Scaling analyses of polyacrylamide gels at swelling equilibrium in water/acetone mixtures by small-angle X-ray scattering

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We experimentally examined the scaling relationship between correlation length ξ and polymer concentration c in homogeneous gels at swelling equilibrium. Polyacrylamide gels having various crosslink densities were synthesized and brought to swell in water/acetone mixtures with various mixing ratios. Their correlation lengths ξ were determined by small-angle X-ray scattering. A $-3/4$ power law ($\xi \propto c^{-3/4}$) was found for the gels swollen in pure water, where c varied with the crosslink density as expressed by r in the as-prepared state. Here r denotes the ratio of the concentration of the monomer to that of the bifunctional monomer at the stage of specimen preparation. On the other hand, a $-1/3$ power law ($\xi \propto c^{-1/3}$) was obtained for the gels having similar values of r when swollen in water/acetone mixtures with various mixing ratios. Both of the power laws are in accord with the predictions given by the c^* theorem introduced by de Gennes for a homogeneous gel swollen in a good solvent.

(Keywords: scaling analyses; polyacrylamide gels; SAXS)

INTRODUCTION

The elucidation of gel structure is becoming more important because of increasing demands upon gels for use in many applications[1,2] following the discovery of the volume phase transition[3–5]. Some approaches to investigate directly the gel structure have been conducted by monitoring crosslinking polymerization[6,7], probe motion[8] and probe diffusion[9] in gels. Other approaches are based on a scaling concept, which was recently introduced by de Gennes[10] for the gel structure by analogy with a semi-dilute polymer solution. The scaling theory can be utilized to describe generally the static and dynamic structures of a homogeneous gel swollen in a good solvent[9,11–19], although the scaling picture does not give a real image of the gel structure. It is also worth noting the 'non-ergodic' behaviour of gels, as observed by dynamic light scattering[15,16], as a recent advance in the understanding of the gel structure.

In this paper, we examine experimentally the scaling relationship between the correlation length ξ in the concentration fluctuation and the polymer concentration c in the homogeneous gel at swelling equilibrium. For this purpose, polyacrylamide (PAAm) gels having various polymer concentrations were prepared and ξ was measured by small-angle X-ray scattering (SAXS) for the gels swollen in water/acetone mixtures with various mixing ratios.

EXPERIMENTAL

PAAm gels were prepared at 30°C by radical copolymerization of acrylamide (monomer) and *N*,*N*′-methylenebis(acrylamide) (bifunctional monomer) in distilled, degassed and nitrogen-saturated water[13,14]. *Table 1* shows the total concentrations c_0 of the monomer and bifunctional monomer, defined by

$$c_0 = c_m + c_b \qquad (1)$$

where c_m and c_b are the concentration of monomer and bifunctional monomer, respectively. The ratios r of the concentrations of monomer to those of bifunctional monomer are also listed in *Table 1*. Here r is given as

$$r = c_m / c_b \qquad (2)$$

which is proportional to the crosslink density in the as-prepared state. Gelation was initiated with ammonium peroxydisulfate and terminated by immersing the as-prepared gel in a large amount of distilled water. Gelation of samples C, F-1 and F-2 was accelerated by adding *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED). Since TEMED causes hydrolysis of acrylamide units, samples

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Table 1 Preparation conditions of gels

Sample code	c_0 (g cm^{-3})	r	Acceleration time with TEMED
A	0.0484	36.9	–
B	0.0493	37.9	–
C	0.0498	36.1	30 d
D	0.0500	454	–
E	0.0502	83.6	–
F-1	0.0524	35.4	1 h
F-2	0.0524	35.4	3 d
G	0.0530	100	–
H	0.0538	70.1	–
I	0.132	111	–
J	0.151	114	–

C, F-1 and F-2 have carboxy groups on the polymer chain which can become ionized in a solvent containing water.

The swelling behaviour was examined in various water/acetone mixtures with mixing ratios from 0 to 40 vol% of acetone. The equilibrium swelling ratio q_m is defined by the ratio of the volume of the gel at swelling equilibrium V_m to the volume of the as-prepared gel V_0. Disc-shaped specimens having $d_0 = 10$ mm were used to measure q_m according to the following equation

$$q_m = V_m/V_0 = (d_m/d_0)^3 \tag{3}$$

where d_m and d_0 denote the diameter of the swollen specimen and the as-prepared specimen, respectively. The polymer concentration c in the gel at swelling equilibrium was evaluated from experimentally determined q_m values, i.e.

$$c = c_0/q_m \tag{4}$$

SAXS measurements were performed at 30°C with a Kratky U-slit camera and a position-sensitive proportional counter (PSPC). The X-ray generator was a Rotaflex (Rigaku Denki Co., Ltd) with a Cu rotating target operated at 60 kV and 200 mA. The CuKβ radiation was eliminated with an Ni filter. The excess scattered intensity from the polymer networks in the gel was obtained by subtracting the scattered intensity of the solvent from that of the gel, taking absorption into account. The thickness of the specimens used for the SAXS measurement was adjusted to be around 1.4 mm at swelling equilibrium. The measured scattered intensity was corrected for inhomogeneity in the sensitivity of the PSPC and for the collimation error owing to a line-shaped cross-section of the incident beam according to the method of Glatter[20]. The absolute intensity of the scattered X-rays was measured using a secondary standard sample, Lupolen platelet, calibrated by Kratky *et al.*[21,22].

RESULTS AND DISCUSSION

The swelling behaviour is presented in *Figure 1* for a gel prepared with $c_0 = 0.0490$ g cm^{-3} and $r = 37.7$, where the swelling ratio q_m on a logarithmic scale is plotted as a function of the volume fraction of acetone ϕ_a in the water/acetone mixture. Note that the specimens shown in this plot do not suffer from hydrolysis with TEMED, since TEMED was not used in the gelation process. The excess scattered intensity $I(q)$ from the polymer networks in the gel can be expressed by a form of Lorentzian in the angular region $q \ll \xi^{-1}$ as[10,11,13,14,18,19]

$$I(q) = \frac{I(q=0)}{1+q^2\xi^2} \tag{5}$$

where q denotes the magnitude of the scattering vector given by

$$q = \frac{4\pi}{\lambda}\sin(\theta/2) \tag{6}$$

with λ and θ being the wavelength of X-rays ($\lambda = 1.54$ Å) and the scattering angle, respectively. *Figure 2* displays a typical example of the plot of $[I(q)]^{-1}$ *versus* q^2 in order to determine the correlation length ξ. This is the result for sample B swollen in pure water at room temperature. The data fall on the straight line in the small-angle region and give $\xi = 44.3$ Å. The deviation between the data points and the approximated straight line in the region $q^2 < 5 \times 10^{-4}$ Å^{-2} may reflect the inhomogeneity of the polymer concentration on a relatively large scale[18,19]; further discussion is beyond the scope of this study.

Figure 3 shows a double logarithmic plot of the correlation length ξ against the polymer concentration c in a gel at swelling equilibrium in pure water. Note that the specimens examined in this plot have different crosslink densities in the as-prepared state (i.e. different r values). The data are aligned on a straight line with slope $-3/4$. Geissler *et al.*[11] also obtained the same $-3/4$ power law by small-angle neutron scattering.

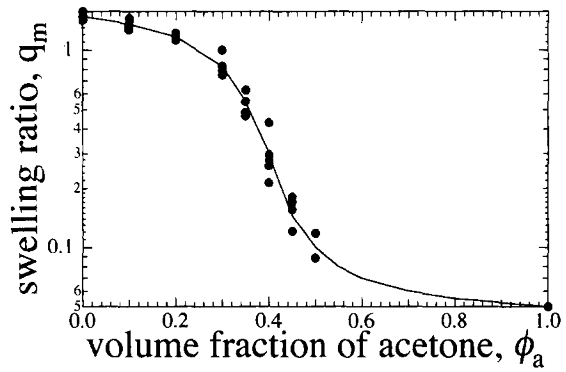

Figure 1 Swelling behaviour for a gel prepared with $c_0 = 0.0490$ g cm^{-3} and $r = 37.7$ at room temperature. Note that the specimens shown in this plot did not suffer from hydrolysis with TEMED, since TEMED was not used in the gelation process

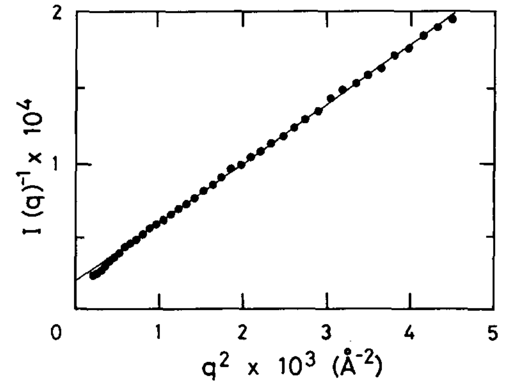

Figure 2 Typical example of the plot of $[I(q)]^{-1}$ *versus* q^2 in order to determine the correlation length ξ. The result for sample B swollen in pure water at room temperature is shown. From this plot $\xi = 44.3$ Å was evaluated

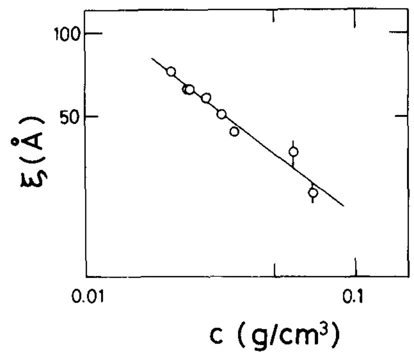

Figure 3 Double logarithmic plot of the correlation length ξ against the polymer concentration c in the gel at swelling equilibrium in pure water. The specimens have different crosslink densities in the as-prepared state. The data are aligned on a straight line with slope $-3/4$

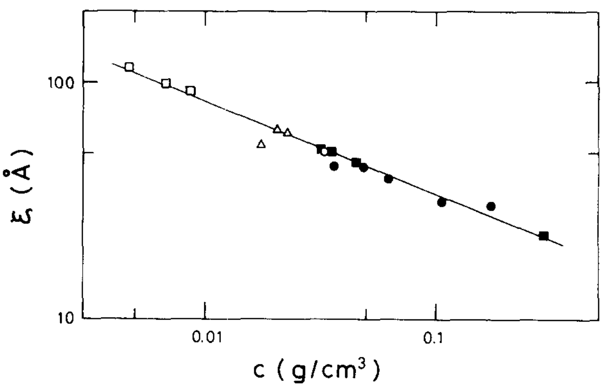

Figure 4 Double logarithmic plot of the correlation length ξ against the polymer concentration c in the gel at swelling equilibrium in water/acetone mixtures for samples A (○), B (●), C (□), F-1 (■) and F-2 (△). The specimens have similar crosslink densities in the as-prepared state, i.e. similar r values. The slope of the approximated line is $-1/3$

Furthermore, we observed another scaling relationship, a $-1/3$ power law, as shown in *Figure 4* for gels having similar values of r when swollen in water/acetone mixtures with various mixing ratios. The specimens used in *Figure 4* were swollen in water/acetone mixtures with various mixing ratios so that we could change the polymer concentration c at the swelling equilibrium.

In order to explain these power laws, let us start with the c^* theorem introduced by de Gennes[10] to describe the structure of polymer gels at swelling equilibrium. According to his theory, a polymer gel at swelling equilibrium can be considered as a semi-dilute solution crosslinked at $c=c^*$, where c^* designates the concentration at the onset of chain overlapping. On the basis of the blob model, c^* is calculated from the number of repeating units N in the chain included in the blob, the size of which is equal to the correlation length ξ. Hence, the polymer concentration c in a gel at swelling equilibrium is represented by

$$c \propto c^* \propto N/\xi^3 \tag{7}$$

From this equation, one can directly obtain the $-1/3$ power law, as observed in *Figure 4* for the case when N is constant. Since the blob size for the polymer gel at swelling equilibrium is considered to be equal to the chain dimension of the single polymer coil in the solution at $c=c^*$, the following relationship for the semi-dilute polymer solution in a good solvent can be used for the swollen gel[10]

$$\xi \propto N^{3/5}(\tfrac{1}{2}-\chi)^{1/5} \tag{8}$$

where χ denotes the Flory–Huggins interaction parameter between the polymer chain and the solvent molecule. By combining equations (7) and (8), one can obtain the following relationship

$$\xi \propto c^{-3/4}(\tfrac{1}{2}-\chi)^{-1/4} \tag{9}$$

The $-3/4$ power law is deduced for the case when χ is constant. As shown in *Figure 3*, this power law was experimentally confirmed for the gels swollen in pure water. It is worth pointing out that the $-3/4$ power law is derived even when χ changes if we examine the scaling relationship between ξ and $\tilde{c}$, where $\tilde{c}$ is defined by

$$\tilde{c} = c(\tfrac{1}{2}-\chi)^{1/3} \tag{10}$$

The scaling relationship $\xi \propto \tilde{c}^{-3/4}$ was experimentally confirmed, as shown in *Figure 5*. Here the χ values were estimated from the literature values[23] of intrinsic viscosity $[\eta]$ through the Flory–Fixman plot for polyacrylamide solutions in water/acetone mixtures. The χ values thus estimated are plotted in *Figure 6* as a function of the volume fraction of acetone ϕ_a. The approximated line expressed by

$$\chi = 0.4654 + (2.63 \times 10^{-2})\phi_a \tag{11}$$

is included in the figure.

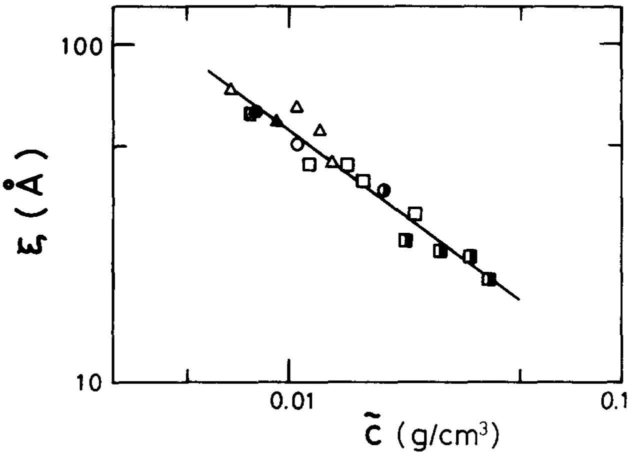

Figure 5 Double logarithmic plot of the correlation length ξ against $\tilde{c}$ for samples A (○), B (□), D (△), E (●), G (■), H (▲), I (◑) and J (◨), where $\tilde{c}=c(\frac{1}{2}-\chi)^{1/3}$. The slope of the approximated line is $-3/4$

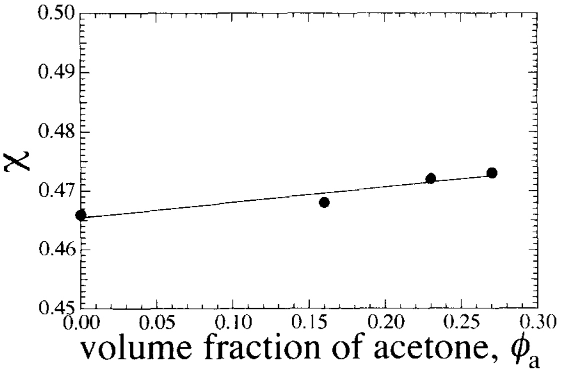

Figure 6 χ values estimated from literature values[23] and plotted as a function of the volume fraction of acetone ϕ_a in the water/acetone mixture. The approximated line given by $\chi=0.4654+(2.63\times10^{-2})\phi_a$ is also shown (solid line)

CONCLUDING REMARKS

The scaling relationships between correlation length ξ and polymer concentration c in homogeneous PAAm gels at swelling equilibrium were experimentally examined by SAXS. A $-3/4$ power law ($\xi \propto c^{-3/4}$) was found for the gels swollen in pure water (for the case of constant χ), where c varied with the crosslink density as expressed by r in the as-prepared state. Here r denotes the ratio of the concentration of the monomer to that of the bifunctional monomer at the stage of specimen preparation. On the other hand, a $-1/3$ power law ($\xi \propto c^{-1/3}$) was obtained for the gels having similar values of r when swollen in water/acetone mixtures with various mixing ratios (for the case of varying χ). It is worth noting that the $-3/4$ power law was also experimentally observed for the gels having various crosslink densities swollen in water/acetone mixtures with various mixing ratios (for the case of varying χ) if we examined the scaling relationship between ξ and the polymer concentration c multiplied by $(\frac{1}{2}-\chi)^{1/3}$. These power laws are in accord with the predictions given by the c^* theorem introduced by de Gennes for a homogeneous gel swollen in a good solvent.

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