

Investigation of PDMS gels and solutions by small angle scattering

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Measurements of swollen end-linked PDMS gels by means of small angle X-ray and neutron scattering are reported. Hexane and octane were used as solvents. The usual excess scattering associated with frozen-in elastic constraints is observed in the small Q region of the spectra. Contrast variation shows the gels to be chemically homogeneous. In the extended Q range explored, the observed structure factor of the gels is satisfactorily described by a two-term expression, the first of which is of Ornstein–Zernike (lorentzian) form, as in polymer solutions, the second being a squared lorentzian. While the scattering amplitudes associated with these two components decrease in a similar way when the gel is deswollen, the respective correlation lengths are distinct, and exhibit different behaviour. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Investigations into the structure of polymer gels using scattering techniques require an appropriate model for their interpretation. Theories behind such models are based on simplifying assumptions about the structure of the network and the constraints imposed by its complex topology^{1–7}. Although the literature contains several studies of scattering properties of gels^{8–13}, in fact a quantitative description in terms of the gel structure is still lacking.

In contrast, polymer solutions, in the absence of associations between chains, display no superstructure. The osmotic pressure ensures that the system is homogeneous at large distance scales, since, at equilibrium, no elastic constraints are present.

Investigations using scattering techniques show unambiguously that cross-linking is in general accompanied by the formation of supermolecular structures^{8–13}. The experimentally observed diversity in such structures is not accounted for in existing theories. These features, which depend on the detailed mechanism of the network

formation, are revealed when the elastic and the osmotic forces become comparable, i.e. when the network approaches its fully swollen condition.

In this paper we report small angle neutron and X-ray scattering measurements (SANS and SAXS) on poly(dimethyl siloxane) (PDMS) solutions and gels in octane at different concentrations. Measurements were also performed in hexane and decane. The aim of the study is to describe the main features of the scattering spectra. For the quantitative description we use a modified version of a scattering function proposed by Onuki⁷.

SCATTERING FORMALISM

In a polymer solution, radiation is scattered by spontaneous thermodynamic concentration fluctuations around the equilibrium state, described by the average volume fraction ϕ of the polymer and the associated osmotic compression modulus K_{os} ($= \phi(\partial\Pi/\partial\phi)$ where Π is the osmotic pressure of the solution). For neutral polymer solutions, the Ornstein–Zernike formalism provides the following expression for the scattered intensity^{14,15}:

$$I_d(\mathbf{Q}) = (\rho_p - \rho_s)^2 \frac{kT\phi^2}{K_{os}} \frac{1}{1 + \mathbf{Q}^2\xi^2} \quad (1)$$

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where ξ is the polymer–polymer correlation length, \mathbf{Q} , is the transfer wave vector (for an incident wavelength λ and scattering angle θ , $\mathbf{Q} = (4\pi/\lambda)\sin(\theta/2)$), and $(\rho_p - \rho_s)^2$ is the contrast factor between the polymer and solvent. In a neutron scattering experiment, ρ_p and ρ_s are, respectively, the scattering length density of the polymer and the solvent; in SAXS, these quantities represent the corresponding electron densities.

Polymer gels differ from solutions in that the connectivity of the chains resulting from the cross-links gives rise to a permanent elastic modulus G . The presence of this elastic modulus modifies the response of the system. Thus, the dynamic concentration fluctuations that scatter radiation from swollen networks are no longer governed simply by K_{os} , as in a solution, but by a longitudinal osmotic modulus^{2,16}

$$M_{os} = K_{os} + \frac{4}{3}G \quad (2)$$

Moreover, in addition to the osmotic component arising from the molecular motion, departures from uniformity of concentration are also generated by the long range elastic forces in gels. As the topology of the elastic constraints is fixed at gelation by the covalent cross-links, the associated concentration fluctuation pattern cannot relax, and is therefore permanent. Such static fluctuations, whose ranges are greater than that of the osmotic fluctuations, produce excess scattering in the lower \mathbf{Q} region of the spectrum.

As the distribution and spatial extent of the elastic constraints is determined by the mechanism and conditions of cross-linking, no universal description, equivalent to equation (1), has been developed from the corresponding static scattering function. Although several theoretical attempts have been made to model the scattering spectra from gels^{4,7}, few experimental studies have been reported over a sufficiently wide \mathbf{Q} range to test their applicability.

Mallam *et al.*⁸ proposed an empirical expression to describe the scattering spectra of gels consisting of two terms, thus

$$I(\mathbf{Q}) = \frac{A}{1 + \mathbf{Q}^2\xi^2} + B \exp(-\mathbf{Q}^2\Xi^2) \quad (3)$$

in which the two correlation lengths ξ and Ξ are governed, respectively, by the liquid-like short range fluctuations, and by the longer range permanent elastic constraints in the system. Owing to the chemically heterogeneous nature of the cross-links in the gel they investigated, however, those authors could not test their expression over a wide range of \mathbf{Q} vectors.

More recently, Onuki⁷ proposed a different form,

$$I(\mathbf{Q}) = \frac{A}{1 + \mathbf{Q}^2\xi^2} + \frac{B}{(1 + \mathbf{Q}^2\xi^2)^2} \quad (4)$$

in which, for a given isotropically swollen network, A and B are constants. The first term is similar to that of equation (1) for a solution, while the second, as in equation (3), is intended to account for the excess intensity due to the frozen-in fluctuations in the swollen network. The parameters A and B , as well as the correlation length ξ , may depend on the elastic deformation of the gel. Unlike equation (3), where the underlying assumption is that two different length scales are needed

to describe a system having two independent force constants (the elastic modulus G and the osmotic modulus K_{os}), the theory of Onuki involves only one correlation length, ξ . As the starting point for our analysis, we investigate the success of equation (4) as a fitting function for the observed spectra.

EXPERIMENTAL

Sample preparation

Uncross-linked PDMS was kindly supplied by Rhône-Poulenc Département Silicones. For this sample, g.p.c. measurements yielded a weight-average molecular weight $M_w = 500\,000$, and $M_n = 250\,000$.

Reagent grade protonated hexane, octane and decane (Prolabo) were used without further treatment. Deuterated octane (99.9% D) was obtained from Janssen Chimica.

The cross-linked PDMS gels were prepared by reacting short PDMS chains ($M_n = 11\,000$), each carrying 10 silane groups, with longer PDMS chains ($M_n = 23\,000$), each carrying eight vinyl groups randomly distributed along the chain¹⁷. Hydrosilylation (100°C, 1 h) catalysed by platinum (Karstedt) induces cross-linking through formation of covalent bonds. Extraction measurements in hexane showed that in these conditions all the chains are bound to the network for a molar ratio $[\text{Pt}]/[\text{silane}] = 10^{-4}$; moreover, measurement of the area of the SiH i.r. absorption band at 2125 cm^{-1} indicated that the conversion is complete after 30 min at 100°C with $[\text{Pt}]/[\text{SiH}] = 10^{-4}$.

Small angle X-ray scattering

SAXS measurements were made on the D24 instrument on the DCI synchrotron at LURE, Orsay, France. The incident white beam is focused by a curved monochromator through a Bragg angular deflection that selects the wavelength required for the experiment, which was chosen to be 1.49 \AA . The beam size was $3 \times 0.5\text{ mm}^2$. The gel sample was placed between two mica sheets separated by a 1 mm annular spacer. A 18 cm linear detector with 512-point resolution was used, with a sample-detector distance of 1.91 m. Pure octane in the same cell was used as background, and the resulting difference signal was normalized by the independently measured detector response. Each run lasted approximately 1500 s.

Normalization of the SAXS data was obtained by measuring the scattering spectrum of poly(vinyl acetate) solutions, for which the osmotic pressure concentration dependence is known^{18,19}. The scattering intensities $I(0)$ were normalized with respect to those of the PVAc solutions by multiplying by the relevant ratio of X-ray contrast factors, i.e.

$$(\Delta\rho_{\text{PVAc-toluene}}/\Delta\rho_{\text{PDMS-hexane}})^2 = 1.210$$

$$(\Delta\rho_{\text{PVAc-toluene}}/\Delta\rho_{\text{PDMS-octane}})^2 = 1.951$$

$$(\Delta\rho_{\text{PVAc-toluene}}/\Delta\rho_{\text{PDMS-decane}})^2 = 2.265$$

Small angle neutron scattering

The small angle neutron scattering (SANS) measurements were made on the D11 instrument at the ILL Grenoble, using an incident wavelength of 6 \AA . The \mathbf{Q}

range explored was $0.003 \text{ \AA}^{-1} \leq Q \leq 0.19 \text{ \AA}^{-1}$. Counting times of between 20 min and 2 h were used. Calibration of the scattered neutron intensity was performed using the signal from a 1 mm thick water sample in conjunction with the absolute intensity measurements of Ragnetti *et al.*²⁰

The sample cells were 1 mm thick quartz windows with a 1.0 mm thick Viton O-ring spacer. For the backgrounds, mixtures of protonated and deuterated solvent were prepared for which the transmission factor was as close as possible to that of the sample.

The dry gels were cut into the form of flat discs, and allowed to swell in the solvent in the available space within the sample cell. The contrast variation measurements were performed on identical gel samples swollen in mixtures of protonated and deuterated octane of varying proportions.

RESULTS AND DISCUSSION

Figure 1 shows the SAXS spectra of PDMS–hexane and PDMS–decane solutions at identical polymer volume fraction $\phi = 0.2$. The continuous curves show the least squares fits of equation (1) to the data points. At low values of Q the signal reaches a plateau, indicating the absence of long range structure in these solutions. The greater intensity scattered by the decane solution shows that decane is a poorer solvent of PDMS than hexane. In Figure 2 the SAXS spectrum of a PDMS gel swollen in hexane is compared with that of the solution of the uncross-linked polymer at a similar concentration ($\phi \approx 0.2$). A qualitative difference between these spectra is apparent. In the low Q region the scattering from the gel significantly exceeds that of the solution, while at higher Q a cross-over occurs. The gel curve cannot be described by the simple Ornstein–Zernike form of equation (1). This result implies that the theoretical scattering functions for gels developed in refs 5 and 6 are inadequate, since these consist also of a single lorentzian.

In principle, the increase of intensity in the gel spectrum at low Q over that of the corresponding solution can have two causes: (i) chemical differences between the network polymer and the cross-links; (ii) differences in the local segment concentration caused by the constraints of the cross-links. These two effects may be distinguished by contrast variation. It can be seen from equation (1) that if the polymer has a unique scattering density ρ_p , then, upon varying the value of the scattering density of the solvent ρ_s , the signal will completely disappear at $\rho_s = \rho_p$. If, however, the network investigated is not chemically uniform, then no single contrast match point exists, and the signal never vanishes.

Neutron scattering affords a simple method of varying the contrast, owing to the large differences in scattering length between protons and deuterons^{21,22}. For chemically homogeneous systems, it follows from equation (1) that a plot of $\sqrt{I(Q)}$ will be linear in $(\rho_p - \rho_s)$. In Figure 3 the values of $\sqrt{I(Q)}$ measured in a PDMS gel at different Q are presented as a function of the deuterated fraction d of the octane content. The straight lines joining $\sqrt{I(Q)}$ at each value of Q have a common intercept at $d = 0.09$, which coincides with the calculated value for pure PDMS. This results indicates that the system behaves as a single chemical species over the whole Q -range investigated.

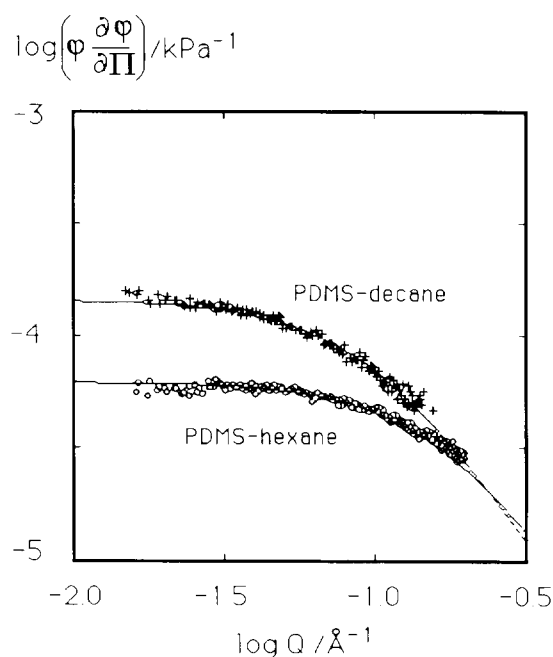


Figure 1 Normalized SAXS spectra of solutions of PDMS in hexane (○) and in decane (+) at volume fraction $\phi = 0.2$

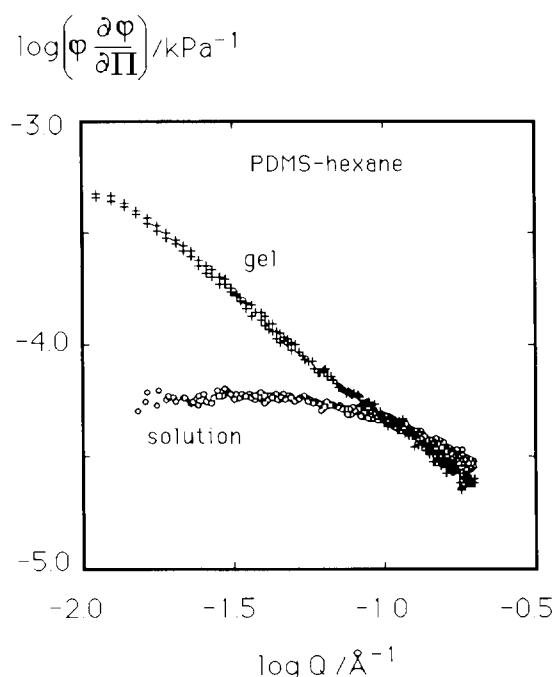


Figure 2 Normalized SAXS spectra of a PDMS–hexane gel at volume fraction $\phi = 0.23$ (+) and solution at $\phi = 0.20$ (○)

Independent evidence of the chemical homogeneity of this system can be seen in Figure 4, where the SAXS and SANS spectra of the same PDMS–octane gel are shown. These measurements, which are expressed in absolute units, are obtained by entirely independent methods (cf. Experimental section). Apart from small differences in the lower part of the spectrum, which probably arises from a slight discrepancy in concentration between the samples, the two techniques yield almost identical results. Since the calibration of these two curves is based on the calculated neutron and electronic densities of the pure polymer, the coincidence of the two curves

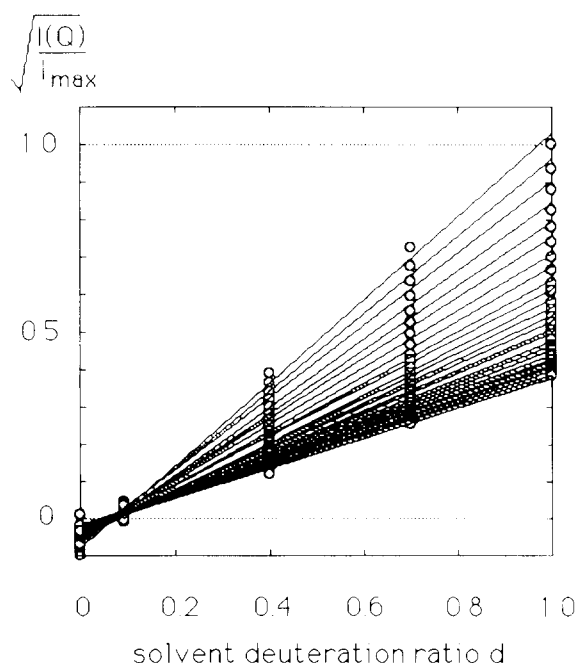


Figure 3 Contrast variation for a PDMS–octane gel as a function of deuteration ratio of the solvent, normalized to the highest scattering intensity I_{\max} . The straight lines connect points of different deuteration ratio belonging to the same Q value. In this representation, data to the left of the contrast match point are attributed negative values of $\sqrt{I(Q)}$

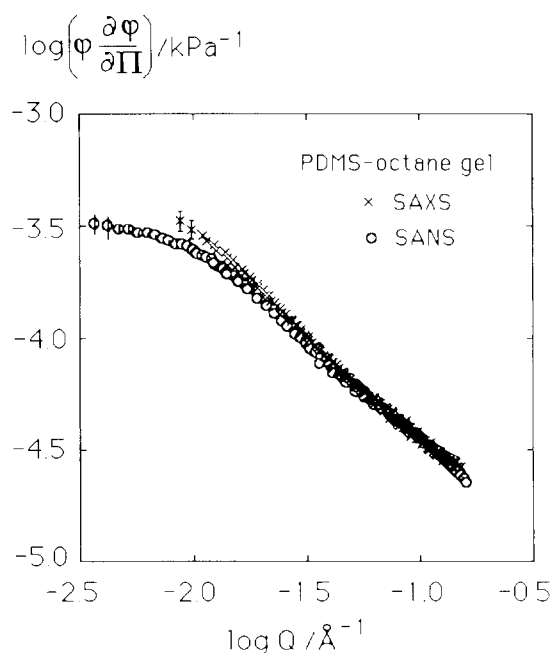


Figure 4 SAXS and SANS spectra of the same PDMS–octane gel at polymer volume fraction $\phi \approx 0.23$

implies the chemical homogeneity of the network, in agreement with the neutron contrast variation measurements.

Figure 5 shows the SANS spectra of the PDMS gel swollen in octane at three different concentrations. The general shape of the three curves is similar. Two shoulders can be distinguished, one at low Q which becomes increasingly prominent as the gel approaches its fully swollen state, while the other, at higher values of Q ,

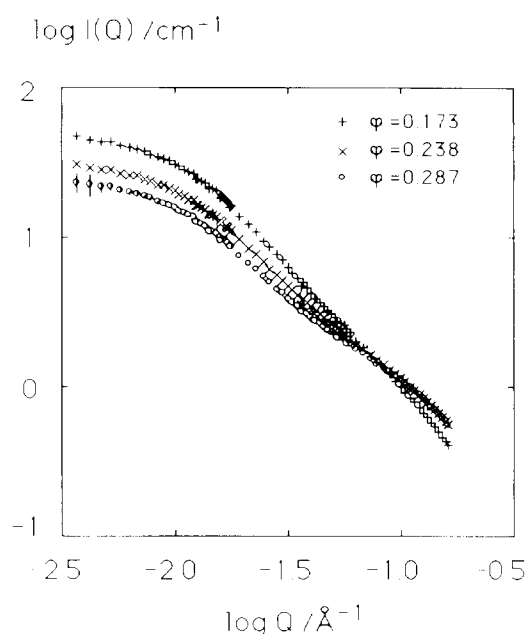


Figure 5 SANS spectra of a PDMS gel at different polymer volume fractions in octane. Volume fractions as indicated

is progressively revealed as the overall concentration increases. The presence of these two features indicates that the scattering response is caused by structures having two different characteristic lengths. The similarity of the second shoulder in the gel to the spectrum of the solution (cf. Figure 1), suggests that the higher Q region of the spectrum is governed by a solution-like component. The separation scheme of equation (4), contains as its first term just such a solution-like component. The whole equation (4), however, gives an unacceptably poor fit to the data, since both terms are controlled by the same correlation length ξ , which therefore cannot describe the observed double shouldered gel spectrum. For this reason, to analyse the data, a second length scale Ξ is necessary. Equation (4) thus becomes

$$I(Q) = (\rho_p - \rho_s)^2 \left[\frac{kT\phi^2}{M_{os}} \frac{1}{(1 + Q^2\xi^2)} + \frac{B}{(1 + Q^2\Xi^2)^2} \right] \quad (5)$$

in which the same contrast factor $(\rho_p - \rho_s)^2$ common to both terms is justified by the contrast variation results. In this expression, ξ is understood to have the same meaning as in equation (1), i.e. the correlation length of the short range thermodynamic concentration fluctuations, corresponding to the size of the blobs. The longer range characteristic length Ξ , however, describes static fluctuations governed by the frozen-in elastic constraints, which act between topologically connected cross-links. The second term in equation (5) is that of the Debye–Bueche formalism²³, and corresponds to a density correlation function for the static concentration fluctuations of the form $\exp(-r/\Xi)$. In the absence of frozen-in elastic constraints in the system, equation (5) reduces to equation (1). As required for a solid with a permanent elastic modulus², however, the osmotic restoring modulus K_{os} is replaced here by M_{os} . The amplitude of the second term in equation (5) can be

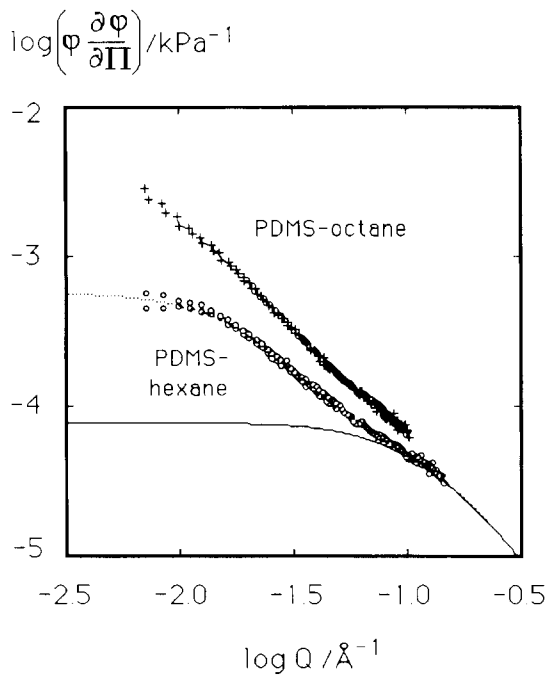


Figure 6 SAXS spectra of a PDMS network in hexane (○) and in octane (+) at identical polymer volume fraction $\phi \approx 0.23$. The dotted line is the fit of equation (5) to the PDMS-hexane spectrum; continuous line is the calculated solution-like component with parameters given in the last line of *Table 1*

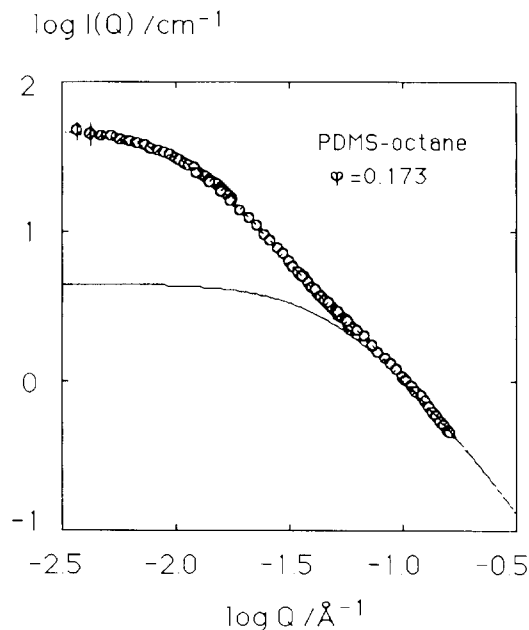


Figure 7 Fit of equation (5) to neutron scattering spectrum of the fully swollen PDMS octane network (dotted line). Continuous line is the solution-like component calculated with the parameters displayed in *Table 1*

shown to be¹⁰

$$B = 8\pi\Xi^3 \langle \delta\phi^2 \rangle \quad (6)$$

where $\langle \delta\phi^2 \rangle$ is the mean square amplitude of the static concentration fluctuations. An expression similar to equation (5) has previously been used to describe the scattering spectrum of gelatin gels²⁴.

In *Figure 6* SAXS spectra are shown of the same

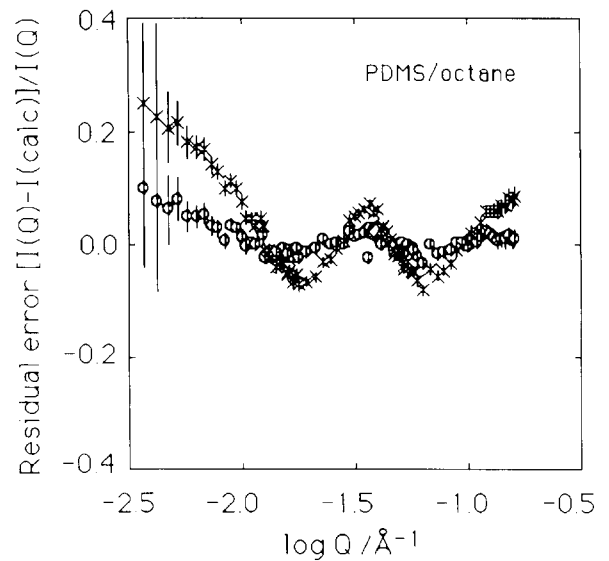


Figure 8 Fractional residuals $[I(Q) - I_{\text{calc}}]/I(Q)$ for the fully swollen PDMS octane gel; (○) I_{calc} given by equation (3); (+) I_{calc} given by equation (5)

PDMS gel swollen to the same degree ($\phi = 0.23$) in octane and in hexane, respectively. The dotted curve represents the least squares fit of equation (5) to PDMS-hexane data, while the continuous curve is its solution-like component. As in the solutions in *Figure 1*, the scattering intensity from the PDMS-hexane system is lower than that of PDMS-octane. The osmotic compressibility of the PDMS-octane system is thus higher than that of PDMS-hexane, reflecting the fact that octane is a poorer solvent. It follows that the maximum swelling degree of the gel is greater in hexane than in octane, i.e. in *Figure 6*, the gel swollen in hexane is further from its maximum swelling than that swollen to the same extent in octane. Inspection of *Figure 6* leads to the conclusion that improvement of the quality of the solvent at constant concentration for a given gel reduces the amplitude not only of the short range fluctuations but also those of the long range. It is also apparent that, within the noise of the SAXS data, equation (5) is quite successful in fitting the scattering spectrum.

A more severe test of the fitting scheme is provided by the SANS spectra of *Figure 5*. Owing to the two-dimensional detector and the lower Q values available on the neutron scattering instrument, the SANS spectra are less noisy and extend over a greater Q range than SAXS. The dotted line in *Figure 7* shows the result of fitting equation (5) to the most highly swollen PDMS-octane sample, the liquid-like component being represented by the continuous line. Although its relative lack of marked features makes this spectrum more difficult in principle to fit than the more deswollen samples, the quality of all the fits is similar. *Figure 8* compares the residual fractional errors of this fit (circles) with those for the gaussian expression, equation (3) (crosses)^{8,12,25}. The quality of the fit for the present end-linked gels is noticeably improved. The parameters obtained from these fits to the gel at different degrees of swelling are listed in *Table 1*. In comparing these values, owing to the restricted Q range and the intrinsically greater uncertainties in the background subtraction procedure, the SAXS measurements at low Q are more delicate than

Table 1 Fitting parameters for equation (5) for PDMS gels

Solvent	ϕ	$\phi(\partial\phi/\partial\Pi)$ (kPa)	B (kPa)	ξ (Å)	Ξ (Å)
Octane	0.173	$2.70 \cdot 10^{-4}$	$2.63 \cdot 10^{-3}$	20.0	53.9
	0.238	$1.74 \cdot 10^{-4}$	$1.65 \cdot 10^{-3}$	13.3	51.2
	0.287	$1.50 \cdot 10^{-4}$	$1.25 \cdot 10^{-3}$	11.9	51.5
Hexane	0.23	$0.77 \cdot 10^{-5}$	$5.00 \cdot 10^{-4}$	9.8	37.0

those of SANS. It is noteworthy that the measured values of Ξ are comparable to the mean end-to-end distances between cross-links calculated for the primary PDMS chains in the gel, i.e. approximately 30 Å. This is considerably larger than either ξ or the persistence length of the polymer (*ca* 6 Å). It is also noticeable from *Table 1* that ξ and the intensity of the liquid-like component decrease with increasing polymer concentration, while Ξ remains practically invariant.

CONCLUSIONS

Measurements using SAXS on poly(dimethyl siloxane) solutions in hexane, octane and decane show that these spectra can be represented by a simple Ornstein–Zernike expression. In the corresponding gels, however, the small Q region of both the SAXS and SANS spectra is dominated by excess scattering associated with frozen-in elastic constraints. Contrast variation showed that the gels were chemically homogeneous. The structure factor of the gels is well described by a two-term expression in which the first term is a lorentzian while the second is a squared lorentzian. The correlation lengths associated with these two components of the structure factor are distinct and exhibit different behaviour when the gel is deswollen.

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