Macromolecules **1995,** *28,* 678–681

Free Chains Trapped in a Swollen Gel under Different Solvent Conditions

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Received July 28, 1994; Revised Manuscript Received October 31, 1994[®]

ABSTRACT: Small-angle neutron scattering measurements are reported on the radius of gyration R_G of free poly(vinyl acetate) (PVAc) chains absorbed into a PVAc network swollen in isopropyl alcohol. Measurements were made at constant concentration on the same gels both at the Θ temperature of this system, 52 °C, and in good solvent conditions at 70 °C. The neutron contrast was ensured by using fully protonated free chains and a partially deuterated network. At 52 °C, the radius of gyration of the trapped polymer, $R_G = 57$ Å, is smaller than in Θ solution ($R_G = 96$ Å). No measurable change was observed in the radius of gyration of the free polymer in the network between the Θ and the good solvent condition. The results can be understood in terms of recent theories describing the behavior of chains trapped in random porous media.

Introduction

The radius of gyration of a polymer coil reflects its thermodynamic interaction with the surrounding medium. Such measurements are made routinely for dilute solutions of polymer in a low molecular weight solvent. It is, however, of practical interest to measure the radius of gyration of polymers in a medium of higher molecular weight, such as polymer melts, concentrated polymer solutions, and polymer networks. In a polymer melt,[1] the individual polymer coils adopt the unperturbed dimensions, while in the solution,[2] the radius of gyration scales with the concentration φ as $\varphi^{-1/8}$ in good solvent conditions. The case of polymer networks is less well understood. The polymer distribution is in general perturbed by the cross-linking process, which is controlled by the details of the chemical mechanism.

Measurements have been reported of labeled chains cross-linked into swollen networks[3-9] and of free chains inside dry networks.[10] The swelling of a network chain linked by its ends inside a swollen network is found to be small[7] and compatible with the expectations of scaling theory.[8] High molecular weight chains that are tied to the network by many cross-links expand more strongly as the gel swells, since they unfold in the same way as the surrounding gel matrix.

For gels containing free chains, swelling properties have been examined,[11] and small-angle scattering behavior of the interchain distribution have been reported.[12,13] For good solvent conditions, the thermodynamic properties of the gel are not significantly affected by the presence of the free chains.[11,12] These studies, however, did not attempt to measure the size of the individual chains in the polymer matrix, a topic on which little work has been reported.[14] The subject not only is important from a theoretical point of view but also has practical importance: e.g., molecular dimensions play an essential role in size exclusion chromatography. Recent theories predict that the presence of random fixed inhomogeneities in the network may cause the coil to shrink.[15-19] The density fluctuations associated with the spatial inhomogeneities are assumed to localize the free chains in certain regions of the network. No localization effect emerges from a simple scaling approach to coils absorbed in swollen networks.

The purpose of this paper is to investigate the effect of the network on the radius of gyration of individual free chains. The theoretical section describes first the expected behavior of the polymer coils according to simple scaling theory and then briefly states the main conclusion of the random medium approach of Baumgärtner and Muthukumar. In the experimental part, we describe a SANS experiment performed on a lightly cross-linked PVAc gel containing a small fraction of free chains. The concentration of the samples was held constant during the measurements. The solvent, isopropyl alcohol, was selected because its Θ temperature with PVAc gels is 52 °C;[20] at 70 °C it is a good solvent. The results obtained in good and Θ solvent conditions are compared.

Background

The unperturbed dimension of a polymer coil is defined by its radius of gyration R_0 in a Θ solvent, with

$$R_0^2 = \frac{1}{6}Nb^2 \tag{1}$$

where N is the number of statistical steps in the coil and b is the step length.[21] According to de Gennes's scaling picture,[22] gels and semidilute polymer solutions are equivalent, the only difference between these states being the lifetime of the contact points. Thus, the chains in a melt and in a dry network are expected to adopt their unperturbed dimension.

If the network is swollen in a Θ solvent the radius of gyration R_G remains unchanged. In a good solvent (excluded volume conditions), however, the free coil should expand to a new radius of gyration given by[2,22]

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[®] Abstract published in *Advance ACS Abstracts,* December 15, 1994.

0024-9297/95/2228-0678$09.00/0

$$R_G = R_0\varphi^{-1/8} \qquad (2)$$

where φ is the polymer volume fraction of the gel. Variations of R_G consistent with this expression have been observed for network chains chemically cross-linked into a gel.[3,7,8]

Equation 2 may serve as a basis to estimate the ratio R_G/R_0 for an arbitrary concentration of the swollen network.

Baumgärtner and Muthukumar[15] and later workers[16-19] discuss the effect of a random field of static obstacles on the size of a polymer molecule in a gel. Here the network cross-links and permanent chain clusters, which are distributed at random, play the role of the static obstacles. The following expression is obtained for the mean square end-to-end distance

$$R^2 = \frac{Nl^2}{z}[1 - \exp(-z)] \qquad (3)$$

where $z = \epsilon u\varrho^2 Nl^6$. Here, ϵ is a numerical coefficient, u is the strength of the pseudopotential between segments, ϱ is the number density of the obstacles, and l is the effective step size.

Expression 3 leads to a reduced radius of the coil. For small values of $u\varrho$, the excluded volume interaction is screened out, while for large $u\varrho$ collapse of the coil occurs.

The prediction of simple scaling thus differs radically from that of the random medium theory. The former makes no statement about the chain dimension in the presence of cross-links and predicts coil expansion on going from the Θ condition to the excluded volume condition. In contrast, the latter theory predicts coil contraction of chains entrapped in a network, both in the Θ and in the excluded volume conditions.

Experimental Section

Partially deuterated PVAc gels were made by cross-linking a 6% poly(vinyl alcohol) (Sigma) aqueous solution in a cylindrical mold with glutaraldehyde (Prolabo). The concentration of glutaraldehyde in the PVA solution defines the ratio of the number of cross-links to the number of vinyl alcohol units, the value of which was chosen to be 1/200. This process yields a fully protonated PVA gel. At the end of the cross-linking reaction, the gel was completely acetylated with perdeuterated acetic anhydride (Janssen) in pyridine, yielding a network of chemical composition $(CHCH_2COOCD_3)_n$. The pyridine was then replaced by toluene, and the swollen PVAc cylinders were cut into disk-shaped slices of thickness about 3 mm. These disks were dried and weighed.

A fully protonated PVAc sample fractionated in an acetone/water mixture was used for the experiments. Characteristics of the fractionated PVAc: M_w = 183 000 (from neutron scattering measurements) and M_w/M_n = 1.5 (from GPC). The fractionated polymer was placed in solution at 3% with toluene and allowed to come to equilibrium with one of the gel disks, a second slice was placed in a 1.5% polymer solution in toluene, and a third was reserved for use as the background. The gels were allowed to remain in contact with their solutions for 1 month, after which they were removed, surface-rinsed, and dried. The weight of absorbed polymer, ca. 15 mg/g, was found by comparing the initial and final dry weights of the slices. The gel slices were then trimmed so that, when swollen in isopropyl alcohol[11] at 52 °C, they just filled the neutron scattering holder.

The neutron scattering cells comprised two 1 mm thick quartz windows separated by a 1.8 mm thick Viton O-ring and held together in a brass housing. Teflon washers of the correct thickness, mounted concentrically inside the Viton seal, maintained the gels in the center of the cell and also minimized the volume of free solvent in contact with the sample: this precaution ensured that the absorbed polymer did not diffuse out.

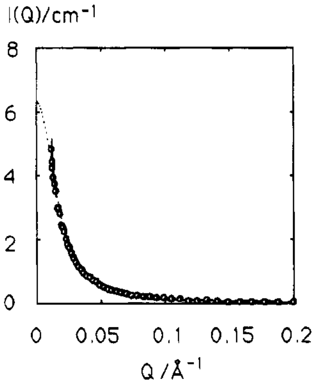

Figure 1. SANS spectrum of a solution of protonated PVAc in deuterated isopropyl alcohol at concentration $c = 0.0116$ g cm^{-3}. The theoretical line shown is the least squares fit of eq 4 to the data, where $I(0) = 6.3$ cm^{-1} and $R_G = 96$ Å.

The equilibrium concentration of the free chains in the gel was measured on a large cylindrical gel specimen ($\phi \approx 1$ cm, height 1 cm) similar to that used for the neutron scattering immersed in the polymer solution.

SANS measurements were made on the LOQ instrument at the ISIS Spallation Neutron Source in the Q range $0.01 \le Q \le 0.22$ Å^{-1}. The gels were swollen in a mixture of protonated and deuterated isopropyl alcohol (Janssen), in a proportion such that the contrast between the network polymer and the solvent was zero. This contrast match point, calculated from the known scattering lengths,[23] occurs at 64% IPA-D + 36% IPA-H. The blank used for background subtraction was the swollen gel containing no absorbed chains. This choice of solvent and background ensures that any resulting signal comes only from the mobile chains absorbed in the sample.

The neutron scattering data were radially averaged and corrected for both the neutron transmission of the samples and the background scattering using the standard LOQ data reduction software.[24] The transmissions of the samples and the background were indistinguishable from each other. This match simplifies the background correction procedure, making it unnecessary to implement more complex incoherent background subtraction schemes.[25] The scattering intensities were put on an absolute scale by reference to the scattering from a well-characterized partially deuterated blend of polystyrene.

The samples were first swollen to equilibrium at 52 °C (Θ temperature) and excess solvent was removed. The temperature was then raised to 70 °C for 2 days prior to the experiment, and the neutron scattering spectrum for that temperature was measured. The temperature was then lowered to 52 °C for 5 h and the scattering behavior measured over the subsequent 16 h period. Throughout the experiment the gel concentration was maintained at $c = 0.171$ g cm^{-3}.

The experiment involves a partially deuterated PVAc system in a mixture of protonated and deuterated isopropyl alcohol. Deuteration of the solvent can modify the Θ temperature. To estimate this effect, light transmission measurements were made at $\lambda = 600$ nm on 1% w/w solutions of the protonated PVAc dissolved in fully protonated and in fully deuterated IPA, respectively. The onset of the cloud point in protonated IPA was 52.6 °C, while that in perdeuterated IPA was 51.8 °C; i.e., replacement of protonated IPA by the deuterated solvent does not seriously affect the Θ temperature of the present system.

Results and Discussion

Figure 1 shows the SANS spectrum of a solution of protonated PVAc in perdeuterated IPA ($c = 0.0116$ g cm^{-3}) at 52 °C. The dotted line shown represents the fit of the data, over the range $0.009 < Q < 0.15$ Å^{-1}, to a Debye scattering function for a random coil,[26]

$$I(Q) = I(0)\frac{2(e^{-x} + x - 1)}{x^2} + \text{bkgrnd} \qquad (4)$$

where $x = (QR_G)^2$ and R_G is the radius of gyration. The parameters of the fit to these data are

$$R_G = 96 \pm 2\ \text{Å}$$

$$I(0) = 6.3 \pm 0.2\ \text{cm}^{-1}$$

$$\text{bkgrnd} = 0.011 \pm 0.006\ \text{cm}^{-1}$$

$$\chi^2 = 0.867 \qquad (5)$$

This value of $I(0)$, together with the contrast factor for neutron scattering between protonated PVAc and fully deuterated isopropyl alcohol, $\Delta\varrho^2 = 2.447 \times 10^{21}$ cm^{-4}, yields for the weight-average molecular weight

$$M_w = (1.83 \pm 0.06) \times 10^5 \qquad (6)$$

In Figure 2 is shown the scattering spectrum for the free PVAc absorbed in the gel at 52 °C. The solvent is a mixture of protonated and deuterated (36/64 vol %) IPA at 52 °C. This mixture, chosen for reasons of contrast matching, reduces the signal from the free polymer by a factor of about 20. The least squares fit of eq 4 to the data yields

$$R_G = 57 \pm 4\ \text{Å}$$

$$I(0) = 0.29 \pm 0.02\ \text{cm}^{-1}$$

$$\text{bkgnd} = 0.005 \pm 0.003\ \text{cm}^{-1}$$

$$\chi^2 = 0.51 \qquad (7)$$

To calculate the molecular weight of the free chains inside the gel, both the concentration and the contrast factor must be known. The volume fraction of free polymer in the swollen network was found to be $\varphi = 2.22 \times 10^{-3}$. Using the neutron contrast factor between protonated PVAc and the solvent mixture at the match point for the network, $\Delta\varrho^2 = 6.67 \times 10^{20}$, together with eq 7, we find for the weight-average molecular weight of the absorbed polymer

$$M_w = (1.4 \pm 0.2) \times 10^5 \qquad (8)$$

This value is slightly smaller than that obtained for the solution. In principle, however, we expect the polymer penetrating into a gel to have a lower molecular weight, since the network acts as a molecular sieve. The experimental result seems to be consistent with this expectation.

On the basis of eq 1, the ratio of molecular weights of the free polymer in the gel and the solution should lead to a small reduction (ca. 12%) in the radius of gyration of the penetrated polymer. The observed reduction is, however, more than 40%. This finding indicates that the chains inside the network are subject to repulsive potentials and is therefore more consistent with the random medium theory.

In Figure 3 the SANS spectrum for the gel at 70 °C is displayed together with the calulated fit to eq 4. The parameters of this fit are

$$R_G = 56 \pm 4\ \text{Å}$$

$$I(0) = 0.23 \pm 0.02\ \text{cm}^{-1}$$

$$\text{bkgrnd} = 0.021 \pm 0.003\ \text{cm}^{-1}$$

$$\chi^2 = 0.47 \qquad (9)$$

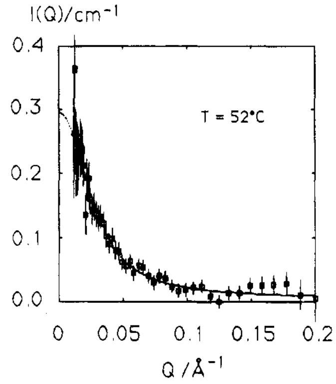

Figure 2. SANS spectrum at $T = 52$ °C from protonated PVAc in the partially deuterated PVAc gel swollen in a mixture of protonated and deuterated isopropyl alcohol. The theoretical line shown is the least squares fit of eq 4 to the data, where $I(0) = 0.29$ cm^{-1} and $R_G = 57$ Å.

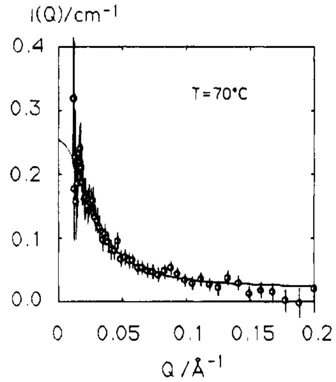

Figure 3. SANS spectrum at 70 °C from protonated PVAc in the partially deuterated PVAc gel swollen in a mixture of protonated and deuterated isopropyl alcohol. The theoretical line shown is the least squares fit of eq 4 to the data, where $I(0) = 0.23$ cm^{-1} and $R_G = 56$ Å.

The radius of gyration of the absorbed coils is practically unchanged on going from the Θ temperature to the good solvent situation. Once again, this result is contrary to the expectation from scaling theory. According to eq 2, the expected increase in R_G is defined by the overall polymer volume fraction $\varphi = 0.149$ of the gel through

$$R_G/R_{G\Theta} = \varphi^{-1/8} \approx 1.26$$

As stated above, the random medium theory predicts a reduction of the coil size inside the swollen network. An order of magnitude estimate of the size of the effect may be made by comparing the radius of gyration with the mean distance between obstacles. In a given network at least two types of random obstacles should be considered: chemical junctions and permanent local concentration fluctuations frozen in by the cross-links.[27] The average distance R_x between the chemical junctions can be estimated from the shear modulus,[28] $G = CkT\varphi^{1/3}/R_x^3$, where the constant C is of the order of unity and depends on the functionality of the junction points. For the present gel at $\varphi = 0.149$, the measured value of G is 8.81 kPa.[20] This yields $R_x \approx 65$ Å. The presence of the large-scale heterogeneities will further reduce the effective distance R_{eff} between obstacles. The finding that the experimental value of R_G is comparable with R_{eff} suggests that the chains are localized in regions of size of the latter. The distance between such obstacles in permanent networks is temperature invariant. It is thus not surprising that the weak excluded volume interaction prevailing at 70 °C does not appreciably modify the chain extension.

Conclusions

The neutron scattering results demonstrate that simple scaling theory fails to account for the radius of gyration of entrapped chains in a swollen cross-linked polymer. The observed variations of the chain dimensions are in qualitative agreement with the theory of random media. This theory shows that randomly distributed obstacles can induce an attractive interaction between the polymer segments, which localizes the macromolecules in a limited region of configuration space. In gels, both the chemical junctions themselves and larger scale static heterogeneities can be classified as such random obstacles. For the system investigated here, the presence of the network reduces the radius of gyration ($R_G = 56$ Å) of the free chains by about 40% with respect to the unperturbed dimension ($R_0 = 96$ Å). The size of the localized chains is comparable with the estimated distance between network cross-links. The theory also predicts a weakening of the excluded volume interaction, which is consistent with the observed independence of the R_G on the thermodynamic quality of the solvent.

Acknowledgment. We are grateful to the UK Science and Engineering Council and ISIS for beam time on the LOQ instrument and to J. Y. Sanchez of the Institut National Polytechnique de Grenoble for carrying out gel permeation chromatography measurements on our PVAc samples. F.H. acknowledges the tenure of a visiting professorship at the Université Joseph Fourier de Grenoble. H.B.S. wishes to thank ICI for a fellowship. This work is part of an agreement between the Centre National de Recherche Scientifique (CNRS) and the Hungarian Academy of Sciences and was supported in part by Grant OTKA No. 2158.

References and Notes

(1) King, J. S.; Boyer, W.; Wignall, G. D.; Ullman, R. *Macromolecules* **1985**, *18*, 709.
(2) 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.
(3) 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.
(4) Davidson, N. S.; Richards, R. W. *Macromolecules* **1986**, *19*, 2576.
(5) Ullman, R. *Macromolecules* **1982**, *15*, 582, 1395.
(6) Clough, S. G.; Maconnachie, A.; Allen, G. *Macromolecules* **1980**, *13*, 774.
(7) Bastide, J.; Duplessix, R.; Picot, C.; Candau, S. J. *Macromolecules* **1984**, *17*, 83.
(8) Geissler, E.; Duplessix, R.; Hecht, A. M. *Macromolecules* **1983**, *16*, 712.
(9) Wu, W.; Jong, L. *Polymer* **1993**, *34*, 2357.
(10) Boué, F.; Farnoux, B.; Bastide, J.; Lapp, A.; Herz, J.; Picot, C. *Europhys. Lett.* **1986**, *11*, 637.
(11) Horkay, F.; Zrínyi, M. *J. Macromol. Sci., Phys.* **1986**, *B25*, 307.
(12) Hecht, A. M.; Stanley, H. B.; Geissler, E.; Horkay, F.; Zrínyi, M. *Polymer* **1993**, *34*, 2894.
(13) Lal, J.; Bastide, J.; Bansil, R.; Boué, F. *Macromolecules* **1993**, *26*, 6092.
(14) Richards, R. W.; Davison, D. A. ISIS Annual Report, 1993 Vol. II, A225.
(15) Baumgärtner, A.; Muthukumar, M. *J. Chem. Phys.* **1987**, *87*, 3082.
(16) Edwards, S. F.; Muthukumar, M. *J. Chem. Phys.* **1988**, *89*, 2435.
(17) Honeycutt, J. D.; Thirumalai, D. *J. Chem. Phys.* **1989**, *90*, 4542.
(18) Muthukumar, M. *J. Chem. Phys.* **1989**, *90*, 4594.
(19) Vilgis, J. *J. Phys. (Les Ulis)* **1989**, *50*, 3243.
(20) Horkay, F.; Geissler, E.; Hecht, A. M.; Zrínyi, M. *Macromolecules* **1988**, *21*, 2589.
(21) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(22) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(23) Sears, V. F. *Neutron News* **1992**, *3* (3), 26.
(24) Heenan, R. K.; King, S. M.; Osborn, R.; Stanley, H. B. COLETTE Users Guide, Rutherford Appleton Laboratory Report RAL-89-128.
(25) Horkay, F.; Hecht, A. M.; Mallam, S.; Geissler, E.; Rennie, A. R. *Macromolecules* **1991**, *24*, 2896.
(26) Debye, P. *Ann. Phys.* **1947**, *46*, 809.
(27) Geissler, E.; Horkay, F.; Hecht, A. M. *Phys. Rev. Lett.* **1993**, *71*, 645.
(28) Treloar, L. R. G. *The Physics of Rubber Elasticity*, 3rd ed.; Clarendon Press: Oxford, 1975.

MA941112B