# Poly(dimethylsiloxane)–silica mixtures: intermediate states of adsorption and swelling properties

**J. P. Cohen Addad* and S. Touzet**
*Laboratoire de Spectrométrie Physique associé au CNRS, BP 87-38402 St Martin d'Hères Cedex, France*
*(Received 26 October 1992)*

The properties of poly(dimethylsiloxane)–silica mixtures are studied by varying the specific area of silica aggregates and the chain molecular weight. The specific area was varied either by changing the nature of the silica (50 or 150 $m^2 g^{-1}$) or by converting silanol groups into trimethylsilyl groups. It is shown that a single kinetic law applies to the description of the chain adsorption process after the mechanical mixing, whatever the chain molecular weight and the silica concentration. In contrast with this result, the time constant is found to depend upon these two variables. Swelling properties of these mixtures were observed in order to investigate statistical structures corresponding to intermediate states of chain adsorption. A quantitative interpretation of swelling effects is given within the framework of percolation. It is shown that the mean number of contact points of one adsorbed chain with the silica surface is proportional to the square root of the chain molecular weight. This result was shown, in previous work, to characterize equilibrium states of adsorption; it is now extended to intermediate states of chain adsorption.

**(Keywords: adsorption; swelling behaviour; poly(dimethylsiloxane))**

## INTRODUCTION

Silica aggregates can be bridged to one another by poly(dimethylsiloxane) (PDMS) chains which are adsorbed on the silica surface. Siloxane–silica mixtures are known to behave like permanent gels when the aggregate concentration and the chain length are appropriate for the formation of an infinite cluster. The elementary mechanism of adsorption arises from the formation of hydrogen bonds between silanol groups on the surface and oxygen atoms of the chain skeletons. In recent years, attention has been focused mainly upon the following three quantitative properties:

(i) At equilibrium, the limiting value of the specific amount of adsorbed polymer $Q_r^1$ exhibits an apparent linear dependence on the square root of the chain molecular weight $\overline{M}_n$:

$$Q_r^1 = \chi_a \overline{M}_n^{1/2} \qquad (1)$$

The $Q_r^1$ quantity is measured when the state of surface saturation of the aggregates is reached. The factor $\chi_a$ depends upon the specific area $A_T$ of silica[1]. This law of adsorption is specific to silica particles fully immersed in molten PDMS; it has already been given an interpretation based upon the probability that a Gaussian random flight collides with a plane[2]. The numerical value of $\chi_a$ is $3 \times 10^{-3}$ $g^{-1/2}$ $mol^{1/2}$ for $A_T = 150$ $m^2 g^{-1}$ and an initial silica concentration $C_{Si}^i$ equal to 0.29 (w/w). It must be noted that the amount of adsorbed polymer $Q_r$ on silica aggregates does not obey equation (1) as long as the state of saturation of the surface is not reached. The process of saturation, observed at room temperature, lasts for about 3 years for end-methylated chains. Consequently, experimental results obtained before reaching the equilibrium adsorption lead to a law different from equation (1). An apparent linear law has been reported when the process of adsorption is observed over time intervals much shorter than 3 years[3], namely $Q_r \propto \overline{M}_n$. Equation (1) is now firmly established for both end-methylated and end-hydroxylated chains. Furthermore, this law has been established not only from microanalysis measurements of the carbon content of siloxane–silica mixtures, but also from n.m.r. measurements. The transverse relaxation of protons linked to adsorbed monomeric units can be distinguished from that of protons linked to chain segments issuing from contact points[4].

(ii) The second quantitative property concerns the kinetics of surface saturation of silica particles. This process begins during the mechanical mixing; then, the adsorption of end-methylated chains lasts for about 3 years, at room temperature. This time interval is reduced to about 3 months when the temperature of adsorption is 343 instead of 300 K. This time-dependent adsorption is well-described according to a law which accounts for both an effect of excluded surface and an effect of absorbing screen. The specific amount $Q_r(t)$ of adsorbed polymer at a time $t$ is expressed as:

$$Q_r^1 - Q_r(t) = [Q_r^1 - Q_r(0)] \exp(-\sqrt{t/\tau}) \qquad (2)$$

where $\tau$ is a time constant of adsorption specific to initial conditions of formation of mixtures[5].

(iii) Finally, swelling properties of mixtures observed after extracting all free chains have been described

---

* To whom correspondence should be addressed

0032-3861/93/163490-09

according to the mean field approximation proposed by Flory[6,7]. The swelling ratio $Q_m$ defined for the polymer part of one mixture is found experimentally to vary as:

$$Q_m^{5/3} - Q_m/2 = Q_r^1 \sigma_e / \rho_p A_T \qquad (3)$$

where $\rho_p$ is the pure polymer density and $\sigma_e$ is the average area associated with one silanol group participating in the formation of one hydrogen bond with a polymer chain. $Q_m$ is defined as the ratio of the volume $V_m$ of swollen polymer over the volume $V_D$ of the dry polymer. The ratio $n_H^0 = A_T/\sigma_e$ is the specific number of bonds which participate in the polymer adsorption on the silica surface. The number $n_H^0$ was varied by applying a partial chemical treatment to silica; $n_H^0$ is called the parameter of efficiency of chain adsorption throughout this work.

A description of PDMS–silica mixtures within the framework of percolation has been recently proposed. Polymer chains are considered as difunctional units while silica particles are assumed to have a high functionality which depends upon the law of adsorption of polymer chains[8]. All relevant quantities which characterize mixture properties are expressed as a function of the chain molecular weight $\overline{M}_n$ on the one hand and of the adsorbed fraction $\Gamma$, on the other hand; $\Gamma$ is defined as the ratio of the amount of adsorbed polymer $Q_r$ to the initial specific amount of polymer $Q_i$, i.e. $\Gamma = Q_r/Q_i$. The threshold of percolation $Q_r^c$ is expressed as a function of $\overline{M}_n$ and $\Gamma$. Above the threshold of percolation, $\Gamma$ can play the role of a gel fraction if all finite clusters are washed out.

The purpose of this work is two-fold:

(i) It is shown that properties observed on silica aggregates characterized by a specific area equal to 150 m$^2$ g$^{-1}$ can be extended to a lower specific area of silica equal to 50 m$^2$ g$^{-1}$. A further reduction of the total mineral surface accessible to polymer chains was induced by mixing two kinds of aggregates. The first kind was obtained by applying a partial chemical treatment to the surface while the second one corresponded to particles without any treatment.

(ii) The kinetics of surface saturation was observed. We also attempted to characterize siloxane–silica mixtures which are in a state of progressive saturation of the silica surface. Investigations into properties associated with different states of partial adsorption are based upon the observation of the swelling effect induced by the osmotic pressure exerted on mixtures by a good solvent.

## EXPERIMENTAL

### *Materials*

End-methylated PDMS chains are commercially available polymers; the polymer chains are methyl terminated. Number-average molecular weights and polydispersity indices are reported in *Table 1*.

The surface area of fumed silica (OX50) determined by the Brunauer–Emmett–Teller (BET) method is 50 m$^2$ g$^{-1}$. Previous studies have been made on another fumed silica (Aerosil 150) characterized by a surface area equal to 150 m$^2$ g$^{-1}$; without any surface treatment, the density of free silanol groups is $1.8 \times 10^{-2}$ Å$^{-2}$. It is assumed that this density also characterizes the OX50 silica. The ultimate particle size varies from 300 to about 400 Å and aggregates are formed from the association of two or three particles bridged by covalent links.

**Table 1** Average molecular weights of PDMS samples

| $\overline{M}_n$ | $\overline{M}_w$ | $I_p$ |
|---|---|---|
| 45 000 | 99 000 | 2.2 |
| 67 500 | 161 400 | 2.4 |
| 229 400 | 441 700 | 1.9 |

Some silica samples were chemically treated; hexamethyldisilazane was used to convert silanol sites on the silica surface into non-functional trimethylsilyl groups; this partial treatment was performed in the gaseous phase by Rhône-Poulenc. The extent of the treatment was estimated using infra-red spectroscopy: about 40% of initial silanol groups were converted into non-functional groups.

### *Sample preparation*

A two-roll stainless steel mill was used to incorporate the mineral particles into the bulk polymer at room temperature. The milling was performed up to the formation of homogeneous samples; after full incorporation of the filler into the polymer, the duration of the milling was about 15 min.

Mixtures differ from one another, both by the initial concentration $C_{Si}^i$ of the products and the ratio $C_{Tr}$ of treated aggregates. All data describing the different mixtures are listed in *Table 1*.

After the milling, samples were placed in an oven regulated at 343 K. This time was chosen as the starting point ($t = 0$) of the study of a given mixture.

### *Polymer extraction*

Methylcyclohexane was used to remove the free polymer chains from silica–siloxane mixtures. At a given time $t$, a small piece of sample (a few mm$^3$) was taken out of the oven and put in a glass vessel with a large excess of solvent at room temperature. The solvent was renewed three times over 5 days. Then the product was dried under free atmosphere. Finally, the product was vacuum dried at room temperature for 48 h, to eliminate traces of solvent.

### *Thermodynamic variables*

The specific residual amount of polymer, $Q_r(t)$, still bound to silica at a time $t$, after removal of all free polymer chains, was determined from microanalysis measurements of carbon content. This analysis was performed by Rhône-Poulenc.

The other quantity appropriate to the approach to statistical properties of these gel-like systems is the swelling ratio, $Q_{mm}$, measured at equilibrium with methylcyclohexane. The ratio $Q_{mm}$ is defined from the polymer part of the system, solely; the silica volume is considered as invariant upon addition of solvent. The value of $Q_{mm}$ is calculated from the weight $m_s$ of the swollen sample, the weight $m_d$ of the dried sample and the amount of adsorbed polymer $Q_r$:

$$Q_{mm} = 1 + \frac{\rho_p}{\rho_s} \frac{(m_s - m_d)}{m_d} \left(1 + \frac{1}{Q_r}\right)$$

where $\rho_p$ and $\rho_s$ are the densities of the polymer and the solvent, respectively.

### *N.m.r. measurements*

Relaxation times of protons attached to adsorbed polymer chains were recorded using an MSL Bruker spectrometer operating at 100 MHz. Relaxation times were determined by observing classical Hahn spin-echoes to eliminate all magnetic field inhomogeneities.

## KINETICS OF SURFACE SATURATION

In this section, it is shown that the specific amount of adsorbed polymer $Q_r(t)$ obeys a general law of kinetics of surface saturation which has a mathematical structure independent of the chain molecular weight and of the content of chemically treated aggregates. This law is first illustrated from the process of saturation of a non-treated surface of silica.

### *Non-treated silica*

The elementary amount of polymer $Q_r(t)$ adsorbed per unit time and per unit mass of silica is expressed according to the differential equation:

$$\frac{dQ_r(t)}{dt}=[Q_r^l-Q_r(t)]/\sqrt{t\tau} \qquad (4)$$

where the quantity $Q_r^l-Q_r(t)$ is proportional to the silica surface still accessible to polymer chains at a time $t$ and the expression $1/\sqrt{t\tau}$ is specific to random flight processes which occur in the presence of an absorbing screen. This differential equation leads to equation (2). The kinetics of surface saturation are illustrated in *Figure 1a* for an initial silica concentration $C_{Si}^i$ equal to 0.29 (w/w); the chain molecular weight was $\overline{M}_n=2.3\times10^5$ g mol$^{-1}$. The limiting value of $Q_r^l$ was found to be equal to 1.1 (w/w) while the time constant of adsorption $\tau$ was equal to 135 h. Values of the time constant $\tau$ corresponding to different concentrations of silica are 83 h for $C_{Si}^i=0.5$ (w/w) and 285 h for $C_{Si}^i=0.17$ (w/w).

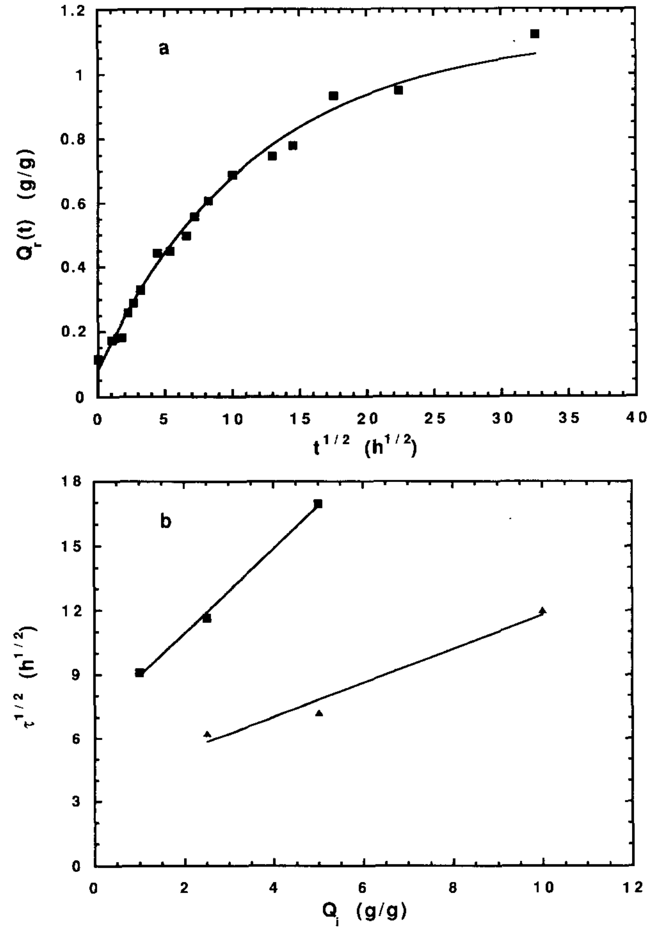

**Figure 1** (a) Kinetics of polymer chain adsorption. The solid curve was drawn according to equation (2). $\overline{M}_n=23\times10^4$ g mol$^{-1}$; $C_{Tr}=0$, $C_{Si}=0.29$ (w/w); specific area of silica: 50 m$^2$ g$^{-1}$. (b) Variation of the square root of the time constant of kinetics of polymer adsorption. ($\overline{M}_n=23\times10^4$ g mol$^{-1}$); specific areas of silica: 50 (■); 150 m$^2$ g$^{-1}$ (▲)

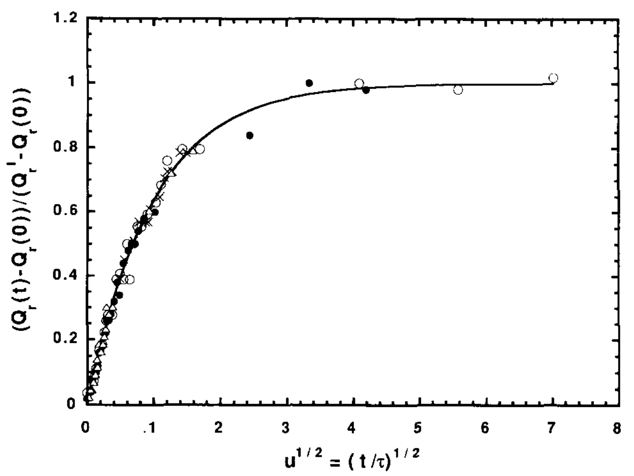

**Figure 2** Property of superposition of curves of kinetics of chain adsorption ($\overline{M}_n=23\times10^4$ g mol$^{-1}$, $C_{Si}=0.5$). Concentrations of chemically treated aggregates: $C_{Tr}=0$ (×); $C_{Tr}=1/3$ (○); $C_{Tr}=2/3$ (●); $C_{Tr}=1$ (△)

The temperature of adsorption was 343 K. Variations of the square root of the time constant $\tau$ are shown as a function of the initial specific amount of polymer, $Q_i$, in *Figure 1b*; a straight line can be drawn, although the number of experimental points is small. Variations of $\sqrt{\tau}$, corresponding to a specific area of silica equal to 150 m$^2$ g$^{-1}$, are also reported in *Figure 1b*; a straight line can again be drawn through the experimental points ($\overline{M}_n=23\times10^4$ g mol$^{-1}$).

### *Treated silica*

Experimental results reported in *Figure 2* were obtained from measurements performed on samples prepared by mixing partly treated aggregates with non-treated aggregates. In *Figure 2*, the initial concentration of silica $C_{Si}^i$ (0.5 (w/w)) and the chain molecular weight ($2.3\times10^5$ g mol$^{-1}$) were kept constant but the concentration $C_{Tr}$ of partly treated aggregates was varied from 0 to 1. The generality of equation (4) is illustrated by showing that curves representing variations of the normalized quantity $(Q_r^l-Q_r(t)/(Q_r^l-Q_r(0))$ as a function of the reduced variable $u=t/\tau$ obey a property of superposition. Values of the time constant of adsorption are $\tau=83$ h for $C_{Tr}=0$, 120 h for $C_{Tr}=0.33$, 330 h for $C_{Tr}=0.66$ and 2310 h for $C_{Tr}=1$. Solid curves were drawn in *Figures 1a* and *2* from equation (4) by applying a least-mean-squares procedure with $Q_r^l$ and $\tau$ as adjustable parameters. Variations of the inverse of $\tau$ as a function of the concentration $C_{Tr}$ are shown in *Figure 3*.

The time constant of adsorption is found to decrease when the concentration of treated aggregates is decreased; this behaviour parallels the result obtained by increasing the concentration $C_{Si}^i$ of non-treated silica. These results show that the kinetics of adsorption depends upon the initial extent of the silica surface which is offered to the unit mass of polymer to form hydrogen bonds. Consequently, it is proposed to modify equation (4)

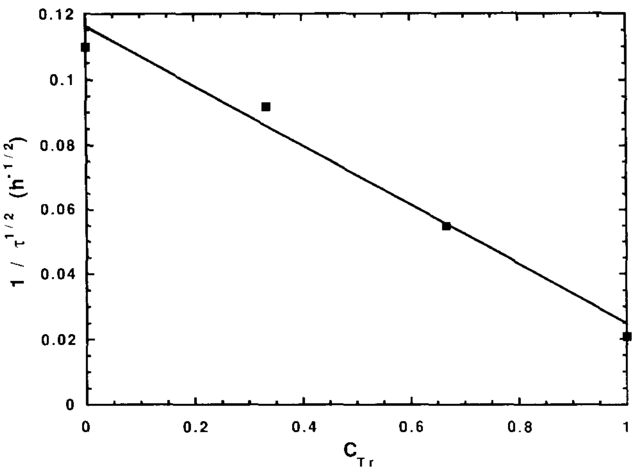

**Figure 3** Variation of the inverse of the square root of the time constant of kinetics of polymer adsorption as a function of the concentration of treated aggregates. $\overline{M}_n = 23 \times 10^4\,\mathrm{g\,mol^{-1}}$, $C_{Si} = 0.5$ (w/w)

empirically by introducing the initial number of binding sites of adsorption per monomeric unit:

$$\sigma_i = A_T(1 - \alpha C_{Tr})M_m/\mathscr{A}\sigma_e(Q_i + \gamma) \tag{5}$$

with $0 \leqslant \alpha \leqslant 1$; the $\alpha$ parameter represents the extent of the chemical treatment of the silica surface and $M_m$ is the molar weight of one monomeric unit. The empirical parameter $\gamma$ may depend upon the chain molecular weight; $\mathscr{A}$ is the Avogadro number. Then, equation (4) is written as:

$$\frac{dQ_r(t)}{dt} = \sigma_i \frac{Q_r^l - Q_r(t)}{\sqrt{t\tau_0}} \tag{6}$$

The apparent correlation time is defined as:

$$\tau = \tau_0 \left[ \frac{(\gamma + Q_i)\mathscr{A}\sigma_e}{A_T(1 - \alpha C_{Tr})M_m} \right]^2 \tag{7}$$

The experimental value of $\alpha$ derived from *Figure 3* is 0.8. According to equation (7), the slope of each straight line drawn in *Figure 1b* is proportional to the parameter of efficiency of chain adsorption $n_H^0 = A_T/\sigma_e$; the ratio of the slopes of the straight lines drawn in *Figure 1b* is found to be equal to $2.5 \pm 0.5$ while the ratio of the specific areas of silica is equal to 3. This discrepancy is probably not significant, taking experimental uncertainties into consideration. However, it may reflect slightly different organizations of silanol groups onto silica surfaces, corresponding to different specific areas.

## SATURATED ADSORPTION

In this section, the limiting value of the specific amount $Q_r^l$ of adsorbed polymer is first reported as a function of the chain molecular weight for several values of the initial concentration of silica; two values of the specific area are also considered. Then, the effect of a chemical treatment of the silica surface is described.

### *Law of adsorption*

Let $\mathscr{P}(r_c, N)$ denote the distribution function of chains which can form $r_c$ contact points with the silica surface; $N$ is the number of skeletal bonds in one chain. The function $\mathscr{P}(r_c, N)$ satisfies the equality:

$$\int r_c \mathscr{P}(r_c, N)\,dr_c = A_T/\sigma_e \tag{8}$$

$\sigma_e^{-1}$ represents the average density of active silanol groups which can be involved in the formation of hydrogen bonds with PDMS chain skeletons. Then, the total number of chains adsorbed per unit mass of silica is:

$$\nu_c = \int \mathscr{P}(r_c, N)\,dr_c \tag{9}$$

The expression of $\mathscr{P}(r_c, N)$ has already been given in ref. 2:

$$\mathscr{P}(r_c, N) = A_T/\sigma_e\sqrt{2/\pi}\,r_c N^{-3/2}\exp(-r^2/2N) \tag{10}$$

Therefore, the number $\nu_c$ is written as:

$$\nu_c = 0.8 A_T/\sigma_e\sqrt{N} \tag{11}$$

The maximum amount of polymer which can be adsorbed on silica without creating any connection between aggregates is:

$$Q_r^m = \nu_c M_n/\mathscr{A} \tag{12}$$

Equation (12) may also be written as:

$$Q_r^m = \beta(n_H^0)\sqrt{M_n} \tag{13}$$

with

$$\beta(n_H^0) = 0.56 A_T\sqrt{M_m}/\sigma_e\mathscr{A} \tag{14}$$

or

$$\beta(n_H^0) = 0.8 A_T 10^{-3}/\sigma_e \tag{15}$$

$A_T$ and $\sigma_e$ are expressed in Å$^2$ units. According to equation (11), the average number of hydrogen bonds formed per adsorbed chain is:

$$\psi(N) = A_T/\sigma_e\nu_c \tag{16}$$

or:

$$\psi(N) = 1.25\sqrt{N} \tag{17}$$

The parameter of efficiency of the chain adsorption process is not involved in equation (17).

### *Percolation framework*

A method of describing the properties of siloxane–silica mixtures within the framework of percolation has already been proposed. For the sake of simplicity, any polymer chain is supposed to connect only two particles; it is then considered as a difunctional unit of percolation. One polymer chain is supposed to carry two $U$ functions. Then, the initial number of $U$-units of percolation per gram of silica is:

$$\mathscr{N}_p^i = Q_i\mathscr{A}/\overline{M}_n \tag{18}$$

Any silica aggregate is considered as one unit of percolation with a multiple functionality. One aggregate is assumed to carry a mean number $f_c$ of sites of chain adsorption. These $f_c$ sites are considered as $V$ functions. Then, the adsorption of one chain on one aggregate is pictured as a chemical reaction which occurs between one $U$-unit and one $V$-unit. The total number of $V$ functions per gram of silica is set equal to $\nu_c$.

Any state of percolation is characterized by the fraction $\phi_p$ of $U$ functions which participate in the determination of the network structure. The number of free chains is written as:

$$\mathcal{N}_p^i(1-\phi_p)^2 \tag{19}$$

This corresponds to the fraction $\phi_{Si}$ of $V$ functions which participate in the percolation process, with:

$$2\phi_p\mathcal{N}_p^i=\phi_{Si}\nu_c \tag{20}$$

The number of adsorbed chains per gram of silica is defined by the ratio $Q_r\mathcal{A}/\overline{M_n}$; it is also expressed as:

$$\mathcal{N}_p^i[1-(1-\phi_p)^2] \tag{21}$$

Therefore:

$$Q_r=Q_i[1-(1-\phi_p)^2] \tag{22}$$

and the fraction $\phi_p$ is a function of the adsorbed polymer fraction $\Gamma=Q_r/Q_i$:

$$\phi_p=\Gamma/(1+\sqrt{1-\Gamma}) \tag{23}$$

In the state of saturated adsorption, the fraction $\phi_{Si}$ is set equal to unity and:

$$\phi_p=\nu_c/2\mathcal{N}_p^i \tag{24}$$

or

$$\phi_p=\nu_c\overline{M_n}/2\mathcal{A}Q_i \tag{25}$$

Therefore:

$$\frac{Q_r^l}{Q_i}=\frac{Q_r^m}{Q_i}\left(1-\frac{Q_r^m}{4Q_i}\right) \tag{26}$$

Two reduced variables are introduced: $q_r^l=Q_r^l/Q_i$ and $q_r^m=Q_r^m/Q_i$; the maximum value of $q_r^l$ is unity while $q_r^m$ is defined from the initial conditions of preparation of the mixtures. The reduced amount of adsorbed polymer is a simple function of the reduced variable $q_r^m$. Experimental results are conveniently presented by using the variable $\sqrt{M_n}/Q_i$:

$$q_r^l=\beta(n_H^0)\frac{\sqrt{M_n}}{Q_i}\left[1-\beta(n_H^0)\frac{\sqrt{M_n}}{4Q_i}\right] \tag{27}$$

All experimental results of measurements performed on two types of silica surfaces are shown in *Figure 4*. For aggregates characterized by a specific area equal to 150 m$^2$ g$^{-1}$, three initial silica concentrations were considered: $C_{Si}^i=0.09$ ($Q_i=10$), $C_{Si}^i=0.17$ ($Q_i=5$) and $C_{Si}^i=0.29$ $(Q_i=2.5)^1$. For aggregates characterized by a specific area equal to 50 m$^2$ g$^{-1}$, the initial concentration was $C_{Si}^i=0.5$ ($Q_i=1$). The ratio of the parameters of efficiency of chain adsorption was found to be equal to 2.2, while the ratio of specific areas is equal to 3. In *Figure 4*, the parameter $\beta$ associated with the specific area equal to 50 m$^2$ g$^{-1}$ was divided by 2.2 to get the experimental points located on the curve drawn for the specific area equal to 150 m$^2$ g$^{-1}$. Considering equation (15), the ratio $A_T/\sigma_e$ is found to be equal to 2.3 for $A_T=50$ m$^2$ g$^{-1}$ and to 5.4 for $A_T/\sigma_e=150$ m$^2$ g$^{-1}$. *Figure 4* can also be considered as an illustration of the law of adsorption $\psi(N)\propto\sqrt{N}$.

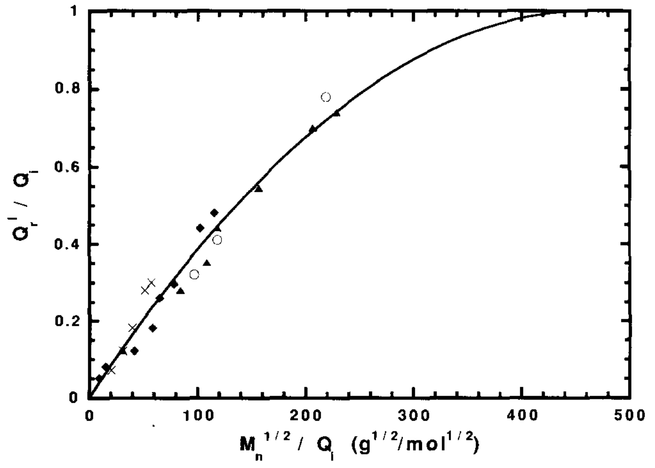

**Figure 4** Representation of the ratio $Q_r^l/Q_i$ as a function of $\sqrt{\overline{M_n}}/Q_i$. For the specific area equal to 150 m$^2$ g$^{-1}$, the initial specific amount of polymer was $Q_i=10$ (×), 5 (◆) and 2.5 (▲). For the specific area equal to 50 m$^2$ g$^{-1}$, the scale of $\sqrt{\overline{M_n}}/Q_i$ was divided by 2.2 (○). The solid curve was drawn as a parabola in accordance with equation (27)

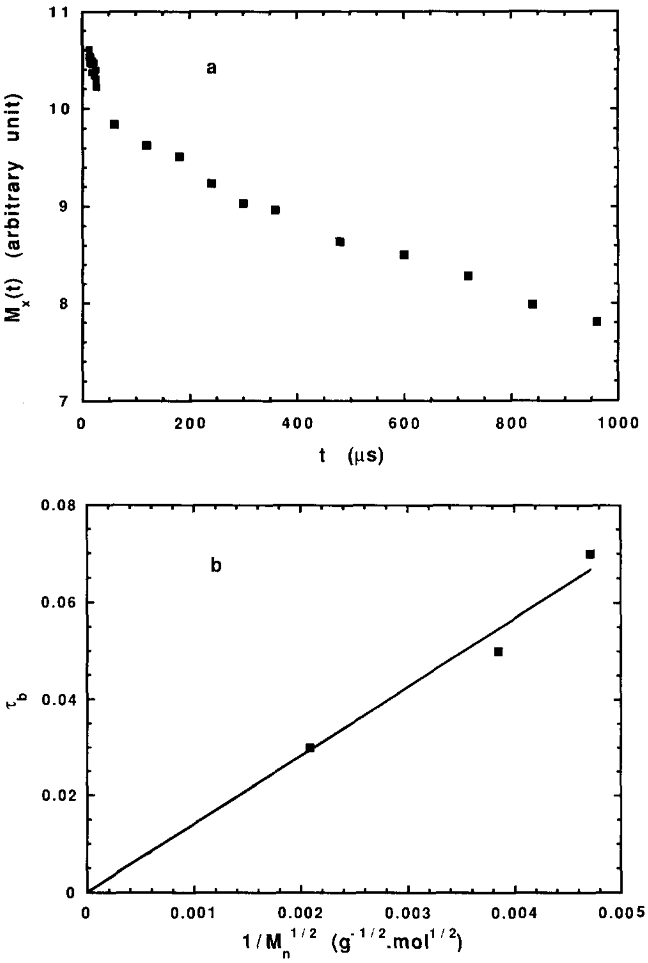

**Figure 5** (a) Transverse magnetic relaxation of protons ($\overline{M_n}=45\times10^4$ g mol$^{-1}$, $C_{Si}=0.5$ (w/w), $C_{Tr}=0$). The temperature of observation was 80°C. Free induction decay (■), Hahn spin-echoes (■). (b) The relative amplitude $\tau_p$ of monomeric units fixed on the silica surface is represented as a function of the inverse of the square root of the chain molecular weight ($C_{Si}=0.5$ (w/w), $C_{Tr}=0.5$)

## *N.m.r. observation of fixed monomeric units*

In this section, the adsorbed layer formed from PDMS chains is observed from the transverse relaxation of the magnetization of protons attached to the polymer. The relaxation process of protons attached to monomeric units tightly bound to the silica surface can be discriminated from the relaxation of protons located on loops and tails. This property is illustrated in *Figure 5a*.

The magnetization assigned to fixed monomeric units behaves as in a solid; a sharp free decay is observed over a time interval equal to about 40 ms. Then, a slowly decreasing relaxation curve is observed by forming spin-echoes. The magnetic relaxation of protons located on loops and tails lasts over about 4 $\mu$s. The relaxation curve was recorded at 80°C; the chain molecular weight was $\overline{M_n} = 4.5 \times 10^4$ g mol$^{-1}$, while the initial silica concentration was $C_{Si}^{i} = 0.5$ ($Q_i = 1$). Free polymer chains were extracted and samples were dried before observing the n.m.r. properties. The specific area of silica was 50 m$^2$ g$^{-1}$.

Relative amplitudes of the magnetizations corresponding to fixed monomeric units and to mobile ones are easily determined from proton relaxation curves corresponding to several molecular weights: $\overline{M_n} = 4.5 \times 10^4$, $6.7 \times 10^4$ and $23 \times 10^4$ g mol$^{-1}$. Variations of the relative number $\tau_B$ of fixed monomeric units are represented as a function of the inverse of the square root of the chain molecular weight in *Figure 5b*. A linear dependence is observed within a reasonable accuracy. This result is interpreted in a simple way by expressing the relative number $\tau_B$ as the ratio of the specific number of fixed monomeric units to the specific residual amount of adsorbed polymer $Q_r^l$:

$$\tau_B = \frac{A_T M_m}{\sigma_e Q_r^l \mathscr{A}} \tag{28}$$

The apparent linear dependence of $Q_r^l$ on $\overline{M_n}^{1/2}$, observed in *Figure 4*, accounts for the dependence of $\tau_B$ on $\overline{M_n}^{-1/2}$ shown in *Figure 5b*. According to equation (28), the number of hydrogen bonds formed between the silica surface and PDMS chains is independent of the chain molecular weight over the range $4.5 \times 10^4 \leqslant \overline{M_n} \leqslant 23 \times 10^4$ g mol$^{-1}$. It may be worth recalling that polymer chains are end-methylated.

### *Treated silica*

The adsorption effect, in the state of surface saturation, was also characterized as a function of the concentration $C_{Tr}$ of treated aggregates.

The relative amount of adsorbed polymer $Q_r^l(C_{Tr})/Q_r^l$ is shown in *Figure 6* as a function of the concentration $C_{Tr}$. The effect induced by the partial chemical treatment is weak; variations of the ratio $Q_r^l(C_{Tr})/Q_r^l$ can be represented by a straight line. It is considered that the mean surface associated with one active silanol group is independent of the chemical treatment; thus, the surface associated with non-converted silanol groups is expressed as:

$$A_c(C_{Tr}) = A_T(1 - \alpha C_{Tr})$$

The parameter $\beta(A_T/\sigma_e)$, defined by equation (14), should be a linear function of $C_{Tr}$ and the slope of the straight line drawn in *Figure 6* should be equal to $-\alpha$, where $\alpha$ is a measure of the extent of the partial chemical treatment of one aggregate. However, the slope of the straight line is smaller than the measured extent of treatment; this result shows that the parameter of efficiency of chain adsorption is not a simple function of $A_c(C_{Tr})$. The mean number of hydrogen bonds participating in the binding of one chain is not invariant when the extent of the chemical treatment is varied. The parameter of efficiency of chain adsorption is now defined as $A_T(1 - \alpha C_{Tr})/\sigma_e(C_{Tr})$ instead of $A_T/\sigma_e$ in the absence of a chemical treatment. The ratio $\alpha\sigma_e/\sigma_e\,(C_{Tr})$ is found to be equal to 0.4. Assuming that $\alpha$ is equal to 0.8, in accordance with *Figure 3*, an estimate of the mean area per link $\sigma_e$ ($C_{Tr}$) is given by $2\sigma_e$. This estimate shows that the chemical treatment of the silica surface cannot be considered as uniform; clusters of converted silanol groups are formed on the surface. The density of converted silanols, within one cluster, may be low enough to allow the binding of one chain. Then, the mean number of hydrogen bonds formed per chain is not $1.25\sqrt{N}$ but somehow smaller than this number (it may be divided by 2). A large number of polymer chains can still be bound to silica, even though the average number of hydrogen bonds accessible per chain is reduced by the chemical treatment.

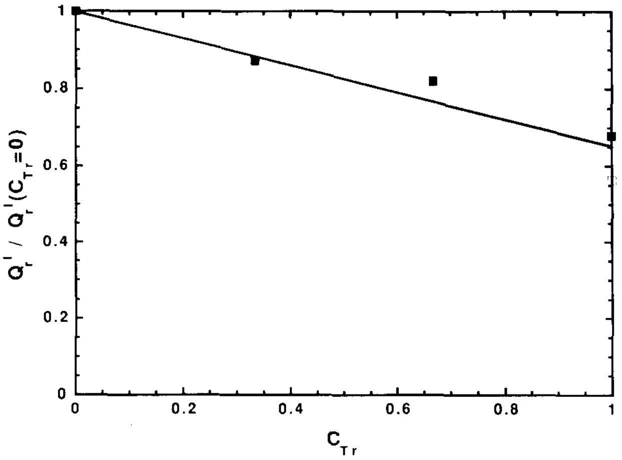

**Figure 6** Relative variation of the amount of adsorbed polymer as a function of the concentration of treated aggregates. $\overline{M_n} = 23 \times 10^4$ g mol$^{-1}$, $C_{Si} = 0.5$ (w/w)

## SWELLING EFFECT

Siloxane–silica mixtures can behave like polymeric gels when the initial silica concentration $C_{Si}^{i}$ and the chain molecular weight $\overline{M_n}$ are given appropriate values. These mixtures have already been described within the framework of percolation. They exhibit a threshold of percolation; the specific amount of polymer $Q_r^c$, adsorbed at the threshold of percolation, depends upon both the initial specific amount of polymer $Q_i$ and the chain molecular weight. The kinetics of chain adsorption, observed at room temperature, are small enough to allow the full study of the physical properties of the mixtures which are in intermediate states of adsorption; the mixtures can also be considered as systems in intermediate states of gelation. A state of saturated adsorption is reached when the amount of adsorbed polymer is equal to $Q_r^l$ as defined by equation (26). In this section, several mixtures defined by a specific amount of adsorbed polymer $Q_r$ smaller than $Q_r^l$ are considered. We attempted to characterize their statistical structures by observing the swelling effect induced by a good solvent.

### *Intermediate states of adsorption*

The description of mixtures in intermediate states of adsorption relies upon the assumption that one polymer chain can connect only two aggregates to each other; the law of chain adsorption is still defined by equation (16). The fraction $\phi_{Si}$ of sites of adsorption occupied by polymer chains is smaller than one as long as the silica surface is not saturated. Then, the number $\nu_{c,2}$ of chains which connect two particles to each other is given by:

$$v_{c,2}=\mathscr{N}^{i}_{p}\phi_p^2 \tag{29}$$

or, according to equation (23), by:

$$v_{c,2}=Q_i\Gamma^2\mathscr{A}/\overline{M_n}[1+\sqrt{(1-\Gamma)}]^2 \tag{30}$$

The number of polymer bridges between aggregates is a function of both the chain molecular weight and the ratio $\Gamma=Q_r/Q_i$.

*Swelling effect*

Statistical structures of mixtures corresponding to intermediate states of adsorption were investigated by observing the effect of swelling induced by a good solvent. The number of active segments per unit volume of polymer is written as:

$$\rho_p v_{c,2}/Q_r=\rho_p\Gamma\mathscr{A}/\overline{M_n}(1+\sqrt{1-\Gamma})^2\psi(N) \tag{31}$$

Within the mean field approximation:

$$(Q_{mm}^{5/3}-Q_{mm}/2)^{-1}=\frac{\langle\xi^2\rangle}{\langle\Delta\xi^2\rangle}\omega_s\rho_p\Gamma/\overline{M_n}(1+\sqrt{1-\Gamma})^2\psi(N) \tag{32}$$

$\omega_s$ is the molar volume of the solvent and the ratio $\dfrac{\langle\xi^2\rangle}{\langle\Delta\xi^2\rangle}$ is a measure of fluctuations of active chain segments. It is worth emphasizing that the above equation applies only to the case where an infinite cluster is formed.

There is a limiting value of $\Gamma_c$ which corresponds to a ratio $\Gamma$ equal to zero. The value of the threshold $\Gamma_c$ is determined experimentally when the quantity $(Q_{mm}^{5/3}-Q_{mm}/2)^{-1}$ is found to be equal to zero. For $\Gamma<\Gamma_c$, particles may be connected to one another but they form clusters with a finite size. By assuming that intermediate states of adsorption are still characterized by the law of adsorption $\psi(N)=1.25\sqrt{N}$, equation (32) may also be written as:

$$(Q_{mm}^{5/3}-Q_{mm}/2)^{-1}=2.5\frac{\langle\xi^2\rangle}{\langle\Delta\xi^2\rangle}\frac{M_s}{M_m}\frac{\rho_p}{\rho_s}\Gamma/\bar{N}^{1/2}(1+\sqrt{1-\Gamma})^2 \tag{33}$$

$M_s$ is the molar weight of one solvent molecule and $\rho_s$ is the solvent density. Considering a given mixture characterized by a chain molecular weight $M_n$ and an initial specific amount of polymer $Q_i$, several samples were left in an oven at 70°C for different time intervals. The adsorption process within a chosen sample was interrupted by lowering the temperature down to 25°C; the sample was then immersed in a large amount of solvent to remove all free chains. Its swelling ratio $Q_{mm}$ was measured at equilibrium. Finally, the sample was dried for several days to eliminate the swelling agent and to weigh the residual amount of adsorbed polymer $Q_r$. Several states of intermediate adsorption were determined according to the above procedure.

Experimental results corresponding to three concentrations of chemically treated aggregates and to numerous intermediate states of adsorption are shown in *Figure 7*; the chain molecular weight was $M_n=2.3\times10^5\,\mathrm{g\,mol^{-1}}$ and the initial amount of polymer was $Q_i=1$ (w/w). The time $t$ of observation during the adsorption process was varied from 0 to about $3.6\times10^3$ h. A strong swelling effect is observed when the concentration of treated aggregates is high ($C_{Tr}=1$). For convenience, the quantity $(Q_{mm}^{5/3}-Q_{mm}/2)^{-1}$ was reported in *Figure 8* as a function of $\Gamma/(1+\sqrt{1-\Gamma})^2$ to obtain linear representations; the three straight lines drawn in *Figure 8* correspond to three molecular weights ($M_n=4.5\times10^4$, $6.7\times10^4$ and $23\times10^4\,\mathrm{g\,mol^{-1}}$). The initial amount of polymer was $Q_i=1$ and the silica surface was not treated chemically (the specific area is 50 m²). In accordance with equation (33), the product of the slopes of the straight lines drawn in *Figure 8* and the square root of the number of skeletal bonds in one chain yields a nearly constant value: 100 for $M_n=23\times10^4$, 87 for $M_n=6.7\times10^4$ and 99 for $M_n=4.5\times10^4\,\mathrm{g\,mol^{-1}}$. The experimental results are also in agreement with equation (33) by assuming that the ratio $\langle\xi^2\rangle/\langle\Delta\xi^2\rangle$ is equal to 4; the value of this ratio is equal to 2 for Gaussian network structures formed by covalent crosslinks. The numerical value of $\langle\xi^2\rangle/\langle\Delta\xi^2\rangle$ shows that the amplitude of fluctuations of coupling junctions is smaller in siloxane–silica mixtures than in usual polymer network structures; such a property is due to the presence of heavy silica aggregates.

Similar straight lines are observed in *Figure 9* where the chain molecular weight ($M_n=23\times10^4\,\mathrm{g\,mol^{-1}}$) and

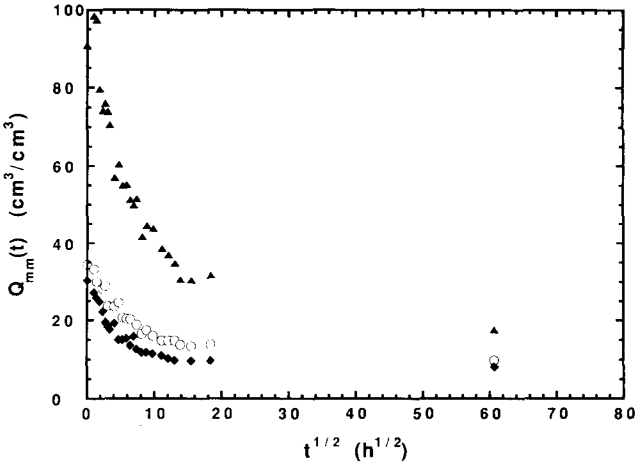

**Figure 7** Variations of the swelling ratio $Q_{mm}$ measured as a function of time during the progressive saturation of the silica surface. The initial amount of polymer was $Q_i=1$ (w/w) and $\overline{M_n}=23\times10^4\,\mathrm{g\,mol^{-1}}$. The concentration of treated aggregates is $C_{Tr}=0.33$ (◆), $C_{Tr}=0.66$ (○) and $C_{Tr}=1$ (▲)

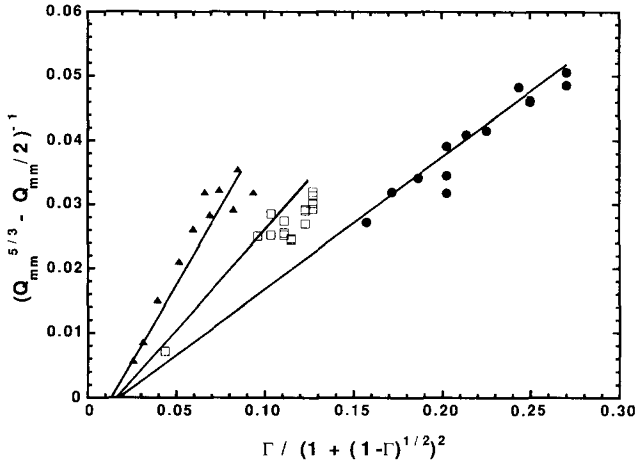

**Figure 8** Representation of the quantity $(Q_{mm}^{5/3}-Q_{mm}/2)^{-1}$ as a function of $\Gamma/(1+\sqrt{1-\Gamma})^2$, according to equation (32). The initial amount of polymer is $Q_i=1$ (w/w) and $C_{Tr}=0$; $\overline{M_n}=4.5\times10^4$ (▲), $6.7\times10^4$ (□) and $23\times10^4\,\mathrm{g\,mol^{-1}}$ (●)

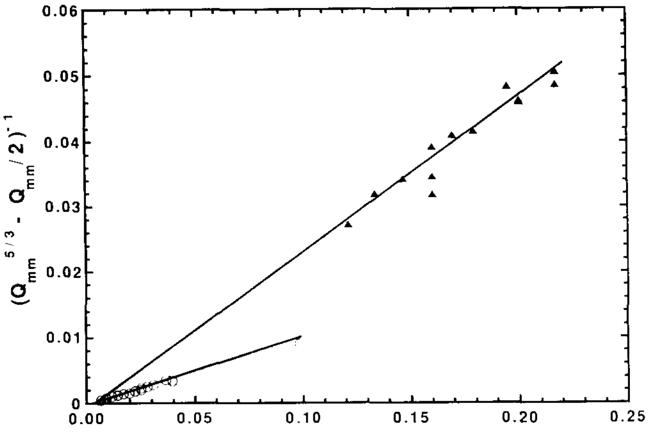

**Figure 9** Representation of the quantity $(Q_{mm}^{5/3} - Q_{mm}/2)^{-1}$ as a function of $\Gamma/(1+\sqrt{1-\Gamma})^2$, according to equation (32). The initial amount of polymer is $Q_i = 1$ (w/w) and $\overline{M}_n = 23 \times 10^4$ g mol$^{-1}$. Two concentrations of treated aggregates are considered: $C_{Tr} = 0$ (▲) and $C_{Tr} = 1$ (○)

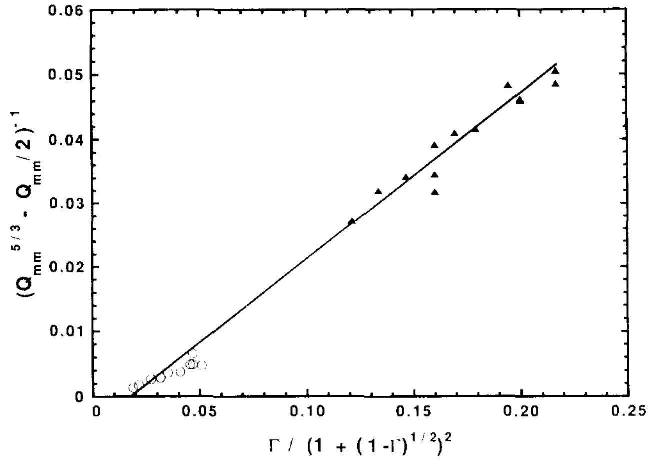

**Figure 10** Representation of the quantity $(Q_{mm}^{5/3} - Q_{mm}/2)^{-1}$ as a function of $\Gamma/(1+\sqrt{1-\Gamma})^2$, according to equation (32) ($\overline{M}_n = 23 \times 10^4$ g mol$^{-1}$ and $C_{Tr} = 0$). Two initial specific amounts of polymer are considered: $Q_i = 5$ (○) and $Q_i = 1$ (w/w) (▲)

the initial specific amount of polymer ($Q_i = 1$) were kept constant while the concentration of chemically treated aggregates was varied ($C_{Tr} = 0$ and 1). The slope of the straight line is divided by two when the concentration $C_{Tr}$ is equal to unity. This result can be ascribed to the modified law of chain adsorption: the mean number of hydrogen bonds formed per chain may be divided by two, in accordance with previous results. Finally, the initial specific amount of polymer $Q_i$ was varied ($Q_i = 5$ and 1) while all other variables were kept constant. A single straight line was drawn in *Figure 10* to obtain the corresponding experimental results.

### *States of maximum adsorption*

In this section, attention is focused on the swelling properties observed in PDMS–silica mixtures which are in a state of maximum adsorption corresponding to given initial conditions. The swelling ratio $Q_{mm}^{1}$ was studied as a function of the residual amount of adsorbed polymer $Q_r^1$ at equilibrium. For the sake of simplicity, $Q_r^1$ was set equal to $Q_r^m$ and equation (33) becomes:

$$(Q_{mm}^{15/3} - Q_{mm}^{1}/2)^{-1} = \frac{\langle \xi^2 \rangle}{\langle \Delta\xi^2 \rangle} \frac{M_s \rho_p}{\rho_s} \frac{A_T}{\mathscr{A}\sigma_e(1+\sqrt{1-\Gamma})^2 Q_i} \tag{34}$$

The quantity $(Q_{mm}^{15/3} - Q_{mm}^{1}/2)^{-1}$ is reported as a function of $(1+\sqrt{1-\Gamma})^{-2} Q_i^{-1}$ in *Figure 11a*; a straight line can be drawn through the experimental points corresponding to different values of the initial specific amount of polymer $Q_i = 5$ and 2.5 (w/w); for $Q_i = 1$, three chain molecular weights are considered; $\overline{M}_n = 4.5 \times 10^4$ and $23 \times 10^4$ g mol$^{-1}$. In *Figure 11b*, four concentrations of treated aggregates are considered: $C_{Tr} = 0$, 0.33, 0.66 and 1 ($\overline{M}_n = 23 \times 10^4$ g mol$^{-1}$ and $Q_i = 1$); the slope of the straight line drawn through the experimental points is equal to 0.8. This slope depends upon the parameter of efficiency of chain adsorption $A_T(1-\alpha C_{Tr})/\sigma_e$. These representations reinforce the description given for systems in states of intermediate adsorption.

## CONCLUSION

Poly(dimethylsiloxane)–silica mixtures can form a broad variety of physical systems which are determined

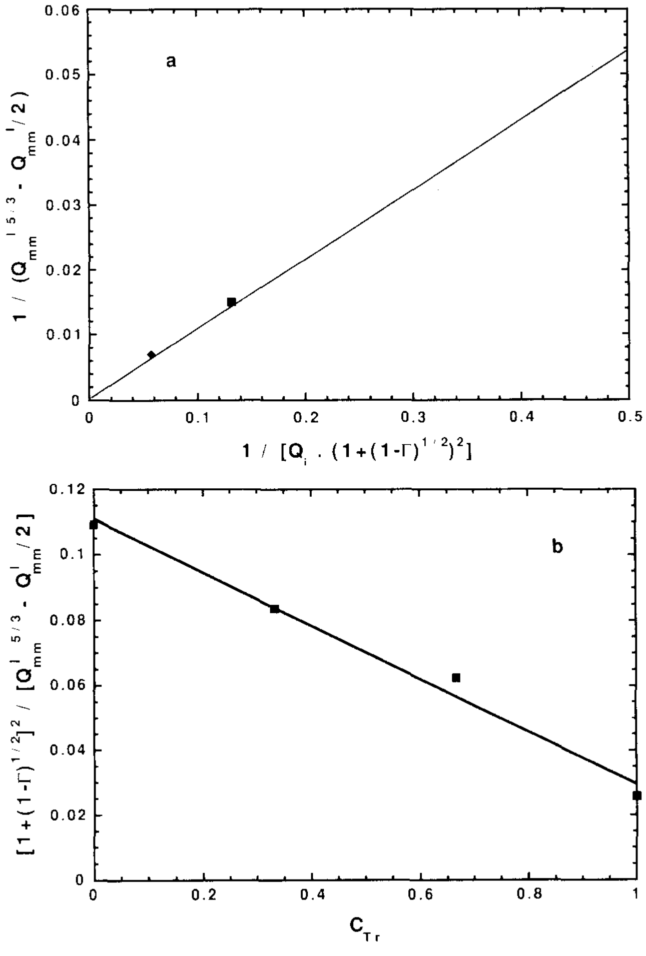

**Figure 11** (a) Representation of the quantity $(Q_{mm}^{15/3} - Q_{mm}^{1}/2)^{-1}$ as a function of $(1+\sqrt{1-\Gamma})^2 Q_i^{-1}$, according to equation (34). The initial amount of polymer is $Q_i = 1$ (w/w) and $C_{Tr} = 0$. Three chain molecular weights are considered: $\overline{M}_n = 4.5 \times 10^4$, $6.7 \times 10^4$ and $23 \times 10^4$ g mol$^{-1}$. (b) Representation of the ratio $(1+\sqrt{1-\Gamma})^2/(Q_{mm}^{15/3} - Q_{mm}^{1}/2)$ as a function of the concentration of chemically treated aggregates. ($\overline{M}_n = 23 \times 10^4$ g mol$^{-1}$; $Q_i = 1$ (w/w))

by the state of chain adsorption on the silica surface. Network structures which behave like permanent gels are created when silica aggregates are connected to one another by polymer chains. Statistical structures of these filled polymers can be conveniently investigated by observing the swelling effect induced by a good solvent. A reasonable description of swelling properties can be developed within the framework of percolation, notwithstanding the complex nature of these systems. Active chain segments connecting two aggregates are numbered in a simple way. Relevant variables are the chain molecular weight and the amount of adsorbed polymer divided by the initial amount of polymer mixed with silica. The observation of the swelling effect proved to be a convenient method for characterization of the structural properties of PDMS–silica mixtures.

Two main features characterized these systems. On the one hand, the number of contact points of one chain with the silica surface is proportional to the square root of the number of skeletal bonds, on average. This property is observed during the progressive adsorption process of polymer chains and also when the silica surface is saturated. This result is in contrast to the usual effect of adsorption observed with silica particles in suspension in a polymer solution[9]. Such a law probably also governs the viscoelastic properties of silica-filled PDMS[10]. On the other hand, the kinetics of chain adsorption is described according to a single law which is independent of the specific area of silica and the chain molecular weight, whereas the characteristic time of adsorption is a function of these variables.

## ACKNOWLEDGEMENT

It is a pleasure to acknowledge the financial support provided by Rhône-Poulenc Recherches.

## REFERENCES

1 Huchot, P. *PhD Thesis*, University of Grenoble, 1988

2 Cohen-Addad, J. P. *Polymer* 1989, **30**, 1820

3 Cohen-Addad, J. P., Roby, C. and Sauviat, M. *Polymer* 1985, **26**, 1231

4 Cohen-Addad, J. P. and Ebengou, R. *Polymer* 1992, **33**, 379

5 Cohen-Addad, J. P., Huchot, P., Jost, P. and Pouchelon, A. *Polymer* 1989, **30**, 143

6 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, 1969

7 Cohen-Addad, J. P. *Polymer* 1987, **28**, 121

8 Cohen-Addad, J. P. *Polymer* 1992, **33**, 2762

9 Di Marzio, E. A. *J. Chem. Phys.* 1965, **42**, 2101

10 Ferry, J. D. 'Viscoelastic Properties of Polymers', Wiley, New York, 1980