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Lattice heterogeneities at various crosslinker contents—a gel swelling study

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Abstract

Disk shaped poly acrylamide (PAAm) gels were prepared from acrylamide (AAm) with various *N,N′*-methylenebis(acrylamide) (Bis) contents by free radical crosslinking copolymerization (FCC) in water and dried before use in swelling experiments. Photon transmission experiments for these gels were performed using an UV–visible (UVV) spectrometer. Transmitted light intensity, I_{tr} from the gel increased at very early times when the PAAm gels are immersed in water, then decreased exponentially as the swelling time increased. Decrease in I_{tr} was attributed to the lattice heterogeneities which might be originated between "frozen blob clusters" and holes in the swelling gel. Decrease in I_{tr} was modeled using the Li–Tanaka equation from which cooperative diffusion coefficients, D_c were determined for various Bis content gels. It is observed that the D_c values increased as the Bis content increased. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Li–Tanaka equation; Poly acrylamide (PAAm) gels; *N,N′*-Methylenebis(acrylamide) (Bis)

1. Introduction

Swelling is directly related to the viscoelastic properties of a gel. The gel elasticity and the friction between the network and solvent play an important role on the kinetics of the gel swelling [1–3]. It has been known that the relaxation time of swelling is proportional to the square of a linear size of the gel [1] which has been confirmed experimentally [3]. One of the most important features of the gel swelling process is that it is isotropic, i.e. when the radius increases 10%, the axial length increases 10% in a long cylindrical gel. The elastic and swelling properties of permanent networks can be understood by considering two opposing effects, the osmotic pressure and the restraining force. Usually the total free energy of a chemically crosslinked network can be separated into two terms: the bulk and the shear energies. In a swollen network the characteristic quantity of the bulk free energy is the osmotic bulk modulus, K. The other important energy, the shear energy, keeps the gel in shape by minimizing the non-isotropic deformation. The characteristic coefficient of these forces is the shear modulus, μ, which can be most directly evaluated by stress–strain measurements [4,5]. Li and Tanaka [6] have developed a model where the shear modulus plays an important role that keeps the gel in shape due to coupling of any change in different directions. This model predicts that the geometry of the gel is an important factor, and swelling is not a pure diffusion process. It has been known that the swelling and elastic properties of gels are strongly influenced by large-scale heterogeneities in the network structure [4,7]. In the swollen state these imperfections manifest themselves in a non-uniformity of polymer concentration. These large-scale concentration heterogeneities do not appear during the gelation but only in the gel swollen at equilibrium [8]. Light scattering experiments by Bastide et al. seem to confirm this picture [9].

The swelling processes of polyacrylamide gels in solvent have been extensively studied [10–12]. It has been reported that PAAm gels undergo continuous or discontinuous volume phase transitions with temperature, solvent composition, pH and ionic composition [10]. When an ionized PAAm gel is allowed to swell in water, an extremely interesting pattern appears on the surface of the gel and the volume expansion increases by adding some amount of sodium acrylate [12]. If PAAm gels are swollen in an acetone–water mixture, gel aging time plays an important role during the collapse of the network [12]. The kinetics of swelling of PAAm gels was studied by light scattering and the cooperative diffusion coefficient of the network was measured [1,13]. Small angle X-ray and dynamic light scattering were used to study the swelling properties

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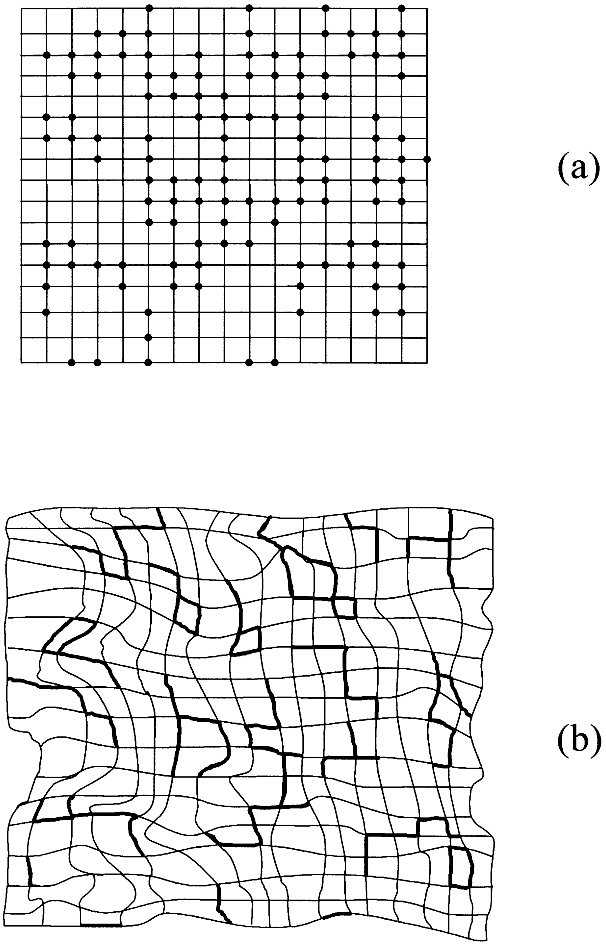

Fig. 1. Schematic representation of the two dimensional gel is shown **a**—before, **b**—after swelling. The black dots in **a** represent the interchain cross-links. The frozen blobs are presented by thick solid lines in **b**.

and mechanical behavior of PAAm gels [14,15]. In situ photon transmission technique for study the aging of acrylamide gels due to multiple swelling was reported from our laboratory [16], where it was observed that the transmitted light intensity I_{tr}, decreases continuously as the PAAm gel swells. The decrease in I_{tr} was attributed to the structural inhomogeneities in the gel. The same technique was employed to study PAAm gel formation in various water [17,18] and crosslinker [19] contents where it was observed that the I_{tr} intensity decreases during gelation in both cases.

In this paper, the Li–Tanaka equation was used to interpret the decrease of transmitted light intensities, I_{tr} during the swelling of PAAm gels in water formed with various Bis contents. It was observed that the values of cooperative diffusion coefficients, D_c were increased as the Bis content is increased by indicating that water molecules move faster in densely formed gels than in loosely formed gels.

2. Swelling of gels

For a disc shape gel, any change in diameter is coupled to a change in thickness. The total energy of a gel can be separated into bulk energy and shear energy. The bulk energy is related to the volume change, which is controlled by diffusion equation [6]. The shear energy, F_{sh} on the other hand, can be minimized instantly by readjusting the shape of the gel i.e. the change of the shear energy in response to any small change in shape that maintains constant volume element within the gel should be zero [6] ($\delta F_{sh} = 0$). Each small diffusion process determined by a diffusion equation must coupled to a small shear process given by $\delta F_{sh} = 0$.

Simultaneous solution of diffusion equation and $\delta F_{sh} = 0$ produces the following equation for the swelling of a gel disk [6].

$$\frac{u(r,t)}{u(r,o)} = \sum_n B_n \exp(-t/\tau_n) \tag{1}$$

where the displacement vector $u(r,t)$ is expressed as a decomposition into components, each of them decaying exponentially with a time constant, τ_n. The first term of the expression is dominant at large shear modulus, μ. Eq. (1) can also be written in terms of solvent uptakes W and W_∞ at time t and at time infinity, respectively, as follows:

$$\left(1 - \frac{W}{W_\infty}\right) = B_1 \exp(-t/\tau_1) \tag{2}$$

where B_1 is given by the following relationship:

$$B_1 = \frac{2(3-4R)}{\alpha_1^2 - (4R-1)(3-4R)} \tag{3}$$

It should be noted from Eq. (1) that $\sum B_n = 1$, therefore B_1 should be less than 1. Here $R = \mu/M$ where M is the longitudinal osmotic modulus $M = (K + 4\mu/3)$. Once the value of B_1 is experimentally obtained, one can determine the value of R, since the dependence of B_1 and R for a disk can be found in the literature [6]. For example; when $R = 3/4$, B_1 is equal to 1 and if R is smaller than 3/4, B_1 is always smaller than 1. τ_1 is related to the collective cooperative diffusion coefficient D_c of a gel disk at the surface by

$$D_c = \frac{3a_\infty}{\tau_1 \alpha_1^2} \tag{4}$$

where α_1 is a function of R only and given in the literature [6], and a_∞ stands for the half thickness of the gel in the final equilibrium state. If R is known α_1 can be determined [6]. Once the quantities τ_1 and B_1 are experimentally obtained, R, α_1 and D_c can be calculated, respectively.

3. Heterogeneities in the gel

A gel can be described as a random distribution of crosslinks on a lattice formed by the interchain contact points.

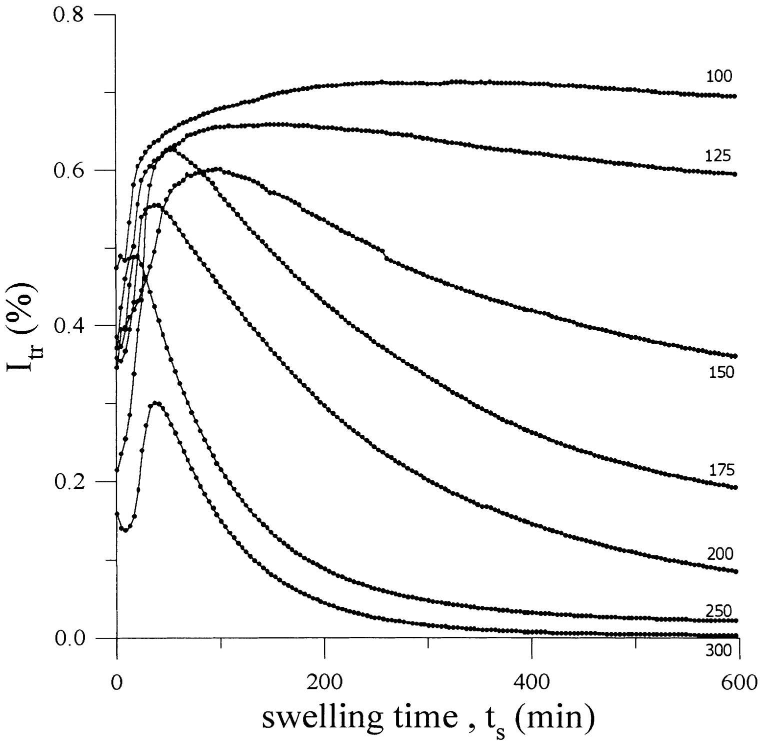

Fig. 2. Variation in transmitted photon intensities, I_{tr} versus swelling time, t_s during swelling process for different Bis content samples at 440 nm wavelength. Numbers on each curve present the Bis content in mg.

When two junctions are located on neighboring lattice sites, a "frozen blob" is formed [8]. In the swollen state of a gel these cross-links cannot move apart from each other, since they are chemically connected by a chain segment which is in an optimal excluded volume conformation. Frozen blobs are often connected and form clusters of first topological neighbors. As a result the random cross-linking of chains can be described as a site percolation on a blob lattice. When the gel is in a good solvent it swells and frozen blob clusters expand less than the interstitial medium. Fig. 1a and b presents a two-dimensional gel before and after swelling, respectively, where the clusters of the first chemical neighbor junctions (frozen blobs) are presented.

When the gel is in a swollen state, small clusters are expelled from bigger ones creating regions of low concentration. Here the correlation length, becomes the typical size of clusters that are not entangled with smaller ones. In other words, correlation length becomes the typical size of holes which are created as a part of the interstitial medium. Here the swelling of gel leads to an excess scattering of light which comes from the contrast between frozen blob clusters and holes created by the dilution. During the dilution process in gel swelling, the partial separation of frozen blob clusters leads to a strong increase of the scattering intensity, I_{sc} or decrease in the transmitted light intensity, I_{tr}.

4. Experimental

Gels were prepared by using 2.5 g of AAm and 40 mg of ammonium persulfate (APS) as an initiator by dissolving them in 25 cc of water in which 10 μl of tetramethyl ethylenediamin was added as an accelerator. Seven different gels were obtained by adding 100, 125, 150, 175, 200, 250 and 300 mg Bis into the each of the gels prepared by the above procedure. Free radical crosslinking copolymerization were performed at room temperature in a cylindrical cell with 1.6 cm diameter in nitrogen atmosphere. Disk shaped gels were obtained by cutting these cylindrical gels. Gels (1.4–1.6 mm thick) in various Bis contents were placed into a 1 × 1 cm quartz cell filled with water for the UVV experiments. Swelling of the gels were monitored in time and in situ photon transmission measurements were performed using a Perkin–Elmer UVV spectrometer. Photon transmission intensities, I_{tr} were measured by using the time drive mode of the spectrometer during the swelling of the gels. Typical normalized I_{tr} curves against swelling time, t_s are given in Fig. 2 for the experiments made at 440 nm wavelength for seven different Bis content samples. In Fig. 2 it is seen that I_{tr} intensities increased suddenly at early times by reaching a highest transparency, then except 100 and 125 mg Bis content samples, I_{tr} decreased exponentially presenting the appearance of the contrasts between frozen blob clusters and holes in these gel samples. The early time

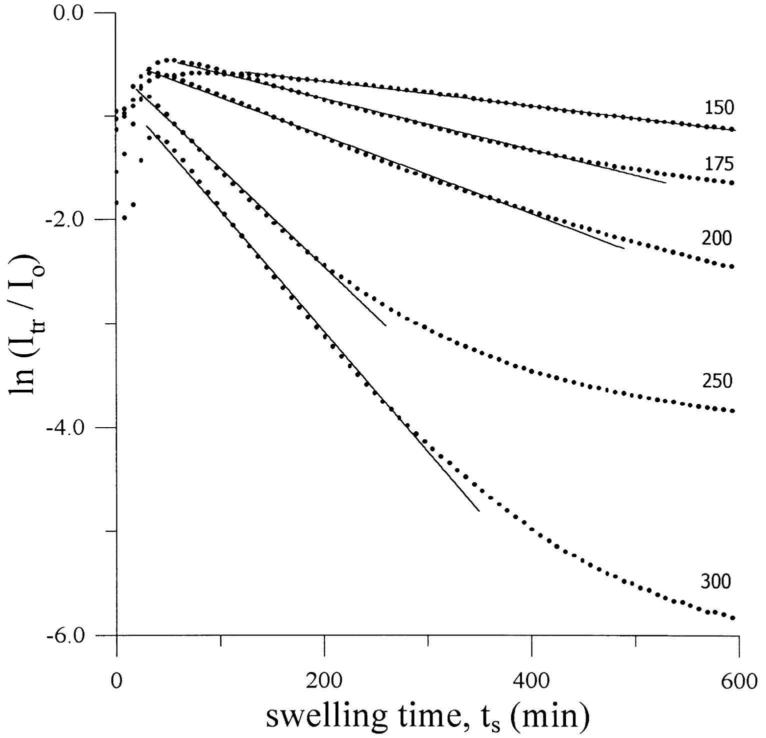

Fig. 3. Plot of the data in Fig. 2 according to Eq. (6). Numbers on each curve present the Bis content in mg.

behavior of I_{tr} most probably comes from the cracks on the surface of the gel which appeared during the cutting process. This behavior of I_{tr} can be named as the surface effect related to the dangling chain ends, which cause some scattering from the gel surfaces before wetting. This effect disappears at early times of wetting and I_{tr} reach the maxima. Further swelling shows that 150, 175, 200, 250 and 300 mg Bis content gels present lattice heterogeneities which increase due to the swelling process. However, gels with 100 and 125 mg Bis contents show perfect, homogeneous lattice structure during the swelling process, where I_{tr} continues to increase and saturates at longer times.

5. Results and discussion

The behavior of I_{tr} above the maxima can be quantified by establishing the relation between Eq. (2) and I_{tr}. At the maxima, before solvent penetration starts the transmitted intensity is I_0. After solvent penetration starts due to the turbidity created by lattice heterogeneities, transmitted light intensity decreases to I_{tr} at time t_s where the amount of solvent uptake is W. At the equilibrium state of swelling, the transmitted intensity decreases to I_∞, where the solvent uptake by the swollen gel is W_∞. The relation between solvent uptake W and transmitted intensities, from the gel during the swelling process can be given by the following relation:

$$\frac{W}{W_\infty} = \frac{I_0 - I_{tr}}{I_0 - I_\infty} \tag{5}$$

Since $I_0 \gg I_\infty$, Eq. (5) becomes

$$\frac{W}{W_\infty} = 1 - \frac{I_{tr}}{I_0} \tag{6}$$

This relation predicts that as W increases, I_{tr} decreases. Combining Eq. (6) with Eq. (2) and taking the logarithm of

Table 1
Experimentally determined swelling parameters given in the text

Bis (mg)	100 ± 1	125 ± 1	150 ± 1	175 ± 1	200 ± 1	250 ± 1	300 ± 1
B_1	0.74	0.68	0.64	0.72	0.65	0.57	0.48
τ_1 (min)	–	–	839	392	258	105	85
D_c (10^{-8} cm^2 s^{-1})	–	–	44	91	144	301	340
W_∞ (g)	0.44 ± 0.01	0.45 ± 0.01	0.42 ± 0.01	0.46 ± 0.01	0.43 ± 0.01	0.44 ± 0.01	0.42 ± 0.01
a_∞ (mm)	1.6 ± 0.05	1.6 ± 0.05	1.75 ± 0.05	1.6 ± 0.05	1.75 ± 0.05	1.75 ± 0.05	1.75 ± 0.05
a_i (mm)	0.75 ± 0.05	0.70 ± 0.05	0.75 ± 0.05	0.70 ± 0.05	0.75 ± 0.05	0.80 ± 0.05	0.80 ± 0.05

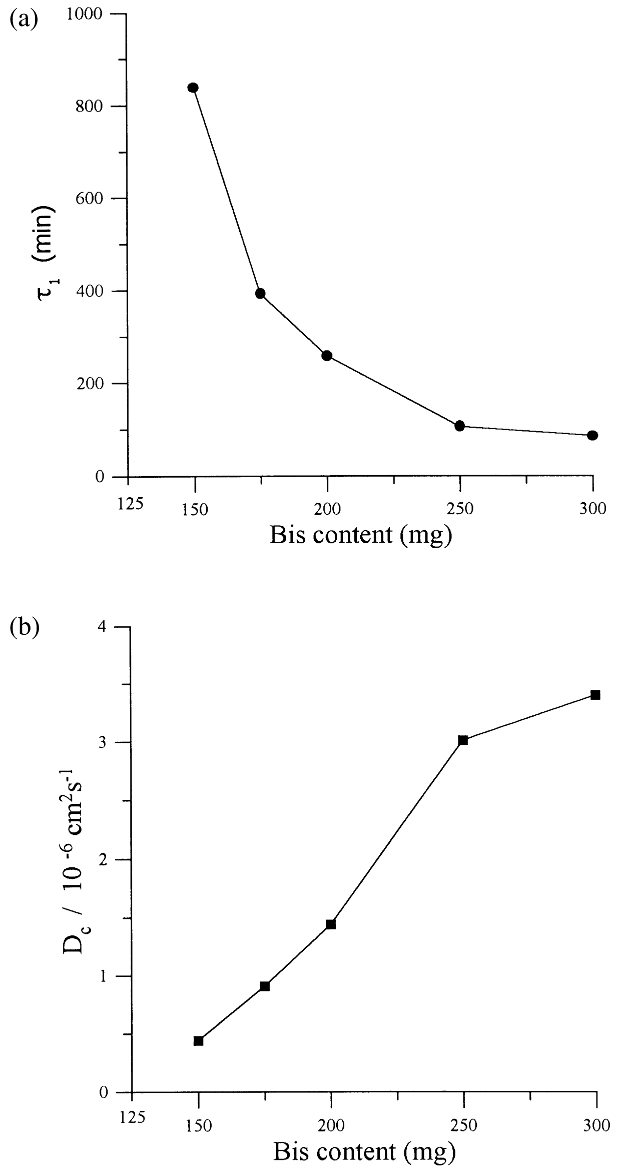

Fig. 4. The plots of a—τ_1 and b—D_c values versus Bis content.

it the following relation can be obtained:

$$\ln(I_{tr}/I_0) = \ln B_1 - \frac{t_s}{\tau_1} \tag{7}$$

The data in Fig. 2 are plotted in Fig. 3 according to Eq. (7) where quite linear relations are obtained. Linear regression of curves in Fig. 3 provide us with B_1 and τ_1 values. Taking into account the dependence of B_1 and R, one obtains R values, and from $\alpha_1 - R$ dependence α values were produced [6]. Then using Eq. (4), cooperative diffusion coefficients D_c were determined for the gel samples and the results are listed in Table 1 together with the τ_1, a_i, a_∞ and W_∞ values. Here a_i and a_∞ are the half thicknesses of the gels before and after swelling. W_∞ is the amount of solvent uptake at the equilibrium of swelling. Here a_i and a_∞ are measured with calipers and optical microscope. W_∞ values were determined by using the digital balance. The measured time constant, τ_1 and cooperative diffusion coefficients, D_c are plotted versus Bis content in Fig. 4a and b, respectively where it is seen that τ_1 values exponentially decrease as the Bis content is increases, which indicates that the swelling of loosely formed gels takes longer than densely formed gels. As seen in Fig. 4b D_c values increase as the Bis content is increased which predicts that water molecules move slower in loosely formed gels than densely formed gels. These behaviors of gels can be understood by realizing the fact that the loosely formed gels are more flexible and the shear energy is much less in these gels than in the densely formed gels. As the crosslinker density of the gels increase, the elastic contribution to the shear energy increases as a result the D_c values increases which is the case in densely formed gels.

In summary, in this work UVV spectrometric technique was employed to study photon transmission intensities, I_{tr} during the swelling of PAAm gels, prepared with various Bis contents. It was observed that the transmitted light intensities I_{tr} at early times increased suddenly and then decreased exponentially as the gels swell. The decrease in I_{tr} was attributed to the increase in the scattered light intensity, I_{sc} from the gel due to lattice heterogeneities which appear the swelling processes. The exponential decrease in I_{tr} against time was modeled using the Li–Tanaka equation [6]. Time constants, τ_1 and cooperative diffusion coefficients, D_c were determined for each gel sample in different Bis contents.

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