

Synthesis and Characterization of Poly(methyl methacrylate)-Grafted Silica Microparticles

Daniel Derouet, Chi Nhan Ha Thuc

LCOM - Chimie des Polymères (UMR du CNRS UCO2M N°6011), Université du Maine, Faculté des Sciences, Avenue Olivier Messiaen, 72085 LE MANS Cedex 9, France

Received 18 July 2007; accepted 20 December 2007

DOI 10.1002/app.28290

Published online 2 May 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A procedure to synthesize poly(methyl methacrylate)-grafted silica microparticles was developed by using radical photopolymerization of methyl methacrylate (MMA) initiated from *N,N*-diethyldithiocarbamate (DEDT) groups previously bound to the silica surface (grafting "from"). The functionalization of silica microparticles with DEDT groups was performed in two steps: introduction of chlorinated functions onto the surface of silica particles, and then nucleophilic substitution of chlorines by DEDT functions via a S_N2 mechanism. The study was performed with a Kieselgel[®] S silica which was initially chlorinated in surface, either by direct chlorination of silanols with thionyl chloride, or by using a condensation reaction between silanols and a chlorofunctional trialkoxysilane reagent, 4-(chloromethyl)phenyltrimethoxysilane and chloromethyltriethoxysilane, respectively. Three types of DEDT-functionalized

silica microparticles were prepared with a good control of the reactions, and then characterized by solid-state ¹³C and ²⁹Si CP/MAS NMR. Their ability to initiate MMA photopolymerization was studied. The kinetics of MMA photopolymerization was followed by HPLC and ¹H-NMR. Whatever the silica used the grafting progresses very slowly. On the other hand, the conversion of MMA in PMMA grafts is depending on the structure of the DEDT-functionalized Kieselgel[®] S used. Poly(methyl methacrylate)-grafted silica microparticles bearing high length grafts (\overline{DP}_n about 100) were synthesized. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2113–2127, 2008

Key words: silicas; modification; photopolymerization; composites; reinforcement; surface; grafting; *N,N*-diethyldithiocarbamate initiating groups; CP/MAS NMR

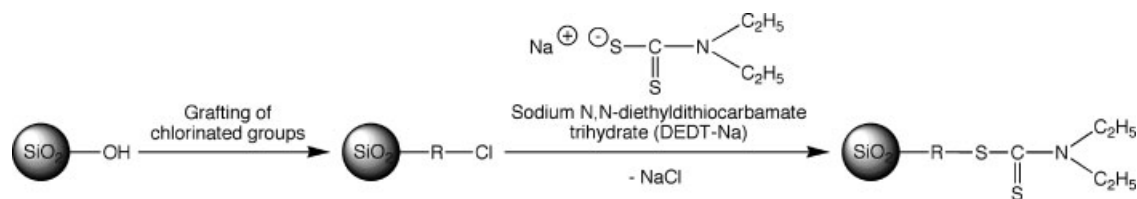
INTRODUCTION

During last years, the surface modification of silica substrates with covalently bound organic functional groups or polymers (polymer brushes) knew a growing interest to prepare new hybrid organo-inorganic silicon materials for various practical applications. In general, the modification involves a reaction between the Bronsted acidic silanols at the silica surface with chloro or alkoxy silanes.¹ This was often used to change the characteristics and properties of silica surfaces such as biocompatibility, wetting, adhesion, and friction, but also to introduce specific organic functional groups for numerous applications, for instance in the fields of chromatography, removal of heavy metals, reinforcement of rubber and composite materials, chemical sensors.

The grafting of polymers onto silica surface is of interest because of the potential applications in colloidal stabilization,² lithography,³ biocompatibility,⁴ and organic-inorganic hybrid micro(nano)composites.^{5,6} Covalent linking of polymer chains onto

silica surface can be achieved by "grafting to" or by "grafting from."⁷ "Grafting to" method involves either the condensation between end-functionalized polymer macromolecules and appropriate functions present on the silica surface,^{8–11} either the propagation of growing chains through polymerizable functions covalently bound to the silica surface.^{12–17} These two approaches lead in general to nonuniform thin films and low surface grafting densities because chemisorption of the first fraction of chains hinders the diffusion of the following ones towards the surface for further linking.¹⁸ "Grafting from" technique, which consists to initiate a monomer polymerization from initiating groups bound to the silica surface is expected to lead to higher surface grafting densities, because monomers can more easily diffuse towards the reactive center. This technique was extremely successful to synthesize polymer-grafted silicas with high and controlled surface grafting densities. It was commonly used to obtain covalently bound vinyl polymers by polymerization chemistry in conjunction with surface-bound initiators. Some works deal with the use of cationic polymerization,^{19,20} but the mainly developed procedures are based on radical polymerization. Conventional radical polymerization of vinyl monomers from radicals created at the silica surface after thermal decomposition of azo groups

Correspondence to: D. Derouet (daniel.derouet@univ-lemans.fr).



Scheme 1 Synthesis of DEDT-functionalized silica microparticles.

previously bound to the solid surface was at first considered.^{21–23} This way was widely investigated by Tsubokawa and coworkers which tested various thermosensitive species: azo,^{24–28} peroxyester,²⁹ or peroxycarbonate³⁰ groups, able to be broken down with formation of radicals on the silica surface. In the above radical grafting systems, polymerization is initiated by both surface and fragment radicals formed by decomposition of azo and peroxide groups on the surface, so leading to production of ungrafted polymer. γ -irradiation was also used to initiate polymerization from silica surface.³¹ On the other hand, it was reported that photopolymerization of vinyl monomers could be initiated by systems consisting of trichloroacetyl groups on the surface with transition metal such as $\text{Mo}(\text{CO})_6$ and $\text{Mn}_2(\text{CO})_{10}$.^{32–34} More recently, photopolymerization of vinyl monomers was initiated from eosin moieties linked to silica surface in presence of ascorbic acid as reducing agent.³⁵ Higher grafting efficiencies and densities were observed with these systems based on photopolymerizations initiated from silica surface by comparison with the polymerizations initiated by thermal decomposition of azo or peroxide groups, because they occur without formation of fragment radicals. *In situ* radical transfer addition polymerization³⁶ and emulsion polymerization³⁷ from silica nanoparticles were also reported, as well as polymer grafting onto colloid silica surface.³⁸ To achieve a better control of molecular weight and molecular weight distribution, and to synthesize new polymer grafts like block copolymer ones, controlled/living radical polymerization methods including nitroxide-mediated free radical polymerization (TEMPO),^{18,39–44} atom transfer radical polymerization (ATRP),^{45–65} and reverse ATRP⁶⁶ were developed.

In the early 1980s, Otsu et al.^{67–71} described a new living-like method for the radical polymerization of vinyl monomers such as styrene and methyl methacrylate (MMA). The polymerization that proceeds under UV irradiation is initiated by dithiocarbamate compounds described as photoiniferters, which mean that they act as an initiator, transfer agent, and terminator. The concept of these nonconventional initiators is based on the formation of a reactive radical and a relatively stable counter radical, where the latter does not participate in the initiation, but merely acts as a transfer agent and termination

species (iniferter). Only few examples of graftings of polymers on silica based on Otsu's work were related in literature. They concern mainly photo-graft-polymerizations performed onto glass surface and initiated from *N,N*-diethyldithiocarbamate (DEDT) groups bound to glass surface.^{48,72–74} The controlled synthesis of polymer-grafted silica (micro)particles with the use of iniferters was less explored.⁷⁵

In the present article, the purpose is to investigate the synthesis of poly(methyl methacrylate)-grafted silica (PMMA-grafted silica) microparticles by using a "grafting from" approach based on Otsu's work, to favor the grafting compared to the undesirable formation of homopolymers.^{67–71} The objective was to initiate radical photopolymerization of MMA from various types of DEDT groups covalently bound to the surface of silica particles. First time, a procedure to synthesize DEDT-functionalized silica microparticles was developed starting from a precipitated Kieselgel[®] S. It consisted to use a two-step reaction: by introduction of chlorinated functions onto the surface of silica particles, followed by nucleophilic substitution of chlorines by DEDT functions via a $\text{S}_{\text{N}}2$ substitution mechanism (Scheme 1). Three types of DEDT-functionalized Kieselgel[®] S were synthesized, and the ability of every type of DEDT function to initiate the MMA photopolymerization was studied and compared. The objective was also to give a precise characterization of the synthesized DEDT-functionalized silica microparticles and to reach a good control of the DEDT group density, as well as that of PMMA-grafted silica particles formed. Solid-state ¹³C and ²⁹Si CP/MAS NMR were used for the product characterization.

EXPERIMENTAL

Materials

Toluene, dichloromethane, ethyl acetate, ethanol, and methanol were purified according to classical methods and re-distilled before use. 4-(chloromethyl)phenyltrimethoxysilane (90% purity, $E_{\text{b}10} = 134\text{--}143^\circ\text{C}$), chloromethyltriethoxysilane (95% purity, $E_{\text{b}33} = 90^\circ\text{C}$), thionyl chloride (99.5% purity, $E_{\text{b}97} = 20^\circ\text{C}$), chlorotrimethylsilane, sodium *N,N*-diethyldithiocarbamate trihydrate (DEDTNa),

bromobutane, and mesitylene were commercial products used as received without further purification. MMA (Aldrich) was carefully distilled under reduced pressure before use ($E_{b_{29 \text{ mmHg}}} = 20^\circ\text{C}$).

Precipitated Kieselgel S (Riedel-de-Haën) with particle size of 63–200 μm , specific surface area of 480 m^2/g , and surface silanol group concentration of 5.6 $\mu\text{mol}/\text{m}^2$, was dried for 24 h at 120°C under vacuum (10^{-2} mbar) before use.

Chlorination of silica microparticles

Chlorination at the surface of silica microparticles was carried out in a Teflon tube fitted with a magnetic stirrer. In a dry nitrogen atmosphere glove box, 2 mL of thionyl chloride (0.03 mol) were added to 2 g of silica particles dispersed in 20 mL of toluene, and the tube was closed. The mixture was magnetically stirred for 24 h in an oil bath thermostated at 110°C. Afterwards, the mixture was extracted with ethyl acetate using a Soxhlet for 24 h, then dried at 40°C under 10^{-2} mbar vacuum for 24 h.

Grafting of chlorofunctional groups onto silica particles

4-(chloromethyl)phenyl[or chloromethyl]-functionalized silicas were prepared under nitrogen atmosphere. In a dry nitrogen atmosphere glove box, 2 g of silica particles dispersed in 20 mL of toluene and trialkoxysilane reagent [4-(chloromethyl)phenyltrimethoxysilane or chloromethyltriethoxysilane] in excess by comparison with silica silanols were placed in a teflon tube successively, and the tube was closed. The mixture was magnetically stirred for 24 h in an oil bath thermostated at 110°C. Afterwards, the mixture was extracted with dichloromethane using a Soxhlet for 48 h, then dried at 40°C under 10^{-2} mbar vacuum for 24 h. Samples were taken at the beginning and the end of the reaction to calculate the rate of chlorinated reactive functions bound onto silica surface (expressed in number of reactive functions per gram of silica), by using $^1\text{H-NMR}$.

Synthesis of DEDT-functionalized silica particles

One gram of 4-(chloromethyl)phenyl[or chloromethyl, or chloro]-functionalized silica and 0.6 g of DEDTNa (2.8 mmol) in 20 mL of ethanol were placed in a 50-mL round-bottom flask. The mixture was magnetically stirred for 92 h at room temperature. Samples were taken at different reaction times, and then analyzed by HPLC to follow the progress of the reaction. After reaction, the mixture was extracted with methanol using a Soxhlet, then dried for 24 h at 40°C under 10^{-2} mbar vacuum.

The progress of the reaction was followed by back titration of residual DEDTNa. 1 mL of reactional mixture was introduced in 25 mL of a solution precisely composed of 0.5 g of *n*-BuBr, 3.5 g of mesitylene used as internal reference, and 100 mL of CH_3OH . The mixture was stirred in the darkness for 24 h, then HPLC analysis was performed using a 70 : 30 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ mixture as mobile phase.

Photopolymerization of MMA initiated from DEDT groups covalently bound to silica particles

MMA photopolymerizations were carried out in toluene under nitrogen atmosphere, and at room temperature. Eleven grams of MMA (0.11 mol) in 25 mL of toluene were introduced in a 250 mL Pyrex reactor containing a quantity of DEDT-functionalized silica microparticles calculated to obtain PMMA grafts of theoretical \overline{M}_n equal to 20,000. Air atmosphere was removed out of the reactor and replaced with nitrogen. The magnetically stirred mixture was then irradiated with a 100 W mercury-vapor lamp from Fisher Bioblock Scientific, placed 10 cm away from the reactor wall. Samples were taken off at various times and analyzed by HPLC and $^1\text{H-NMR}$ to determine MMA conversions.

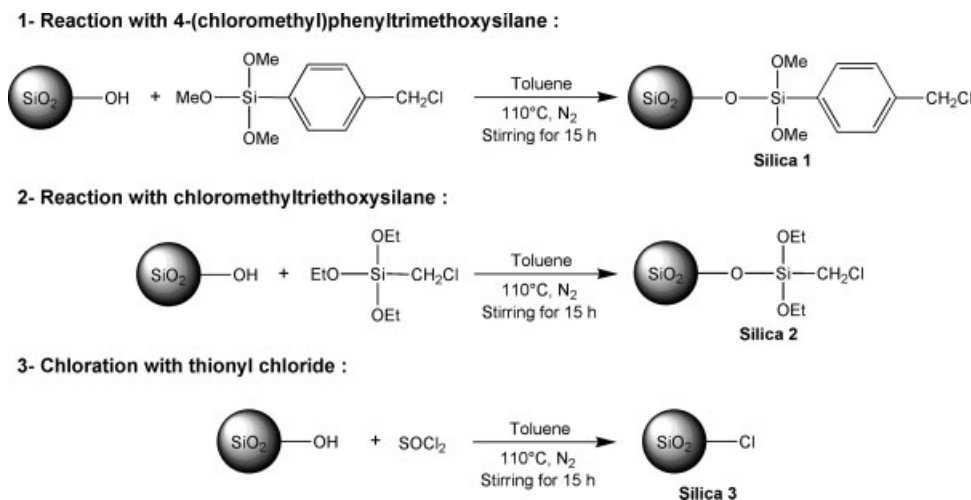
HPLC measurements were carried out as follows. A 10 mg sample was introduced in 1 mL of mobile phase (90 : 10 methanol/water). After filtration, the solution was fractionated by HPLC. MMA conversion was calculated by comparison of the area of residual MMA peak to that of toluene peak, the MMA peak/toluene peak area ratio at t_0 being used as reference for the calculation.

Measurements

Solid-state ^{13}C and ^{29}Si CP/MAS NMR measurements were carried out on a Bruker MSL300 spectrometer. Magic Angle Spinning was performed at 5 kHz spinning rate. For $^{13}\text{C-NMR}$ measurements (at 75.47 MHz), the proton 90° pulse was 3.5 μs , and the contact time 3.5 ms. For $^{29}\text{Si-NMR}$ measurements (at 59.63 MHz), the proton 90° pulse was 3.5–4.4 μs , and the repetition time 2 s. Each NMR spectrum was referred to tetramethylsilane (TMS) as internal reference. Chemical shifts (δ) were given in parts per million (ppm).

Liquid NMR spectra were recorded on a Bruker AC 400 Fourier-transform spectrometer, at 400.13 MHz for ^1H and at 100.61 MHz for ^{13}C . Samples were analyzed in solution in chloroform-*d* (99.8% purity; Spectrométrie Spin et Techniques). In ^1H and $^{13}\text{C-NMR}$, the chemical shifts were expressed in ppm in the δ scale, compared with the singlet of TMS, as internal reference.

Analyses in High Performance Liquid Chromatography (HPLC) were performed on a Waters modu-



Scheme 2 Reactions used to prepare chlorofunctional Kieselgel[®] S.

lar equipment including a Model 510 pump module, a Model U6K injector, an AIT CHROMATO Kromasil C18 column (4.6 mm I.D. \times 15 cm length; particle size = 5 μm ; pore size = 100 \AA), and a double detection system (a Model 996 UV/vis photodiode array spectrophotometer and a Model 410 differential refractometer). System command, data acquisition, and data processing were carried out using a microcomputer equipped with Empower software (Waters). The analyses were performed in isocratic mode with

acetonitrile-water or methanol-water as mobile phase, at a flow rate adjusted to 1 mL min^{-1} .

RESULTS AND DISCUSSION

Functionalization of silica microparticles with DEDT groups

The functionalization of silica microparticles with DEDT groups was considered using a two step procedure:

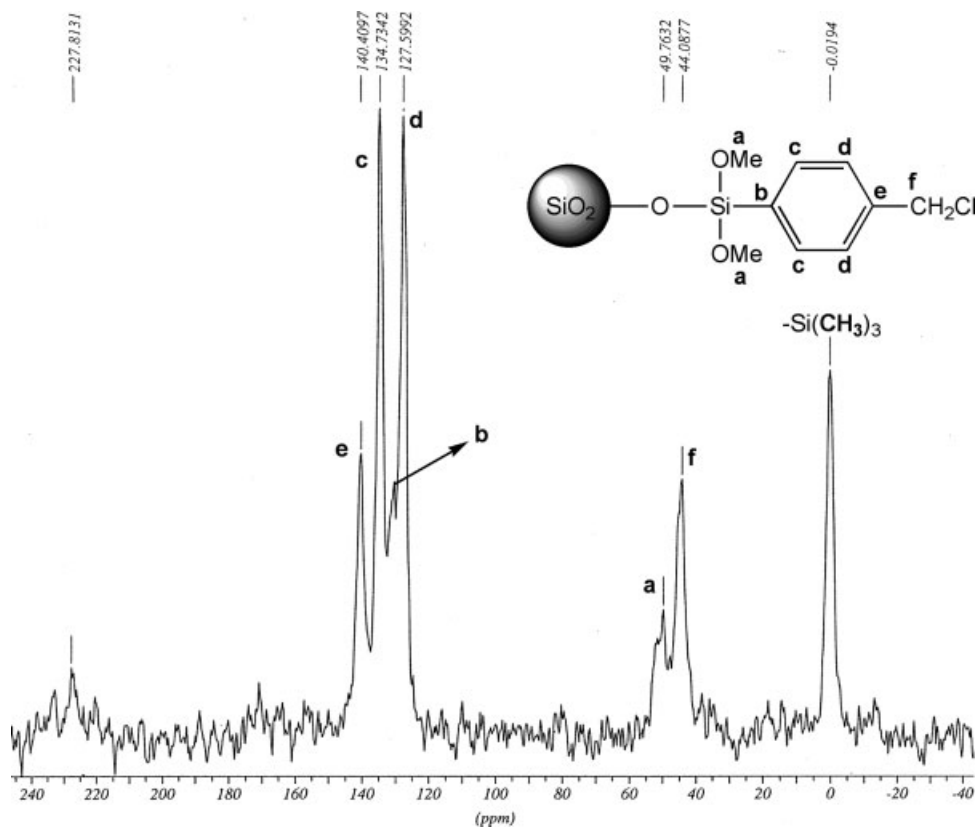


Figure 1 ^{13}C CP/MAS NMR spectrum of Silica 1.

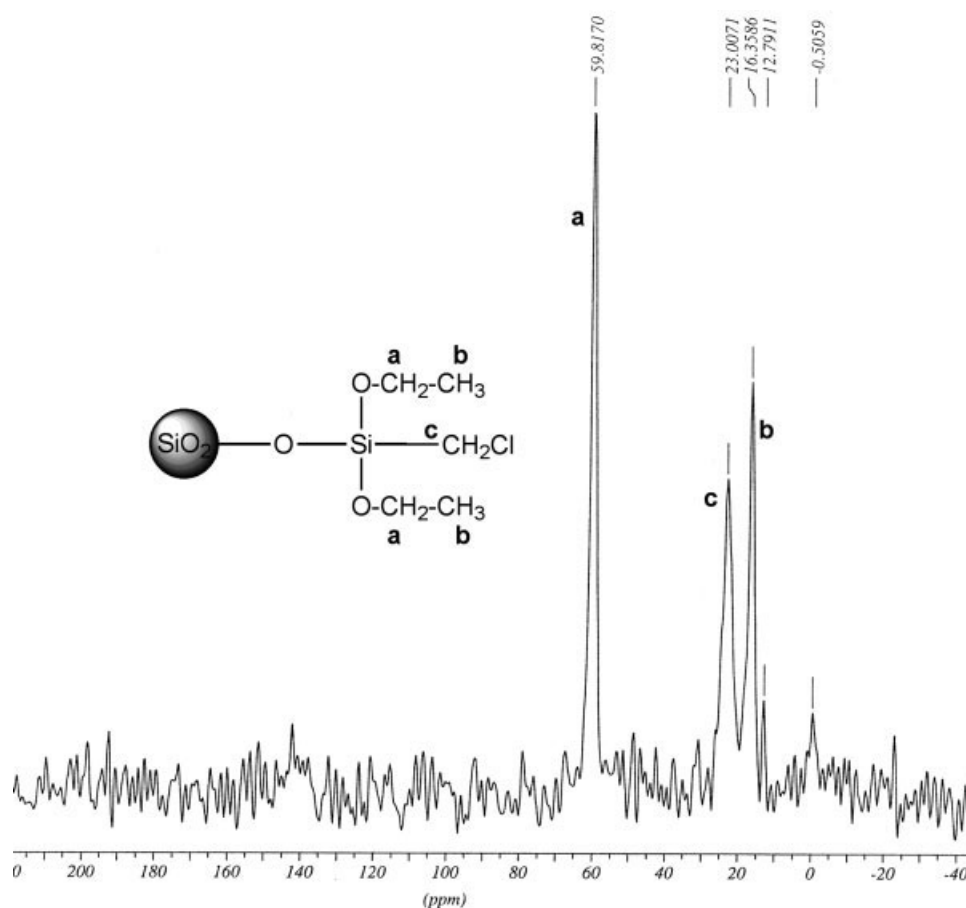


Figure 2 ^{13}C CP/MAS NMR spectrum of Silica 2.

At first, an intermediate functionalization reaction of the silica particles was performed to create functions able to react with DEDT salts to lead to the silica macroiniferter. The purpose was to introduce chlorine atoms at the silica surface of Kieselgel[®] S particles. Because of the well-known reactivity of silanols towards alkoxy-

lane functions,¹ this reaction was considered to insert chlorine atoms by means of trialkoxysilane reagents bearing a chlorofunctional group, 4-(chloromethyl)phenyltrimethoxysilane and chloromethyltriethoxysilane respectively (Scheme 2). Chlorination of silanols by action of thionyl chloride was also considered.

TABLE I
 ^{13}C CP/MAS NMR Analysis of 4-(chloromethyl)phenyl[and Chloromethyl]-Functionalized Kieselgel[®] S:
Chemical Shifts of the Various Carbons

Chlorofunctionalized Kieselgel ^a S	Chemical shifts of the different carbons (δ in ppm)					
	a	b	c	d	e	f
	49.8	131.1	134.7	127.6	140.4	44.1
	59.8	16.4	23.0			

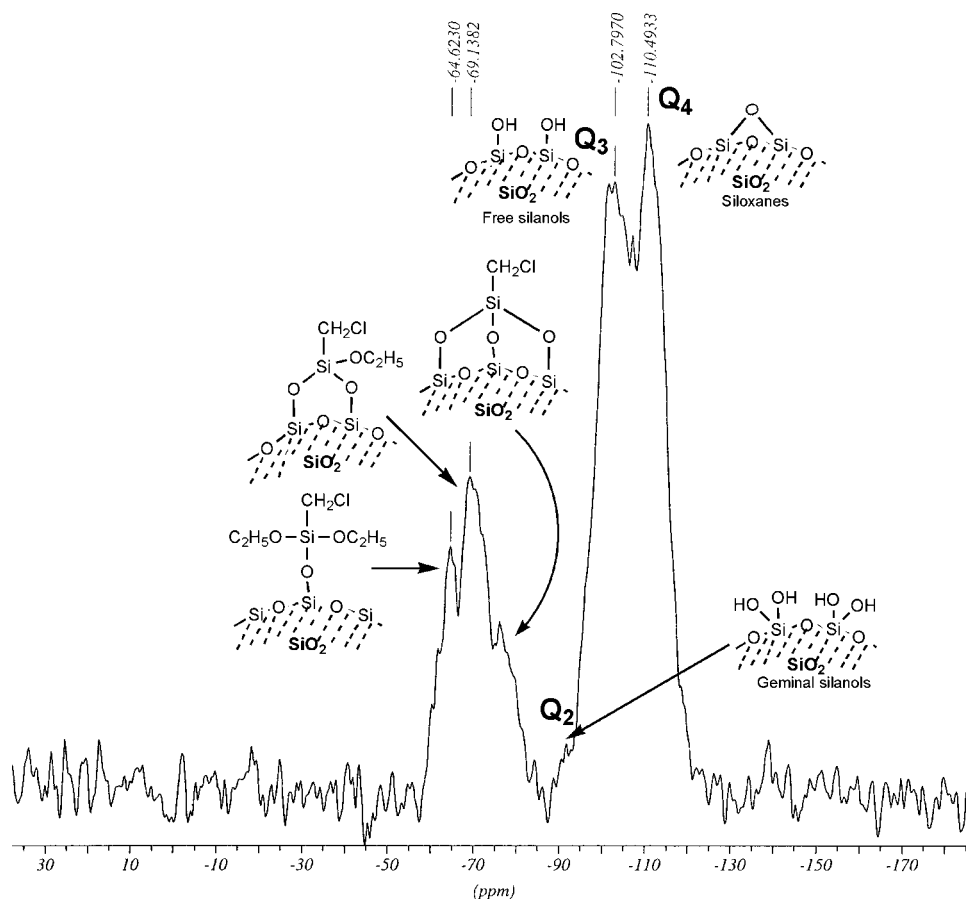


Figure 4 ^{29}Si CP/MAS NMR spectra of Silica 2.

chemical shifts and corresponding assigned structures onto silica surface.⁷⁶ To identify the signals characteristic of the silicons bearing 4-(chloromethyl)phenyl functions (or chloromethyl functions), the spectra of the respective chlorofunctionalized silicas synthesized here were compared with that of the starting Kieselgel[®] S.

In ^{29}Si CP/MAS NMR, the nontreated Kieselgel[®] S shows three signals at $\delta = -90$ ppm, $\delta = -100$ ppm, and $\delta = -109$ ppm, respectively, assigned to Q₂ geminal silanols, Q₃ free silanols, and Q₄ siloxane groups⁷⁶ (Scheme 3).

By comparison with that of the initial nontreated Kieselgel[®] S, the spectra of the chlorofunctionalized

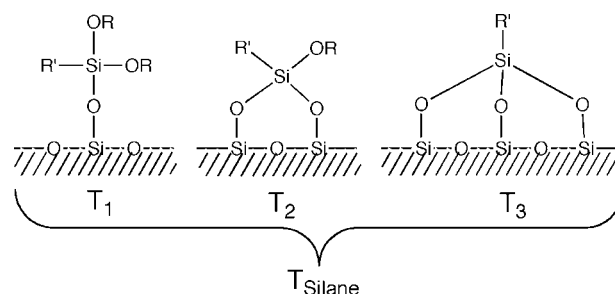
Kieselgel[®] S (Figs. 3 and 4) showed always two groups of signals (Table II):

As expected, the first one, from -90 to -120 ppm, is representative of the silica surface silicon atoms nonmodified during the grafting process. By referring to the siloxane signal, we can note a decrease of the silicon signal characteristic of free silanols and the almost disappearance of the one corresponding to geminal silanols. This showed that grafting mainly involves geminal silanols.

The second group of signals, in the range of $\delta = -50$ ppm to $\delta = -91$ ppm, is significant of the silica functionalization with 4-(chloromethyl)phenyl

TABLE II
 ^{29}Si CP/MAS NMR Analysis of
4-(chloromethyl)phenyl[and Chloromethyl]-
Functionalized Kieselgel[®] S: Chemical Shifts of the
Silicons Support of Chlorofunctional Group in Relation
with the Grafted Structures

Chlorofunctionalized Kieselgel [®] S	T ₁ (ppm)	T ₂ (ppm)	T ₃ (ppm)
4-(chloromethyl)phenyl	-62.5	-70.0	-79.0
Chloromethyl	-64.6	-69.1	-77.5



Scheme 4 Types of grafted structures present at the silica surface.



Scheme 5 Grafting of chlorofunctional groups on silica via two alkoxy functions.

or chloromethyl groups. As deduced from the spectra of the respective chlorofunctionalized silica microparticles synthesized, the reaction of the chlorofunctional trialkoxysilane [4-(chloromethyl)phenyl or chloromethyl] onto silica leads to the formation of three types of grafted structures (Scheme 4, Table II) characterized by as many signals characteristic of silicons bound to chlorofunctional groups, that is bound to silica surface by one, two, or three siloxane bonds. T_{Silane} represents the total concentration in $R'-\text{Si}-\text{O}-\text{Si}$ chlorofunctional groups at the silica surface, T_x that of the respective types of chlorofunctional-grafted structures ($x = 1$: with one siloxane bond, $x = 2$: with two siloxane bonds, $x = 3$: with three siloxane bonds). For **Silica 1**, the three signals characteristic of mono, bi, and tridentate silicons are noted at $\delta = -62.5$ ppm (T_1), $\delta = -70.0$ ppm (T_2), and $\delta = -79.0$ ppm (T_3), respectively, while for **Silica 2** at $\delta = -64.6$ ppm (T_1), $\delta = -69.1$ ppm (T_2), $\delta = -77.5$ ppm (T_3), respectively. The comparison of the area of the signals corresponding to T_1 , T_2 , and T_3 structures, respectively, showed that the grafting of the trialkoxysilane reagents considered in the present study involves mainly two alkoxy functions, more especially in the case of 4-(chloromethyl) phenyltrimethoxysilane. Consequently, it can be supposed that the condensation onto geminal silanols would be favored, which could mean that the formation of bidentate structures would be prevalent (Scheme 5).

On the other hand, the solid-state NMR analyses of the two chlorofunctionalized Kieselgel[®] S showed

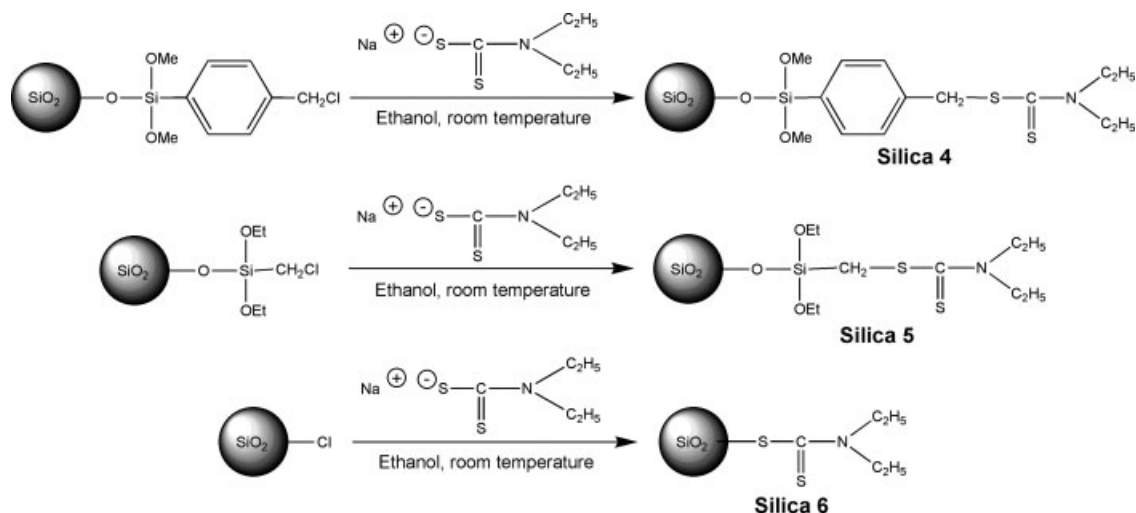
TABLE III
Quantitative Characterization of the Chlorofunctionalized Kieselgel[®] S Synthesized

Chlorofunctionalized Kieselgel [®] S	Number of chlorofunctional groups bound per gram of silica
4-(chloromethyl)phenyl	1.52×10^{-3}
Chloromethyl	1.95×10^{-3}

that the end-capping with chlorotrimethylsilane is only noted in the case of the functionalization with 4-(chloromethyl)phenyltrimethoxysilane. Signals characteristic of trimethylsilyl groups anchored to the silica surface of **Silica 1** were noted at $\delta = 13$ ppm on its ²⁹Si-NMR spectrum (Fig. 3) and $\delta = 0$ ppm on its ¹³C-NMR spectrum (Fig. 1). This can be explained by the big size of 4-(chloromethyl)phenyltrimethoxysilane molecule by comparison with that of chloromethyltriethoxysilane. In addition, the characterization of free silanols on the spectrum (Fig. 3), shows that residual silanols cannot be totally transformed, even after end-capping.

Quantitative characterization of the chlorofunctionalized Kieselgel[®] S

¹H-NMR in solution was used to estimate the content of chlorofunctional groups bound to the surface of silica microparticles (Table III), the area of the signal characteristic of toluene methyl protons being used as a reference for the calculation. The comparison of the ¹H-NMR spectrum of the sample taken at the beginning of the reaction with that of the sample taken at the end, that is after 48 h, indicated a decrease of the area of the singlet characteristic of chloromethyl protons (at $\delta = 4.6$ ppm and $\delta = 2.8$ ppm, for the reac-



Scheme 6 DEDT-functionalized silica microparticles prepared from the various chlorofunctionalized Kieselgel[®] S.

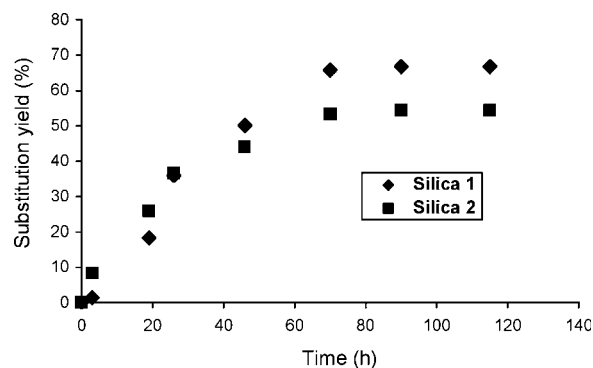


Figure 5 Progress of the nucleophilic substitution yield in the case of **Silica 1** and **Silica 2**. Reaction conditions: 1 g of chlorofunctional silica, 0.6 g (2.8 mmol) of DEDT Na, 20 mL of EtOH.

tions performed with 4-(chloromethyl)phenyltrimethoxysilane and chloromethyltriethoxysilane, respectively) at the end of the reaction. This area decrease confirmed the grafting of part of the trialkoxysilane reagent onto the surface of Kieselgel S.

To calculate the number of chlorofunctional groups bound per gram of silica (F_c), it was considered that two alkoxy silane functions are involved for the grafting of one molecule of trialkoxysilane reagent (Scheme 5). This was supposed because of T2

structures are mainly formed during grafting (Figs. 3 and 4). Consequently, F_c was obtained by applying the following relation that takes into account the weight increase of silica caused by the grafting of the chlorofunctional trialkoxysilane:

$$F_c = \frac{n_c}{m + n_c(M_{\text{alkoxysilane}} - 2M_{\text{ROH}})}$$

in which:

- m is the weight (in gram) of Kieselgel[®] S used for the reaction.
- n_c is the number of chlorofunctional trialkoxysilane molecules grafted onto Kieselgel[®] S at the end of the reaction (determined by ¹H-NMR).
- $M_{\text{alkoxysilane}}$ is the molecular weight of the chlorofunctional trialkoxysilane.
- M_{ROH} is the molecular weight of the alcohol formed during reaction.

The results summarized in Table III show that, after 48 h of reaction between 30 mmol of alkoxy silane and Kieselgel[®] S (initial weight = 2 g), the numbers of 4-(chloromethyl)phenyl and chloromethyl functions grafted per gram of silica were of the same order of magnitude: 1.52×10^{-3} and 1.95×10^{-3} mol, respectively.

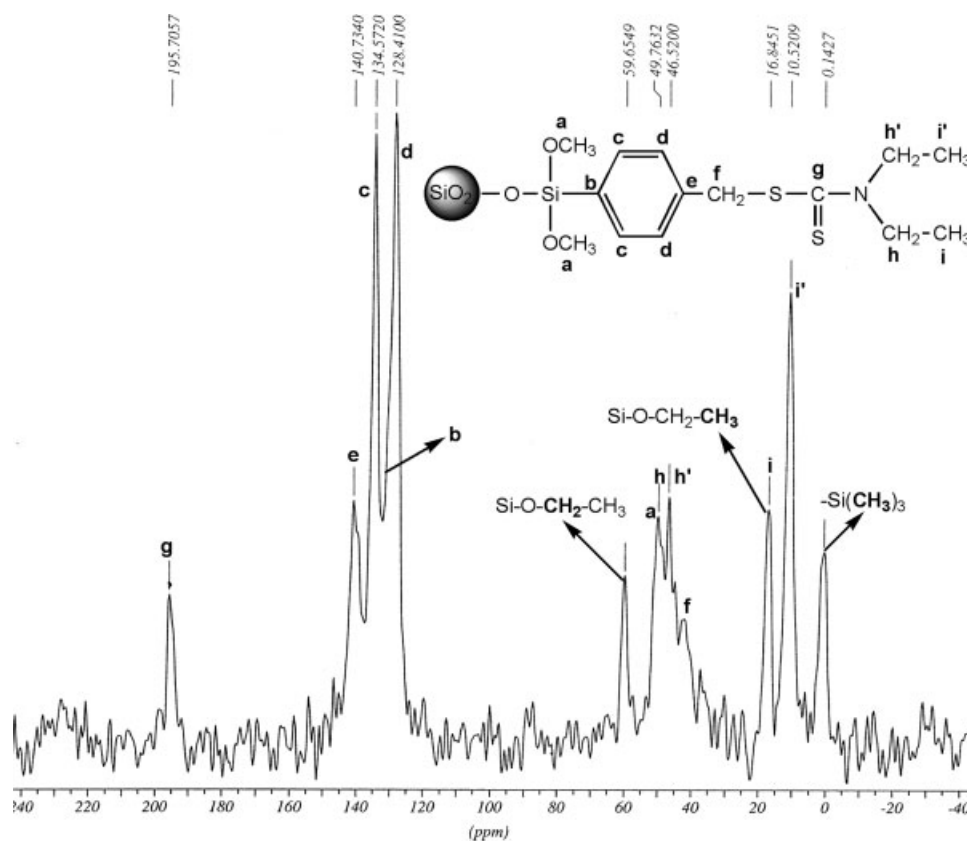


Figure 6 ¹³C CP/MAS NMR spectrum of **Silica 4**.

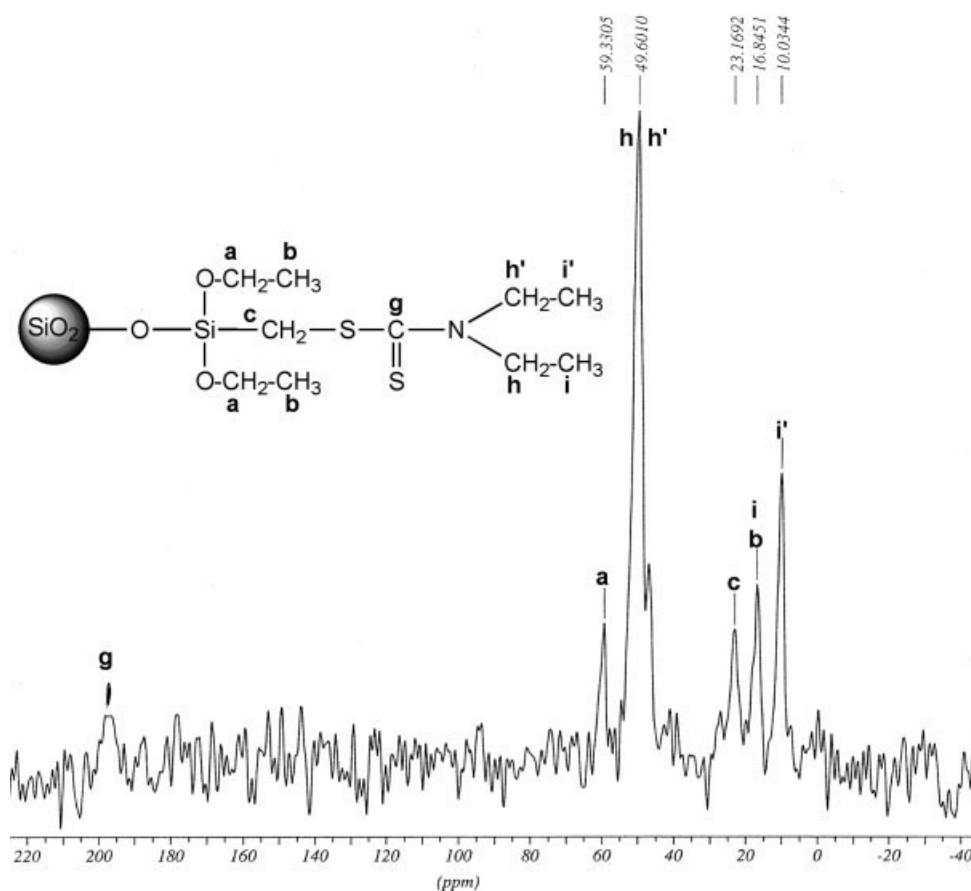


Figure 7 ^{13}C CP/MAS NMR spectrum of **Silica 5**.

In addition to the chlorofunctionalized silicas prepared by condensation of chlorofunctional trialkoxy-silane reagents with silanols of Kieselgel[®] S, chlorinated silica microparticles (**Silica 3**) were also prepared by chlorination of Kieselgel[®] S with thionyl chloride, introduced in large excess by comparison with silanols.

Grafting of DEDT groups onto chlorofunctionalized silica particles

Grafting of DEDT groups onto silica particle surface was performed according to a $\text{S}_{\text{N}}2$ substitution mechanism, by reaction of DEDTNa upon chlorine atoms of **Silica 1**, **Silica 2**, and **Silica 3**, respectively, (Scheme 6). The reactions were carried out in ethanol at room temperature.

Determination of grafting rate by measurement of residual DEDTNa by HPLC

The progress of the reactions performed on **Silica 1** and **Silica 2** was followed by isocratic HPLC using 70 : 30 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ mixture as mobile phase. Because DEDTNa is eluted at the dead volume, the

rate of DEDT anchored onto the silica particles were determined by back titration of the residual DEDTNa. Residual DEDTNa was transformed in *n*-butyl DEDT by reaction with 1-bromobutane, and then the proportion of *n*-butyl DEDT formed was measured by HPLC (mesitylene was chosen as internal reference) [eq. (1)]. A calibration was previously carried out to make sure that bromine substitution by DEDT was really quantitative.

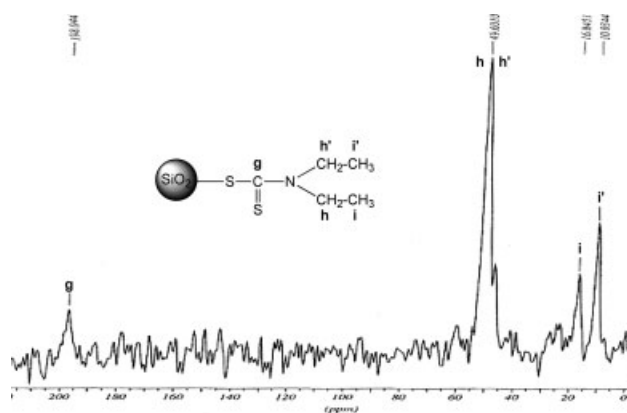
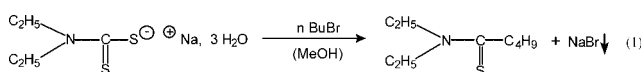


Figure 8 ^{13}C CP/MAS NMR spectrum of **Silica 6**.

TABLE IV
¹³C NMR Characteristics of the Various DEDT-Grafted Silica Synthesized

Type of DEDT-functionalized silica particles	Chemical shifts of the different carbons (δ in ppm)								
	a	b	c	d	e	f	g	h,h'	i,i'
	49.8	131.0	134.6	128.4	140.7	42.5	195.7	46.6 49.2	10.5 16.8
	59.3	16.8	23.2				196.9	47.1 49.6	10.0 16.8
							198.0	47.0 49.6	10.0 16.8



Knowing the quantity of salt consumed at t time, it was then possible to calculate the number of DEDT groups grafted per gram of silica (F) by applying the following relation:

$$F = \frac{n_{\text{DEDT}}}{m + n_{\text{DEDT}}(M_{\text{DEDT}} - M_{\text{Cl}})}$$

in which

- m is the weight (in gram) of chlorofunctionalized silica (**Silica 1** or **Silica 2**) used for the reaction.
- n_{DEDT} is the number of DEDT molecules which have reacted at t time with chlorines of chlorofunctionalized silica to form DEDT grafts (determined by HPLC).

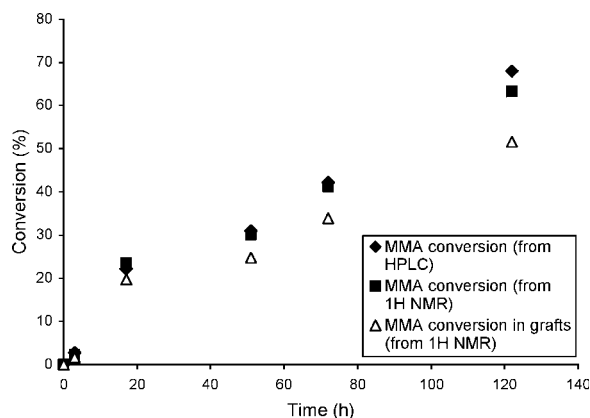


Figure 9 Progress of MMA photopolymerization initiated from **Silica 4**.

- M_{DEDT} is the molecular weight of DEDT group.
- M_{Cl} is the atomic weight of chlorine atom.

The substitution yield at t time was calculated by comparing the number of DEDT functions bound per gram of silica at t time to the number of reactive functions per gram of initial reactive silica.

The results summarized in Figure 5 show that the nucleophilic substitution used to graft DEDT groups onto silica microparticles progresses very slowly. After 90 h of reaction, the substitution yields obtained with **Silica 1** and **Silica 2** were 67 and 55%, respectively. It was also noted that, at the end of the reaction, the rates of DEDT functions contained per gram of DEDT-functionalized Kieselgel[®] S were practically identical for the two silicas prepared: 9.13×10^{-4} for **Silica 1** and 9.45×10^{-4} for **Silica 2**. These very close values are surprising, because of the difference that is observed between

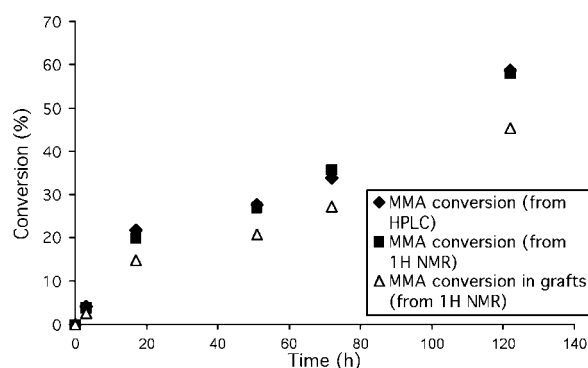


Figure 10 Progress of MMA photopolymerization initiated from **Silica 5**.

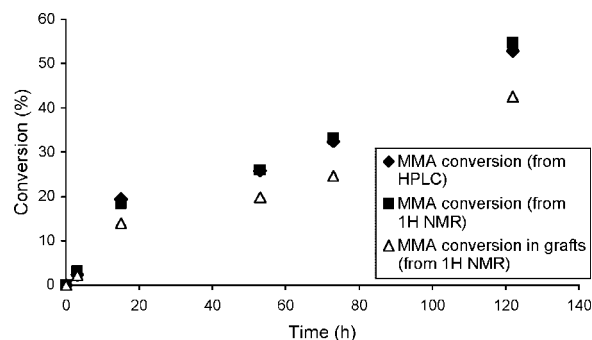


Figure 11 Progress of MMA photopolymerization initiated from **Silica 6**.

the yields obtained. This result could be explained by the inaccuracy of the measurement of chlorine functionalities in **Silica 1** and **Silica 2** because the calculation mode used for this determination supposed that two alkoxy silane bonds are involved in the grafting of one molecule of chlorofunctional trialkoxysilane (Table III).

Characterization of DEDT-functionalized silica microparticles

Because of their insolubility in solvents, DEDT-functionalized silica microparticles were characterized by using ^{13}C CP/MAS NMR (Figs. 6–8).

The ^{13}C -NMR chemical shifts of the carbons characteristic of the various DEDT-functionalized silica synthesized are given in Table IV.

Whatever the origin of the DEDT-functionalized silica microparticles analyzed after treatment with DEDTNa (from **Silica 1**, **Silica 2**, or **Silica 3**), the substitution reaction was confirmed by the presence of carbon signals characteristic of DEDT groups towards $\delta = 198$ ppm (C=S) ppm and $\delta = 10$ ppm (N-CH₂-CH₃). On the other hand, it was noted that the chemical shifts of the carbons of the grafted DEDT groups depend on the nature of the spacer which links DEDT groups to silica microparticle surface.

Photopolymerization of MMA initiated from DEDT groups covalently bound to silica microparticles

Photopolymerizations of MMA initiated from DEDT groups bound to the silica surface of microparticles were performed under oxygen-free nitrogen in toluene at room temperature (about 25°C). UV radiation was produced with a 100 W mercury-vapor lamp that showed an intense emission line at 365 nm. The proportions of MMA and DEDT-functionalized Kieselgel[®] S used for the studies were determined to obtain PMMA grafts of molecular weight equal to $\overline{M}_n = 20,000$.

The progress of MMA photopolymerization initiated from DEDT groups was followed by HPLC and ^1H -NMR, respectively, (Figs. 9–11) and the results were compared. MMA conversion at t time was calculated by using the following equation:

$$T_t (\%) = \frac{[\text{MMA at } t_0] - [\text{MMA at } t]}{[\text{MMA at } t_0]} \times 100$$

HPLC measurements led only to a global value of MMA conversion. In ^1H -NMR, it was possible to follow the progress of MMA conversion by referring to the signal of aromatic protons of toluene considered as a reference, but also to determine the proportion of homopolymer possibly formed during the grafting reaction, thanks to the difference that exists in the chemical shift of OCH₃ protons, respectively, noted at $\delta = 3.7$ ppm in MMA and $\delta = 3.55$ ppm in poly(methyl methacrylate) (PMMA). The quantity of MMA transformed in PMMA homopolymer during the grafting was thus compared with that transformed in PMMA grafts. Knowing the proportion of MMA consumed and that of MMA converted in homopolymer, the proportion of PMMA really grafted on silica microparticles could be determined, and then the average PMMA graft length (\overline{DP}_n) (Table V). \overline{DP}_n was calculated from the following equation:

$$\overline{DP}_n = \frac{[\text{PMMA units in grafts}]}{[\text{DEDT initiating functions}]}$$

TABLE V
Study of MMA Photopolymerization Initiated from the Different DEDT-Functionalized Kieselgel[®] S:
Results after 5 Days of Irradiation

DEDT-functionalized Kieselgel [®] S	Number of DEDT functions per grams of silica	MMA conversion ^a (%)	Distribution of PMMA formed ^a		Graft length	
			In grafts ^a (%)	In homopolymer ^a (%)	\overline{M}_n	\overline{DP}_n
Silica 4	9.13×10^{-4}	63.2	81.8	18.2	10,300	103
Silica 5	9.45×10^{-4}	58.1	77.3	22.7	9,000	90
Silica 6	–	54.4	77.6	22.4	–	–

^a Determined from ^1H NMR spectrum of the liquid phase.

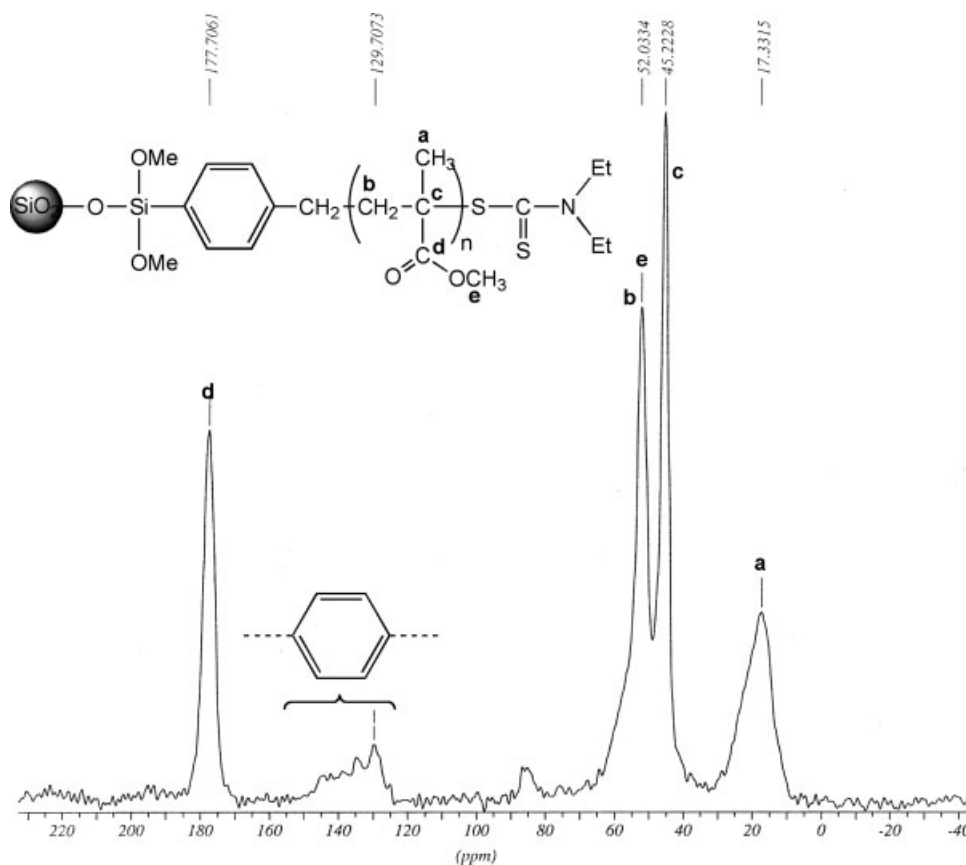


Figure 12 ^{13}C CP/MAS NMR spectrum of PMMA-grafted silica microparticles coming from **Silica 4**.

The results summarized in Figures 9–11 show a good accordance between the MMA conversion values determined from HPLC chromatograms and that calculated from ^1H -NMR spectra. On the other hand, conversion versus time curves show a very slow progress of grafting polymerizations whatever the DEDT-functionalized silica used: MMA consumption after 20 h of UV exposure is always lower than 25%. However, after 5 days of reaction, good grafting rates were obtained, depending on the DEDT-functionalized Kieselgel[®] S used (Scheme 6). The proportions of MMA converted in PMMA grafts decrease as follows: 51.7% (**Silica 4**) > 44.9% (**Silica 5**) > 42.2% (**Silica 6**). This corresponds to the formation of high length grafts with an average polymerization degree ($\overline{\text{DP}}_n$) of about 100 (Table V). In addition, formation of PMMA homopolymer was simultaneously noted during the grafting, but the proportions of MMA transformed in homopolymer remains low compared to that converted in grafts (Table V).

Characterization of PMMA-grafted silica microparticles

Because of their insolubility in solvents, PMMA-grafted silica microparticles were characterized by using ^{13}C CP/MAS NMR. The various samples of

PMMA-grafted silica particles obtained at the end of the functionalization were previously extracted with acetone to eliminate the PMMA homopolymer possibly formed. The presence of PMMA grafts was confirmed whatever the DEDT-functionalized Kieselgel[®] S used. A spectrum of PMMA-grafted silica particles prepared from **Silica 4** is given as an example in Figure 12. The formation of PMMA grafts is proved by the peaks at $\delta = 17.98, 45.38, 52.03, 41.00,$ and 178 ppm characteristic of the various carbons of the PMMA structures.

CONCLUSIONS

The purpose was to develop a procedure to synthesize well-defined poly(methyl methacrylate)-grafted silica microparticles. This was achieved by using radical photopolymerization of MMA initiated from DEDT groups covalently bound to the silica surface (grafting “from”).

At first, DEDT-functionalized silica microparticles were prepared from a Kieselgel[®] S silica, with a good control of the content in DEDT functions onto the silica surface. The procedure developed includes two steps: the grafting of organochlorinated functions onto the surface of silica particles, followed by the nucleophilic substitution of the chlorines by DEDT functions

via a S_N2 mechanism. Kieselgel[®] S silica was initially chlorinated, either by direct chlorination of silanols at its surface with thionyl chloride, either by using a condensation reaction between silanols at the silica surface and an alkoxy silane reagent, 4-(chloromethyl)phenyltrimethoxysilane and chloromethyltriethoxysilane, respectively. Three types of DEDT-functionalized silica microparticles were so prepared with a good control of the reaction, and then characterized by solid-state ^{13}C and ^{29}Si CP/MAS NMR. A method using HPLC chromatography was perfected to determine the DEDT group contents in the DEDT-functionalized silica particles obtained from chlorofunctionalized Kieselgel S modified with 4-(chloromethyl)phenyltrimethoxysilane and chloromethyltriethoxysilane, respectively. The results showed that, in the two cases, the contents in DEDT functions obtained after substitution of chlorine atoms by DEDT groups were same, that is about 9.3×10^{-4} DEDT function per gram of DEDT-functionalized Kieselgel[®] S.

The ability of the respective DEDT-functionalized silica microparticles to initiate MMA photopolymerization was studied. HPLC and 1H -NMR were used to follow the kinetics of MMA photopolymerizations initiated from the different types of DEDT-functionalized silica microparticles. In spite of very low kinetics of polymerization, high grafting rates were generally obtained after 5 days of reaction even if the formation of PMMA grafts is always accompanied with the formation of low proportions of PMMA homopolymer. At this time, the proportions of MMA converted in PMMA grafts decrease as follows: 51.7% (**Silica 4**) > 44.9% (**Silica 5**) > 42.2% (**Silica 6**), which shows that the grafting rates depend on the structural characteristics of the DEDT-functionalized Kieselgel[®] S used. This corresponds to the formation of high length grafts with an average polymerization degree (\overline{DP}_n) of about 100.

J.Y Buzaré and J. Emery of the Laboratoire de Physique de l'Etat Condensé in the Université du Maine in Le Mans are gratefully acknowledged for performing and handling the CP/MAS NMR measurements.

References

- Brinker, C. J.; Scherer, G. W. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Academic Press: New-York, 1990.
- Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv Polym Sci* 1992, 100, 31.
- Prucker, O.; Schimmel, M.; Tovar, G.; Knoll, W.; Rühle, J. *Adv Mater* 1998, 10, 1073.
- Ratner, B. J. *Biomed Mater Res* 1993, 27, 837.
- Alexandre, M.; Dubois, P. *Mater Sci Eng* 2000, 28, 1.
- Giannelis, E. P.; Krishnamoorti, R.; Manias, E. *Adv Polym Sci* 1999, 138, 108.
- Zhao, B.; Brittain, W. J. *Prog Polym Sci* 2000, 25, 677.
- Bridger, K.; Fairhurst, D.; Vincent, B. *J Colloid Interface Sci* 1979, 68, 190.
- Vincent, B. *Chem Eng Sci* 1993, 48, 429.
- Bridger, K.; Vincent, B. *Eur Polym J* 1980, 16, 1017.
- Auroy, P.; Auvray, L.; Leger, L. *J Colloid Interface Sci* 1992, 150, 187.
- Espiard, Ph.; Guyot, A. *Polymer* 1995, 36, 4391.
- Pu, Z.; Mark, J. E.; Jethmalani, J. M.; Ford, W. T. *Chem Mater* 1997, 9, 2442.
- Bourgeat-Lami, E.; Lang, J. *J Colloid Interface Sci* 1998, 197, 293.
- Buchmeiser, M. R.; Sinner, F.; Mupa, M.; Wurst, K. *Macromolecules* 2000, 33, 32.
- Barthet, C.; Hickey, A. J.; Cairns, D. B.; Armes, S. P. *Adv Mater* 1999, 11, 408.
- Zhang, K.; Zheng, L.; Zhang, X.; Chen, X.; Yang, B. *Colloids Surf A* 2006, 277, 145.
- Husseman, M.; Malmström, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. *Macromolecules* 1999, 32, 1424.
- Spange, S.; Simon, F.; Schütz, H.; Schramm, A.; Winkelmann, H. *J Macromol Sci Pure Appl Chem A* 1992, 29, 997.
- Jordan, R.; Ulman, A. *J Am Chem Soc* 1998, 120, 243.
- Prucker, O.; Rühle, J. *Macromolecules* 1998, 31, 602.
- Prucker, O.; Rühle, J. *Macromolecules* 1998, 31, 592.
- Boven, G.; Oosterling, M. L. C. M.; Challa, G.; Schouten, A. J. *Polymer* 1990, 31, 2377.
- Tsubokawa, N.; Satoh, M. *J Appl Polym Sci* 1997, 65, 2165.
- Tsubokawa, N.; Kogure, A.; Maruyama, K.; Sone, Y.; Shimomura, M. *Polym J* 1990, 22, 827.
- Ueda, J.; Sato, S.; Tsunokawa, A.; Yamauchi, T.; Tsubokawa, N.; *Eur Polym J* 2005, 41, 193.
- Yokoyama, R.; Suzuki, S.; Shirai, K.; Yamauchi, T.; Tsubokawa, N.; Tsuchimochi, M. *Eur Polym J* 2006, 42, 3221.
- Tsubokawa, N.; Hayashi, S.; Nishimura, J. *Prog Org Coat* 2002, 44, 69.
- Tsubokawa, N.; Ishida, H. *Polym J* 1992, 24, 809.
- Hayashi, S.; Fujiki, K.; Tsubokawa, N. *React Funct Polym* 2000, 46, 19331.
- Tsuchida, A.; Suda, M.; Ohta, M.; Yamauchi, T.; Tsubokawa, N. *J Polym Sci Part A: Polym Chem* 2006, 44, 2972.
- Yokoyama, R.; Suzuki, S.; Shirai, K.; Yamauchi, T.; Tsubokawa, N.; Tsuchimochi, M. *Eur Polym J* 2006, 42, 3221.
- Shirai, Y.; Shirai, K.; Tsubokawa, N. *J Polym Sci Part A: Polym Chem* 2001, 39, 2157.
- Shirai, Y.; Tsubokawa, N. *React Funct Polym* 1997, 32, 153.
- Satoh, M.; Shirai, K.; Saitoh, H.; Yamauchi, T.; Tsubokawa, N. *J Polym Sci Part A: Polym Chem* 2005, 43, 600.
- Liu, P.; Liu, W. M.; Xue, Q. *J. Eur Polym J* 2004, 40, 267.
- Ding, X.; Zhao, J.; Liu, Y.; Zhang, H.; Wang, Z. *Mater Lett* 2004, 58, 3126.
- Yoshinaga, K.; Teramoto, M. *Bull Chem Soc Jpn* 1996, 69, 2667.
- Parvole, J.; Laruelle, G.; Khoukh, A.; Billon, L. *Macromol Chem Phys* 2005, 206, 372.
- Ghannam, L.; Parvole, J.; Laruelle, G.; Francois, J. F.; Billon, L. *Polym Int* 2006, 55, 1199.
- Parvole, J.; Montfort, J.-P.; Billon, L. *Macromol Chem Phys* 2004, 205, 1369.
- Laruelle, G.; Parvole, J.; Francois, J.; Billon, L. *Polymer* 2004, 45, 5013.
- Kasseh, A.; Ait-Kadi, A.; Riedi, B.; Pierson, J. F.; *Polymer* 2003, 44, 1367.
- Bailly, B.; Donnenwirth, A.-C.; Bartholome, C.; Beyou, E.; Bourgeat-Lami, E. *J Nanomater* 2006, Article ID 76371, 10.
- Zheng, G.; Stöver, H. D. H. *Macromolecules* 2002, 35, 6828.
- Vestal, C. R.; Zhang, J. *J Am Chem Soc* 2002, 124, 14312.
- Huang, W.; Kim, J.-B.; Bruening, M. L.; Baker, G. L. *Macromolecules* 2002, 35, 1175.
- Liu, P.; Tian, J.; Liu, W.; Xue, Q. *Polym Int* 2004, 53, 127.
- Liu, P.; Liu, W. M.; Xue, Q. *J Macromol Sci Pure Appl Chem* 2004, 41, 1001.
- von Werne, T.; Patten, T. E. *J Am Chem Soc* 1999, 121, 7409.
- von Werne, T.; Patten, T. E. *J Am Chem Soc* 2001, 123, 7497.

52. von Werne, T.; Farmer, S.; Suehiro, I. M.; Patten, T. E. *Polym Mater Sci Eng* 2000, 82, 294.
53. Ejaz, M.; Ohno, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* 2000, 33, 2870.
54. Pyun, J.; Jia, S.; Kowalewski, T.; Patterson, G. D.; Matyjaszewski, K. *Macromolecules* 2003, 36, 5094.
55. Liu, T.; Jia, S.; Kowalewski, T.; Matyjaszewski, K. *Langmuir* 2003, 19, 6342.
56. Perruchot, C.; Khan, M. A.; Kamitsi, A.; Armes, S. P.; von Werne, T.; Patten, T. E. *Langmuir* 2001, 17, 4479.
57. Mori, H.; Chan Seng, D.; Zhang, M.; Müller, A. H. E. *Langmuir* 2002, 18, 3682.
58. Böttcher, H.; Hallensleben, M. L.; Nuss, S.; Wurm, H. *Polym Bull* 2000, 44, 223.
59. Gu, B.; Sen, A. *Macromolecules* 2002, 35, 8913.
60. Ohno, K.; Koh, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* 2002, 35, 8989.
61. Ohno, K.; Koh, K.; Tsujii, Y.; Fukuda, T. *Angew Chem Int Ed* 2003, 42, 2751.
62. Percy, M. J.; Michailidou, V.; Armes, S. P.; Perruchot, C.; Watts, J. F.; Greaves, S. J. *Langmuir* 2003, 19, 2072.
63. Mori, H.; Müller, A. H. E.; Klee, J. E. *J Am Chem Soc* 2003, 125, 3712.
64. El Harrak, A.; Carrot, G.; Oberdisse, J.; Eychenne-Baron, C.; Boué, F. *Macromolecules* 2004, 37, 6376.
65. Kobayashi, T.; Takahara, A. *Chem Lett* 2005, 34, 1582.
66. Wang, Y.-P.; Pei, X.-W.; He, X.-Y.; Yuan, K. *Eur Polym J* 2005, 41, 1326.
67. Otsu, T.; Matsumoto, A. *Adv Polym Sci* 1998, 136, 75.
68. Otsu, T.; Yoshida, M. *Makromol Chem Rapid Commun* 1982, 3, 127.
69. Otsu, T.; Yoshida, M.; Tazaki, T. *Makromol Chem Rapid Commun* 1982, 3, 133.
70. Otsu, T.; Matsunaga, T.; Doi, T.; Matsumoto, A. *Eur Polym J* 1995, 31, 67.
71. Otsu, T.; Yamashita, K.; Tsuda, K. *Macromolecules* 1986, 19, 287.
72. Kobayashi, T.; Takahashi, S.; Fujii, N. *J Appl Polym Sci* 1993, 49, 417.
73. Kobayashi, T.; Takahashi, S.; Nosaka, Y.; Fujii, N. *Chem Lett* 1992, 7, 1321.
74. de Boer, B.; Simon, H. K.; Werts, M. P. L.; van der Vegte, E. W.; Hadziioannou, G. *Macromolecules* 2000, 33, 349.
75. Zaremski, M. Y.; Chernikova, E. V.; Izmailov, L. G.; Garina, E. S.; Olenin, A. V. *Macromol Rep A* 1996, 33(Suppl 3 and 4), 237.
76. Derouet, D.; Forgeard, S.; Brosse, J. C.; Emery, J.; Buzaré, J. Y. *J Polym Sci Part A: Polym Chem* 1998, 36, 437.