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# Structure of silica-filled poly(dimethyl siloxane) gels and solutions

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Small-angle neutron scattering measurements are described for poly(dimethyl siloxane) solutions and gels containing fumed silica filler, swollen in toluene. Contrast variation with solvent deuteration is used, first to determine the density of the silica, and then to distinguish the three different partial structure factors of the filled polymer samples. The concentration of the polymer solution immediately surrounding the filler particles is found to be enhanced over a distance range of about 20 Å, and then depleted beyond this range. The distribution of the filler particles is described by a stretched exponential with an exponent $n=\frac{1}{3}$. Comparison of the partial structure factors of the silica and the polymer indicates that less than 10% of the free surface of the filler particles is in contact with polymer. [S1063-651X(99)03002-0]

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## INTRODUCTION

Filler particles have been used for many years in rubbers as reinforcing materials for innumerable goods such as automobile tires, industrial sealants, elastomer mouldings, etc. To investigate the properties and structure of these fillers in their polymer environment, a wide range of different experimental techniques has been employed. The effect of these particles on their surroundings depends on the spatial range considered, and although some techniques, such as nuclear magnetic resonance or Raman scattering, can supply valuable information of a local nature, the interpretation of the results is not straightforward and is strongly model dependent.

Small-angle neutron and x-ray scattering (SANS and SAXS) have been used to investigate the distribution of carbon black dispersed in natural rubber [1] and of silica particles in polydimethyl siloxane (PDMS) [2]. Carbon black particles are found to possess an internal structure, which complicates the analysis and limits the amount of information that can be deduced about the distribution of the surrounding polymer. With silica, fractal-like behavior has been observed in the clusters when the concentration is sufficiently high [2,3], and the role played by this secondary network in the mechanical properties remains a subject of considerable interest. SANS measurements have also been reported on polymer molecules attached to porous silica under dilute conditions, in which scaling behavior is observed for the concentration profile [4]. Relatively little attention, however, appears to have been paid to the influence of the filler particles on their immediate polymer surroundings when they are incorporated in a concentrated solution or a gel [5–7]. This interaction is important because the existence of free silica surfaces modifies the local polymer distribution, and the polymer and the silica networks are therefore not simply additive. In this article we report SANS measurements on silica-filled PDMS elastomers, in which contrast variation is used to separate the partial structure factors of the different components.

## EXPERIMENT

The polymer, kindly supplied by Rhône-Poulenc Silicones, was linear polydimethyl siloxane hydroxylated at both extremities. Three systems were investigated.

(1) A high molecular weight fraction of pure polymer, $M_w \approx 500\,000$, with polydispersity index $M_w/M_n=2$, where $M_n$ and $M_w$ are, respectively, the number average and the weight average molecular weights.

(2) A lower molecular weight oil of viscosity 20 Pa s, containing 9% w/w fumed silica (Degussa) with trimethylsilyl groups grafted to its surface. The BET specific surface area of this treated silica is 60 $\mathrm{m}^2\,\mathrm{g}^{-1}$. Prior to grafting, the nominal BET surface area of the untreated silica (code name Æ300) is stated to be 300 $\mathrm{m}^2\,\mathrm{g}^{-1}$. A sample of this untreated silica was used in these experiments to measure the properties of the pure filler.

(3) The same as (2), but with in addition 4.3% w/w ethyl triacetoxysilane. This additive binds to the hydroxyl end groups and establishes cross links when the system is exposed to atmospheric moisture. After completion of the reaction, during which acetic acid is released, the residual weight fraction of this cross-linking additive falls to 1%.

Both these samples were prepared by mechanically mixing the filler and PDMS melt in a ball mill under dry nitrogen at room temperature until the mixtures were homogeneous. A third set of samples was similarly prepared with untreated fumed silica of surface area 300 $\mathrm{m}^2\,\mathrm{g}^{-1}$. Between the sample mixing and the SANS experiments, more than three years elapsed. This delay is sufficient to allow equilibrium adsorption to be established on the filler surface [8].

The samples were swollen in mixtures of hydrogenated toluene (Prolabo, analytical grade) and deuterated toluene

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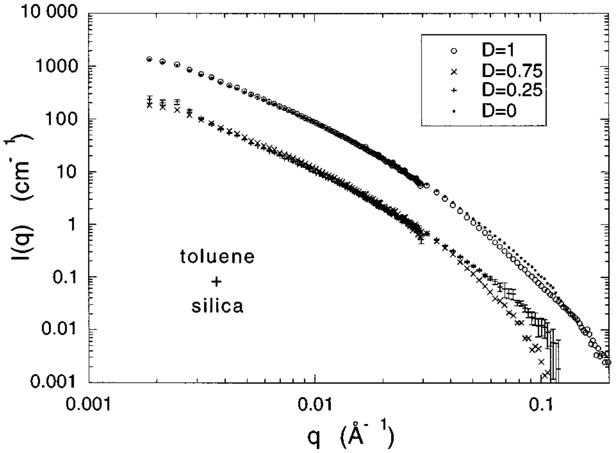

FIG. 1. SANS spectra $I(q,D)$ of silica aerogel (300 $m^2\,g^{-1}$) in toluene at different degrees of deuteration $D$.

(Acros) with deuterium content >99%. The specimens for SANS were contained in a cell consisting of 1-mm thick quartz windows separated by a 1-mm spacer sealed with a Viton O ring. Measurements of the equivalent set of samples containing untreated silica particles (300 $m^2\,g^{-1}$) at the same concentration yielded results that are closely similar to those from the treated system, and are not described here.

The SANS experiments were carried out on the $D17$ and $D22$ instruments at the ILL, Grenoble, using wavelengths of 12 and 10 Å, respectively. For the former instrument, the sample-detector distance was 2.9 m, and for the latter, two distances were used, 2 and 18 m. Counting times were between 20 min and 1 h. Calibrations were made with water at 25 °C using the measurements of Ragnetti *et al.* [9]. Corrections for incoherent background were made with a method described elsewhere [10]. All measurements were made at room temperature (20 °C).

Experimental errors were estimated using the mean square deviations of the data from the area detector for the sample, the empty cell and the background, together with the Poisson noise in the transmission measurements. The resulting mean square deviation of the intensity provides the statistical weights employed in inverting the matrix [Eq. (4) below]. This process yields the partial structure factors and their errors.

The density of the fumed silica used in the filled elastomers was not known with precision. As a knowledge of the density of each component is essential to analyse a ternary system, contrast variation measurements were made on the pure filler. This was done by preparing slurries of untreated silica aerogel Æ300 with toluene at four different values of deuteration content $D$. The resulting SANS spectra are shown in Fig. 1. In this double logarithmic representation, the four curves appear to lie parallel to each other within the experimental error. Since the toluene-aerosol mixture constitutes a binary system, the observed intensity is given by

$$I(q,D)=(\rho_p-\rho_s)^2 kTS(q), \tag{1}$$

where $S(q)$ is the structure factor of the silica particles in suspension, and the Boltzmann factor ($kT=4.11\times10^{-21}$ Js) expresses $S(q)$ in terms of $\mathrm{Pa}^{-1}$. In Eq. (1), $\rho_p$ is the scattering length density of the polymer; the scattering length

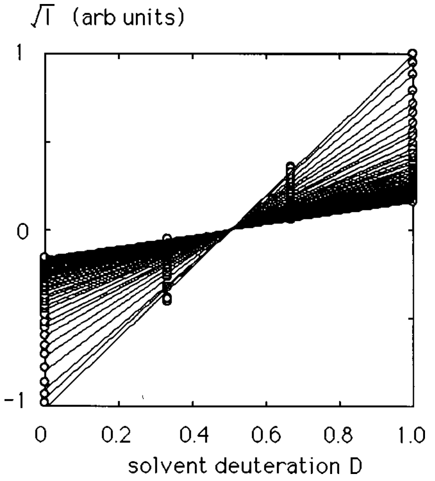

FIG. 2. Least square fits of $\sqrt{I(q,D)}$ vs $D$ for different values of $q$. The intersection at $D=0.497$ is the contrast match point for all values of $q$.

density of the solvent $\rho_s(D)$ depends linearly on the deuterium content $D$. For any fixed value of $q$ therefore, the square root of Eq. (1)

$$\sqrt{I(q,D)}=(\rho_p-\rho_s)\sqrt{kTS(q)} \tag{2}$$

should yield a straight line when plotted as a function of $D$. For this to be true, in Eq. (2) the sign of the square root must be chosen to be positive on one side of the contrast match point, at which $\rho_s(D)=\rho_p$, and negative on the other. As $q$ varies, this procedure generates a family of linear regression lines, shown in Fig. 2. All these lines meet at a single point, indicating that the mass density of the silica particles, $d_{\mathrm{SiO}_2}$, is uniform. The point of intersection, $D=0.497$, combined with a knowledge of the scattering lengths of the constituent nuclei of toluene and silica [11], then yields for this sample

$$d_{\mathrm{SiO}_2}=2.089\ \mathrm{g\,cm^{-3}}. \tag{3}$$

This value, which is lower than the density of bulk fused silica, is a sign that the material is porous.

## RESULTS AND DISCUSSION

In ternary systems such as those investigated here, the scattered intensity $I(q)$ can be expressed in terms of three partial structure factors $S_{ij}(q)$, where the subscripts $i$ and $j$ refer to polymer ($p$) and filler ($f$). Thus Eq. (1) transforms to

$$I(q)=kT[(\rho_p-\rho_s)^2 S_{pp}(q) + (\rho_p-\rho_s)(\rho_f-\rho_s)S_{pf}(q)+(\rho_f-\rho_s)^2 S_{ff}(q)]. \tag{4}$$

Here, $\rho_p$, $\rho_f$, and $\rho_s$ are the scattering length densities of the polymer, the filler, and the solvent, respectively. The values calculated from the literature for these quantities are

$$\rho_p=6.34\times10^{8}\ \mathrm{cm}^{-2}, \tag{5a}$$

$$\rho_s=(0.944+4.738D)\times10^{10}\ \mathrm{cm}^{-2}, \tag{5b}$$

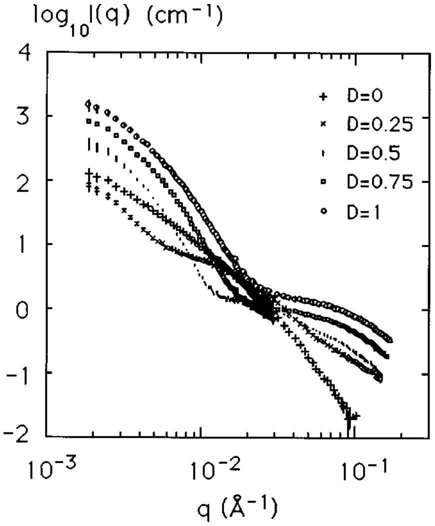

FIG. 3. SANS spectra of filled uncross-linked PDMS solution in toluene at five different values of *D*.

$$\rho_f = 3.30\times10^{10} \ \mathrm{cm}^{-2}, \tag{5c}$$

where $\rho_f$ is the result of substituting the isopyknic point $D = 0.497$ of Fig. 2 into Eq. (5b).

Figure 3 shows the normalized SANS spectra from the filled uncross-linked polymer solutions in toluene, at five different values of *D*. The total volume fraction of polymer+silica is $\varphi = 0.20$. The curves obtained from the cross-linked gel fully swollen in toluene ($\varphi = 0.24$), not reproduced here, closely resemble those of Fig. 3. The structure factors $S_{ij}(q)$ are found by inserting the corresponding intensities $I(q)$ into Eq. (4) and inverting the matrix. Each of the resulting curves $S_{ij}(q)$ yields information on the distribution of matter in the sample.

In the double logarithmic plot of Fig. 1 it is clear that $I(q)$ does not follow a straight line: the distribution of the silica particles is therefore not fractal in this $q$ range. The same result is also true for the partial structure factors $S_{ff}(q)$, calculated from Eq. (4), for the filled solution and the swollen gel, respectively. In Fig. 4 these data are shown in a stretched exponential representation. The stretched exponential form

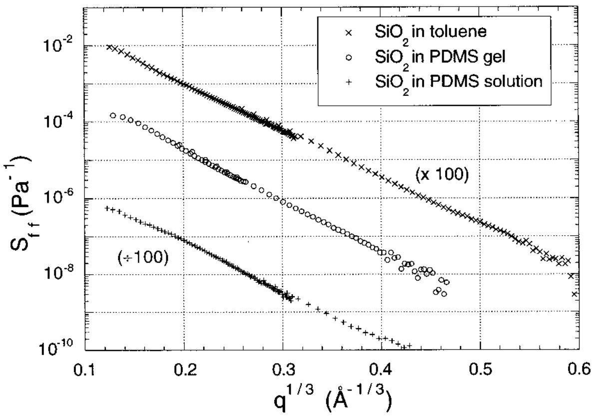

FIG. 4. $S(q)$ of silica aerogel in Fig. 1 (×), and partial structure factor $S_{ff}(q)$ of silica in swollen gel (○) and in uncross-linked solution (+), plotted in a stretched exponential representation with $n = \frac{1}{3}$.

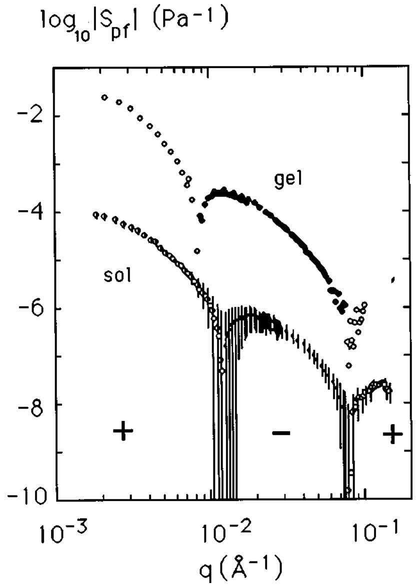

FIG. 5. Modulus of the partial structure factor $|S_{pf}(q)|$ for filled gel and for uncross-linked solution (open symbols: positive values; filled symbols: negative values). For clarity, the error bars are shown only for the uncross-linked solution, and gel data have been shifted upwards by two decades.

$$S_{ff}(q) = a\exp[-(qR_A)^n], \tag{6}$$

where the exponent $n = \frac{1}{3}$, produces a straight line plot for the three filler systems investigated. The explanation of this behavior is not at present clear, but is related to the method of production of the silica aggregates. The similarity between the structure factors of the silica in the free state and inside the polymer matrix shows that the mechanical mixing does not modify the aggregates. Results for a similar filled PDMS system [12] indicate that the validity of Eq. (4) extends well into the light scattering region at low $q$ and is limited by the Porod $q^{-4}$ behavior at the high $q$ end. Values of the apparent radius $R_A$ in Fig. 4 lie in the range 2–3 $\mu$m.

The off-diagonal term $S_{pf}(q)$ is shown in Fig. 5 both for the uncross-linked solution and the gel. The error bars shown are those calculated from the covariant matrix of Eq. (4), as outlined in the Experimental section. $S_{pf}(q)$ displays an oscillation, with a minimum (in this representation negative values are distinguished from positive values) at $q \approx 0.02\,\text{Å}^{-1}$. Such a minimum implies a region that is depleted in polymer at about 100 Å from the silica particles. In the cross-linked system, this depleted feature shifts to lower $q$, indicating that the permanent elastic forces expand the range of the corresponding concentration fluctuation. This observation may also be due in part to deposition of a layer of polymerized ethyl triacetoxysilane at the surface of the silica particles. At higher $q$, in both samples, $S_{pf}(q)$ changes sign once again to become positive. Close to the filler surface, therefore, the polymer concentration is enhanced. Over a limited range at the low $q$ end of Fig. 5, the data from these two samples satisfy the Guinier relation

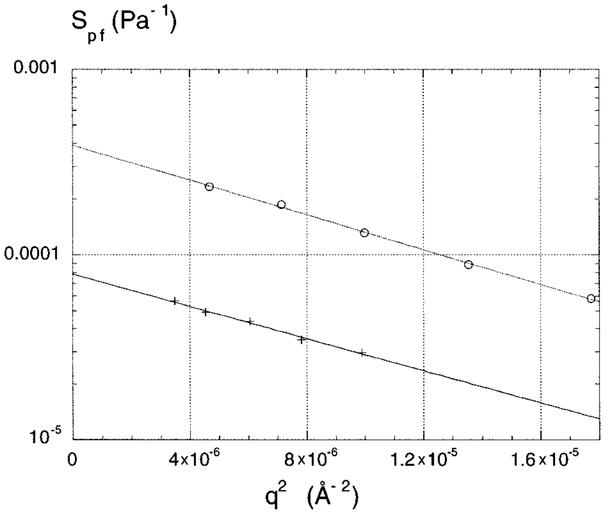

FIG. 6. Guinier plot of $\log_{10} S_{pf}(q)$ vs $q^2$ for the lowest $q$ data points of Fig. 5. ○: filled gel, +: filled solution. The slopes of the straight lines yield $R_G = 570$ Å and $R_G = 550$ Å, respectively.

$$S_{pf}(q) = S_{pf}(0)\exp\left(\frac{-q^2R_G^2}{3}\right), \qquad (7)$$

where $R_G$ is the radius of gyration of the polymer clusters around the silica. The results are shown in Fig. 6, where the straight line fits yield $R_G = 550$ Å for the filled solution, and $R_G = 570$ Å in the gel.

The polymer-polymer scattering functions $S_{pp}(q)$ obtained from these experiments are shown in Fig. 7. The lowest data points (crosses) are those of the unfilled uncross-linked solution in the semidilute state. It can be described satisfactorily by an Ornstein-Zernike expression

$$S_{\mathrm{sol}}(q) = \frac{S_{\mathrm{osm}}(0)}{(1+q^2\xi^2)}, \qquad (8)$$

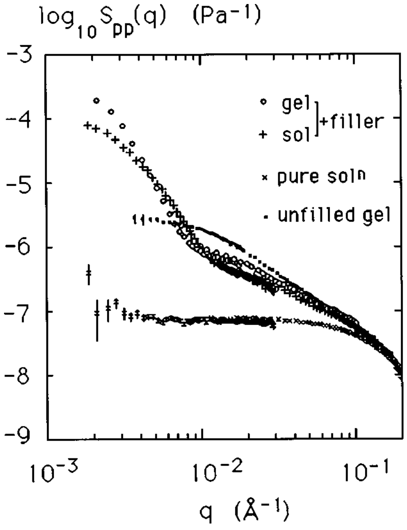

FIG. 7. Polymer-polymer partial structure factors $S_{pp}(q)$ in swollen PDMS gel containing silica (○), and in the corresponding uncross-linked solution (+). Also shown are the structure factors of a PDMS-toluene solution without filler (pure solution) (×), and a randomly cross-linked PDMS gel [24] fully swollen in octane to approximately the same concentration (●).

where $\xi$ is the polymer-polymer correlation length and $S_{\mathrm{osm}}(0) = \varphi/\partial\Pi/\partial\varphi$ is the osmotic susceptibility, $\varphi$ being the polymer volume fraction and $\Pi$ the osmotic pressure exerted by the solvent in the solution. For this sample, $\xi = 11.5$ Å and $S_{\mathrm{osm}}(0) = 0.9\times10^{-7}$ Pa$^{-1}$. The broad plateau in the region $q < 0.03$ Å$^{-1}$ indicates that large scale associations are absent from this solution.

By contrast, for the filled polymer solution and gel the curves of $S_{pp}(q)$ in Fig. 7 exhibit a complex pattern over their entire range. The physical picture of silica beads surrounded by a corona of polymer chains makes it tempting to interpret these scattering functions in terms of star polymers [13–16]. This approach seems attractive in the present case, since the scattering functions of solutions of star polymers qualitatively resemble those observed in Fig. 7. The appearance of regions with slope in excess of 3, which is the signature of scattering from surfaces, is, however, inconsistent with stars, and this concept is therefore abandoned in favor of a phenomenological approach.

In Fig. 7 the scattering function of the filled polymer solution (plusses) displays three different characteristic lengths. First, at high $q$ a shoulder is present that is analogous to that of the pure binary solution. This feature, which is shared with the signal from the cross-linked gel (open circles), comes from the osmotic fluctuations of the constituent polymer network, and may be described by an expression similar to Eq. (8). In cross-linked systems, however, owing to their finite elastic modulus $G$, the osmotic susceptibility can be expressed as [10,17]

$$S_{\mathrm{osm}}(0) = \frac{\varphi^2}{[\varphi\partial\omega/\partial\varphi + 4G/3]}, \qquad (9)$$

where $\omega = \Pi - G$ is the swelling pressure of the solvent in the gel. Second, at intermediate values of $q$, extra scattering is visible compared with that from the unfilled solution. In chemically cross-linked gels, an equivalent feature is identified with static concentration fluctuations due to elastic constraints in the polymer network [18]. This feature can be simulated by an additional term in the scattering function of the form [19]

$$S_1(q) = \frac{A}{(1+q^2\Xi_1^2)^2}, \qquad (10)$$

where $A$ describes the amplitude of the static fluctuations and $\Xi_1$ their spatial range. In the present filled solutions, analogous concentration fluctuations are expected to develop around the filler particles, since the free ends of polymer chains adsorbed on the silica are stretched elastically by osmotic forces. For these solutions, therefore, the region of high concentration is situated in a layer immediately surrounding the silica particles. As stated above, this expectation is corroborated by the positive values of the cross-term $S_{fp}(q)$ at high $q$. Lastly, at the lowest values of $q$ in Fig. 7, a region is distinguished with slope close to $-4$, characteristic of Porod scattering [20]. To describe this feature a third characteristic length $\Xi_2$ is necessary.

In the lowest $q$ range no feature equivalent to the upturn in $S_{pp}(q)$ is observed in the partial structure factor of the silica $S_{ff}(q)$ for which the Porod region occurs at higher $q$

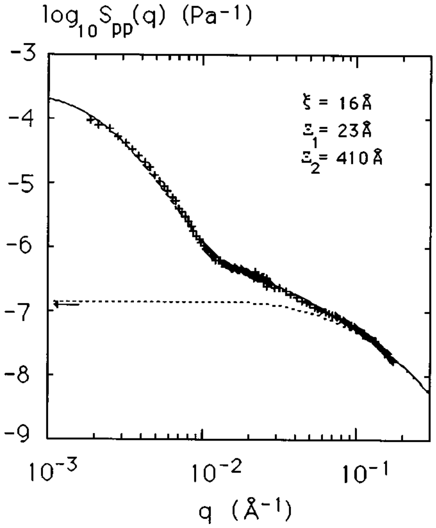

FIG. 8. Least squares fit of Eq. (10) to the partial structure factor $S_{pp}(q)$ of the filled uncross-linked solution. The dotted curve is the first term in Eq. (11), and the arrow is the intensity calculated from the swelling pressure of the equivalent gel [21].

($q \geqslant 0.1$ Å$^{-1}$). If the concentration of the polymer surrounding the silica particles were uniform, then, by virtue of Babinet's principle, $S_{pp}(q)$ and $S_{ff}(q)$ would have the same shape. That this is not the case shows that the silica clusters are surrounded by a layer of concentrated polymer that is unrelated to the interparticle distances of the silica.

These considerations are illustrated by representing the scattering of the polymer-polymer contribution phenomenologically as

$$S_{pp}(q) = \frac{S_0(0)}{(1+q^2\xi^2)} + \frac{A_1}{(1+q^2\Xi_1^2)^2} + \frac{A_2}{(1+q^2\Xi_2^2)^2}. \tag{11}$$

Equation (11) contains six adjustable parameters, which, under normal circumstances, is unduly many to describe a monotonically decreasing curve of the type shown in Fig. 7. However, the low $q$ and high $q$ features of these curves are sufficiently distinctive to yield an unambiguous least squares fit to the data. This is shown in Fig. 8 for the filled uncross-linked solution [for the gel, the data do not extend to large enough values of $q$ to give a reliable fit to Eq. (11)]. The values of the characteristic lengths found are $\xi = 16$ Å, $\Xi_1 = 23$ Å, and $\Xi_2 = 410$ Å. Although these numerical estimates may be viewed with reserve, their magnitude is significant: the thickness $\Xi_1$ of the concentrated layer around the silica clusters is, as expected for physical reasons, comparable to the correlation length $\xi$ of the free polymer chains. Both these lengths are much smaller than the apparent cluster radius $\Xi_2$, the value of which is more consistent with the radius of gyration $R_G$ estimated from the cross partial scattering function $S_{pf}(q)$.

Independent evidence for these results is found by comparing the value of $S_{\mathrm{osm}}(0)$ obtained by SANS with that obtained from swelling pressure measurements in the cross-linked gels [21]. For the filled gel fully swollen at $\varphi = 0.24$, it is found from these osmotic measurements that $\varphi \partial\omega/\partial\varphi + 4G/3 = 470$ kPa. The corresponding value of $\varphi^2/[\varphi \partial\omega/\partial\varphi + 4G/3] = 1.24 \times 10^{-7}$ Pa$^{-1}$ is indicated by an arrow at the left of Fig. 8. The agreement with the intensity of the osmotic term in Eq. (11) lends support to this approach.

TABLE I. Specific surface area of silica filler measured by SANS, from Eq. (12). (The error in these estimates is approximately 25%.)

| Sample | $\frac{\Sigma_p}{Vd_{\mathrm{SiO}_2}}$ (m$^2$ g$^{-1}$) | $\frac{\Sigma_f}{Vd_{\mathrm{SiO}_2}}$ (m$^2$ g$^{-1}$) | $\frac{\Sigma_p}{\Sigma_f}$ | $\frac{\Sigma_{\mathrm{nom}}}{Vd_{\mathrm{SiO}_2}}$ (m$^2$ g$^{-1}$) |
|---|---|---|---|---|
| silica Æ300 | | 330 | | 300 |
| filled solution | 35 | 440 | 0.08 | 60 |
| filled gel | 21 | 270 | 0.08 | 60 |

The standard method for estimating the size of the large scale (low $q$) feature in Fig. 7 is to calculate the specific surface area $\Sigma_p/V$ [22]

$$\frac{\Sigma_p}{V} = \pi \frac{\lfloor_{q\to\infty} S_{pp}(q) q^4}{\int S_{pp}(q) q^2 dq} \tag{12}$$

(where $\lfloor_{q\to\infty}$ is the limit as $q$ tends to infinity) in the Porod region where the intensity varies as $q^{-4}$. The subscript $p$ in $\Sigma_p$ refers to the fact that this quantity is calculated from the polymer partial scattering function $S_{pp}(q)$, for which the Porod region lies in the range $q \leqslant 0.01$ Å$^{-1}$. For the filled gel, use of Eq. (12) yields $\Sigma_p/V = 4.4 \times 10^{-3}$ Å$^{-1}$, while for the filled solution, $\Sigma_p/V = 7.3 \times 10^{-3}$ Å$^{-1}$. These numbers may be compared with the nominal specific surface area of this filler, namely, 60 m$^2$ g$^{-1}$, which, combined with the measured density $d_{\mathrm{SiO}_2}$ in Eq. (3), corresponds to $\Sigma_{\mathrm{nom}}/V = 1.25 \times 10^{-2}$ Å$^{-1}$. The results of these measurements are listed in Table I. Also listed are the values of specific surface area calculated from the Porod region ($q \geqslant 0.1$ $A^{-1}$) for $S_{ff}(q)$, namely, $\Sigma_f/V$. For this calculation, $S_{ff}(q)$ is substituted for $S_{pp}(q)$ in Eq. (12). From Table I it can be seen, first, that the measured value $\Sigma_f/V$ of the untreated silica aerogel is consistent with its nominal value; second, the ratio $\Sigma_p/\Sigma_f$ of the free surface of the polymer to that of the filler with which it is in contact is of the order of 10%. This result implies that the majority of the silica surface is inaccessible to the polymer chains, probably owing to steric hindrance. The ratio for the fractional occupation $\Sigma_p/\Sigma_f$ by this direct measurement is lower than indirect estimates [8,23] based on chemical analysis and NMR, which lie in the range 0.25–0.5.

Finally, as a comparison with the filled system, in Fig. 7 is also shown the SANS spectrum of a randomly cross-linked unfilled PDMS gel (dots), swollen to approximately the same concentration in deuterated octane (volume fraction 0.173) [24]. The difference in solvent does not qualitatively modify the SANS response of the system. At low $q$, no $q^{-4}$ behavior is revealed in this case, since no filler is present. In the intermediate $q$ range, however, the intensity is significantly enhanced compared with the filled system. The corresponding concentration fluctuations are thus larger in the unfilled gel.

## CONCLUSIONS

Contrast variation measurements with SANS on silica-filled PDMS solutions and gels swollen in toluene reveal that the filler particles are surrounded by a layer of concentrated polymer, the thickness of which (around 20 Å) is comparable with the correlation length of the polymer in the rest of the solution. A region depleted in polymer occurs outside this layer. At the low (9% w/w) filler concentration studied, fractal behavior is not observed. The silica distribution instead displays a stretched exponential form, in which the stretching exponent *n* is equal to $\frac{1}{3}$. Evaluations from the SANS spectra of the internal free surfaces reveal that less than 10% of the surface area of the filler particles is in direct contact with the polymer.

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[1] R. P. Hjelm, W. A. Wampler, P. A. Seeger, and M. Gerspacher, J. Mater. Res. **9**, 3210 (1994).

[2] M. Dorget, Ph.D. thesis, Université J. Fourier de Grenoble, 1995.

[3] J. Hyeon-Lee, L. Guo, G. Beaucage, and M. A. Macip-Boulis, J. Polym. Sci., Polym. Phys. Ed. **34**, 3073 (1996).

[4] L. Auvray, P. Auroy, and M. Cruz, J. Phys. I **2**, 943 (1992).

[5] R. P. Hjelm and W. A. Wampler, Proc. SPIE **2867**, 144 (1996).

[6] D. W. McCarthy, J. E. Mark, and D. W. Schaefer, J. Polym. Sci., Polym. Phys. Ed. **36**, 1167 (1998).

[7] D. W. McCarthy, J. E. Mark, S. J. Clarson, and D. W. Schaefer, J. Polym. Sci., Polym. Phys. Ed. **36**, 1191 (1998).

[8] J. P. Cohen Addad and N. Morel, J. Phys. III **6**, 267 (1996).

[9] M. Ragnetti, D. Geiser, H. Höcker, and R. C. Oberthür, Makromol. Chem. **186**, 1701 (1985).

[10] F. Horkay, A. M. Hecht, S. Mallam, E. Geissler, and A. R. Rennie, Macromolecules **24**, 2896 (1991).

[11] V. F. Sears, Neutron News **3** (3), 26 (1992).

[12] A. M. Hecht and E. Geissler (unpublished).

[13] M. Daoud and J. P. Cotton, J. Phys. (Paris) **43**, 531 (1982).

[14] G. S. Grest, K. Kremer, and T. A. Witten, Macromolecules **20**, 1376 (1987).

[15] D. Richter, B. Farago, L. J. Fetters, J. S. Huang, and B. Ewen, Macromolecules **23**, 1845 (1990).

[16] D. Lairez, M. Adam, J. P. Cotton, and E. Raspaud, Macromolecules **30**, 6798 (1997).

[17] T. Tanaka, L. O. Hocker, and G. B. Benedek, J. Chem. Phys. **59**, 5151 (1973).

[18] E. Geissler, F. Horkay, and A. M. Hecht, Phys. Rev. Lett. **71**, 645 (1993).

[19] P. Debye and R. M. Bueche, J. Appl. Phys. **20**, 518 (1949).

[20] G. Porod, Acta Phys. Austriaca **2**, 133 (1951).

[21] F. Horkay, M. Zrínyi, E. Geissler, A. M. Hecht, and P. Pruvost, Polymer **32**, 835 (1991).

[22] O. Glatter and O. Kratky, *Small Angle X-ray Scattering* (Academic, London, 1982).

[23] J. P. Cohen Addad and S. Touzet, Polymer **34**, 3490 (1993).

[24] E. Geissler, F. Horkay, A. M. Hecht, C. Rochas, P. Lindner, C. Bourgaux, and G. Couarraze, Polymer **38**, 15 (1997).