on either physicochemical routes or polymerization methods. Chemical grafting techniques include “grafting onto” and “grafting from” methods.^{2,3} “Grafting from” method begins by the fixation of initiating groups on the surface of the particles followed by in situ polymerization. Organofunctional silanes such as 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) are widely used for “grafting from” processes since it contains simultaneously a silicon–alcoxy function and a double-bond end-group. So, free double bonds can be fixed at the surfaces of particles using a condensation step of $\text{Si}(\text{OMe})_3$ with Si-OH groups.⁴⁻⁷ A variety of polymerization techniques, including conventional free radical,⁸ cationic,⁹ anionic,¹⁰ ring-opening¹¹ and controlled radical polymerizations (CRPs)¹²⁻¹⁵ have been used for the growth of polymer chains from the solid surface of different inorganic particles. “Grafting onto” route is another effective method. It involves the reaction of functional end groups of polymers onto the silica nanoparticles bearing reactive groups.²

In this paper, we propose a new method to obtain fluorinated silica nanoparticles bearing free double bond making them reactive in a polymerization process. Most often, fluorinated silica nanoparticles are obtained either by a sol-gel process using a perfluoroalkyl di- or tri-alkoxysilane¹⁶ or by condensation of perfluoroalkyl di- or tri-alkoxysilane onto preformed silica nanoparticles.¹⁷ In our process, cotelomers bearing one unsaturation were condensed onto silica nanoparticles. So, new poly[(3-(trimethoxysilyl)propyl methacrylate)-*stat*-(perfluorodecylacrylate)] P(TMSPMA-*stat*-PFDA) were synthesized by cotelomerization

leading to oligomers with α -functional end-group. As already said in a previous paper,¹⁸ only perfluoroacrylate polymers which short chains can be obtained due to the insolubility of longer ones in most organic solvents. The telomerization of perfluorodecylacrylate with 2-mercaptoethanol has been explored and the efficiency of this transfer agent has been outlined in several previous investigations.¹⁸⁻²²

Experimental Section

Materials

Nanosized silica (AEROSIL TT 600, Evonik) with an average diameter of 40 nm and a specific area of $200 \text{ m}^2\cdot\text{g}^{-1}$ was used as received. Perfluorodecyl acrylate (PFDA) (Fluorochem, 98%) was distilled under vacuum (8 mmbar, 130°C). 2,2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization in methanol and dried under vacuum. 3-(Trimethoxysilyl)propyl methacrylate (TMSPMA) (Aldrich, 98%), 2-mercaptoethanol (Aldrich, 99%), 2-isocyanatoethyl methacrylate (IME) (Aldrich, 98%), triethylamine (Acros), acetonitrile (Acros), toluene (Acros), acetone (Fluka) and CDCl_3 (Aldrich, 99.8%) were used as received.

TMSPMA, ^1H NMR (200 MHz, CDCl_3 , δ , ppm): 6.09 and 5.54 (s, $\text{CH}_2=\text{C}$), 4.11 (t, O- CH_2), 3.57 (s, Si-O- CH_3), 1.93 (s, C- CH_3), 1.86-1.63 (m, O- CH_2 - CH_2), 0.69 (m, CH_2 - CH_2 -Si). ^{13}C NMR (300 MHz, CDCl_3 , δ , ppm): 166.95 (COO), 136.23 (C= CH_2), 124.78 ($\text{CH}_2=\text{C}$), 66.19 (O- CH_2), 50.15 (Si-O- CH_3), 27.80 (C- CH_3), 17.95 (CH_2 - CH_2 - CH_2), 166.95 (CH_2 -Si). FTIR (cm^{-1}): 2944 (CH), 2841 (O CH_3), 1717 (C=O), 1638 (C=C), 1100 (Si-O).

PFDA, ^1H NMR (200 MHz, CDCl_3 , δ , ppm): 6.50-6.40 (dd, H_f -CH=CH), 6.19-6.05 (dd, $\text{CH}_2=\text{CH}$), 5.91-5.85 (dd, H_c -CH=CH), 4.47 (t, O- CH_2), 2.52 (m, CH_2 - CH_2 - CF_2). ^{13}C NMR (300 MHz, CDCl_3 , δ , ppm): 165.63 (COO), 131.41 ($\text{CH}_2=\text{CH}$), 127.78 (CH= CH_2), 125-108 ((CF_2) $_7$ - CF_3), 56.37 (O- CH_2), 27.80 (CH_2 - CF_2). FTIR (cm^{-1}): 2944 (CH), 1735 (C=O), 1200-1000 (C-F).

2-Mercaptoethanol, ^1H NMR (200 MHz, CDCl_3 , δ , ppm): 3.71 (dt, HO- CH_2), 2.70 (dt, HS- CH_2), 2.18 (s, OH), 1.38 (t, SH). ^{13}C NMR (300 MHz, CDCl_3 , δ , ppm): 63.41 (HO- CH_2), 26.71 (HS- CH_2).

Characterization

^1H NMR spectra were recorded using a Bruker AC 200 with CDCl_3 as solvent. Chemical shifts were referenced to the peak of residual CHCl_3 at 7.26 ppm. ^{13}C NMR spectra were recorded using a Bruker AC 300 with CDCl_3 as solvent. Chemical shifts were referenced to CDCl_3 at 77 ppm. 2D NMR was recorded on a Bruker AC 400. ^{29}Si cross-polarization magic-angle-spinning (CP/MAS) NMR spectra were recorded using a Bruker AC 400 operating at 99 MHz. Magic-angle spinning was performed at a spinning rate of 6 kHz. Fourier Transform Infrared (FTIR) spectra were recorded with a Perkin Elmer Spectrum 100 spectrometer equipped with an attenuated total reflectance (ATR) crystal. Thermogravimetric measurements were performed using a TGA51 TA Instruments apparatus. Samples were heated in a nitrogen flow (60 mL/min) at $20^\circ\text{C}/\text{min}$ from room temperature to 800°C . Carbon elemental analysis was performed on a homemade microanalyzer by combustion of the sample at 1050°C in a stream of oxygen followed by infrared detection.

Synthesis of P(TMSPMA-*stat*-PFDA) statistical copolymer

Cotelerization of TMSPMA with PFDA was performed in acetonitrile at 80°C with 2-mercaptoethanol as transfer agent. Special care was needed for handling TMSPMA because it was easily hydrolyzed. In a 100 mL flask 11.175 g (0.045 mol) of TMSPMA, 2.590 g (0.005 mol) of PFDA, 0.390 g ($5 \cdot 10^{-3}$ mol) of 2-mercaptoethanol and 0.041 g ($2.5 \cdot 10^{-4}$ mol) of 2,2'-azobisisobutyronitrile (AIBN) ($n_{\text{initiator}}/n_{\text{monomer}}=0.5\%$) were diluted to 50 mL with anhydrous acetonitrile. The solution was bubbled with nitrogen for 30 min before heating at 80°C . To avoid any foaming phenomenon during the evaporation of acetonitrile, anhydrous heptane was added at the end of reaction. Then, polymer was washed three times with anhydrous n-hexane and dried under vacuum. The obtained copolymer was a colorless viscous liquid.

Functionnalization of cotelomer by isocyanatoethyl methacrylate (IME)

3 g (1.36 mmol, 2200 g.mol⁻¹) of P(TMSPMA-*stat*-PFDA), 276 mg (1.78 mmol) of 2-isocyanatoethyl methacrylate (IEM), 0.2 wt% (6 mg) of triethylamine and 50 mL of dried toluene were introduced in a round-bottom flask fitted with a condenser. The reaction was stirred and heated at 60°C for 20h. The solvent was removed under vacuum and the polymer was washed three times with anhydrous n-hexane and dried under vacuum.

Grafting of TMSPMA onto silica nanoparticles

Grafting of TMSPMA onto silica nanoparticles was performed with three different experimental methods:

A-method: 1.9 g of silica were mixed with 2.15 g of TMSPMA, while vigorously stirring in boiling acetone.²³⁻²⁷ 30 mg of maleic anhydride diluted in 0.2 mL of water and 30 mL of acetone were added as catalyst. The mixture was refluxed for 2h.

B-method: 1.9 g of silica were dispersed in 30 mL of ethanol-water solution (4/1 weight ratio) by sonication to give a suspension of particles.²⁸ 2.15 g of TMSPMA were hydrolyzed while vigorously stirring in 60 mL of ethanol-water solution (4/1 weight ratio) at room temperature and pH condition was controlled at 4.5 by acetic acid. After this step the hydrolyzed silane was added to the particle suspension and this mixture was stirred continuously for 2h at room temperature and then followed by refluxing for 4h at 70°C.

C-method: 2.15 g of TMSPMA was added to a suspension of silica (1.9 g) in toluene (48 g) and stirred for 30 min at room temperature.²⁹ The mixture was heated to 110°C for 24h.

Finally, in each method, the TMSPMA-grafted silica nanoparticles were washed three times by centrifugation with acetone and dried under vacuum.

Grafting of copolymer onto silica nanoparticles

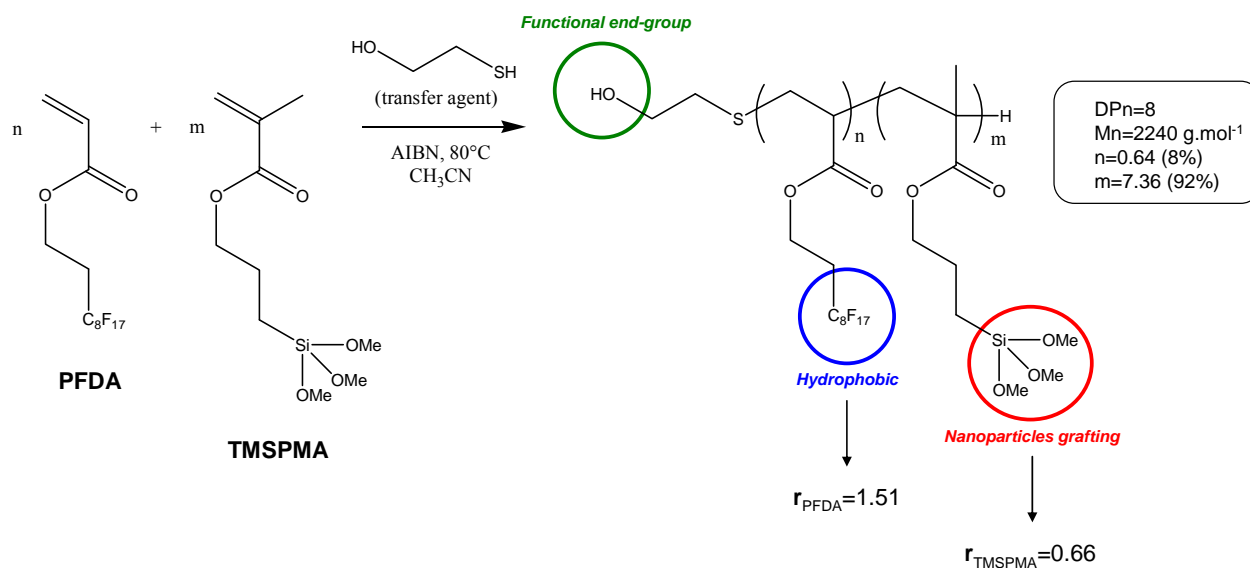
Grafting of copolymers onto silica nanoparticles was performed in toluene with different initial amounts of copolymer. As an example, a solution of 2.26 g of P(TMSPMA-*stat*-PFDA) in 7 g of toluene was added to a suspension of silica (1 g) in toluene (22 g). The mixture was stirred for 30 min at room temperature and then heated to 110°C for 24h. Finally the copolymer-grafted silica nanopowder was washed three times with acetone, separated by centrifugation and dried under vacuum.

Results and Discussion Section

Cotelomerization of TMSPMA with PFDA

Statistical copolymers of TMSPMA and PFDA were prepared by telomerization with 2-mercaptoethanol as transfer agent and AIBN as initiator in acetonitrile at 80°C. The characteristics of the copolymer are summarized in Scheme 1. The efficiency of 2-mercaptoethanol was demonstrated in a previous publication by the determination of the transfer constant (C_T).¹⁸ The corresponding value reveals a good control of the number-average polymerization degree ($\overline{DP}_n=8$). The incorporation of PFDA moieties was limited to 10% initial content because of the poor solubility of the fluorine groups in organic solvents. Moreover, no hydrolysis of the $-\text{Si}(\text{OCH}_3)_3$ groups was confirmed by the signals integration of $9H_m$ than $2H_j$ as shown in Figure 1. Thus, telomerization appears to be a good method for synthesizing oligomers containing fluorine groups.

The monomer reactivity ratios were determined by Jaacks ($r_{\text{TMSPMA}}=0.67$) and Macret ($r_{\text{TMSPMA}}=0.66$ and $r_{\text{PFDA}}=1.51$) methods.¹⁸ The obtained values illustrated that the copolymer was statistical ($r_{\text{TMSPMA}} \times r_{\text{PFDA}}=0.99$) and that PFDA reacts preferentially than TMSPMA. At the early stage of the polymerization (first hour), the resulting chains were enriched in PFDA whereas at higher conversion, they were enriched in less reactive TMSPMA monomer.



Scheme 1: Synthesis of P(TMSPMA-*stat*-PFDA) copolymer.

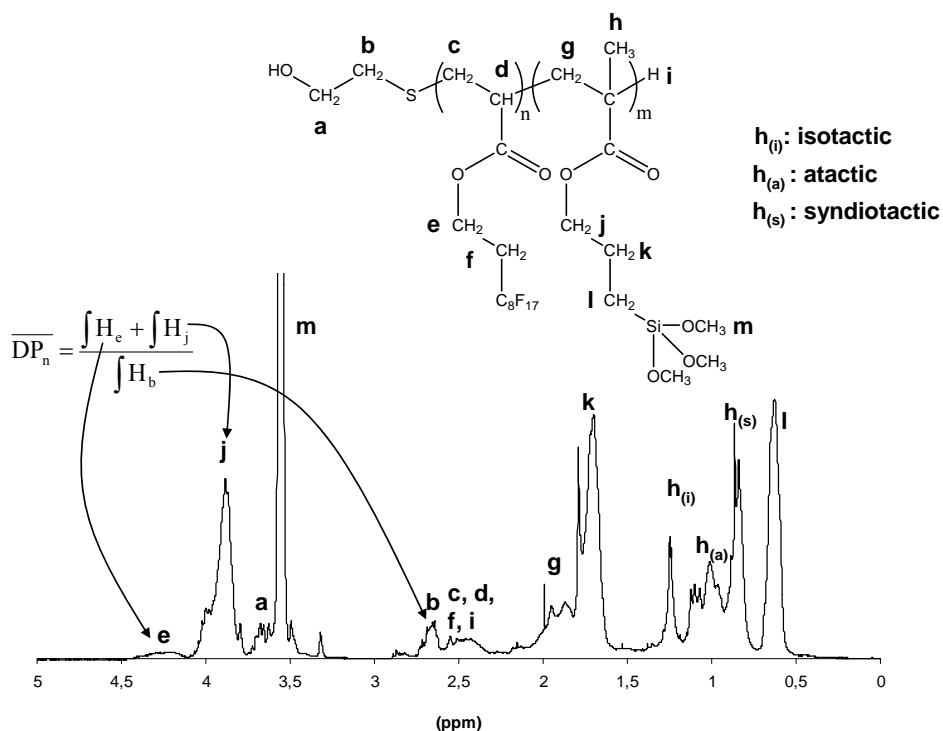


Figure 1: ¹H NMR spectrum in CDCl₃ of P(TMSPMA-*stat*-PFDA) after precipitation in n-hexane.

^1H NMR spectrum of P(TMSPMA-*stat*-PFDA) allows the determination of $\overline{\text{DP}}_n$ (eq. 1) by comparing signals integration: H_e , H_j and H_b which appear at 4.2, 3.9 and 2.7 ppm respectively (Figure 1). The final composition of the cotelomer was also deduced following equations (2) and (3). The ratio between the integration of PFDA unit proton (H_e) and that of end-group ones (H_b) gave the number of PFDA units n in the cotelomer. The same equation was used with H_j and to determine the TMSPMA units m in the cotelomer.

$$\overline{\text{DP}}_n = \frac{\int \text{H}_e \text{ (at 4.2 ppm)} + \int \text{H}_j \text{ (at 3.9 ppm)}}{\int \text{H}_b \text{ (at 2.7 ppm)}} \quad (1)$$

$$n = \frac{\int \text{H}_e \text{ (at 4.2 ppm)}}{\int \text{H}_b \text{ (at 2.7 ppm)}} \quad (2)$$

$$m = \frac{\int \text{H}_j \text{ (at 3.9 ppm)}}{\int \text{H}_b \text{ (at 2.7 ppm)}} \quad (3)$$

^1H NMR and two-dimensional ^1H - ^1H COSY spectral analysis unambiguously reveal the microstructure of P(TMSPMA-*stat*-PFDA). ^1H NMR analysis shows the tacticity of TMSPMA units with three signals: isotactic $\text{H}_{h(i)}$, atactic $\text{H}_{h(a)}$ and syndiotactic $\text{H}_{h(s)}$ between 1.4 and 0.7 ppm as previously reported Chen et al.³⁰ However $\text{H}_{h(a)}$ overlapped $\text{H}_{h(s)}$ protons and prevented from the calculation of syndio-, iso- and atacticity ratios (Figure 1). Moreover in the two-dimensional ^1H - ^1H COSY spectral analysis, the peak at 3.7 ppm was correlated to the proton peak at 2.7 ppm (H_a, H_b) and proved the incorporation of the telogen agent in the backbone of the copolymer while the other correlations concern both PFDA and TMSPMA units (Figure 2). Two serial correlations between H_j , H_k and H_l as well as the interaction between further protons H_g and H_h demonstrated the presence of TMSPMA units in the

copolymer. Moreover PFDA unit was detected by the correlation between the protons on the backbone H_c to H_d in the region of 2.5 ppm.

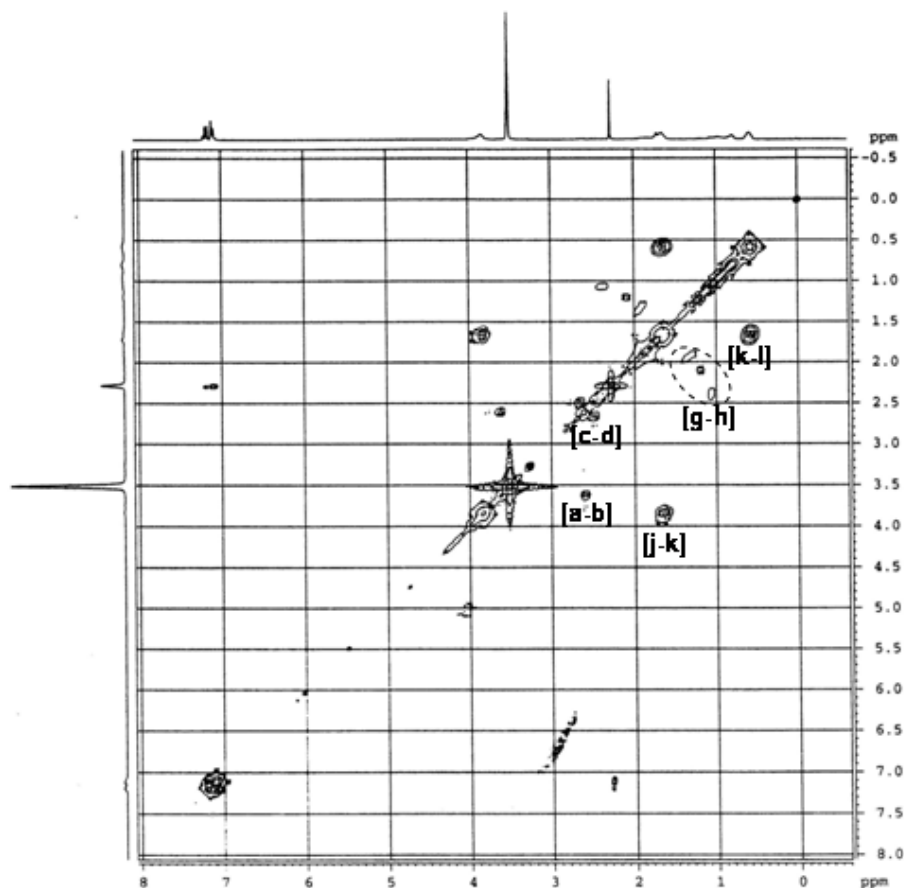
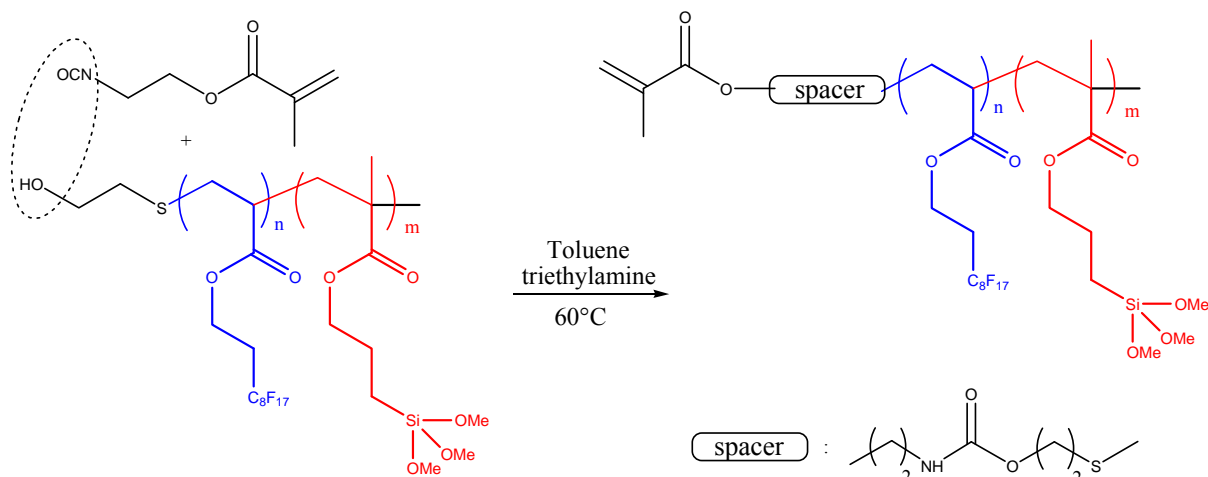


Figure 2: ¹H-¹H COSY NMR spectrum of P(TMSPMA-*stat*-PFDA) copolymer in CDCl₃.

Functionnalization of P(TMSPMA-*stat*-PFDA) by isocyanatoethyl methacrylate (IME)

Telomers are good precursors for the synthesis of macromonomers by conversion of the terminal function coming from the telogen into unsaturation.¹⁹ The reaction of isocyanate functions from IME onto alcohol ones was performed with triethylamine as catalyst (Scheme 2).



Scheme 2: Chemical modification of P(TMSPMA-*stat*-PFDA) hydroxyl end-group by IME.

Usually this reaction can be monitored by FTIR since the large and intense isocyanate band at 2250 cm^{-1} disappears after few hours of reaction at 60°C .²⁰ In our case, IME was used in excess so, FTIR analysis could not be used due to the high absorption band of the unreacted NCO groups. The structure of the purified macromonomer was checked by ^{13}C NMR (Figure 3). The appearance of two peaks was observed at 156.02 ppm (-NH-COO-) and at 39.97 ppm (-CH₂-NH-) which prove the formation of urethane groups. Peaks at 135.87 and 126.20-125.70 ppm corresponding to the terminal unsaturation was also observed. Thus, this study showed that the terminal alcohol function of P(TMSPMA-*stat*-PFDA) is enough reactive to give a macromonomer.

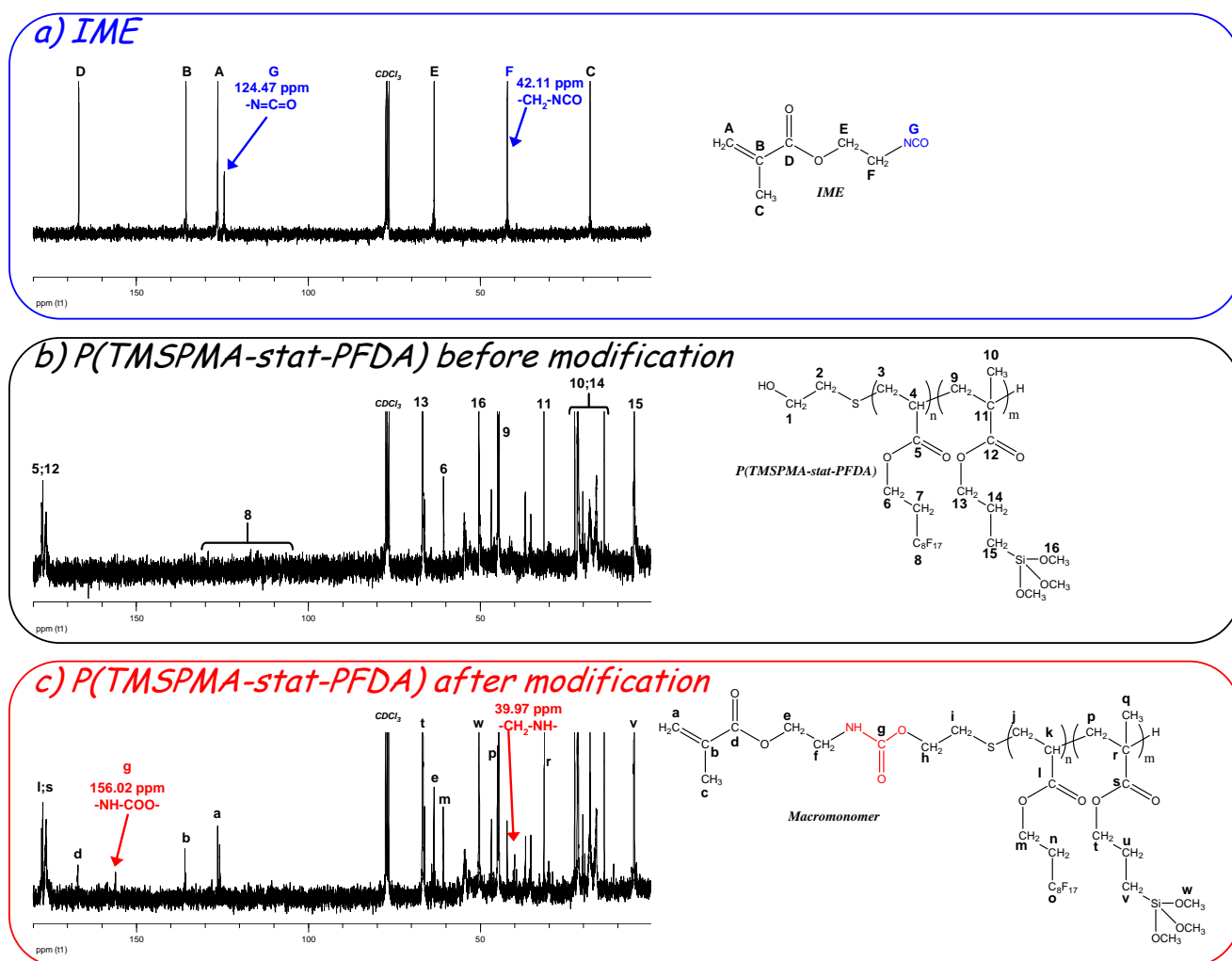


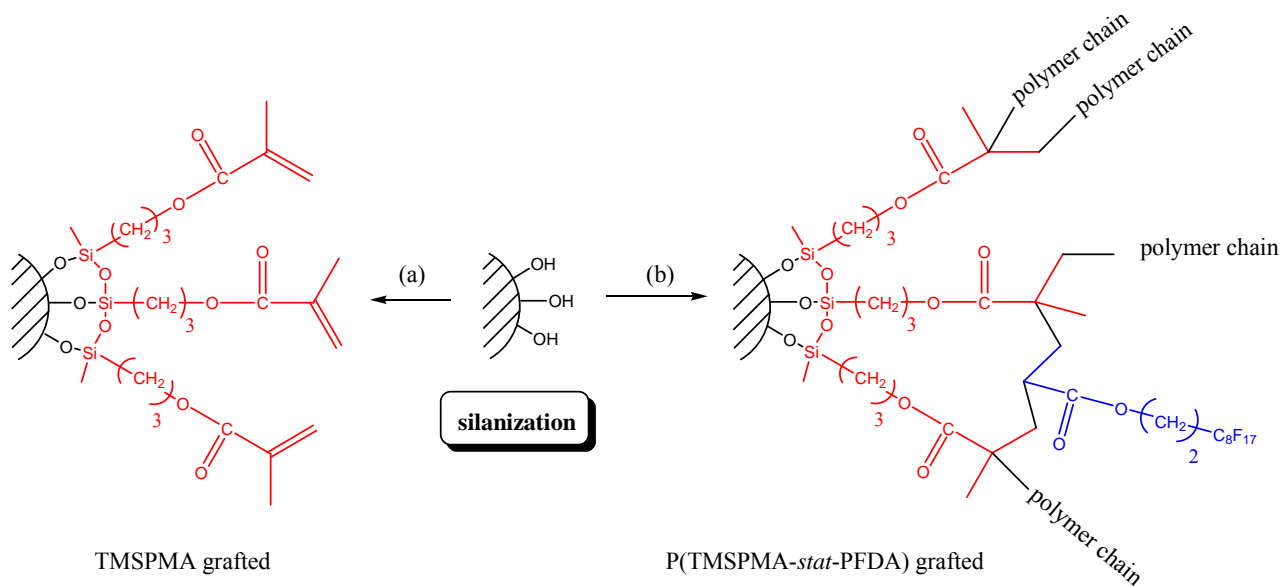
Figure 3: ^{13}C NMR spectra of a) IME compound, b) P(TMSPMA-*stat*-PFDA) before chemical modification and c) P(TMSPMA-*stat*-PFDA) after chemical modification.

So various NMR studies permitted to characterize P(TMSPMA-*stat*-PFDA) cotelomer. Its chemical composition in PFDA and TMSPMA units was calculated from ^1H NMR study and the microstructure was determined by additional two-dimensional ^1H - ^1H COSY analysis. Finally the reactivity of the hydroxy end-group of the cotelomer was proved by ^{13}C NMR analysis.

Grafting of cotelomers onto silica nanoparticles

Preliminary experiments were performed with TMSPMA monomer in order to determine the optimal conditions to graft organosilane molecules on silica nanoparticles. Hydrolyzed silanes react by condensation with the silica surface bearing significant concentration in silanol groups. Three experimental methods named A, B and C differing by the natures of the solvent and of the catalyst, the temperature, were compared.^{21,28,29} Experiments were performed in a mixture of acetone and water with maleic anhydride as catalyst at 60°C for A-method, in a mixture of ethanol and water with acetic acid as catalyst at 70°C for B-method and in toluene at 110°C for C-method. In all cases, silane was in excess in respect to silica and the targeted silane grafting density was arbitrarily fixed at 22.80 $\mu\text{mol.m}^{-2}$. C-method provided the best results (Table 2 runs 1, 2 and 3) and thus was used for the grafting of the cotelomer.

Herein, we report the grafting results for TMSPMA and P(TMSPMA-*stat*-PFDA) on silica nanoparticles (Scheme 3). The grafting was qualitatively evidenced by FTIR spectroscopy and ²⁹Si NMR solid state analysis. Figure 4 shows the infrared spectra of untreated silica and silica after grafting with the cotelomer. In both spectra a peak appearing around 3400 cm^{-1} was characteristic of O-H stretching. Infrared spectra of cotelomer grafted silica revealed new absorptions at 1700 cm^{-1} which could be assigned to carbonyl group (C=O) and 2900 cm^{-1} corresponding to aliphatic carbons of silane moieties. These FTIR analysis disclose the presence of cotelomer with silica even if the formation of covalent bonds between silica and hydrolyzed silanes could not be proved by this analytical method.



Scheme 3: Schematic grafting routes to prepare: (a) P(TMSPMA) grafted silica nanoparticles, (b) P(TMSPMA-*stat*-PFDA) grafted silica nanoparticles.

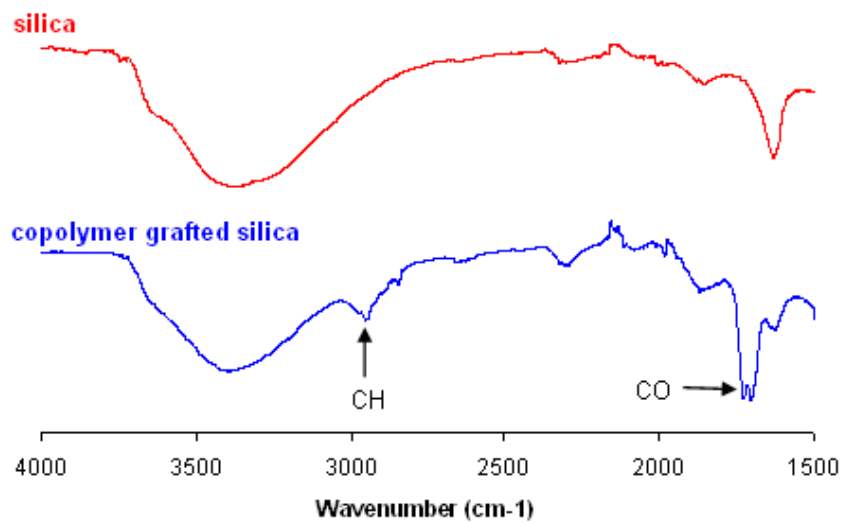


Figure 4: FTIR spectra of untreated silica and copolymer grafted silica.

^{29}Si cross-polarization magic-angle-spinning (CP/MAS) NMR investigations were used to determine the structure of silane grafted onto silica. Organosilane can theoretically react with one (monodentate structure), two (bidentate structure) or three silanols (tridentate structure). A previous work detailed the chemical shifts of the silanol and siloxane functions of silica and silyl grafted.²³ The spectrum of the cotelomer modified silica revealed two groups of signals as shown in Figure 5. The first group is characteristic of unreactive silica and the signals at -92 (Q^2), -102 (Q^3) and -110 (Q^4) ppm are assigned to geminal silanols, free silanols and siloxane groups, respectively. The second group is only observed for modified silica. The signals at -43 (T^1), -48 (T^2) and -57 (T^3) ppm are attributed to organosilane condensates and show that various species are formed onto silica surface. This observation is of great importance for the calculation of the grafting density which depends on the number of formed bonds.

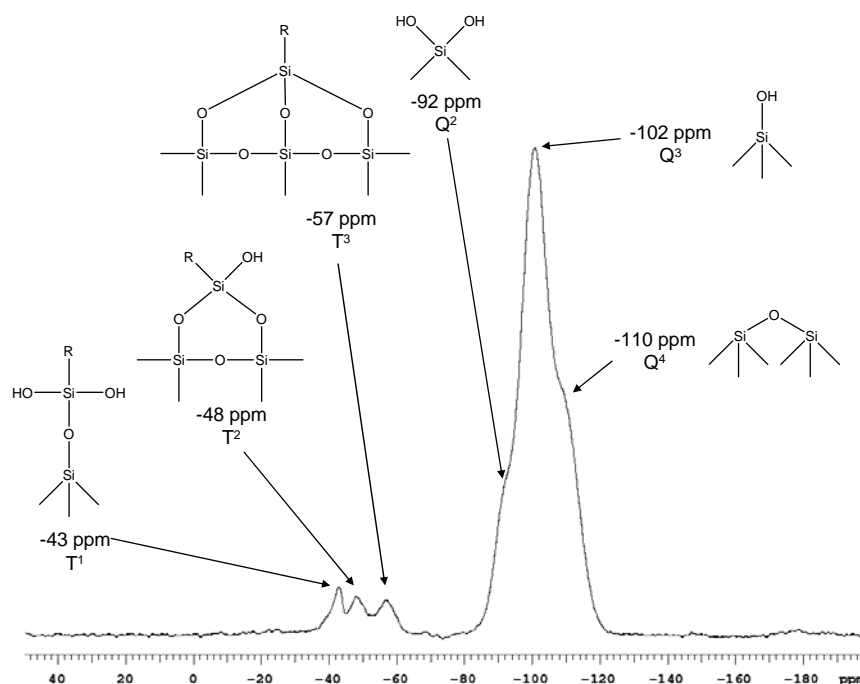


Figure 5: ^{29}Si CP/MAS NMR spectrum of P(TMSPMA-*stat*-PFDA) grafted silica.

The silane grafting onto silica was also quantified by elemental analysis and thermogravimetric analysis. These two methods permitted the determination of the silane coverage of silica surface. First, the organosilane grafting density was determined by elemental analysis from the carbon content using the Berendsen equation (4).³¹

$$\text{Grafting density } (\mu\text{mol.m}^{-2}) = \frac{10^6 \times \Delta C}{[100 \times M_c \times N_c - \Delta C(M_{\text{silane}} - 1)] \times S} \quad (4)$$

where ΔC is the difference of carbon content (wt %) between the sample and the unreactive silica $C_{\text{silica}}=0.23\%$, M_c and N_c are the atomic mass ($M_c=12 \text{ g.mol}^{-1}$) and the number of the carbon atoms of the grafted silane, respectively. M_{silane} is the molecular weight of the silane and S is the specific area of the silica ($S=200 \text{ m}^2.\text{g}^{-1}$). N_c and M_{silane} are function of the number (1, 2 or 3) of formed bonds between the three methoxy groups of the silane and the silica surface. As ^{29}Si CP/MAS NMR demonstrates that the three types of anchoring (mono-, bi- and tri-dental) exist, one can consider a bidental average anchoring of silanes. N_c and M are easily calculated for TMSPMA (Table 1). For the P(TMSPMA-*stat*-PFDA) copolymer one needs to consider a molar mass and average carbon number since a chain contains many silane groups (Equations 5-6).

$$N_{C \text{ P(TMSPMA-} \textit{stat}\text{-PFDA)}} = \frac{\text{carbon number of the grafted copolymer}}{\text{number of silane units}}$$

$$N_{C \text{ P(TMSPMA-} \textit{stat}\text{-PFDA)}} = \frac{N_{C(\text{silane})} \times DP_n \times f_{\text{silane}} + N_{C(\text{PFDA})} \times DP_n \times f_{\text{PFDA}} + N_{C(\text{end-group})}}{DP_n \times f_{\text{silane}}} \quad (5)$$

$$M_{\text{P(TMSPMA-} \textit{stat}\text{-PFDA)}} = \frac{M_{(\text{silane})} \times DP_n \times f_{\text{silane}} + M_{(\text{PFDA})} \times DP_n \times f_{\text{PFDA}} + M_{(\text{end-group})}}{DP_n \times f_{\text{silane}}} \quad (6)$$

where f_{silane} and f_{PFDA} are the molar ratio of the silane (92%) and of the fluorine (8%) moieties respectively, determined by ^1H NMR (see composition of the copolymer in Scheme 1). M_{PFDA} ($\text{C}_{13}\text{H}_7\text{O}_2\text{F}_{17}$) and M_{ext} (sum of $\text{C}_2\text{H}_5\text{OS}$ and H end-chains) values are 518 and 78 $\text{g}\cdot\text{mol}^{-1}$ respectively. These precisions appear to be important since these details of calculations are slightly detailed in the literature and thus confusion can occur.

Table 1: Carbon numbers and molecular weights of the grafted P(TMSPMA-*stat*-PFDA) supposing average bidental anchoring and TMSPMA.

	$N_{\text{C (silane)}}$	$M_{\text{(silane)}} (\text{g}\cdot\text{mol}^{-1})$
TMSPMA	8	186
P(TMSPMA- <i>stat</i> -PFDA)	$\frac{8 \times 8 \times 0.92 + 13 \times 8 \times 0.08 + 2}{8 \times 0.92} = 9.4$	$\frac{186 \times 8 \times 0.92 + 518 \times 8 \times 0.08 + 78}{8 \times 0.92} = 241.6$

Moreover, the grafting yield, which corresponds to the fraction of silane grafted onto silica, can be calculated using following equation:

$$\text{Grafting yield (\%)} = \frac{\text{grafting density}}{[\text{silane}]_x} \times 100 \quad (7)$$

where $[\text{silane}]_x$ ($\mu\text{mol}\cdot\text{m}^{-2}$) is the initial concentration of silane, which is not hydrolyzed yet, and can be calculated using the following equation:

$$[\text{silane}]_x = \frac{m_x}{m_{\text{silica}} \times S \times M_x}$$

$$x = \text{copolymer} \quad M_x = \frac{\overline{M}_n}{\text{number of silane units}} = \frac{186 \times 8 \times 0.92 + 518 \times 8 \times 0.08 + 78}{8 \times 0.92} = 304 \text{ g.mol}^{-1} \quad (8)$$

$$x = \text{TMSPMA} \quad M_x = M_{\text{TMSPMA}} = 248 \text{ g.mol}^{-1}$$

where m_x and m_{silica} are the weight of TMSPMA or P(TMSPMA-*stat*-PFDA) and the weight of silica added before reaction. M_x corresponds to the molecular weight of TMSPMA with their three OMe groups. The grafting density was also determined by thermogravimetric analysis using equation (9):

$$\text{Grafting density } (\mu\text{mol.m}^{-2}) = \frac{\left(\frac{W_{60-730}}{100 - W_{60-730}} \right) \times 100 - W_{\text{silica}}}{M_{\text{silane}} \times S \times 100} \times 10^6 \quad (9)$$

where W_{60-730} is the weight loss from 60 to 730°C, corresponding to the degradation of the silane and W_{silica} is the weight loss of silica before grafting ($W_{\text{silica}}=2.51\%$). All the results of TGA and elemental analysis on silane grafting are summarized in Table 2.

For TMSPMA, the grafting density ranged from 0.07 to 1.37 and from 0.10 to 0.90 $\mu\text{mol.m}^{-2}$ by elemental and thermogravimetric analysis respectively. In a previous study of Bourgeat-Lami et al. similar results were obtained for a silane concentration of 20 $\mu\text{mol.m}^{-2}$ using silica with a specific area of 228 $\text{m}^2.\text{g}^{-1}$.¹⁴ Although, it is difficult to compare these values since hypothesis made for calculation differs regarding to the authors (i.e. molar mass and number of carbon atoms of the grafted silane). Moreover different silica grades are commercially available and bear different specific area. The solvent nature has a greater influence on TMSPMA grafting reaction than temperature and catalyst, meaning that good dispersion of

silica favors the reaction onto silica surface. Indeed, among the three experimental protocols, the highest weight loss of 5.52% and the highest carbon content were observed in toluene using the C-method (Table 2, run 3). Thus, this experimental protocol was selected for the grafting of P(TMSPMA-*stat*-PFDA).

Table 2: TGA and elemental analysis of TMSPMA and of copolymer grafted silica nanoparticles using different experimental methods.

Run	Silane	Silane / silica weight ratio	[silane] _s (μmol.m ⁻²)	Elemental analysis			Thermogravimetric analysis		
				Carbon content (%)	Grafting density (μmol.m ⁻²)	Grafting yield (%)	Weight loss (%)	Grafting density (μmol.m ⁻²)	Grafting yield (%)
1 ^{a)}	TMSPMA	1.13	22.80	0.94	0.50	2.19	3.79	0.38	1.69
2 ^{b)}	TMSPMA	1.13	22.80	0.13	0.07	0.30	2.81	0.10	0.45
3 ^{c)}	TMSPMA	1.13	22.80	2.5	1.37	6.00	5.52	0.90	3.93
4 ^{a)}	P(TMSPMA- <i>stat</i> -PFDA)	0.38	6.60	3.42	1.63	24.76	7.83	1.24	18.74
5 ^{a)}	P(TMSPMA- <i>stat</i> -PFDA)	0.77	12.66	3.76	1.81	14.32	8.65	1.44	11.38
6 ^{a)}	P(TMSPMA- <i>stat</i> -PFDA)	1.50	23.48	4.31	2.10	8.96	8.92	1.51	6.42
7 ^{a)}	P(TMSPMA- <i>stat</i> -PFDA)	2.26	33.83	4.60	2.26	6.69	9.82	1.73	5.12
8 ^{a)}	P(TMSPMA- <i>stat</i> -PFDA)	4.15	59.63	4.38	2.14	3.59	9.20	1.67	2.80

^{a)} in acetone/H₂O/maleic anhydride at 60°C.

^{b)} in ethanol/H₂O/acetic acid at 70°C.

^{c)} in toluene at 110°C.

Figure 6 represents the TGA curves of initial silica and of copolymer grafted silica with various silane concentrations. The TGA measurement of unreacted silica with a weight loss of around 2.51% was due to the loss of water molecules absorbed onto the surface. Different TGA studies provided informations on the relative amounts of grafted copolymer (Table 2, runs 4-8). The weight loss was caused by the decomposition of P(TMSPMA-*stat*-PFDA) with degradation temperature close to 400°C. For example, for P(TMSPMA-*stat*-PFDA)/silica weight ratio=0.77 the weight loss was about 6% ($W_{P(TMSPMA-*stat*-PFDA)}(60-730) - W_{silica} = 8.65 -$

2.51) (Table 2, run 5) corresponding to a grafting yield of 11.38 %. The highest weight loss of 9.82 % was measured for a silane concentration of 33.83 $\mu\text{mol.m}^{-2}$ (Table 2, run 7).

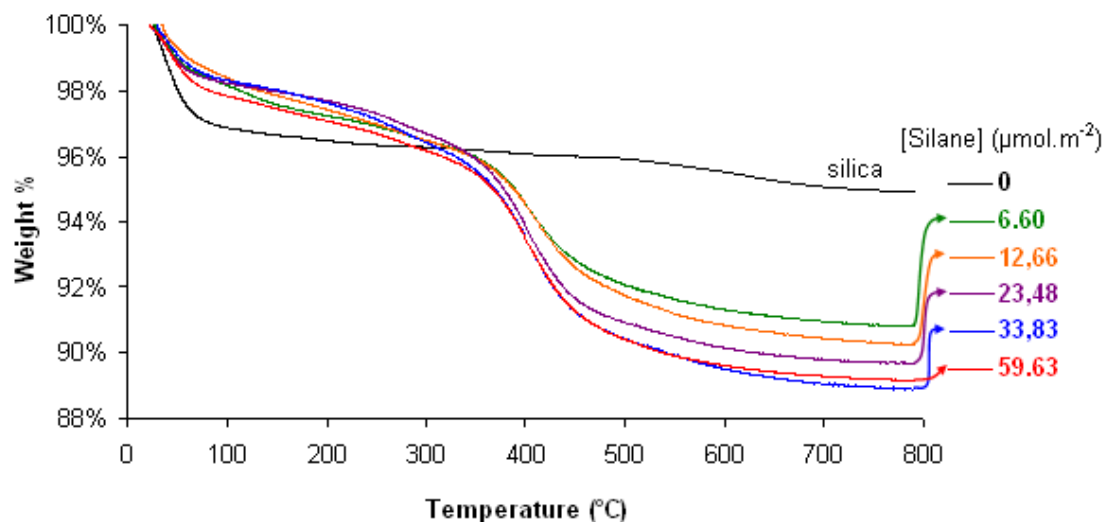


Figure 6: TGA curves of silica nanoparticles grafted by P(TMSPMA-*stat*-PFDA).

To find optimum grafting conditions, increasing amounts of copolymer were added to the silica (Table 2, runs 4-8). Figure 7 represents the grafting density (determined by elemental analysis) and the grafting yield as a function of the copolymer/silica weight ratio. The grafting density increases while increasing the copolymer/silica weight ratio until a plateau value at 2.26 $\mu\text{mol.m}^{-2}$. In parallel the grafting yield coherently decreased due to steric effects appearing on the silica surface. Beyond this limit, the supplementary added silane enhanced the unreacted reactant amount and decreased the grafting yield. Although, grafting density values were probably overestimated since one cannot quantify precisely the quantity of unreacted silane groups. In the case of P(TMSPMA-*stat*-PFDA) the low chemical compatibility of hydrophobic PFDA with silica particles doesn't seem to be the main reason

of the low grafting density because in the same grafting experimental conditions similar results were observed in the case of TMSPMA which didn't contain fluorinated part (Table 2, run 3 and 6). In our case, steric hindrance effects cannot explain this partial grafting since monomers and cotelomers with low molecular weights were used. Consequently the main explanation could be that the grafting is kinetically limited by chain diffusion with this type of particle.

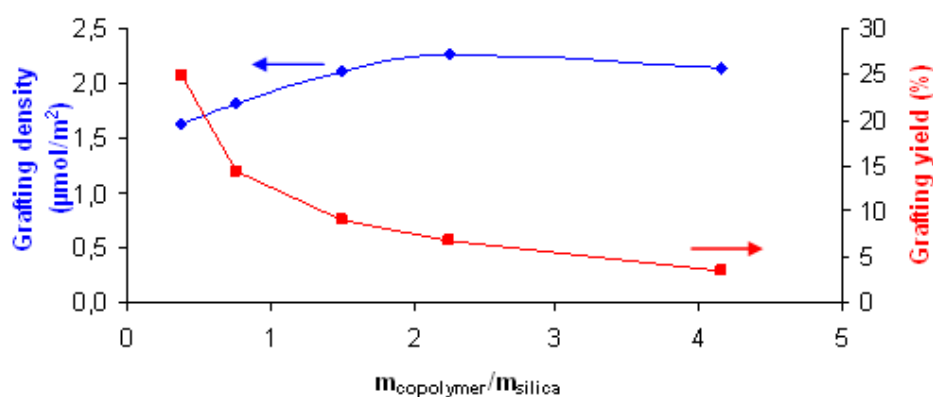


Figure 7: Grafting density and grafting yield versus cotelomer/silica weight ratio.

For P(TMSPMA-*stat*-PFDA) the grafting density values obtained by elemental analysis and by TGA are in good agreement (Figure 8). TGA values were lower than those obtained by elemental analysis. This can be explained by the use of the molecular weight value of the grafted cotelomer in the TGA calculation while Fontanille et al. have shown that one should only consider the molecular weight of the grafted silane without their silicon atoms because they stayed on the silica particles after the thermal degradation.³² Indeed, it has been shown that thermal degradation of TMSPMA proceeds as follows: at the first stage of degradation, a cleavage of C-O bonds (methacrylic acid loss) is observed and followed by the cleavage of Si-

C bonds (allylic radical loss). Considering that the mechanism could be the same for the copolymer, we should use the molar mass corresponding to $\text{CH}_2\text{-C}(\text{CH}_3)\text{-COCH}_2\text{CH}_2$ unit.

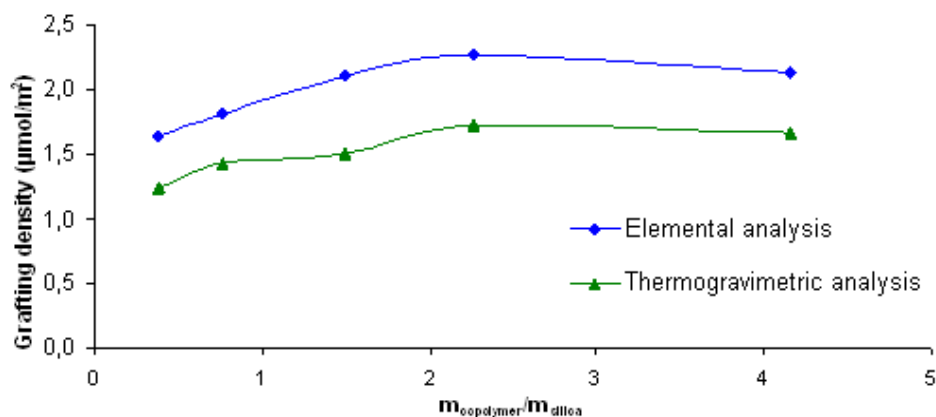


Figure 8: Comparison of copolymer grafting density values obtained by elemental analysis and thermogravimetric analysis.

Conclusions

P(TMSPMA-*stat*-PFDA) cotelomers were successfully synthesized by radical telomerization controlling the molecular weight and incorporating around 10% of fluorinated monomer. The latter provides hydrophobic property whereas the further grafting onto silica nanoparticles was realized from TMSPMA. In a preliminary study the optimal conditions of grafting were calculated and some details were explained on the calculations of silane/silica weight ratio which were little explained in the literature. Modification of silica surface by cotelomers was qualitatively checked by FTIR and ^{29}Si solid-state NMR analyses and various organosilane species were detected. Moreover grafting density in cotelomers was quantified by thermogravimetric and elemental analyses with similar values. A maximum grafting density value has been observed while increasing the silane/silica weight ratio. As to the potential

uses, such hydride nanocomposites can be considered as building blocks to fabricate more complex nanomaterials using the reactive polymer end-chains.

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References

- 1-H. Zou, S. Wu, J. Shen. *Chem. Rev.* 2008, 108, 3893.
- 2-N. Tsubokawa. *Pol. J.* 2007, 39, 983.
- 3-J.-M. Yeh, C.-J. Weng, W.-J. Liao, Y.-W. Mau. *Surface Coatings Technol.* 2006, 201, 1788.
- 4-E. Bourgeat-Lami, N. Negrete Herrera, J.-L. Putaux, A. Perro, S. Reculosa, S. Ravaine, E. Duguet. *Macromol. Symp.* 2007, 248, 213.
- 5-J. Parvole, G. Laruelle, C. Guimon, J. François, L. Billon. *Macromol. Rapid Commun.* 2003, 24, 1074.
- 6-D.-M. Qi, Y.-Z. Bao, Z.-X. Wenig, Z.-M. Huang. *Polymer* 2006, 47, 4622.
- 7-T. H. Zhou, W. H. Ruan, J. L. Yang, M. Z. Rong, M. Q. Zhang, Z. Zhang. *Compos. Sci. and Technol.* 2007, 67, 2297.
- 8-G. K. Raghuraman, J. Ruhe, R. Dhamodharan. *Journal of Nanoparticle Research* 2008, 10, 415.
- 9-N. Tsubokawa, T. Kimoto, T. Endo. *Polym. Bull.* 1994, 33, 187-194.
- 10-Q. Zhou, S. Wang, X. Fan, R. Advincula, J. Mays. *Langmuir* 2002, 18, 3324-3331.
- 11-M. Joubert, C. Delaite, E. Bourgeat-Lami, P. Dumas. *J. Polym. Sci., Part A: Polym. Chem.* 2004, 42, 1976-1984.
- 12-Y.-P. Wang, X.-W. Pei, X.-Y. He, K. Yuan. *Eur. Pol. J.* 2005, 41, 1326.
- 13-S. Blomberg, S. Ostberg, E. Harth, A. W. Bosman, B. V. Horn. *J. Polym. Sci., Part A: Polym. Chem.* 2002, 40, 1309.
- 14-C. Bartholome, E. Beyou, E. Bourgeat-Lami, P. Chaumont, F. Lefebvre N. Zydowicz. *Macromolecules* 2005, 38, 1099.
- 15-B. Bailly, A.-C. Donnenwirth, C. Bartholome, E. Beyou, E. Bourgeat-Lami. *Journal of nanomaterials* 2006, 1, 76371.
- 16-H. Sawada, A. Sasaki, K. Sasazawa, K.-I. Toriba, H. Kakehi, M. Miura, N. Iso. *Polym. Adv. Technol.* 2008, 19, 419.
- 17-Y.-C. Sheen, Y.-C. Huang, C.-S. Liao, H.-Y. Chou, F.-C. Chang. *J. Polym. Sci., Part B: Polym. Phys.* 2008, 46, 1984.
- 18-F. Pardal, V. Lapinte, J.-J. Robin. *Eur. Pol. J.* 2009, 45, 1198.
- 19-C. Boyer, G. Boutevin, J.-J. Robin, B. Boutevin. *J. Polym. Sci. Part A: Polym. Chem.* 2007, 45, 395-415.
- 20-C. Boyer, G. Boutevin, J.-J. Robin, B. Boutevin. *Polymer* 2004, 45, 7863.
- 21-M. Teodorescu, M. Dimonie, I. Cerchez. *Eur. Pol. J.* 1999, 35, 247.
- 22-B. Boutevin. *J. Polym. Sci. Part A: Polym. Chem.* 1990, 38, 3235.
- 23-F. Bauer, H. Ernst, U. Decker, M. Findeisen, H.-J. Gläsel, H. Langguth, E. Hartmann, R. Mehnert, C. Peuker. *Macromol. Chem. Phys.* 2000, 201, 2654.
- 24-H.-J. Gläsel, F. Bauer, H. Ernst, M. Findeisen, E. Hartmann, H. Langguth, R. Mehnert, R. Schubert. *Macromol. Chem. Phys.* 2000, 201, 2765.
- 25-F. Bauer, H.-J. Gläsel, U. Decker, H. Ernst, A. Freyer, E. Hartmann, V. Sauerland, R. Mehnert, C. Peuker. *Progress in Organic Coatings* 2003, 47, 147.
- 26-F. Bauer, R. Flyunt, K. Czihal, M. R. Buchmeiser, H. Langguth, R. Mehnert. *Macromol. Mat. Eng.* 2006, 291, 493.
- 27-F. Bauer, V. Sauerland, H.-J. Gläsel, H. Ernst, M. Findeisen, E. Hartmann, H. Langguth, B. Marquardt, R. Mehnert. *Macromol. Mat. Eng.* 2002, 287, 546.
- 28-M. Du, Y. Zheng. *Polymer composites* 2007, 28, 198.
- 29-C. Bartholome, E. Beyou, E. Bourgeat-Lami, P. Chaumont, N. Zydowicz. *Macromolecules* 2003, 36, *Macromolecules*
- 30-J. Du, Y. Chen. *Macromolecules* 2004, 37, 6322.
- 31-E. Bourgeat-Lami, P. Espiard, A. Guyot. *Polymer* 1995, 36.

32-M. Abboud, M. Turner, E. Duguet, M. Fontanille. *J. Mater. Chem.* 1997, 7, 1527

Graphical Abstract

After the free-radical cotelomerization of 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) with perfluorodecylacrylate (PFDA) in the presence of 2-mercaptoethanol, the P(TMSPMA-*stat*-PFDA) cotelomers, containing fluoro and silane groups, were grafted onto silica nanoparticles. The article focuses on the characterization of the structure of the modified silica by FTIR and ^{29}Si solid-state NMR as well as the detailed calculations of the amount of grafted P(TMSPMA-*stat*-PFDA) from thermogravimetric and elemental analyses.

