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Investigation by Small-Angle Neutron Scattering of the Chain Conformation in Equilibrium-Swollen Poly(dimethylsiloxane) Networks

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ABSTRACT: The influence of swelling on the dimensions of the elastic chains in poly(dimethylsiloxane) (PDMS) networks prepared by "end-linking" has been investigated by small-angle neutron scattering. Within the limit of experimental accuracy the radius of gyration of the elastic chains in a network swollen in a good solvent of PDMS is the same as that of the linear homologue of the same molecular weight in dilute solution. The functionality of the cross-links and the conditions of network preparation such as the polymer concentration at network formation have no influence on the chain dimensions. No simple general relation exists between the macroscopic and the molecular behavior. However, the results obtained strongly support de Gennes' approach based on the analogy between a semidilute solution of high molecular weight polymer and a cross-linked gel swollen to equilibrium in a good solvent.

Introduction

Swollen networks have been the subject of many investigations during the past 30 years. The experimental results reported in the literature concern mainly their macroscopic behavior, for example, equilibrium swelling and modulus. The interpretation of the network behavior upon swelling in relation to the deformation thus involved at the molecular level has given rise to many controversial discussions.

The recent development of the SANS technique allows one to obtain quantitative information concerning the dimensions of the network strands: the radius of gyration of an elastic chain can be measured accurately and it can be compared with theoretically predicted values.

A recent investigation by SANS of poly(dimethylsiloxane) (PDMS) model networks in the dry state has led to the conclusion that cross-linking (by an "end-linking" reaction) does not affect the dimensions of the polymer chains.[1] This is established regardless of the concentration at which the networks have been generated. Thus, at the molecular level, no memory effect or supercoiling of the elastic chains can be detected.

In the present paper the experimental results of a SANS investigation on the same type of PDMS networks, swollen to equilibrium in cyclohexane, a good solvent of PDMS, are reported and discussed.

Theory of the Swelling Process

In the early theories of rubber elasticity,[2-4] the cross-links of a rubbery network were considered to be firmly embedded in the medium. As a consequence, in a deformed network, the displacement of the cross-links is affine in the macroscopic strain, i.e., the macroscopic swelling.

An alternative approach to rubber elasticity was first developed by James and Guth.[5,6] In their model called "phantom network", the physical role of the chains is to transmit the forces exerted on the junctions. The volume and material existence of the chains are ignored: the latter may go through one another freely and they are consequently not restricted by neighboring chains. The junction points of a phantom network can be characterized by the following behavior: (i) their mean positions are defined by the macroscopic dimensions, (ii) the displacements of these mean positions are affine in the macroscopic strain, and (iii), the fluctuations of the junctions from these mean positions are Gaussian and their magnitude is independent of the strain.

Recently, Flory[7,8] reviewed these rubber elasticity theories. He suggests that these two deformation processes correspond to the upper and lower limits of a chain deformation in a real network. The experimentally observed discrepancies from the phantom network theory could be due to restrictions of the fluctuations around the mean positions of the cross-links. These restrictions are imposed by the neighboring chains and are the chief consequence of entanglements in polymer networks.

de Gennes[9] has proposed a more intuitive model based on the analogy between a swollen gel and a semidilute solution of high molecular weight polymer chains. The mesh size of the network corresponds to the "screening length" of the polymer solution.

As a consequence, the equilibrium segment concentration c_e of the swollen gel is related to the c^* concentration

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of a solution of macromolecules of the same molecular weight. c^* is the crossover concentration between the dilute regime, where the coils are separated, and the semidilute regime, where the coils overlap:

$$c_e = k(f)c^* \quad (1)$$

where $k(f)$ is a constant depending on the functionality f of the cross-links and on the preparation conditions. In a very good solvent, the c^* concentration depends on the degree of polymerization N according to the following law:

$$c^* \propto N/R_F^3 \propto N^{-4/5} \quad (2)$$

where R_F is the radius of gyration of a chain of degree of polymerization N in the dilute regime.

The information on the chain conformation of swollen PDMS networks that was obtained by SANS measurements will be discussed within the framework of these different theories.

Small-Angle Neutron Scattering Experiments

Swollen Networks. Semidilute Solutions. As was shown recently both theoretically[10,11] and experimentally,[12-14] SANS experiments can be performed on polymer samples containing any volume fraction of deuterated species.

The theoretical treatment has been extended to three-component systems. In the simple case of mixtures of deuterated and nondeuterated linear polymers dissolved in a solvent, Akcasu[10] suggested adjusting the coherent scattering length b_s of the solvent to the average scattering length of the polymer mixture b_0.

The use of a mixture of deuterated and nondeuterated solvents allows an adjustment of b_s such that $b_s = b_0$. In this case the interchain contribution to the scattering intensity is canceled and the scattered intensity reduces to

$$I(q) \sim N\phi_D(1 - \phi_D)(b_D - b_H)^2P(q) \quad (3)$$

where N is the total number of chains in the medium, $b_D - b_H$ is the difference of scattering lengths of the deuterated and undeuterated species, ϕ_D is the volume fraction of deuterated polymer, $P(q)$ is the intrachain scattering function, also called the single-chain form factor, and q is the momentum transfer ($q = (4\pi/\lambda) \sin(\theta/2)$).

It thus appears that the single-chain form factor can be derived from the intensity scattered by a three-component system provided Akcasu's condition is obeyed. The accuracy of the measurements increases with the volume fraction of deuterated component and reaches a maximum for $\phi_D = 0.5$.

We have verified earlier experimentally the validity of relation 3 on swollen PDMS networks and on semidilute solutions of linear PDMS.[1]

As mentioned in ref 1, eq 3 is strictly valid only for mixtures of identical deuterated and undeuterated polymer species. However, it has been shown that in the present case a correction which takes into account the polydispersity of the H and D molecules is within the limit of experimental accuracy.

The results reported in the present paper refer to samples containing about 20% PDMS(D). An investigation of the same network samples in the dry and undeformed state has already been published.[1]

Dilute Solutions. The classical Zimm formulation[15] of the intensity $I(q)$ scattered by a dilute solution of polymer can be expressed in the low q range as

$$\frac{Kc}{I(q)} \simeq \frac{1}{M_w}\left(1 + q^2\frac{\langle R^2\rangle_z}{3}\right) + 2A_2c \quad (4)$$

Table I
Equilibrium Swelling Degrees of the PDMS Networks in a Mixture of Deuterated and Undeuterated Cyclohexane

M_n(D)	M_n(H)	ϕ_D	v_c	f	Q
3 100	3 150	0.189	0.71	4	5.4
6 100	6 400	0.189	1	4	5.2
6 100	6 400	0.197	0.71	4	6.7
10 500	9 700	0.187	1	6	5.2
10 500	9 700	0.268	0.71	6	6.6
10 500	9 700	0.188	1	4	6.0
10 500	9 900	0.196	0.71	4	7.4
10 500	9 700	0.188	0.60	4	8.2
23 000	25 000	0.076	1	6	6.7
23 000	25 000	0.188	1	4	10
23 000	25 000	0.188	0.71	4	15

where M_w is the weight-average molecular weight, $\langle R^2\rangle_z$ is the z average of the mean square radius of gyration, A_2 is the second virial coefficient, and c is the polymer concentration.

Experimental Section

Preparation of the Samples. The synthesis of the PDMS networks containing a known fraction of deuterated chains has been described elsewhere.[1] The samples were obtained by submitting mixtures of deuterated PDMS (PDMS(D)) and undeuterated PDMS (PDMS(H)) to an end-linking process. α,ω-Difunctional polymers of average molecular weights M_n ranging from 3000 to 25 000 were used. The networks were prepared in the bulk or in concentrated toluene solution. The volume fraction of total PDMS, v_c, ranged from 0.6 to 1. The volume fraction of PDMS(D) with respect to total PDMS was always 0.2 in this set of experiments.

A small fraction of unreacted polymer was extracted with toluene from the network.

The equilibrium swelling degree Q of the gels was determined by a weighing technique.[16] Q is related to the equilibrium segment concentration (by volume) of PDMS, c_e, by the expression

$$c_e = Q^{-1} \quad (5)$$

Solvents. Cyclohexane, C_6H_{12}, was distilled twice. Perdeuterated cyclohexane, C_6D_{12} (CEA, Service des Molécules Marquées, 99.7% D), was used without further purification.

SANS Experiments. The neutron scattering experiments were performed on either of the two small-angle scattering devices (D11 and D17) of the Institut von Laue-Langevin (Grenoble, France). The following samples were studied: (i) networks (see Table I) swollen to equilibrium in a mixture of deuterated and undeuterated cyclohexane (volume fraction of $C_6D_{12} \equiv X_D = 0.17$), (swollen gels were placed in 1-mm-thick quartz cells); (ii) the corresponding semidilute solutions of the linear deuterated and undeuterated polymer mixtures in cyclohexane characterized by $\phi_D = 0.2$ and $X_D \simeq 0.17$ (volume fractions of polymer were set equal to the equilibrium volume fraction c_e in the corresponding swollen networks; 1-mm quartz cells were used); and (iii) dilute solutions of undeuterated PDMS in deuterated cyclohexane (in this case the incoherent contribution is much lower than for a solution of PDMS(D) in undeuterated cyclohexane and, as a consequence, the signal/noise ratio is more favorable).

For each PDMS sample, the measurements were carried out at three concentrations. The solutions were placed in 2-mm quartz cells (1-mm cells for the samples of molecular weight $M_n = 25\,000$).

Determination of the Radius of Gyration. The following treatment has been applied to the data obtained from the neutron scattering measurements: (i) radial integration of the measured neutron counts, (ii) subtraction of the incoherent scattering background (account being taken of thickness and transmission), and (iii) normalization of the resulting scattering distribution by means of an incoherent scatterer (pure water) in order to correct for detector efficiency.

(a) Swollen Networks and Semidilute Solutions. For these samples, the background incoherent scattering was measured by means of a solution of a mixture of deuterated and undeuterated octamethylcyclotetrasiloxane (D_4) in the solvent used (C_6D_{12} + C_6H_{12}, $X_D = 0.17$).

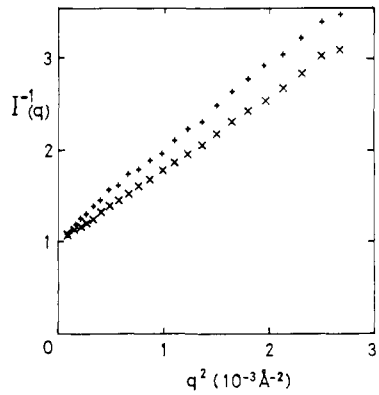

Figure 1. Scattered intensities vs. q^2 (Zimm representation): (+) equilibrium-swollen PDMS network; (×) semidilute solution of the linear homologue (M_n = 9700; concentration $c_e = Q^{-1}$).

Table II
Radii of Gyration of the Linear PDMS Chains in Dilute Solution

M_n	M_z[a]	R_F, Å
3 150	7 800	27 ± 2
6 400	16 000	39 ± 3
9 700	24 000	58 ± 3
25 000	61 000	85 ± 5

[a] Determined by GPC.

Typical scattered intensities are shown in Figure 1 in the Zimm representation. The radius of gyration, $R_g = (\langle R^2\rangle_z)^{1/2}$, is given by the slope of the curve in the Guinier range ($q^2\langle R^2\rangle \ll 1$):

$$\frac{1}{I(q)} \simeq \frac{1}{I(0)}\left(1 + q^2\frac{\langle R^2\rangle}{3}\right) \qquad (6)$$

In fact, because of the polydispersity of the labeled species ($M_w/M_n \sim 1.6$), the linear regression leading to the determination of $\langle R^2\rangle$ can be performed on values even outside the range $q^2\langle R^2\rangle \ll 1$.[17] Under these conditions the deviation from the true value of the radius of gyration is insignificant.

(b) Dilute Solutions. In the case of dilute solutions, we chose as "background" the intensity scattered by solutions of D_4 in deuterated cyclohexane. The mean square radius of gyration at infinite dilution, $(\langle R^2\rangle_z)_{c=0} = R_F^2$, is given by the slope of the inverse scattering intensity, extrapolated to $c = 0$, $(c/I(q))_{c=0}$, as a function of q^2 according to the classical Zimm representation (see Figure 2).

Figure 3 shows a plot of $(c/I(q))_{c=0}$ vs. q^2 for the linear PDMS samples studied. The corresponding radii of gyration calculated by linear regression are listed in Table II.

Results and Discussion

The values of the equilibrium swelling degrees of the PDMS networks are presented in Table I. These results are consistent with those of previous studies on swollen networks.[18] It is thus established that the equilibrium swelling degree not only depends on the molecular weight of the elastic chains and on the functionality of the cross-slinks but is also function of the volume fraction v_c at which the networks were prepared. Quasi-elastic light scattering experiments on PDMS networks swollen in heptane led to the conclusion that trapped entanglements are responsible for a decrease of the effective mesh size.[19]

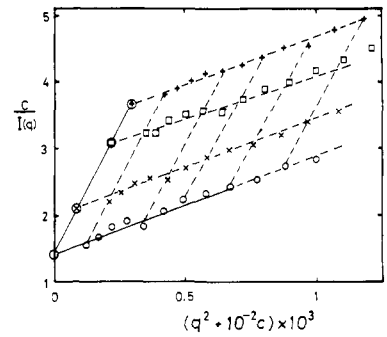

Figure 2. Zimm representation of PDMS in cyclohexane solution (M_n = 9700): (+) c = 0.0283 g·cm^3; (□) c = 0.0214 g·cm^3; (×) c = 0.0086 g·cm^3; (○) values of $c/I(q)$ extrapolated to $c = 0$. The circled symbols represent values extrapolated to $q = 0$ for a given concentration.

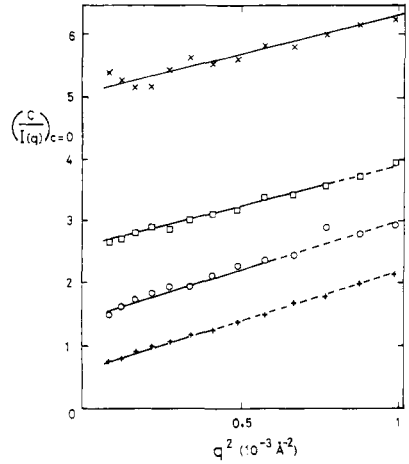

Figure 3. $c/I(q)$ extrapolated at zero concentration vs. q^2: (×) M_n = 3050; (□) M_n = 6400; (○) M_n = 9700; (+) M_n = 25 000.

Table III summarizes the experimental values of the radius of gyration, $R_g = (\langle R^2\rangle)^{1/2}$, of the elastic chains of molecular weight $M_n \simeq 10\,000$ (M_n(PDMS(D)) = 10 500, M_n(PDMS(H)) = 9700). The networks with tetrafunctional cross-links (f = 4) were prepared at three different volume fractions ($0.6 \leq v_c \leq 1$) and the hexafunctional gels (f = 6) were cross-linked at v_c = 1 (bulk) and at v_c = 0.71.

The radius of gyration measured for the corresponding free chains in semidilute solution at the same concentration ($c_e = Q^{-1}$) is R_g = 49 ± 2 Å, whereas for the same linear PDMS at infinite dilution we have found R_F = 58 ± 3 Å.

The values of R_g predicted by the rubber elasticity theories can be calculated in first approximation for the

Table III[a]
Experimental and Calculated Radii of Gyration of Elastic Chains in Swollen PDMS Networks

				R_F,[b] Å			
Q	f	v_c	R_F,[b] Å	swollen networks	semidilute solutions[c]	junction affine	phantom networks
			58				
5.2	6	1		57 ± 2		58.0	53.0
6.0	4	1		59 ± 2	49 ± 2	60.5	51.5
6.6	6	0.71		59 ± 2		58.5	53.0
7.4	4	0.71		61 ± 2	49 ± 2	60.5	51.0
8.2	4	0.60		60 ± 2	49 ± 2	62	52.0

[a] $M_n \simeq 10\,000$. [b] Radius of gyration of the free chain at infinite dilution. [c] Concentration $c_e = Q^{-1}$.

Table IV[a]
Experimental and Calculated Radii of Gyration of Elastic Chains in Swollen Networks

				R_g, Å			
Q	f	v_c	R_F,[b] Å	swollen networks	semidilute solutions[c]	junction affine	phantom network
			85 ± 8				
6.7	6	1		88 ± 5		87.5	80
10	4	1		87 ± 5	71	101	83
15	4	0.71		89 ± 5	79	113	90

[a] $M_n \simeq 25\,000$. [b] Radius of gyration at infinite dilution. [c] Concentration $c_e = Q^{-1}$.

Table V
Experimental and Calculated Radii of Gyration of Elastic Chains in Swollen Networks

				R_g, Å			
M_n	v_c	Q	R_F,[a] Å	swollen networks	semidilute solutions[b]	junction affine	phantom network
3050			27				
3100	0.71	5.4		27	24	31	27
6400			39				
6100	1	5.2		41	35	45	39
6100	0.71	6.7		41	35	47.5	40

[a] Radius of gyration at infinite dilution. [b] Concentration $c_e = Q^{-1}$.

swollen gels. Under the assumption that the statistics of the chains remains Gaussian, the swelling can be identified with the macroscopic strain of deformation ratio $\lambda = Q^{1/3}$.

If the induced displacements of the junction points are affine, the expected value of R_g is given by[20]

$$R_g = R_{g_0}\left(\frac{\lambda^2 + 1}{2}\right)^{1/2}$$

where R_{g_0} is the radius of gyration of the elastic chains in the dry undeformed network.[1]

For an f-functional phantom network, the predicted value can be written as[21]

$$R_g = R_{g_0}\left(\frac{f + 2 + (f-2)\lambda^2}{2f}\right)^{1/2}$$

The experimental values of R_g of the elastic chains are consistent with the predictions of a "junction affine" deformation. On the other hand, the agreement with the dimensions of a single coil in the dilute regime is remarkable.

In the classical theories—"phantom network" or "junction affine"—the chain expansion is directly related to the macroscopic deformation. For this reason, networks with longer elastic chains are interesting: indeed, the cross-linking conditions (v_c and f) strongly influence the equilibrium swelling degree of the gels prepared with precursor polymers of higher molecular weight ($M_n \simeq 25\,000$) as shown in Table I.

Table IV summarizes the experimental values of the radii of gyration R_g obtained for these networks: the dimensions of the elastic chains are the same within experimental accuracy, and they correspond to the dimensions of the single coil in the dilute regime.

A similar agreement is obtained for samples prepared with two other precursor polymers (molecular weights $M_n \simeq 3000$ and $M_n \simeq 6000$) as shown in Table V.

In these cases, the behavior at the molecular level can be described roughly by the phantom network model.

Conclusion

In the present paper, we have compared the observed radius of gyration of the elastic chains in a swollen network with the theoretical predictions.

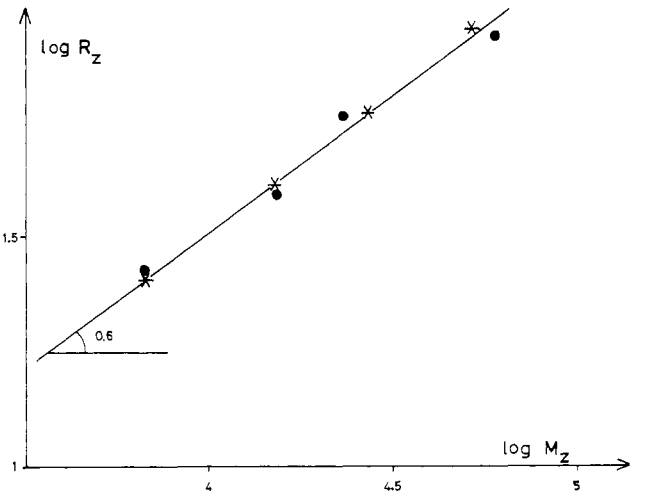

Figure 4. Double-logarithmic plot of the radii of gyration R_z of elastic chains and the corresponding free PDMS chains vs. the molecular weight M_z (z average of the molecular weight measured by GPC): (*) PDMS networks swollen to equilibrium in cyclohexane; (●) dilute solutions of linear PDMS in cyclohexane.

In first approximation, we considered a Gaussian network submitted to a deformation which should not affect the statistics (deformation ratio $\lambda = Q^{1/3}$). Under that assumption, the major part of the results are roughly consistent with the predictions arising from the phantom network model. However, for some of them (particularly those corresponding to the precursor PDMS of molecular weight $M_n \simeq 10\,000$) an important discrepancy was observed.

On the other hand, using de Gennes' approach of swollen gels, a simple and coherent interpretation of the network behavior is possible. The c^* theorem predicts that the equilibrium concentration c_e is proportional to c^*.

Indeed the radii of gyration of the elastic chains in the swollen networks are, within the limits of experimental accuracy, the same as those of the corresponding free chains in the dilute regime.

This is illustrated by Figure 4, where the radii of gyration of the elastic chains of the networks and of the free chains of the precursor polymers are plotted vs. the mo-

lecular weight on a double-logarithmic scale. In both cases excluded volume affects the chain dimensions. The radius of gyration is related to the molecular weight by the expression

$$R_g = 0.17 M_z^{0.58}$$

where M_z is the z average of the molecular weight measured by GPC.

In the semidilute regime, where screening leads to dimensions smaller than in dilute solutions, the experimental values of R_g of the PDMS chains at a concentration $c = c_e$ are significantly different from the radii of gyration of the elastic chains in the corresponding swollen networks.

We can conclude that the conformation of an elastic chain in a swollen network is mainly governed by the local polymer–solvent interaction, whereas the equilibrium swelling degree of the gel depends on the functionality of the junctions points and on the volume fraction v_c at which the network was prepared.

This study corroborates several other investigations on swollen networks[19,22] and strongly supports de Gennes' approach of the behavior of a network swollen at equilibrium in a good solvent.

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Dynamic Light Scattering Studies of Polymer Solutions. 1. Histogram Analysis of Internal Motions

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ABSTRACT: The efficiency of the histogram method in the study of internal motions by dynamic light scattering has been tested for a narrow-distribution polystyrene having a weight-average molecular weight of 5.50×10^6 in dilute solutions in *trans*-decalin at 25 °C. The bimodal histogram analysis has been proved to be adequate for estimating the characteristic parameters of internal relaxation motions separately from those of translational diffusive motions. The results are compatible with theoretical predictions by the non-free-draining chain model with preaveraged hydrodynamic interaction.

Introduction

Dynamic light scattering can be used to study the internal motions of a flexible polymer in dilute solution. For example, the longest intramolecular relaxation time τ_1 is obtainable from the intensity autocorrelation function $A(\tau)$ measured in the intermediate q region, where the reciprocal magnitude q^{-1} of the scattering vector is comparable to the root-mean-square radius of gyration R_G of the polymer. This feature of dynamic light scattering is remarkable, because the τ_1 in dilute solutions can hardly be determined by other means such as viscoelastic measurements.

Several groups of investigators have attempted the two-exponential-term analysis[1-5] or the cumulant analysis[6-9] of $A(\tau)$ to estimate τ_1 or the first cumulant Ω, respectively, and have compared the results with predictions of various theories. However, extrapolation of the estimated values of τ_1 and Ω to zero scattering angle and zero concentration, which is necessary to precisely test the theories, has not been fully performed in these studies. Thus the results are still not conclusive, though two latest studies[5,9] seem to support predictions obtained for the nondraining polymer model with the preaveraged hydrodynamic interaction,[10,11] rather than that without preaveraging.[12]

Chu and co-workers[13] have recently presented the histogram method for determining the distribution of decay rate $G(\Gamma)$ from the measured correlation function $A(\tau)$. The method has been proved to be effective, especially in the analysis of bimodal distributions of Γ which appear, for example, in binary mixtures of polystyrene latex particles of different sizes.[14]

In this paper, we apply the histogram method to the analysis of $A(\tau)$ measured in the intermediate q region and examine whether the method is effective in estimating τ_1 of flexible polymers separately from the translational diffusion coefficient D. For the purpose, we used a nar-

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