Silica–siloxane mixtures. Investigations into adsorption properties of end-methylated and end-hydroxylated chains

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The adsorption process of end-hydroxylated poly(dimethylsiloxane) chains upon silica particles is compared with that of end-methylated chains. Four variables were used to analyse the adsorption process: the chain molecular weight $\bar{M}_n$, the initial concentration of silica c^i_{Si}, the amount of adsorbed polymer Q^1_r and the relative number of fixed monomeric units τ_B, observed from n.m.r. Both polymer species were found to obey two simple equivalent laws of adsorption: $Q^1_r \propto \sqrt{\bar{M}_n}$ and $\tau_B \propto 1/\sqrt{\bar{M}_n}$. Several features characterize the adsorption process: equal specific amounts of hydroxylated chains are adsorbed for two silica concentrations, $c^i_{Si} = 0.17$ or 0.29 (w/w); for a given chain length, the specific amount of adsorbed hydroxylated chains is higher than that of methylated ones; a partial desorption of methylated chains is induced by washing mixtures with $c^i_{Si} = 0.17$ (w/w); the process of adsorption of hydroxylated chains is about 10 times faster than that of methylated ones, at 343 K.

(Keywords: silica; siloxane; adsorption; n.m.r.; kinetics)

INTRODUCTION

The purpose of this work is to analyse the process of adsorption of end-methylated or end-hydroxylated siloxane chains upon the surface of silica particles. The insertion of silica into siloxane polymers is obtained by mechanical mixing. The adsorption process occurs through the formation of hydrogen bonds between silica and oxygen atoms of siloxane chains.

It has already been shown both experimentally and theoretically that the law of adsorption of end-methylated siloxane chains obeys the formula:

$$Q^1_r = \chi^M_a \bar{M}_n^{1/2} \tag{1}$$

where Q^1_r denotes the amount of polymer left bound to 1 g of silica when the adsorption process is completed (after ~30 months)[1] and $\bar{M}_n$ is the number average molecular weight of polymer chains. This formula applies within the range $2 \times 10^3 \leqslant \bar{M}_n \leqslant 3.6 \times 10^5$ g mol^{-1} with $\chi^M_a = 3.3 \times 10^{-3}$ g$^{-1/2}$ mol$^{1/2}$. It has been shown that the average number of contact points $\langle r_c \rangle$ of one Gaussian chain upon the silica surface is proportional to the square root of the number of skeletal bonds N:

$$\langle r_c \rangle = \varepsilon^M_a \sqrt{N} \tag{2}$$

where ε^M_a is a numerical constant close to unity. The average value $\langle r_c \rangle$ is calculated from the probability distribution function

$$P(r_c, N) \propto \frac{r_c}{N^{3/2}} \exp(-r_c^2/2N) \tag{3}$$

where $P(r_c, N)$ gives the probability that a chain which contains N skeletal bonds forms r_c contact points of adsorption with the silica surface[2]. Let A denote the specific area of silica ($A = 150$ m^2 g^{-1}) and σ_e^{-1} the density of hydrogen bonds which can be formed between the silica surface and one oxygen atom of the siloxane chains ($\sigma_e \approx 55$ Å^2). Then:

$$Q^1_r = \frac{A M_p^{1/2}}{\sigma_e \varepsilon^M_a \mathcal{A}} \bar{M}_n^{1/2} \tag{4}$$

where M_p is the molecular weight of one skeletal bond and $\mathcal{A}$ is the Avogadro number. Consequently, $\chi^M_a = 2.8 \times 10^{-3}/\varepsilon^M_a$ and $\varepsilon^M_a \approx 0.85$. One of the aims of this work was to observe the magnetic relaxation of protons attached to polymer chains to determine the relative number of monomeric units linked firmly to the silica surface. According to equation (2), this relative number τ^M_B is expressed as:

$$\tau^M_B = \gamma^M_v \langle r_c \rangle / N \quad \text{or} \quad \tau^M_B = \gamma^M_v \varepsilon^M_a \sqrt{M_p}/\sqrt{\bar{M}_n} \tag{5}$$

where γ^M_v is a numerical factor which accounts for the number of monomeric units which are very close neighbours of adsorbed monomers along one chain; these neighbours may be observed from n.m.r. as fixed units even though they undergo slow motions. The determination of this relative number was applied to hydroxylated and end-methylated chains.

Another aim of this work was to analyse the effect of the formation of hydrogen bonds between ends of hydroxylated chains and the silica surface upon the law of adsorption expressed by equation (1). Furthermore, the kinetics of adsorption of such chains was observed as a function of the chain molecular weight $\bar{M}_n$.

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EXPERIMENTAL

Samples

The surface area of fumed silica (Aerosil 150) determined by the BET method is 150 m^2 g^{-1}. A two-roll stainless steel mill was used to incorporate silica particles into the polymers at room temperature. The average duration of the milling was 15 min. Poly(dimethylsiloxane) samples were supplied by Rhône-Poulenc. The $\overline{M}_n$ values of end-methylated chains were: 1.8 × 10^3, 5.6 × 10^3, 42 × 10^3, 85 × 10^3, 110 × 10^3, 50 × 10^3, 257 × 10^3 and 325 × 10^3 g mol^{-1}; the polydispersity index was 1.9. The $\overline{M}_n$ values of end-hydroxylated chains were: 12 × 10^3, 24 × 10^3, 36 × 10^3 and 54 × 10^3 g mol^{-1}. The c_{Si}^i values in the mixtures were 0.17 or 0.29 (w/w).

All end-methylated samples were observed after the completion of the adsorption process. The state of equilibrium was reached after ~2 years[3].

Extraction of free chains

Free polymer chains were removed from mixtures by keeping each sample in a large flask in the presence of methylcyclohexane over 2 days.

The solvent was removed twice during this time interval. Then, the liquid phase was gently pumped out with a small pipette. The mixture was vacuum dried at room temperature for 2 days and at 90°C for a further 2 days. Finally, each sample was kept in a n.m.r. tube sealed under vacuum. The amount of polymer Q_r^1 left absorbed on the silica surface was determined by microanalysis measurements of the carbon–silicon ratio.

Kinetics of adsorption

The kinetics of adsorption of end-hydroxylated chains was studied by dividing each initial sample into small pieces. These were supposed to evolve simultaneously under external conditions, at 70°C. The amount of polymer linked to silica particles, at a time t, was determined from the irreversible analysis of a single piece, chosen at random. The initial time t_0 of the process of adsorption was chosen as the end of the milling.

N.m.r. measurements

N.m.r. measurements were performed using a Bruker pulsed relaxation spectrometer operating at 60 MHz. Transverse magnetic relaxation functions of protons were analysed from spin-echoes which were formed by applying Carr-Purcell pulse sequences to the spin system.

ADSORPTION OF END-METHYLATED CHAINS

Here the relative number of monomeric units adsorbed upon the silica surface τ_B^M is analysed from n.m.r. observations made in mixtures which contain end-methylated chains.

Principle of the n.m.r. observation

The transverse magnetic relaxation of methyl protons is observed when the adsorption process is achieved and after eliminating all free chains from the mixture. Then, the relaxation function is found to consist of two parts. The fast decay is assigned to fixed monomeric units whereas the long decay corresponds to protons attached to polymer parts which form loops and tails (*Figure 1*). The $c_{Si}^i = 0.29$ (w/w) and $\overline{M}_n = 110 \times 10^3$ g mol^{-1}. Observations were made at several temperatures to induce a strong contrast between the proton relaxation of fixed monomeric units and the proton relaxation of mobile ones. The relaxation function of fixed monomers $M_x^B(t)$ is expected to be insensitive to small variations of temperatures whereas amplitudes of diffusional motions of units forming loops and tails are increased when the temperature is raised; correspondingly, the relaxation function $M_x^L(t)$ ascribed to loops and tails is lengthened. Consequently, the whole relaxation function is expressed as:

$$M_x(t) = \tau_B^M M_x^B(t) + (1 - \tau_B^M) M_x^L(t)$$

where τ_B^M is the relative number of monomeric units fixed on the silica surface.

High silica concentration

Relative numbers of fixed monomeric units were determined for mixtures which contained $c_{Si}^i = 0.29$ (w/w); in such mixtures, silica particles are linked to one another to form an infinite cluster. This behaves like any polymeric gel when free chains are removed from the mixture. It can be reversibly swollen. The ratio τ_B^M was found to vary as a function of $\overline{M}_n^{-1/2}$ in accordance with equation (4). The experimental value of the slope of the straight line is equal to 19.6 g$^{1/2}$ mol$^{-1/2}$; therefore, $\gamma_v^M = 3.8$ (*Figure 2*). Consequently, the two independent ways of observing the law of adsorption (equation (1)) are in agreement with each other.

Partial desorption

Deviations from the laws $Q_r^1 = \chi_a^M \overline{M}_n^{1/2}$ or $\tau_B^M = \gamma_v^M \varepsilon_a^M \sqrt{M_p}/\sqrt{\overline{M}_n}$ are observed when $c_{Si}^i = 0.17$ (w/w) in the mixtures.

Variations of the ratio τ_B^M measured from n.m.r. as a function of the chain molecular weight are reported in *Figure 3*; more precisely the graph shows that the product $\tau_B^M\sqrt{\overline{M}_n}$ is not constant when $\overline{M}_n$ is varied. This result is interpreted in the following way. When $c_{Si}^i = 0.17$ (w/w) an infinite cluster is still formed by mineral particles

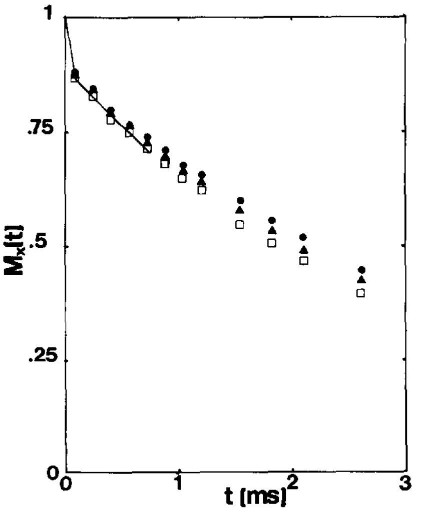

Figure 1 Transverse magnetic relaxation functions of protons linked to end-methylated poly(dimethylsiloxane) chains adsorbed on silica ($\overline{M}_n = 110 \times 10^3$ g mol^{-1}). The two components of the relaxation functions are well observed. Three temperatures of observation were chosen: 298 K (□), 310 K (▲) and 330 K (●); $c_{Si}^i = 0.29$ (w/w)

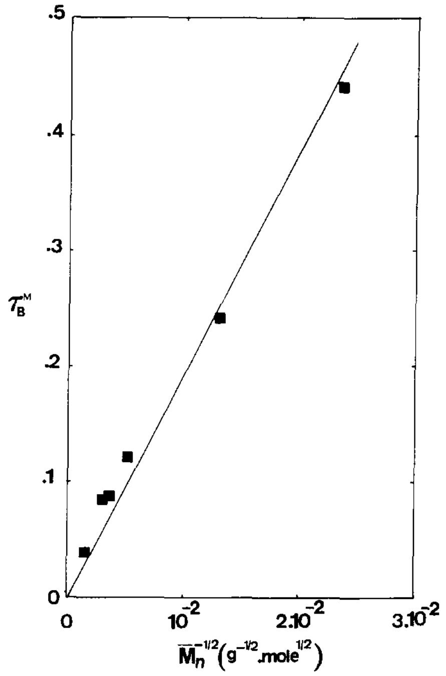

Figure 2 Relative number of adsorbed monomeric units (derived from *Figure 1*) τ_B^Mas a function of the inverse of the square root of the chain molecular weight $\bar{M}_n^{-1/2}$

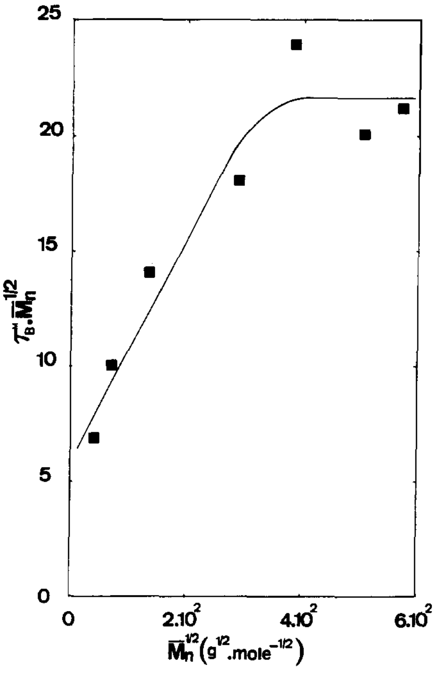

Figure 3 Product $\tau_B^M \bar{M}_n^{-1/2}$ corresponding to $c_{Si}^i = 0.17$ (w/w) as a function of $\bar{M}_n^{1/2}$

attached to one another. It behaves like any permanent gel; however, the amount of solvent that can be absorbed by this gel is larger than the amount absorbed by the infinite cluster obtained with $c_{Si}^i = 0.29$ (w/w). This means that the mesh size of the first species of gel is larger than the mesh size of the second species. Correspondingly the chemical potential of the free chain in the state of maximum swelling is much lower in the first case than in the second case. Consequently, polymer chains which are not linked tightly to the silica surface can be desorbed when the infinite cluster is washed. Experimental results show that this desorption effect is negligible in mixtures where $c_{Si}^i = 0.29$ (w/w); it is no longer negligible when $c_{Si}^i = 0.17$ (w/w).

After washing the polymeric gel ($c_{Si}^i = 0.17$), the area covered by adsorbed polymer chains is not A but $A - \Delta A$ and the total amount of polymer adsorbed per gram of silica is:

$$Q_r^l = (A - \Delta A)\sqrt{M_p}\sqrt{\bar{M}_n}/\sigma_e \varepsilon_a^M \mathscr{A} \qquad (6)$$

However, the value of the deviation ΔA is not constant; it is supposed to depend upon the chain molecular weight $\Delta A(\bar{M}_n)$.

When the infinite cluster is dried, the average distance between particles is shortened and part of the surface $\Delta A(\bar{M}_n)$ may be covered by chains which are already adsorbed. Let $\delta A(\bar{M}_n)$ denote the corresponding area: $\delta A(\bar{M}_n) \leqslant \Delta A(\bar{M}_n)$. Then, the ratio τ_B^M is expressed as:

$$\tau_B^M = \gamma_v^M (A - \Delta A + \delta A) M_p / \sigma_e \mathscr{A} Q_r^l \qquad (7)$$

The product $\tau_B^M Q_r^l$ is proportional to the area covered by all monomeric units fixed to the silica surface after drying the infinite cluster:

$$\tau_B^M Q_r^l = \gamma_v^M M_p (A - \Delta A + \delta A)/\sigma_e \mathscr{A} \qquad (7')$$

Variations of the product $\tau_B^M Q_r^l$ determined as a function of $\sqrt{\bar{M}_n}$ are shown in *Figure 4*. The area of the silica surface involved in the adsorption process is not a constant. It increases when the chain molecular weight is increased. Furthermore, the average area σ_a covered by one chain is:

$$\sigma_a = \bar{M}_n (A - \Delta A + \delta A)/\mathscr{A} Q_r^l \qquad (8)$$

or, from equation (7):

$$\sigma_a = \sigma_e \tau_B^M \bar{M}_n / \gamma_v^M M_p \qquad (8')$$

In the absence of any deviation from equation (5), the area σ_a should be proportional to $\bar{M}_n^{1/2}$. Therefore, it is convenient to represent variations of the ratio $\sigma_a/\sqrt{\bar{M}_n}$; the value of this ratio is constant for $\bar{M}_n > 90 \times 10^3$ g mol^{-1} (*Figure 3*). On close inspection of *Figures 3* and *4*, it is considered that the law of adsorption $Q_r^l \propto \sqrt{\bar{M}_n}$ is observed when the molecular weight of polymer chains is $> 90 \times 10^3$ g mol^{-1}; then, $\chi_a^M = 4 \times 10^{-3}$ g$^{-1/2}$ mol$^{1/2}$, for $c_{Si}^i = 0.17$ (w/w). This result shows that a tighter binding of polymer chains occurs when the number of contact points is sufficiently large ($\sqrt{N} \geqslant 50$)

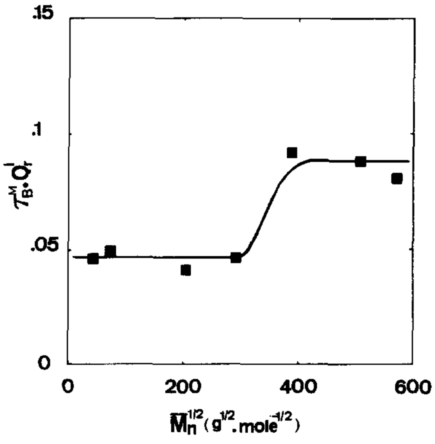

Figure 4 Product $\tau_B^M Q_r^l$ (proportional to the area covered by the polymer adsorption) as a function of $\bar{M}_n^{1/2}$; $c_{Si}^i = 0.17$ (w/w)

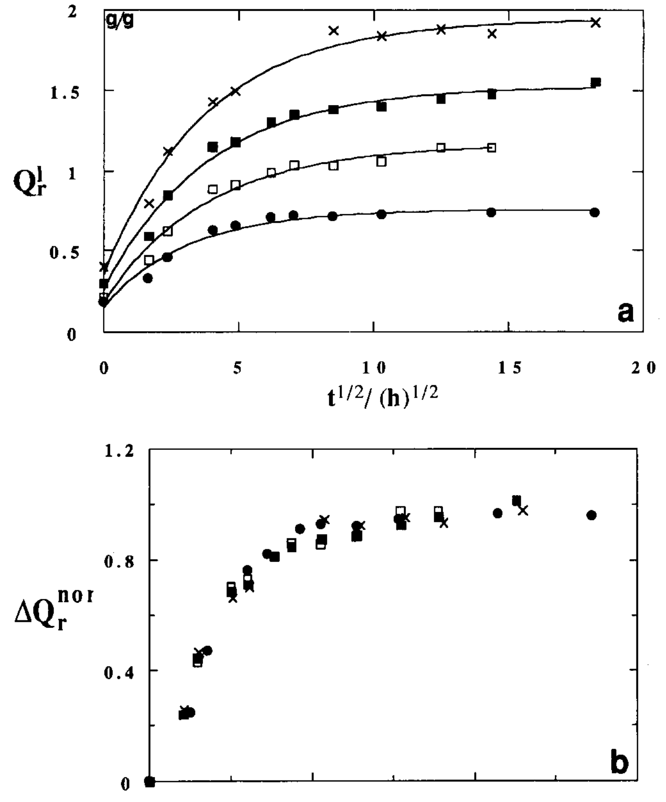

Figure 5 (a) Kinetics of adsorption of end-hydroxylated chains: $c_{Si}^i = 0.17$ (w/w). Continuous curves were drawn according to equation (9). $\bar{M}_n = 12 \times 10^3$ (●), 24×10^3 (□), 36×10^3 (■) and 54×10^3 g mol^{-1} (×). (a) Normalized experimental curves of adsorption kinetics obey superposition. The time scale is defined by the time constant τ of each mixture

to avoid a desorption process induced by the presence of solvent.

ADSORPTION OF HYDROXYLATED CHAINS

The purpose of this section is to analyse the role played by hydroxylated ends of siloxane chains in the process of adsorption.

Kinetics of adsorption

Before considering the limiting value Q_r^l of the amount of polymer fixed on the silica surface, it is worth describing the kinetics of adsorption which follows after mechanical mixing. The duration of the mixing is 15 min; at the end of the mixing, the surface of silica particles is not covered entirely by polymer chains. The completion of the adsorption process occurs according to a law which has been already described[3]; it is represented by the time function:

$$Q_r^l - Q_r(t) = [Q_r^l - Q_r(0)]\exp\left(-\sqrt{\frac{t - t_0}{\tau}}\right) \quad (9)$$

where t_0 corresponds to the end of the mixing and τ is a time constant specific to the mixture. This function has been established by assuming that the rate of adsorption at a time t results from a random collision with an absorbing screen on the one hand and excluded surface effect on the other hand. The rate of adsorption depends upon the accessible area which is proportional to $Q_r^l - Q_r(t)$. The kinetics of adsorption of end-hydroxylated chains corresponding to $c_{Si}^i = 0.17$ (w/w) is represented in *Figure 5a*. Four chain molecular weights were considered ($\bar{M}_n = 12 \times 10^3, 24 \times 10^3, 36 \times 10^3$ and 54×10^3 g mol^{-1}); correspondingly, the values of the time constant τ were 11 h for $\bar{M}_n = 12 \times 10^3$ g mol^{-1} and 16 h for the three other values of $\bar{M}_n$. The good agreement between experimental points and theoretical curves is seen in *Figure 5a*. Experimental points obey superposition when amplitudes $Q_r^l - Q_r(t)$ are normalized and when a shift factor is applied to the time scale of evolution (*Figure 5b*).

Similar curves are obtained when $c_{Si}^i = 0.29$ (w/w). Values of $\tau = 7.0$ and 9.5 h for $\bar{M}_n = 12 \times 10^3$ and 54×10^3 g mol^{-1} (*Figure 6*). The time constant is ~20 times shorter than that associated with the kinetics of end-methylated chains[3].

Law of adsorption

Numerical values of the limiting amount of polymer Q_r^l adsorbed on the silica surface are determined from the fit associated with equation (9). It is shown in *Figure 7* that Q_r^l is proportional to the square root of the chain

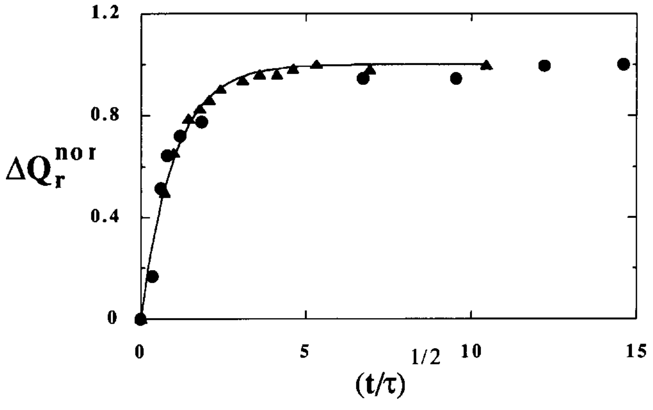

Figure 6 Normalized experimental curves of adsorption kinetics obey superposition when $c_{Si}^i = 0.29$ (w/w). $\bar{M}_n = 12 \times 10^3$ (▲) and 54×10^3 (●) g mol^{-1}

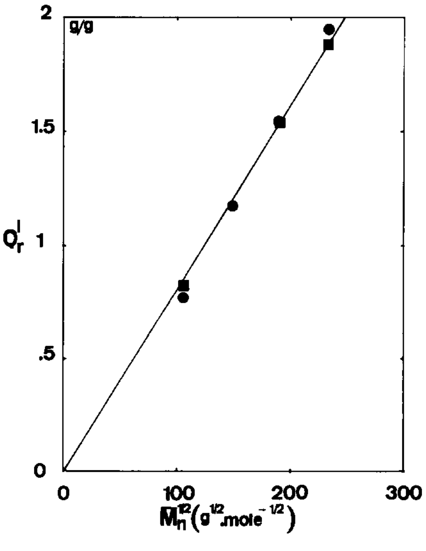

Figure 7 Residual amount of polymer adsorbed on the silica surface Q_r^l as a function of $\bar{M}_n^{1/2}$: $c_{Si}^i = 0.17$ (w/w) (●) and 0.29 (w/w) (■)

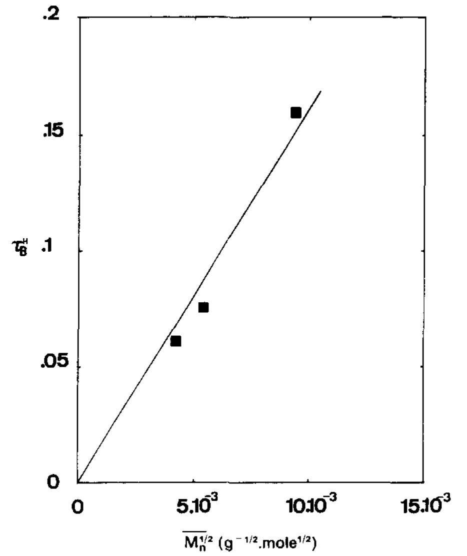

Figure 8 Relative number of adsorbed monomeric units τ_B^H as a function of $\bar{M}_n^{-1/2}$ of hydroxylated chains

molecular weight within the range $12 \times 10^3 \leqslant \overline{M_n} \leqslant 54 \times 10^3$ g mol^{-1}:

$$Q_r^i = \chi_a^H \overline{M_n}^{1/2} \qquad (10)$$

with $\chi_a^H = 8.0 \times 10^{-3}$ for both $c_{Si}^i = 0.17$ and 0.29 (w/w) and $\varepsilon_a^H = 0.34$ is the corresponding value of the contact constant (equation (2)) for the two concentrations. For $c_{Si}^i = 0.29$ (w/w), the presence of hydroxylated ends does not change the law of adsorption except for the value of the constant χ_a^H. For $c_{Si}^i = 0.17$ (w/w), there is no partial desorption induced by washing the infinite cluster. The amounts of adsorbed polymers are equal to each other although the initial concentrations c_{Si}^i have very different values.

The relative number τ_B^H of monomeric units fixed upon the silica surface can be measured from n.m.r. Variations of τ_B^H as a function of $\overline{M_n}^{-1/2}$ are reported in *Figure 8*. The numerical value of the slope of the straight line is 15.5 g$^{1/2}$ mol$^{-1/2}$. This must be compared with the value of $\gamma_v^H \varepsilon_a^H \sqrt{M_p}$. Thus, $\gamma_v^H = 7.4$ for $c_{Si}^i = 0.29$ (w/w) and the number of monomeric units which are perceived from n.m.r. as fixed above the silica surface is higher for hydroxylated chains than for methylated ones.

CONCLUSIONS

The law of adsorption of end-methylated or end-hydroxylated chains upon silica surfaces is specific to the full immersion of particles in a melt. This law is completely different from that observed from mineral particles in suspension in a polymer solution[4]. The number of contact points of one chain with the surface is not proportional to the number of skeletal bonds but to the square root of this number. It is worth emphasizing that hydroxylated chain ends play a non-negligible role in the adsorption process of poly(dimethylsiloxane). The specific amount of adsorbed polymer for a given chain length is increased by the presence of hydroxylated ends; and an increase in the rate of saturation of the silica surface is induced by the presence of the hydroxylated ends. These observations lead to the conclusion that all hydroxylated chain ends are probably linked to the surface because of the formation of double hydrogen bonds. Consequently, there are no tails. Also, once a chain end is fixed upon the surface, there is an anchoring effect on the chain.

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