Scattering from Network Polydispersity in Polymer Gels

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Swollen networks possess permanent elastic constraints that induce static variations $\langle \delta\varphi^2 \rangle_s$ at a microscopic scale in the polymer volume fraction φ. It is shown that the concentration polydispersity $\langle \delta\varphi^2 \rangle_s/\varphi^2$ is related to the macroscopic osmotic and elastic properties of the gel. An expression is derived for the dependence of $\langle \delta\varphi^2 \rangle_s/\varphi^2$ on swelling. Good agreement is found with previously reported small-angle neutron scattering measurements in randomly cross-linked polyvinyl acetate and end-link polydimethyl siloxane networks swollen in toluene.

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Chemically cross-linked gels are composed of flexible polymer molecules that are mutually connected to form a three-dimensional structure of unlimited size. The principal observable macroscopic difference between such systems and polymer solutions is the appearance of a finite zero-frequency elasticity. In a gel the local polymer concentration may differ significantly from the average, since the cross-linking process is in general accompanied by a redistribution of the polymer segments [1]. This local variation in concentration is an analog of molecular weight polydispersity in dilute polymer solutions, since a spread in concentration in a gel is equivalent to a spread in molecular weight per unit volume. For this reason we designate it by the term concentration polydispersity.

The phenomenon is of broad relevance. Concentration polydispersity affects important macroscopic parameters in gels including their swelling, elastic, transport, and optical properties; it seems probable that it is also related to their rupture strength.

The architecture of a network depends on the manner of the cross linking. A consequence of concentration polydispersity is that a certain fraction of the polymer in the network is restrained from participating fully in the thermodynamic concentration fluctuations that prevail in uncross-linked polymer solutions.

The microscopic structure of the gel can be characterized by applying scattering techniques suited to the different length scales of the polymer distribution. We have found [2,3] that the scattering spectra of swollen gels can be treated as the sum of two separate components, a static and a dynamic scattering function $I_s(Q)$ and $I_d(Q)$, respectively. $I_s(Q)$ is determined by the permanent mechanical constraints imposed by the cross links, and $I_d(Q)$, which exhibits solutionlike behavior, reflects the thermodynamic fluctuations of the polymer segments. Here, $Q=(4\pi/\lambda)\sin(\theta/2)$ is the transfer vector at scattering angle θ for an incident radiation of wavelength λ. It was also found that the form and relative intensity of $I_s(Q)$ depends upon the particular system investigated.

In this Letter we propose a relationship between the microscopic polydispersity of the network structure and the macroscopic osmotic and elastic parameters of the system (swelling pressure, shear modulus, and polymer volume fraction). The polydispersity of the polymer density distribution is calculated from the second moment of the static scattering function $I_s(Q)$, which is an experimentally accessible quantity. A comparison is made between the theoretical expression and the results from small-angle neutron scattering (SANS) experiments on chemically cross-linked polyvinyl acetate (PVAc) and polydimethyl siloxane (PDMS) gels.

The free energy function of a gel is expressed as the sum of two terms [4,5], $F_{\text{mix}}+F_{\text{el}}$, where the former, of osmotic origin, is the free energy of mixing between polymer and solvent, and the latter, the elastic free energy of deformation of the network chains, is mainly entropic. At equilibrium, the derivative of the total free energy with respect to concentration (i.e., the swelling pressure, ω) is constant throughout the sample. Hence, at fixed overall concentration, the swelling pressure

$$\omega = \Pi - G = \text{const}\,, \tag{1}$$

where Π is the osmotic pressure exerted by the network and G is the elastic modulus. In a real network fluctuations arise in the cross-linking density, thereby affecting the local value of G. Since both Π and G depend on the polymer volume fraction φ, we have

$$\delta\omega = (\partial\Pi/\partial\varphi)\delta\varphi - \delta G = 0\,. \tag{2}$$

Here [5],

$$G = aNkT\varphi^{1/3}/V\,, \tag{3}$$

where N is the number of cross links in a volume V of the dry network, k is the Boltzmann constant, T the absolute temperature, and the constant a is a topological factor of the order of unity [5,6]. In the concentration range explored here, the exponent of φ indicated in Eq. (3) is observed [7,8] to be accurate to within 1%.

The nonuniformities in cross-linking density are of

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finite size defined by some average volume v. We define $n=Nv/V$ as the mean number of cross links within v. Local variations in the number of cross links, $\delta n=\delta N\times(v/V)$, develop when the gel forms. Hence, from Eqs. (2) and (3),

$$(K-G/3)(\delta\varphi/\varphi)=\delta n(akT/v)\varphi^{1/3}\,, \tag{4}$$

where $K=\varphi(\partial\Pi/\partial\varphi)$ is the osmotic compression modulus of the system. For gels in which the cross-link clusters obey Gaussian statistics, the mean value $\langle\delta n\rangle^2=n$, the angular bracket denoting an average over the sample. Assuming small relative concentration excursions, one then has $\langle(\delta\varphi/\varphi)^2\rangle=\langle\delta\varphi^2\rangle_s/\varphi^2$, where $\langle\delta\varphi^2\rangle_s$ is the mean square concentration fluctuation due to the static concentration polydispersity. Thus

$$\begin{aligned}\frac{\langle\delta\varphi^2\rangle_s}{\varphi^2}&=CG^2\Big/\left(\varphi\frac{\partial\omega}{\partial\varphi}\right)^2\\&=CG^2\Big/\left(K-\frac{G}{3}\right)^2,\end{aligned} \tag{5}$$

where the constant $C=1/n$. The value of C consequently depends on the nature of the cross-link distribution.

For not too high concentrations (say $\varphi\leq 0.4$), a scaling approach gives a fair approximation [7-9] to the behavior of the parameters in Eq. (5). In scaling theory of polymer solutions in the semidilute regime [6], the concentration dependence of the osmotic pressure obeys a power law of the form

$$\Pi=A\varphi^m\,, \tag{6}$$

where the exponent m depends on the thermodynamic quality of the solvent. In excluded volume conditions, $m\approx\frac{9}{4}$. For a gel, the equilibrium swelling concentration φ_e in the pure solvent is defined by the condition $\omega=0$, and we thus have

$$(ankT/v)=A\varphi_e^{m-1/3}\,. \tag{7}$$

Substitution into Eq. (5) yields

$$\frac{\langle\delta\varphi^2\rangle_s}{\varphi^2}=C\left[m\left(\frac{\varphi}{\varphi_e}\right)^{m-1/3}-\frac{1}{3}\right]^{-2}. \tag{8}$$

Equation (8), although in agreement with the known concentration dependence of the swelling pressure and the elastic modulus of the gel [7-9] is a simplification based on scaling considerations, and so in principle applies only in the semidilute concentration range. At high polymer concentrations, where the osmotic pressure increases faster than indicated by Eq. (6), the osmotic modulus K may be better approximated by a Flory-Huggins type expression [4].

Estimates of the concentration polydispersity $\langle\delta\varphi^2\rangle_s/\varphi^2$ are obtained from the small-angle neutron scattering spectra of the gels. In statistically isotropic two-phase systems exhibiting no long range order the second moment of the normalized scattering intensity

$$\begin{aligned}M_2&=\int_0^\infty[I_s(Q)+I_d(Q)]Q^2dQ\\&=2\pi^2\Delta\rho^2\langle\delta\varphi^2\rangle\end{aligned} \tag{9}$$

is an invariant [10]. Here, $\Delta\rho^2$ is the contrast factor, and $\langle\delta\varphi^2\rangle=(1-\varphi)\varphi$ is the mean square amplitude of the total fluctuation in polymer volume fraction. [The restriction of this treatment to two phase systems with sharp boundaries does not in fact apply to the low Q region of the scattering spectra. Low resolution scattering experiments cannot distinguish between a uniform object with sharp boundaries and a real structural element having an uneven nuclear density distribution. Thus, provided the principal contribution of the static scattering intensity $I_s(Q)$ is confined to the low Q spectral region, its second moment belongs to an invariant.]

Application of this concept to swollen polymer networks gives

$$M_2=2\pi^2\Delta\rho^2[\langle\delta\varphi^2\rangle_s+\langle\delta\varphi^2\rangle_d]\,, \tag{10}$$

where $\langle\delta\varphi^2\rangle_d$ is the mean square amplitude of the thermodynamic fluctuations of φ.

It is found [2,3,11,12] that $I_d(Q)$ corresponding to $\langle\delta\varphi^2\rangle_d$ can be represented in the low Q region by an Ornstein-Zernike function [13,14]

$$I_d(Q)=\frac{kT\Delta\rho^2\varphi^2}{K+4G/3}\frac{1}{1+Q^2\xi^2}\,, \tag{11}$$

where ξ is the polymer correlation length (a correction for the finite cross section of the polymer chain is included [3] at higher values of Q).

The static scattering intensity $I_s(Q)$ is approximated satisfactorily by the empirical form

$$I_s(Q)=I_s(0)\exp[-(Q\Xi)^p]\,, \tag{12}$$

where Ξ is the mean radius of the static concentration fluctuations. The exponent p may depend on the network structure. For randomly cross-linked PVAc gels swollen in toluene [3], $p\approx 0.7$, while for end-linked PDMS [12], an acceptable fit to the neutron scattering spectra was found with $p=2$. The second moment of Eq. (12) then yields

$$\langle\delta\varphi^2\rangle_s=\frac{I_s(0)\Gamma(3/p)}{2\pi^2p\Delta\rho^2\Xi^3}\,, \tag{13}$$

where $\Gamma(x)$ is the gamma function. The scattering function is not unique. A model for gels close to the percolation threshold, developed by Bastide and co-workers [15,16] gives an alternative expression whose central property is the slope of the scattering curve. For the present PVAc data, however, this model gives an unsatisfactory fit to the spectra and yields unphysical values for $I_d(Q)$.

We now apply these relations to experimental observations made on two sets of chemically cross-linked PDMS

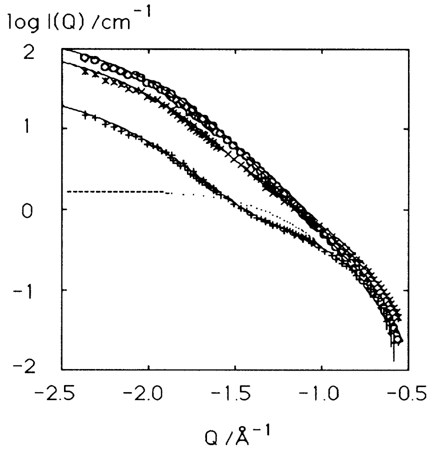

FIG. 1. SANS scattering curves for a PVAc gel ($\varphi_e=0.146$) at different swelling degrees in toluene; ○: $\varphi=0.146$; ×: $\varphi=0.208$; +: $\varphi=0.399$. Continuous curves are the fits of $I_d(Q)+I_s(Q)$ to the data using Eqs. (11) and (12). Dots: data from a PVAc/toluene solution at $\varphi=0.114$ [dashed line is the low Q extrapolation of these data from Eq. (11)].

and PVAc network systems swollen in toluene. The PVAc gels were prepared by cross linking of polymer chains in solution following a method described elsewhere [17]. The PDMS gels were synthesized by end linking undiluted hydroxyl terminated PDMS chains using triacetoxysilane as the cross-linking agent [2,7].

SANS measurements were made on the D11 instrument at the Institut Laue Langevin, Grenoble, using an incident wavelength of 6 Å, and sample-detector distances in the range 1.2 to 15 m. A 64×64 element area detector was used. The gel samples of area approximately 2 cm^2 and thickness 1 mm were held between 1 mm thick quartz plates in a thermostated sample holder at 25 °C. The concentration dependence of the swelling pressure ω was measured in the range up to 100 kPa, using an osmotic deswelling technique [17]. The osmotic pressure of the network polymer, Π, was calculated from these independent measurements of ω and the shear modulus.

In Fig. 1 are shown the SANS spectra from a randomly cross-linked PVAc gel in deuterated toluene at three different degrees of swelling. The spectrum composed of dots in the figure are the experimental data points from an uncross-linked solution. The excess scattering visible in the gel spectra at low Q is due to the static concentration polydispersity.

The above analysis refers to binary systems. It is essential that the samples should be chemically homogeneous. Previous contrast variation measurements performed on these lightly cross-linked PVAc and PDMS gels demonstrated [2,3] that the neutron scattering signal originates from the pure polymer, and on the length scales investigated, is unperturbed by the chemically different nature of the cross linker.

TABLE I. Measurements of scattering parameters from PVAc and PDMS gels swollen to different degrees in toluene [3,12].

Sample	φ	$\langle\delta\varphi^2\rangle_s/\varphi^2(\times 10^2)$
PDMS	0.166	0.91
$\phi_e=0.166$	0.177	0.60
	0.223	0.44
	0.254	0.25
	0.353	0.06
PVAc[a]	0.146	35.2
$\varphi_e=0.146$	0.208	9.7
	0.270	2.9
	0.315	1.4
	0.399	0.5
PVAc[b]	0.074	34.7
$\varphi_e=0.074$		

[a] Mean number of monomer units between cross links equal to 50.

[b] Mean number of monomer units between cross links equal to 400.

Values of the polydispersity $\langle\delta\varphi^2\rangle_s/\varphi^2$, calculated from the fit of Eqs. (11) and (12) to the gel spectra (Table I) were given in Refs. [3] and [12]. It can be seen that $\langle\delta\varphi^2\rangle_s/\varphi^2$ decreases as the gels deswell, i.e., concentration differences between nonuniformly cross-linked regions of the gel progressively disappear. The numerical values of the polydispersity for the PVAc system are significantly larger than for the PDMS gel.

In Fig. 2 the values of $\langle\delta\varphi^2\rangle_s/\varphi^2$ are plotted against the right-hand side of Eq. (8). For both PVAc and PDMS, reasonable agreement is found with the straight line behavior predicted by Eq. (8). For the PVAc system, the slope C is approximately 1.25; this corresponds to a wide distribution of structural nonuniformities, as expected from a randomly cross-linked gel. In the figure is also displayed a datum (open circle) obtained from a more lightly cross-linked PVAc sample in the fully swollen state: the $\langle\delta\varphi^2\rangle_s/\varphi^2$ values for the two gels almost coincide. For the PDMS gel, the corresponding value of C is approximately 0.033. This small value reflects the fact that in the randomly cross-linked PVAc gels the permanent structural perturbations extend to much higher Q vectors (smaller spatial separations) than in the end-linked PDMS system.

The numerical values of these slopes obviously must depend on the analytical form chosen for the static scattering function $I_s(Q)$ in the decomposition procedure. To estimate the uncertainty introduced by different forms, the scattering spectra of the PDMS gels were reanalyzed replacing $p=2$ by $p=0.7$ in Eq. (12). In this case, although the quality of the fits to the scattering spectra becomes poorer, the linear dependence described by Eq. (8) remains valid. The slope C, however, increases by about 25%. The much larger difference in slopes between the PVAc and the PDMS gels (one and a

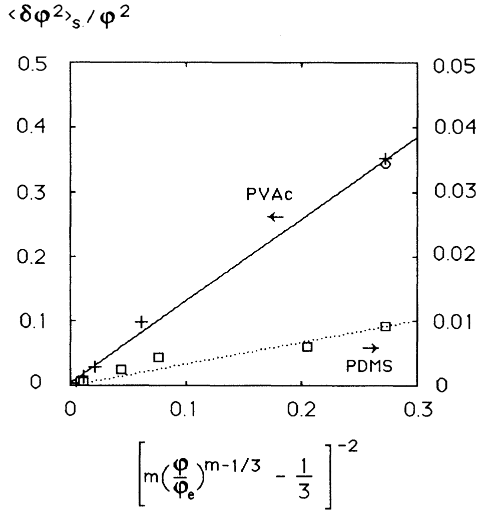

FIG. 2. Dependence of network polydispersity $\langle\delta\varphi^2\rangle_s/\varphi^2$ on the function of $[m(\varphi/\varphi_e)^{m-1/3}-\frac{1}{3}]^{-2}$ for PVAc/toluene (+: $\varphi_e=0.146$; ○: $\varphi_e=0.074$) and for PDMS/toluene gels (□: $\varphi_e=0.166$). The value for m is taken to be $\frac{9}{4}$. Note the factor of 10 difference in vertical scale between the PVAc data (left-hand scale) and the PDMS data (right-hand scale).

half orders of magnitude) is therefore not a consequence of the choice of the function $I_s(Q)$. It reflects, instead, intrinsic structural differences between the two networks.

In summary, in contrast to polymer solutions, where the osmotic pressure ensures long range uniformity in the structure, swollen networks possess permanent elastic constraints, which induce a static concentration polydispersity $\langle\delta\varphi^2\rangle_s/\varphi^2$ on a microscopic scale. We have shown that $\langle\delta\varphi^2\rangle_s/\varphi^2$ is related to the macroscopic osmotic and elastic properties of the gel. Its amplitude is determined by the molecular architecture of the network. The concentration dependence of $\langle\delta\varphi^2\rangle_s/\varphi^2$ predicted by the model proposed here is in agreement with the SANS data of PVAc and PDMS gel systems.

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