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Synthesis of Polyisoprene-Grafted Silicas by Free Radical Photopolymerisation of Isoprene Initiated from Silica Surface

DANIEL DEROUET*# AND CHI NHAN HA THUC*

Synthetic silicas are used increasingly in tyre tread compounds. However, their use as fillers for hydrophobic rubbers (synthetic polydienes, natural rubber) is questionable unless a silane-coupling agent is introduced to bind the silica to the rubbers and to prevent it from interfering with the reaction mechanism of the sulphur-cure system. In order to improve the interphase strengths between silica and hydrophobic rubber, as well as to suppress the effects of silanol groups on sulphur-cured systems, polyisoprene-grafted silicas were synthesised. The principle of the synthesis was based on the "living" radical photopolymerisation initiated from the silica surface. For that, a two-step procedure was adopted. First, silica particles were functionalised with N,N-diethyldithiocarbamate iniferter groups, by using a SN2 substitution of chlorine atoms previously bound on silica surface. Following this, photopolymerisation of isoprene was carried out from the N,N-diethyldithiocarbamate iniferter groups and the polymerisation progress was simultaneously followed by HPLC and NMR. Functionalised silicas and polyisoprene-grafted silicas were characterised by solid-state ^{13}C and ^{29}Si CP/MAS NMR.

Key words: fillers; polyisoprene-grafted silicas; polyisoprene rubber; photopolymerisation; radical polymerisation; iniferter

For most technological applications, mechanical and thermal properties of rubber are commonly improved by addition of fillers. Fillers improve the physical and mechanical properties such as tear, abrasion resistance, hardness and tensile strength[1]. The choice of filler thus has a major influence on the service life, performance and durability of rubber products.

Carbon black has been widely used since the beginning of the 19th century to reinforce the properties of rubber compounds[2–4]. However, in recent years, synthetic silica has also been proved to be beneficial to rubber properties and is replacing carbon black in many applications. By using treads based on SBR-silica filled compounds, remarkable improvements in terms of wet grip and rolling resistance have been obtained[5–8]. The wider use of silica is hindered by the polarity of the silica surface, because of the presence of silanol groups. Silanol groups are acidic[9] and interact with the basic accelerators, causing

*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.

Corresponding author (e-mail: daniel.derouet@univ-lemans.fr)

detrimental effects such as unacceptably long cure times, slow cure rates[10] and also loss of crosslink density[11] in sulphur-cured systems. Moreover, the silica surface, due to its high polarity, has a strong tendency to absorb moisture[12,13], *i.e.* water, which affects the ionisation of silanols[14], which in turn adversely influences cure and hence properties of the cured rubbers. Consequently, contrary to carbon black, coupling agents must be used to reduce the strong filler-filler interactions between silica particles and to improve the dispersion of silica in the elastomer[15,16]. Generally, multifunctional molecules are able to establish molecular bridges between the polymer matrix and the filler surface. Among them, *bis*(3-triethoxysilylpropyl) tetrasulfane (TESPT) is most often used in the tyre industry because it reduces the hydrophilic character of the silica surface and promotes the adhesion between silica aggregates and elastomers through the formation of sulphur bridges. Good interactions are obtained, because triethoxy groups of TESPT react with the silanol groups of the silica during compounding with loss of ethanol and the rubber-reactive group of the silane (*e.g.* tetrasulfane) has a strong tendency to form rubber-to-filler bonds during curing of the rubber compound. In order to obtain optimum in-rubber properties, it is necessary to ensure that both reactions, but particularly the reaction between silica and silane, take place under specific, closely controlled conditions.

An improvement of interactions between surface silica and non-polar rubbers can also be obtained by bonding non-polar polymer chains on silica surface. The coating of a surface by irreversible grafting of a stable preformed polymer[17] or by selective adsorption of a diblock copolymer[18–20] leads in general to non-uniform thin films and poor surface coverage, due to the formation of islands and mushrooms on the surface. To overcome this, initiation of a polymerisation from a surface can be performed, which is expected to lead to higher surface grafting densities, because monomers can more easily diffuse toward the reactive center, whereas the grafting (or selective adsorption) of polymers is limited by steric and entropic forces. To initiate a polymerisation from the surface, initiator groups must be previously created at the surface of the inorganic particles. In most cases, conventional radical initiating species[21,22] or ionic moieties[23,24] are introduced on the surface. In order to achieve a good control of molecular weight and molecular weight distribution, and to synthesise new polymer grafts like block copolymer ones, controlled/living radical polymerisation methods including nitroxide-mediated free radical polymerisation (TEMPO)[25,31], atom transfer radical polymerisation (ATRP)[32–52], and reverse ATRP[53] have been developed.

In the early 1980s, Otsu *et al.* reported that living-like radical polymerisation of styrene and methyl methacrylate in solution proceeds with a new type of initiators classified as dithiocarbamate derivatives, and described them as photoiniferters, which means that they act as an initiator, transfer agent and terminator[54–58]. The concept of this non-conventional polymerisation 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). "Living" free radical polymerisation shows some advantages

(a) linear increase of molecular weight, leading to a steady growth of the polymer chains,
(b) possibility of formation of block copolymers by reinitiating the polymerisation with a different monomer solution, and
(c) compatibility with a wide variety of monomers, *e.g.* acrylates, methacrylates, styrenes, acrylonitrile and derivatives.

In this paper, the purpose is to investigate the synthesis of polyisoprene-grafted silica microparticles by using a "grafting from" approach based on Otsu's works. We describe the synthesis of densely grafted silica particles with stable iniferter groups and the "living" free radical photopolymerisation of isoprene initiated from these initiating groups anchored onto the silica particle surface. The purpose of the study was to generate hybrid inorganic/organic particles by photopolymerisation, in order to elaborate a core-shell composite with a hard core of silica coated by a rubbery shell (polyisoprene with T_g of about –60ºC).

EXPERIMENTAL

Materials

Toluene, dichloromethane, ethanol and methanol were purified according to classical methods and carefully re-distilled before use. p-Chloromethylphenyltrimethoxysilane (90% purity, $Eb_{10\ mbar}$ = 134–143ºC) is commercially available and was used as received. Isoprene (Aldrich, $Eb_{670\ mm\ Hg}$ = 34ºC) was carefully distilled under nitrogen atmosphere before use. Sodium N,N-diethyldithiocarbamate trihydrate (DEDTNa), bromobutane and mesitylene were pure commercial products used without further purification.

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

Synthesis of p-chloromethylphenyl-functionalised silica

p-Chloromethylphenyl-functionalised silica was prepared under nitrogen atmosphere as follows. In a dry nitrogen atmosphere glove box, 2 g of silica particles dispersed in 20 mL of toluene and p-chloromethylphenyltrimethoxysilane in excess by comparison with silica silanols, were placed in a clean Teflon tube successively, and the tube was closed. The mixture was magnetically stirred for 24 h in an oil bath thermostated at 110ºC. The mixture was extracted with dichloromethane using a Soxhlet for 48 h, then dried at 40ºC under 10^{-2} mbar vacuum for 24 h. Samples were taken at the beginning and at the end of the reaction and, after filtration, analysed by ^1H NMR in order to calculate the rate of chlorofunctional groups anchored onto silica particles (expressed as the number of chlorofunctional groups per g of silica).

Synthesis of N,N-diethyldithiocarbamate-functionalised silicas

1 g of 4-(chloromethyl)phenyl-functionalised 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. After reaction, it was filtered, and the functionalised particles were extracted with methanol using a Soxhlet for 24 h, then dried for 24 h at 40ºC under 10^{-2} mbar vacuum.

The rate of functionalisation was determined from back titration of residual DEDTNa contained in the solution at the end of the reaction. 1 mL of the solution (the filtrate) 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 CH_3CN/H_2O mixture as mobile phase. Knowing the quantity of salt consumed at the end of the reaction, it was then possible to calculate the number of N,N-diethyldithiocarbamate

functions bonded per g of silica by applying the following equation:

$$F = \frac{n}{m + n(M_{DEDT} - M_{Cl})} \quad \ldots 1$$

where,

m = the weight (in g) of reactive chloro-functionalised silica.

n = is the number of DEDT functions bound to silica particles at the end of the reaction (determined by HPLC).

M_{DEDT} = the molecular weight of DEDT group.

M_{Cl} = the atomic weight of chlorine atom.

Synthesis of the polyisoprene-grafted silica microparticles

Isoprene photopolymerisations were carried out under nitrogen atmosphere, in toluene and at room temperature. 0.6 g of the synthesised N,N-diethyldithiocarbamate-functionalised silica microparticles and 11 g of isoprene (161 mmol) in 25 mL of toluene were placed in a 250 mL Pyrex reactor, that is reagent proportions calculated to obtain polyisoprene grafts of theoretical $\overline{Mn}$ equal to 20 000. Air atmosphere was removed out of the reactor and replaced with nitrogen. The magnetically stirred mixture was then irradiated for 125 h with a 100 W mercury-vapor lamp placed 10 cm away from the reactor.

The kinetic studies were performed as above. Samples were taken off at various times and analysed by HPLC and ^{1}H NMR to determine isoprene conversions.

HPLC measurements were carried out as follows. A 10 mg sample was introduced in 1 mL of mobile phase (58:42 acetonitrile/water). After filtration, the solution was fractionated by HPLC. Isoprene conversion was calculated by comparison of the area of residual isoprene peak (at t_R = 7.2 min) to that of toluene peak (at t_R = 7.7 min), the isoprene peak/toluene peak area ratio at t_0 being used as reference for the calculation.

In ^{1}H NMR measurements, isoprene conversion was determined by comparing the area of the signal of CH_2=C(CH_3)-C**H**=CH_2 isoprene proton at δ = 6.4 p.p.m. to that of aromatic toluene protons at δ = 7.0 – 7.3 p.p.m., the ratio at t_0 being used as reference for the calculation.

Irradiations

UV-irradiation was performed using a 100 Watts Blak-Ray® mercury-vapor lamp (Model B 100 AP), marketed by Fisher Bioblock Scientific. It shows an intense emission ray at 365 nm. The intensity measured at 30 cm of the filter was equal to 7000 μW.cm^{-2}.

Measurements

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

Liquid ^{1}H and ^{13}C NMR measurements were recorded on a Bruker AC 400 Fourier-transform spectrometer, at 400.13 MHz for ^{1}H and at 100.61 for ^{13}C. Samples were analysed in chloroform-d (99.8% purity; Spectrometrie Spin et Techniques). The chemical shifts were expressed in p.p.m. in the δ scale, compared

with the singlet of tetramethylsilane (TMS), as internal reference.

Analyses in High Performance Liquid Chromatography (HPLC) were performed on a Waters modular equipment including a Model 510 pump module, a Model U6K injector, an AIT CHROMATO Kromasil C18 column (4.6 mm I.D., and 15 cm in length; particle size: 5 µm), and a double detection system (a Model 996 photodiode array spectrophotometer and a Model 410 differential refractometer). The command of the various modules, the acquisition of the data, and the data processing were carried out using a microcomputer equipped with Empower Waters program. The analyses were performed in isocratic mode with acetonitile-water or methanol-water mobile phases, at a flow rate adjusted to 1 $mL.min^{-1}$.

Thermo Gravimetric Analyses (TGA) were performed on an ATD-ATG TA Instrument apparatus (SDT 2960). The analyses were performed in argon from 30ºC to 1000ºC with a heating rate of $10ºC.min^{-1}$.

RESULTS AND DISCUSSION

The aim was to synthesise polyisoprene-grafted silicas to be used as reinforcing fillers for rubber vulcanisates. The purpose is to improve the interaction strengths between the silica surface and rubber matrix. To achieve this objective, the "living" free radical photopolymerisation of isoprene initiated from iniferter groups previously bonded onto the surface of the silica particles was considered. Isoprene photopolymerisation was initiated from N,N-diethyldithiocarbamate previously bonded on the silica surface (*Figure 1*). The first stage was to perform the functionalisation of silica particles with N,N-diethyldithiocarbamate functions. A two-step synthesis was considered.

First step - a chlorofunctionalisation step of the silica particles was carried out to create functions able to react with N,N-diethyldithiocarbamate salts to lead to the silica iniferter.

Second step - the nucleophilic substitution of the chlorine atoms by N,N-diethyldithiocarbamate groups was conducted (reaction with sodium N,N-diethyldithiocarbamate trihydrate).

Finally, the photopolymerisation of isoprene was initiated from the N,N-diethyldithiocarbamate-functionalised silicas.

Synthesis of the N,N-diethyldithiocarbamate-functionalised silicas

Functionalisation of silicas is generally achieved by grafting of functional alkoxy (or chloro) silanes used as coupling agents[59]. This reaction was at first selected to introduce the chlorofunctional groups at the surface of silica microparticles. Then, the chlorine atoms were substituted by N,N-diethyldithiocarbamate anions by reaction with sodium N,N-diethyldithiocarbamate trihydrate.

Introduction of chlorine atoms onto Kieselgel® S microparticles was performed by using a condensation reaction between p-chloromethylphenyltrimethoxysilane and silanols at the surface of silica particles (*Figure 1*). In order to anchor a maximum of chlorobenzyl groups onto the surface of Kieselgel® S particles, the functionalisation reactions were carried out using chlorofunctional trialkoxysilane in large excess by comparison with silica silanols. At the end of the reaction, chlorotrimethylsilane was added to deactivate the accessible residual silanols. The rate of chlorofunctional groups anchored onto silica particles was evaluated to 1.52×10^{-3} chlorobenzyl groups per g of silica.

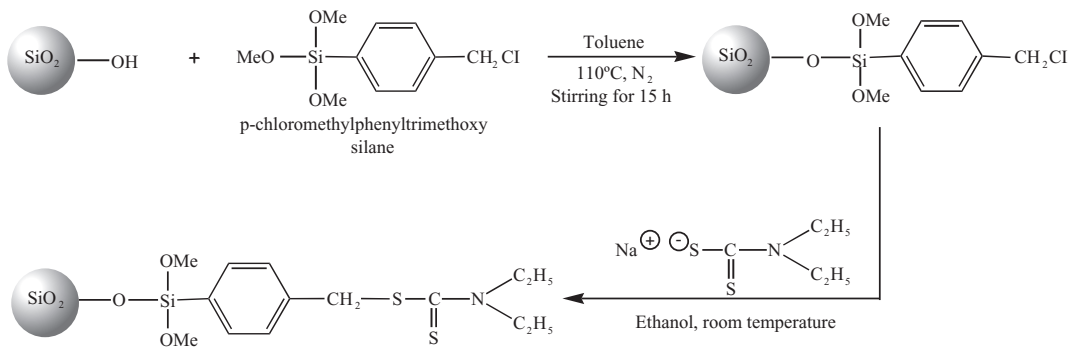
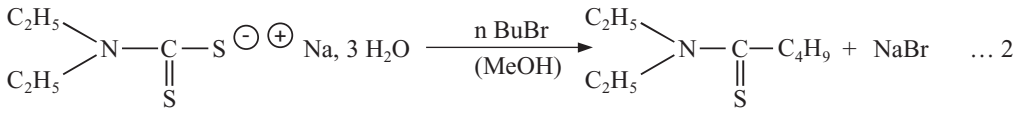


Figure 1. Synthesis of N,N-diethyldithiocarbamate-functionalised silica microparticles.

The synthesised chlorobenzyl-functionalised silicas were characterised by solid-state ^{13}C and ^{29}Si CP/MAS NMR. In ^{13}C NMR (*Figure 2*), the presence of peaks characteristic of chlorobenzyl groups shows that the condensation reaction occurred onto the silica particles. In addition, the presence of a peak characteristic of methoxy carbons at δ = 44.2 p.p.m. from the chlorofunctional reagent indicates that methoxy functions were not totally consumed during the condensation reaction. On the other hand, the presence of a peak at δ = 13 p.p.m. corresponding to methyl carbons of trimethylsilane functions, is a significance of complete neutralisation of the accessible reactive silanols. In ^{29}Si CP/MAS NMR, by comparison with that of the starting Kieselgel® S^{60}, the spectrum of the chlorofunctionalised silica showed three signals characteristic of three types of grafted structures: mono, bi, and tridentate silicons (T_1, T_2, T_3) that are noted at T_1 = –62.5 p.p.m., T_2 = –70.0 p.p.m., and T_3 = –79.0 p.p.m. respectively. However, only free silanols of Q_3 type and Q_1 siloxanes were noted at the end of the reaction.

N,N-diethyldithiocarbamate functions were introduced onto the silica particle surface by SN2 nucleophilic substitution of the chlorine atoms previously introduced, that is by reaction with sodium N,N-diethyldithiocarbamate trihydrate (DEDTNa) (*Figure 1*). The reactions were carried out in ethanol at room temperature. The rate of DEDT anchored onto the silica particles was determined by back titration of the residual DEDTNa contained in the solution at the end of the reaction. Residual DEDTNa was transformed into n-butyl N,N-diethyldithiocarbamate by reaction with 1-bromobutane, and then the quantity of n-butyl N,N-diethyldithiocarbamate formed was measured by HPLC (mesitylene was chosen as internal reference) (*Equation 2*). A calibration was previously carried out to make sure that the bromine substitution by DEDT group is quantitative.



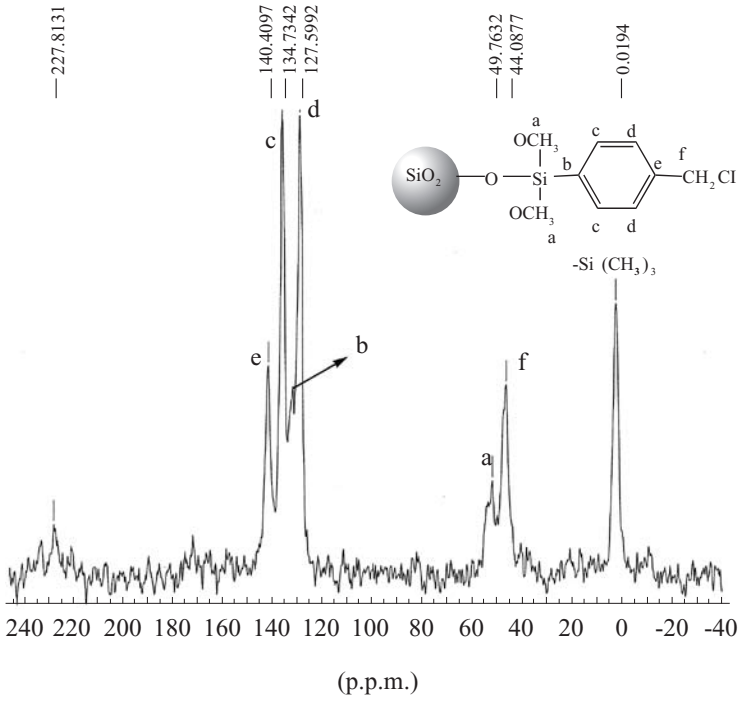


Figure 2. ^{13}C CP/MAS NMR spectrum of chlorobenzyl-functionalised silica microparticles.

After 92 h of reaction, the rate of N,N-diethyldithiocarbamate functions contained per g of N,N-diethyldithiocarbamate-functionalised Kieselgel® S was equal to 9.13×10^{-4}. This measurement showed that the substitution reaction of chlorine atoms by the N,N-diethyldithiocarbamate groups was not quantitative (yield = 60%).

Because of their insolubility in solvents, N,N-diethyldithiocarbamate-functionalised silica microparticles were characterised by using ^{13}C CP/MAS NMR (*Figure 3*). Before analysis, the functionalised silica particles were purified by extraction with MeOH, and then dried at 40ºC under vacuum. The presence of peaks at δ = 195.7 p.p.m. (**C**=S), δ = 10.5 and 16.8 p.p.m. (N-CH_2-**C**H_3), and δ = 46.6 and 49.2 p.p.m. (N-**C**H_2-**C**H_3) on the spectra confirmed the anchoring of N,N-diethyldithiocarbamate functions onto the silica surface. A detailed ^{13}C NMR characterisation of the functionalised silica microparticles is given in *Table 1*.

Synthesis of polyisoprene-grafted silica microparticles

Synthesis of polyisoprene-grafted silica microparticles was conducted by photo-polymerisation of isoprene initiated from N,N-diethyldithiocarbamate functions bound to the silica surface. Polymerisations were carried out in toluene at room temperature (about 25ºC), under oxygen-free nitrogen atmosphere. UV radiation was produced with a 100 W mercury-vapor lamp that showed

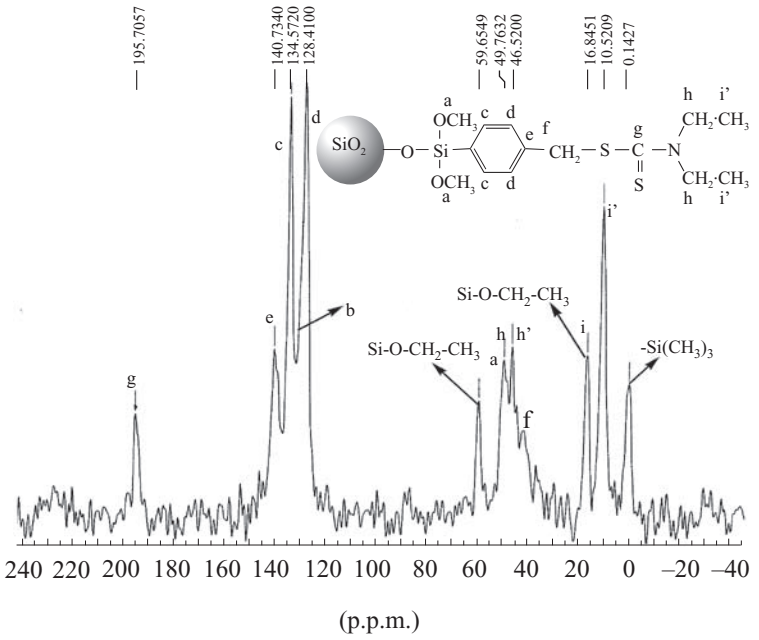
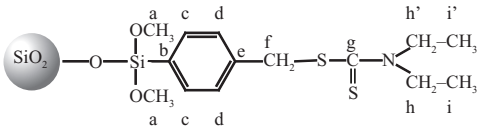


Figure 3. ^{13}C CP/MAS NMR spectrum of N,N-diethyldithiocarbamate-functionalised silica microparticles.

TABLE 1. CHARACTERISATION OF THE SYNTHESISED N,N-DIETHYLDITHIOCARBAMATE-FUNCTIONALISED SILICAS BY ^{13}C NMR

N,N-diethyldithiocarbamate-functionalised silica	Chemical shifts of the different carbons (δ in p.p.m.) 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

an intense emission line at 365 nm. The lamp was placed at 10 cm from the reactor glass wall. Proportions in isoprene and N,N-diethyldithiocarbamate-functionalized Kieselgel® S were chosen to obtain polyisoprene grafts of molecular weight equal to $\overline{Mn}$ = 20 000.

In a first time, the progress of isoprene polymerisation initiated from N,N-diethyldithiocarbamate groups at the silica surface was followed simultaneously by HPLC and ^1H NMR (*Figure 4*) and the respectively obtained results were compared. Isoprene conversion at t time was calculated from the following equation:

$$T_t\,(\%) = ([isoprene\ at\ t_0] - [isoprene\ at\ t])/[isoprene\ at\ t_0] \times 100 \quad \ldots 3$$

HPLC measurements led only to a global value of isoprene conversion. In ^{1}H NMR, it was possible to follow the progress of isoprene conversion by referring to the signal area of aromatic protons of toluene considered as a reference, but also to characterise the possible formation of homopolymer during the grafting reaction, by comparing the area of the signal at δ = 6.4 p.p.m. characteristic of CH_2=C(CH_3)-C**H**=CH_2 proton of residual isoprene to the total area of signals between 4.5 and 5.5 p.p.m. that includes C**H**$_2$=C(CH_3)-CH=C**H**$_2$ protons of residual isoprene and the unsaturated protons (at δ = 5.14 p.p.m. and δ = 4.7 p.p.m.) of the homopolyisoprene possibly formed. However, ^{1}H NMR analyses carried out with the various samples taken during isoprene photopolymerisation showed that none contained polyisoprene, which indicated that isoprene homopolymerisation did not occur during the grafting course.

Finally, knowing the proportion of isoprene consumed at the end of the reaction, that is after 125 h, the grafting rate (G) defined as the weight % of polyisoprene contained in the polyisoprene-grafted silica microparticles, could be determined by applying the following equation:

$$G\,(\%) = m_1/(m_0 + m_1) \times 100 \quad \ldots 4$$

where, m_0 = the weight of silica particles at t_0, m_1 = that of isoprene consumed after 125 h.

Then, the average length of grafts could be evaluated by the measurement of the number average molecular weight of polyisoprene grafts ($\overline{Mn}$), obtained from the following equation:

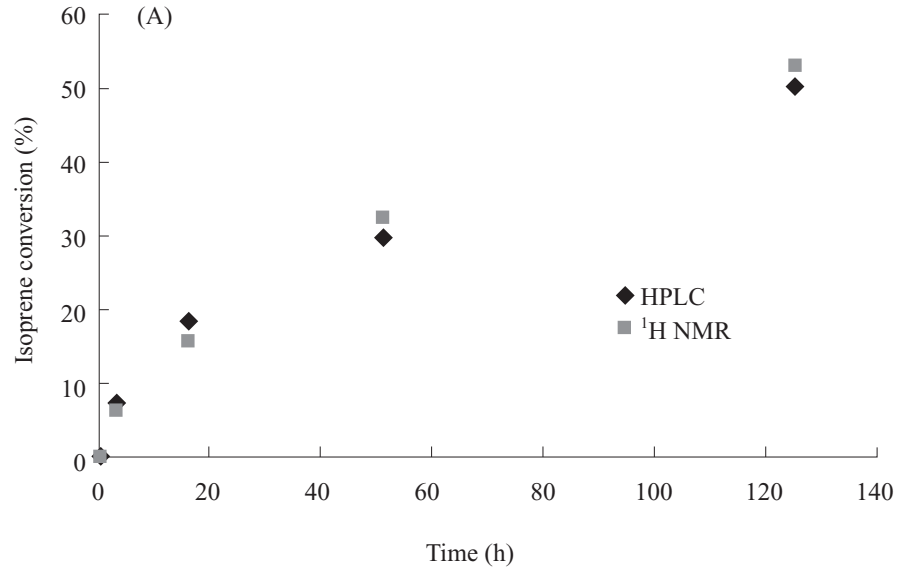
$$\overline{Mn} = m_1 \,/\, \textit{number of N,N-diethyldithiocarbamate functions used} \quad \ldots 5$$

Results summarised in *Figure 4A* showed that the kinetic of photodissociation was very low: only 20% of the initial isoprene was consumed after 17 h of irradiation and about 50% after 125 h. They also showed that the isoprene conversion values determined from HPLC chromatograms were in good accordance with the ones calculated from ^{1}H NMR spectra. However, after 125 h of reaction, good grafting rates were obtained (90%). This corresponded to the formation of high length grafts with a number average molecular weight number ($\overline{Mn}$) higher than 10 000 (*Figure 4B*).

A kinetic plot of Ln($[M]_0/[M]_t$) *versus* time is shown in *Figure 5*. The resulting slope indicates that polymerisation proceeds with a non-constant number of active species during the reaction. This is the significance of a non-controlled radical polymerisation, the concentration in growing macroradicals being affected by non-reversible terminations and/or transfer reactions.

In addition to the reaction followed by HPLC and ^{1}H NMR, a second experiment was performed in same conditions, in order to determine the grafting rate and the graft length, on one hand by measuring the increase in weight of silica and on the other hand by comparing the proportions of silica and polyisoprene contained in the obtained polyisoprene-grafted silica by using Thermo Gravimetric Analysis (TGA).

Polyisoprene-grafted silica particles obtained after grafting, 125 h of reaction, were extracted with dichloromethane using a Soxhlet to separate the homopolymer possibly formed from polyisoprene-grafted silica particles. By comparing the weight of the extracted sample with that of the initial sample of N,N-diethyldithiocarbamate-functionalised silica, it was possible to determine the quantity of polyisoprene really grafted, and afterwards the grafting rate and graft $\overline{Mn}$.



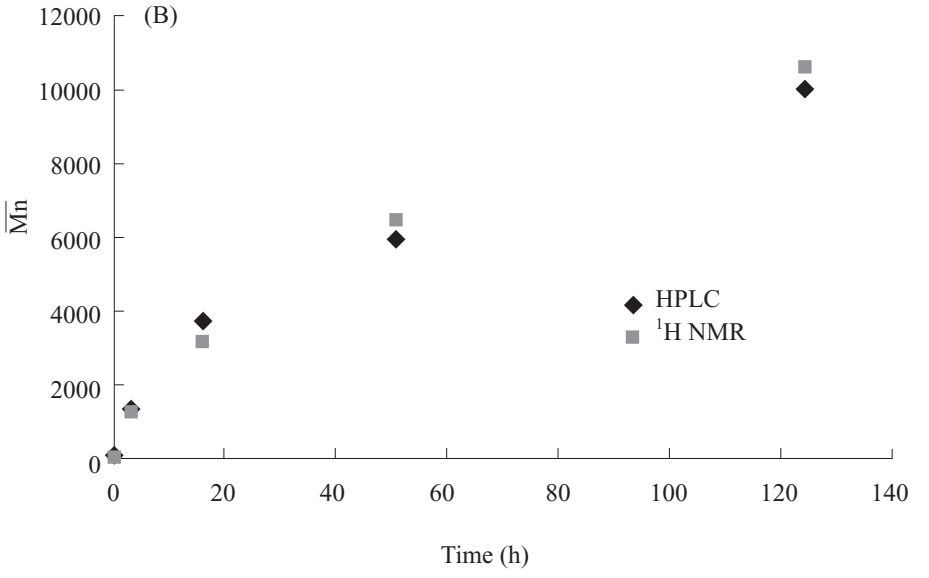


Figure 4. Control of polyisoprene graft growing by HPLC and ^{1}H NMR respectively: (A) isoprene conversion and (B) $\overline{Mn}$ progress

In the present study, the grafting rate (G) was determined from the following equation:

$$G\,(\%) = (m_1 - m_0)/m_1 \times 100 \quad \ldots 6$$

where, m_0 = the weight of silica particles at t_0, m_1 = the weight of the silica particles at the end of polyisoprene grafting (after extraction and drying).

Isoprene conversion in grafts was given by the equation:

$$C\,(\%) = (m_1 - m_0)/m_2 \times 100 \quad \ldots 7$$

where, m_2 = the weight of isoprene at t_0.

The results of the experiment are given in *Table 2*. Polyisoprene grafting was confirmed by the weight increase of the global weight of the particles. It was noted that the rate of polyisoprene grafted per g of silica was very high (89 %). This corresponded to a graft $\overline{Mn}$ equal to about 8500.

TGA analysis was performed with a dry sample of polyisoprene-grafted silica microparticles previously extracted with dichloromethane. Decomposition of polyisoprene-grafted silica particles occurred in two steps: a first step corresponding to the degradation of polymer grafts (between 300ºC and 520ºC), and a second step corresponding to the decomposition of silica (>1200ºC). From the thermograms, it was then possible to compare the weight of the organic part to that of silica and so to calculate the proportion of grafted polyisoprene contained in the polyisoprene-grafted silica. In the present case, this led to a grafting rate equal to 86% and a graft $\overline{Mn}$ = 6800.

A summary of grafting rates and graft lengths ($\overline{Mn}$) in relation with the method used for their determination is given in *Figure 6*. Apart from the values measured by TGA, a good agreement is observed in the measurements of the grafting rates and $\overline{Mn}$ made by ^{1}H NMR, HPLC, and weighing respectively. The lower values obtained using TGA, can be explained by the difficulty to distinguish the transition between degradations of organic and mineral phases. As a whole, in spite of termination reactions, the grafting rate (>90%) was high, with an isoprene conversion in polyisoprene grafts higher than 50%, which resulted in graft $\overline{Mn}$ equalling to approximately half of the expected values.

NMR analyses of synthesised polyisoprene-grafted silica microparticles were performed on samples that were previously extracted dichloromethane, and thus removed from the homopolymer possibly formed. Because of their insolubility in solvents, polyisoprene-grafted silica microparticles were at first characterised by using ^{13}C CP/MAS NMR (*Figure 7*). However, an analysis was also performed in Liquid ^{13}C NMR on a sample of polyisoprene-grafted silica

TABLE 2. ASSESSMENT OF THE GRAFTING FOLLOWED BY WEIGHT CONTROL OF THE SILICA PARTICLES. m_0 = 0.6 g; m_2 = 11 g

Weight of particles after extraction on Soxhlet (m_1 in g)	Isoprene conversion in grafts (C in %)	Grafting rate (G in %)	$\overline{Mn}$
5.24	42.3	89	8500

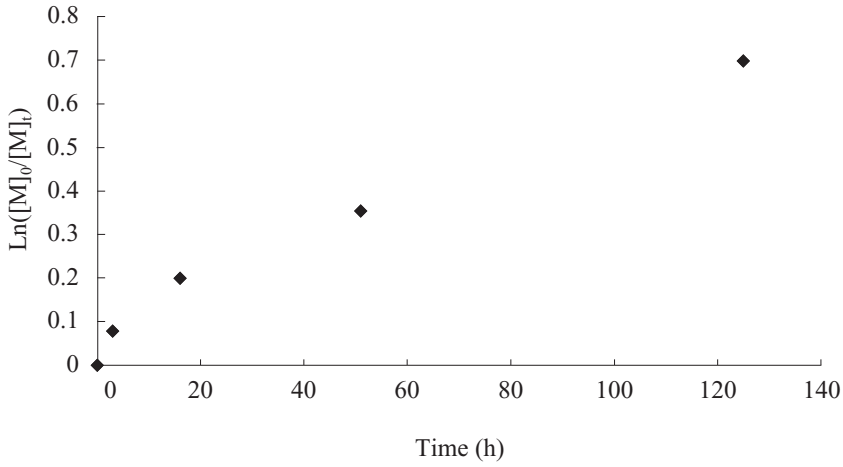


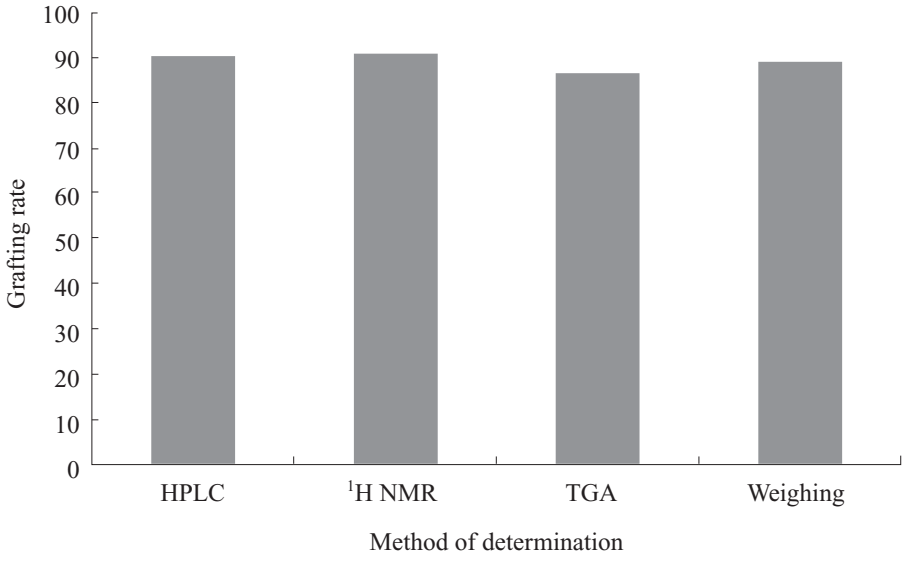
Figure 5. Plot of Ln($[M]_0/[M]_t$) versus time for isoprene photopolymerisation initiated from N,N-diethyldithiocarbamate-functionalised silica microparticles.

microparticles dispersed in chloroform-d (*Figure 8*). The spectra obtained were similar, but the spectrum obtained in liquid NMR was resolved better. These analyses confirmed the formation of polyisoprene grafts. The most important peaks are noted at δ = 23.4, 30.0, 36.2, 128.1 and 135.4 p.p.m. characteristic of the various carbons of polyisoprene units[61]. They are primarily composed of 1,4-polyisoprene units[61], the proportion in *trans* ones being higher than that in *cis* ones. This was confirmed by the higher area of the peak characteristic of methyl carbons in *trans* units at δ = 16.04 p.p.m. by comparison with that of the peak corresponding to methyl carbons in *cis* units at δ = 23.51 p.p.m. (*Figure 8*). On the other hand, it was not possible to identify the presence of N,N-diethyldithiocarbamate functions at the graft ends.

CONCLUSION

The objective of the study was to synthesise polyisoprene-grafted silica microparticles to be used as fillers for the reinforcement of natural rubber (or synthetic polyisoprenes) vulcanisates. The study was performed with precipitated Kieselgel® S silica, a silica composed of microparticles of 63 µm to 200 µm size. The polyisoprene grafting was achieved according to the « grafting from » method by initiating an isoprene photopolymerisation from iniferter functions previously bound at the surface of the silica microparticles. For that, N,N-diethyldithiocarbamate initiating functions were at first created at the silica surface by using a two-step procedure: by chlorofunctionalisation of the silica surface of microparticles, followed by the SN2 nucleophilic substitution of the chlorine atoms by N,N-diethyldithiocarbamate carbanions. Then, N,N-diethyldithiocarbamate-functionalised silica microparticles were used as macroiniferter to initiate isoprene photopolymerisation under UV irradiation.

The procedure developed to synthesise polyisoprene-grafted silica microparticles is particularly interesting because it leads to very



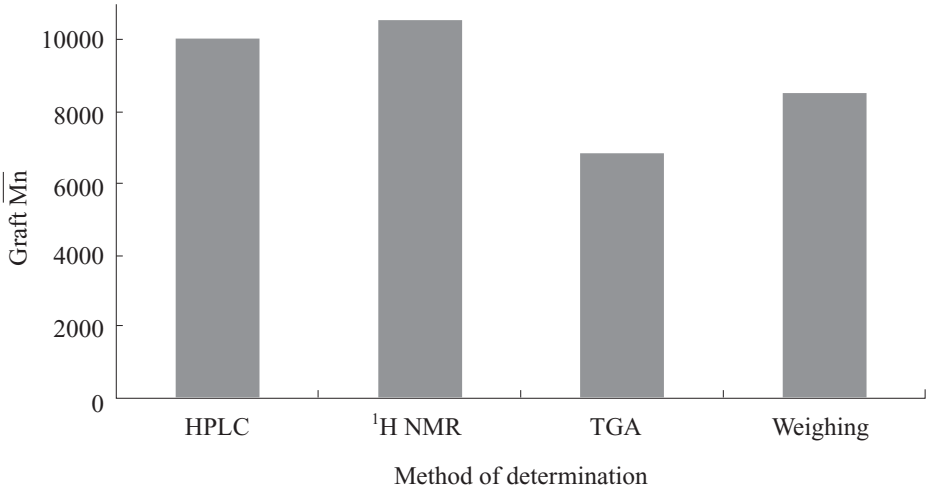


Figure 6. Grafting rates and graft $\overline{Mn}$ in relation with the method used for their determination.

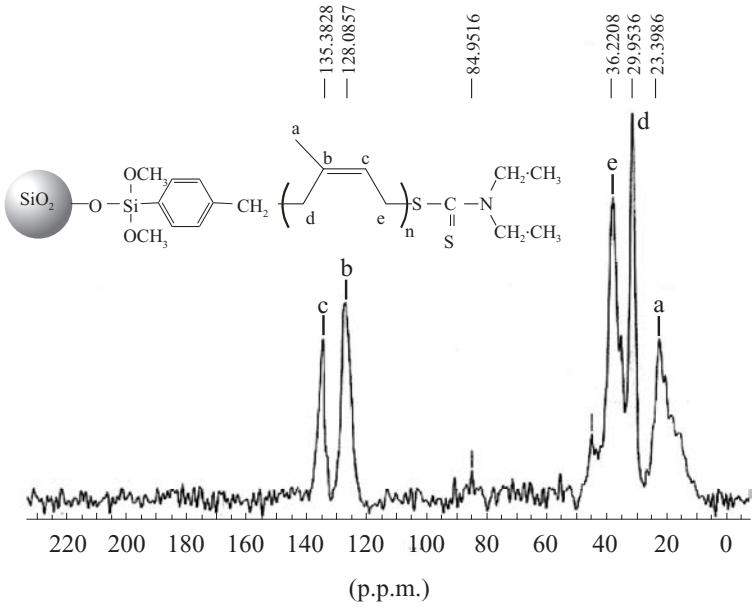


Figure 7. Solid-state ^{13}C CP/MAS NMR spectrum of polyisoprene-grafted silica microparticles.

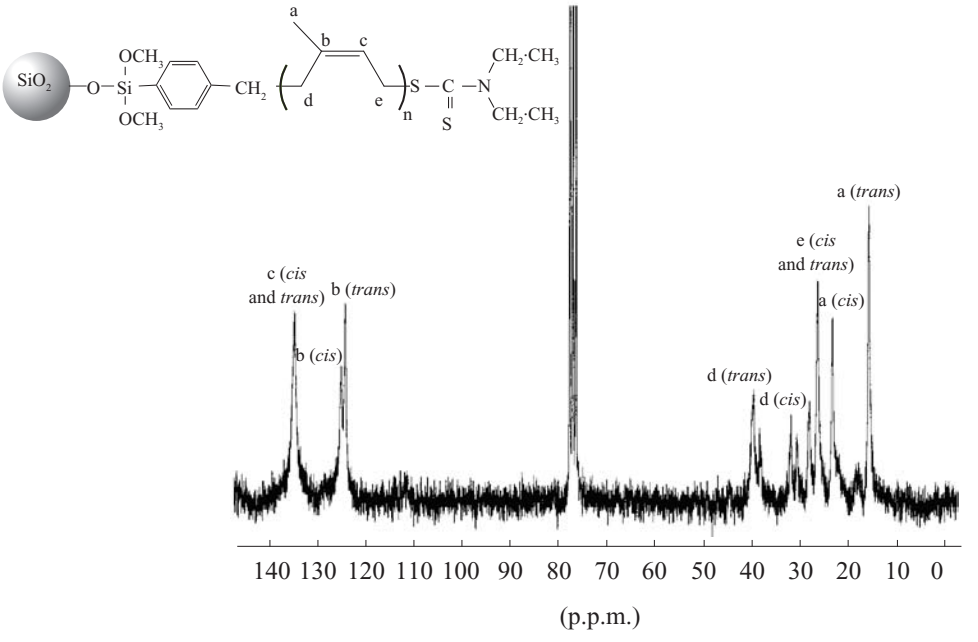


Figure 8. Liquid ^{13}C NMR spectrum of polyisoprene-grafted silica microparticles.

high grafting rates (polyisoprene contents in polyisoprene-grafted silica microparticles are higher than 90 %), with grafts whose lengths are half of that theoretically waited ($\overline{Mn}$) > 10 000). Moreover, it occurs without formation of homopolymer. Normally, it should be easily generalised to nano size particles.

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