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Radius of Gyration in Anisotropically Swollen Gels[†]

Several reports have appeared concerning the effects produced by an external strain on the dimensions of a given polymer coil in polymer melts[1,2] and in dry gels.[3–5] Somewhat less attention seems to have been paid to the case of gels swollen in a good solvent,[6] probably because any anisotropy is expected to be dwarfed by overwhelming isotropic effects of the osmotic pressure.

In this communication we describe small-angle neutron scattering (SANS) measurements of the radius of gyration of deuterated chains, end-linked in a strongly deformed swollen gel. The samples, made at the Centre de Recherche sur les Macromolécules, Strasbourg, were model polystyrene gels consisting of chains of M_w = 26 000 Daltons, with 7% of the chains being deuterated. In the dry state the radius of gyration was found[6] by SANS to be 43 Å; more recent measurements on the same gels[7] gave 44 Å for the same parameter.

We discuss first the isotropic swelling of gels, which proceeds in a manner proposed qualitatively by Bastide.[8] The mean distance between spatially nearest-neighbor cross-link points, R_s, is assumed to increase affinely as the cube root of the swelling ratio $q = V/V_0$, where V_0 is the volume of the dry gel. Now it has been shown[9] that a characteristic length relation exists between R_s and the topologically (i.e., on the same chain) nearest-neighbor distance R_t between cross-links

$$R_s^3 = AR_t^2\xi \qquad (1)$$

where ξ is the static screening length and A is a constant, proportional to the functionality of the cross-links, whose value is close to unity at low functionalities. Equation 1 was derived to describe the distance between entanglement points in a semidilute polymer solution; the application to gels is achieved by imagining each entanglement to be transformed into a cross-link. Then, assuming that good solvent conditions prevail,[10] i.e.

$$\xi \propto q^{0.75} \qquad (2)$$

one finds for the gel

$$R_t^2 \propto q^{0.25} \qquad (3)$$

A similar relation holds for the radius of gyration of a free coil in semidilute solution.[11]

Since in the range of concentration being considered the radius of gyration R of the molecule is much larger[11] than ξ, one may use Gaussian statistics as an approximation to define the dependence of R upon the mean square end-to-end length[12]

$$\begin{aligned} R^2 &= \tfrac{1}{12}(Nb^2 + R_t^2) \\ &= R_0^2(1 + q^{0.25})/2 \qquad (4) \end{aligned}$$

Equation 4 is in good qualitative agreement with recent measurements by Bastide et al. on polystyrene gels.[7] In this equation, we have, however, neglected the fact that at high polymer concentrations the scaling relation (2) should be replaced by[13]

$$\xi \propto q^{0.5} \qquad (5)$$

Inclusion of this effect causes R^2 to increase initially as $(1 + q^{0.5})/2$ until the semidilute region is reached and thereafter as $(1 + q^{0.25})/2$.

Turning now to the anisotropic case, we make the basic assumption that there is no difference between a gel which has been swollen isotropically and then subjected to a uniaxial constraint and one which has been swollen anisotropically to the same degree of constraint. We therefore examine the situation in which a dry gel placed in a container such that swelling along one of the axes is constrained. Light scattering measurements in a similar situation, that of gels deswollen uniaxially, have shown that the intensity of the dynamically scattered light and the collective diffusion coefficient are isotropic,[14] even with compression ratios as high as 5. We assume therefore that here also ξ will remain isotropic to a good approximation, even though the gel is swollen anisotropically.

Table I
Neutron Scattering Measurements from Anisotropically Swollen Polystyrene Gels

	sample		
	1	2	3
relative Debye scattering intensity	2.0	1.6	1.0
calcd relative intensity from concentration, thickness, and transmission	2.15	1.62	1.0
dry sample major axis α, mm	13.5	9.9	5.7
dry sample minor axis β, mm	5.8	6.0	5.7
cell inner diameter γ, mm	14.7	14.7	14.0
applied constraint $\delta = \alpha/\beta$	2.34	1.65	1.0
swelling ratio q_1[a]	1.28	3.25	14.5
swelling ratio q_2[a]	7.01	8.85	14.5
measd $R_\perp$, Å	55.4	51.7	53.1
measd $R_\parallel$, Å	48.8	47.8	53.1
induced anisotropy $R_\perp/R_\parallel$ (exptl)	1.14	1.08	1.0
calcd $R_\perp = 44\{(1 + q_2^{0.25})/2\}^{0.5}$, Å	50.4	51.4	53.5
calcd $R_\parallel = 44\{(1 + q_1^{0.25})/2\}^{0.5}$, Å	44.7	47.6	53.5
calcd $R_\perp/R_\parallel$	1.13	1.08	1.0
anisotropy of cluster scattering $a_\perp/a_\parallel$ measd at distance $1/Q$			
200 Å	1.7		
186 Å		1.2	
118 Å	1.8		
75 Å		1.3	
90 Å	1.7		

[a] The swelling ratio q_1 is taken to be $(\gamma/\alpha)^3$. The subsequent swelling takes place only along the two axes perpendicular to α; the total swelling ratio is thus $q_2 = (\gamma/\alpha)^3\delta^2$.

We shall imagine that the swelling takes place in two stages: first, the gels swells *isotropically* in the solvent to some value of q, say q_1, at which point one of the gel dimensions encounters the constraining wall of the container; the second, *anisotropic*, stage then occurs, with the gel swelling only in the two directions perpendicular to the initial constraint. The total swelling ratio at the end of the process is q_2. The simplest assumption one can make is that eq 4 applies to each of the principal axes in the swollen gel, and therefore

$$R_\perp/R_\parallel = \{(1 + q_2^{0.25})/(1 + q_1^{0.25})\}^{0.5} \qquad (6)$$

For the experimental observations, three pairs of model polystyrene gels, fully protonated and partially deuterated, were used, each prepared with three molecules of divinylbenzene per living end of polystyrene. The experiments were performed on the small-angle scattering instrument D11 at the Institut Laue Langevin at Grenoble, using an incident wavelength of 7.0 Å, the sample–detector distance being set at 10 m.

The samples were made of thin slices of gel cut into the form of ellipses of varying aspect ratio: 2.4, 1.7, and 1.0 (circular). When the samples were allowed to swell in carbon disulfide inside a circular quartz cell, the swelling gave rise to a homogeneous uniaxial constraint in the sample, with the symmetry axis lying in the plane of the

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[†] Measurements performed at the Institut Laue Langevin, Grenoble.

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cell. The spacer between the cell windows was chosen so that the sample could swell freely along the cylinder axis.

The scattering patterns, after appropriate background subtraction, were found to contain two regions of interest.

(a) At forward angles, an intense, strongly anisotropic scattering, extending up to wave transfer vectors $Q = 1.5 \times 10^{-2}$ Å^{-1}, was found.

(b) For higher values of Q, a nearly linear region in a Zimm plot was obtained. The values of the radii of gyration deduced from these plots are obtained from the region $1 < QR < 2$, i.e., outside the Guinier region. On the basis of the argument used above that the Gaussian approximation should be acceptable, the analysis of the data from this region was performed by using the full Debye scattering function and a nonlinear regression procedure.

In region b, for each azimuthal angle ϕ with respect to the constraint in the gel, the values of $R(\phi)$ were calculated, and a mean ellipticity was deduced. In Table I are shown the relative intensities of this contribution for each sample, compared with the relative intensities expected from a knowledge of the sample concentration and thickness. The agreement between these two sets of data suggests that the decomposition of the spectra into two separable parts is a satisfactory approximation.

It can be seen from Table I that the induced anisotropy is much smaller than the applied constraint. In order to interpret this result, it is first necessary to verify that the polymer coils are effectively coupled to the network. This was done by assuming that p is the probability that a given labeled chain end is poisoned so that it cannot bind to the lattice when the gel is formed; then the number of doubly poisoned chains is proportional to p^2 and the residual number of deuterated molecules left in the gel after washing in solvent is proportional to $1 - p^2$. The original concentration of deuterated chains at preparation is known $7 \pm 1\%$. By comparing the Raman spectra of a mixture of known composition of protonated and deuterated polystyrene in solution with CCl_4, we used the relative intensities of the features at 3060 and 2290 cm^{-1} (protons and deuterium, respectively) to calibrate the Raman spectra of the gels. The relative concentration of deuterated polystyrene was found to be 0.065 ± 0.009, in agreement with a value of p close to zero. The majority of the deuterated coils are therefore fully coupled to the network.

We are thus in a position to compare the observed anisotropies with a model, for example, that defined by eq 6. From Table I it can be seen that there is good qualitative agreement between eq 6 and the experimental observations of $R_\perp/R_\parallel$. The agreement between the calculated and the observed values of $R_\perp$ and $R_\parallel$ taken separately is, however, not so good for sample 1; this may be due in part to the neglect of the initially strong increase in R expected from eq 5. It should also be remembered that while the experimental ratios $R_\perp/R_\parallel$ are each obtained from a single corrected spectrum and are therefore expected to be relatively insensitive to errors of background subtraction, comparisons of the absolute value of R between different samples is intrinsically more sensitive to this source of error.

As for the anisotropic forward scattering (region a), we assume that this is caused by regions of higher coil density and is simply additive to that of the single coils. Although such a deconvolution is not likely to be rigorous, it is supported by the different anisotropic behavior of the two components. When the calculated Debye scattering function is subtracted from the total intensity and the difference is smoothed by interpolation, it is found that the excess intensity varies as Q^{-n}, where n lies between 3.5 and 4. This suggests a Porod type[15] of distribution for the density fluctuations. The contours of the intensity profile allow an effective constraint $a_\perp/a_\parallel$ to be calculated at different characteristic distances $1/Q$. It can be seen from Table I that this anisotropy, attributed to clusters, is comparable to but smaller than the applied constraint and, in the range 90–200 Å, is independent of the scale of observation.

In conclusion, the samples we used appear to be inhomogeneous, with some of the marked chains separated into well-defined zones with sharp boundaries, corresponding to a Porod law. The elastic response of these zones suggests that they are regions of high cross-linking density. Such features are common in other gels.[16]

The single coils, which seem dispersed throughout the rest of the gel, produce a weakly anisotropic scattering pattern in the strained gels. Both the magnitude of this anisotropy and the change in coil dimensions on swelling are in good qualitative agreement with a model relating the spatial and the topological nearest-neighbor distances between cross-links with the screening length of the gel.

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References and Notes

(1) Picot, C.; Duplessix, R.; Decker, D.; Benoit, H.; Boué, F.; Cotton, J. P.; Daoud, M.; Farnoux, B.; Jannink, G.; Nierlich, M.; de Vries, A. J.; Pincus, P. *Macromolecules* **1977**, *10*, 436.

(2) Boué, F.; Nierlich, M.; Jannink, G.; Ball, R. *J. Phys.* (*Paris*) **1982**, *43*, 137.

(3) Hinkley, J. A.; Han, C. C.; Mozer, B.; Yu, H. *Macromolecules* **1978**, *11*, 836.

(4) Clough, S. B.; Maconnachie, A.; Allen, G. *Macromolecules* **1980**, *13*, 774.

(5) Beltzung, M.; Herz, J.; Picot, C.; Bastide, J.; Duplessix, R. *27th Int. Symp. Macromol. IUPAC Strasbourg 1981*, Proceedings, p 728.

(6) Benoit, H.; Decker, D.; Duplessix, R.; Picot, C.; Rempp, R.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Ober, R. *J. Polym. Sci., Polym. Phys. Ed* **1976**, *14*, 2119.

(7) Bastide, J.; Duplessix, R.; Picot, C.; Candau, S. J. *Macromolecules*, to be published.

(8) Bastide, J.; Picot, C.; Candau, S. J. *J. Macromol. Sci. Phys.* **1981**, *B19*, 13.

(9) Geissler, E.; Hecht, A. M. *C. R. Hebd. Seances Acad. Sci., Ser. II* **1981**, *293*, 865. *28th Macro. Symp. IUPAC*, Amherst, MA, 1982, Proceedings, p 509.

(10) de Gennes, P. G. *Macromolecules* **1976**, *9*, 594.

(11) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P. G. *Macromolecules* **1975**, *8*, 804.

(12) Volkenstein, M. V. "Configurational Statistics of Polymeric Chains"; Wiley-Interscience: New York, 1963.

(13) Muthukumar, M.; Edwards, S. F. *Polymer* **1982**, *23*, 345.

(14) Hecht, A. M.; Geissler, E., unpublished measurements on polyacrylamide–water gels.

(15) Porod, G. *Kolloid-Z.* **1951**, *124* (2), 83.

(16) Weiss, N.; van Vliet, T.; Silberberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 2229.

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