

# Photon Transmission Technique for Monitoring Drying Processes in Acrylamide Gels Formed with Various Crosslinker Contents

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**ABSTRACT:** *In situ* photon transmission experiments were performed using UV-visible (UVV) spectrometer during the drying of polyacrylamide (PAAm) gels. These gels are formed from acrylamide (AAm) with various *N,N'*-methylenebis(acrylamide) (Bis) contents by free radical crosslinking copolymerization (FCC) in water. The transmitted light intensity,  $I_{tr}$ , increased continuously as PAAm gels are dried. Increase in  $I_{tr}$  was attributed to the decrease in the scattered light intensity,  $I_{sc}$ , which might be originated from the contrast between “frozen blob clusters” and holes in the drying gel. Decrease in  $I_{sc}$  was modeled using Rayleigh’s equation, where drying times with various exponents were found to be proportional to the volume of frozen blob clusters. It was observed that the radius of frozen blob cluster (correlation length),  $\xi_c$  increased in various power of time, depending on Bis contents during drying of gels. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1898–1906, 2001

**Key words:** photo transmission; drying process; acrylamide gels

## INTRODUCTION

Polymer networks or gels are known to exist generally in two forms—swollen, and shrunken. Volume transitions may occur between these forms either continuously or sudden jumps between them.<sup>1,2</sup> The equilibrium swelling and shrinking of gels in solvents have been extensively studied.<sup>3–5</sup> The swelling, shrinking, and drying kinetics of physical and chemical gels are very important in many technological applications, especially in pharmaceutical industries in designing slow-release devices for oral drugs and in using of cosmetic ingredients. Understanding the mecha-

nism of swelling, shrinking, and drying kinetics is highly desirable. In agricultural industry for producing storable foods and in medical applications in developing artificial organs the knowledge of gel kinetics is an important requirement for the scientist in the field.

The swelling properties of chemically cross-linked gels can be understood by considering the osmotic pressure versus the restraining force.<sup>6–10</sup> The total free energy of a chemical gel consists of bulk and shear energies. In fact, in a swollen gel the bulk energy can be characterized by the osmotic bulk modulus, which is defined in terms of the swelling pressure and the volume fraction of polymer at a given temperature. On the other hand, the shear energy that keeps the gel in shape can be characterized by shear modulus. Here, shear energy minimizes the nonisotropic

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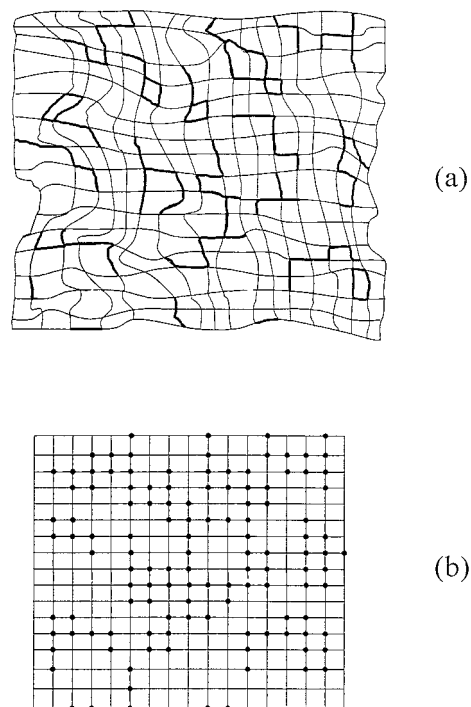
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deformations in gel. The theory of kinetics of swelling for a spherical chemical gel was first developed by Tanaka et al.<sup>11</sup> where the assumption is made that the shear modulus is negligible compared to the osmotic bulk modulus. Later, Li and Tanaka<sup>6</sup> 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 gel is an important factor and swelling is not a pure diffusion process. In our knowledge, however, so far no serious model has developed to explain the drying processes. Several experimental techniques have been employed to study the kinetics of swelling, shrinking, and drying of chemical and physical gels, among which are neutron scattering,<sup>12</sup> quasielastic light scattering,<sup>13</sup> and *in situ* interferometric<sup>14</sup> measurements. Recently, several fluorescence studies on swelling and drying kinetics of poly(methyl methacrylate) gels has been reported from our laboratory.<sup>15–18</sup>

The equilibrium swelling and shrinking processes of polyacrylamide (PAAm) gels in solvent have been extensively studied.<sup>19–21</sup> It has been reported that PAAm gels undergo continuous or discontinuous volume phase transitions with temperature, solvent composition, Ph, and ionic composition.<sup>19</sup> Ph-induced volume phase transition of PAAm gels in an acetone/water mixture was studied using fluorescence technique.<sup>20</sup> 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.<sup>21</sup> If PAAm gels are swollen in acetone–water mixture, gel aging time plays an important role during collapse of the network.<sup>21</sup> The kinetics of swelling of PAAm gels was studied by light scattering and the cooperative diffusion coefficient of the network was measured.<sup>11,13</sup> Small-angle X-ray and dynamic light scattering were used to study the swelling properties and mechanical behavior of PAAm gels.<sup>23,24</sup> It has been known that the swelling and elastic properties of gels are strongly influenced by large-scale heterogeneities in the network structure.<sup>25,26</sup> In the swollen state, these imperfections manifest themselves in a nonuniformity of polymer concentration. These large-scale concentration heterogeneities do not appear during the gelation but only in the gel swollen at equilibrium.<sup>27</sup> Light-scattering experiments by Bastide et al. seem to confirm this picture.<sup>28</sup>

The formation of the heterogeneities of crosslinked polymer gels has been the subject of great interest for many years. These structural inhomogeneities of a gel affects its physical properties such as optical and phase properties. Extensive studies have been made on the characterization of the gel heterogeneities. The effects of inhomogeneities of the polymer network on the swelling equilibrium of PAAm gels during the diffusion of water molecules was studied by Hsu et al.<sup>29</sup> Recently, Photon transmission technique was used to study the existence of frozen blob clusters in PAAm gels, which caused strong light scattering during swelling.<sup>30</sup>

In this article *in situ* photon transmission experiments are reported during the drying of PAAm gels with various Bis contents. It was observed that the transmitted light intensities  $I_{tr}$  increased continuously as the gels are dried. Increase in  $I_{tr}$  was attributed to the decrease in scattered light intensity,  $I_{sc}$ , from the gel due to spatial heterogeneities, which disappear during drying processes.  $I_{tr}$  intensities were measured

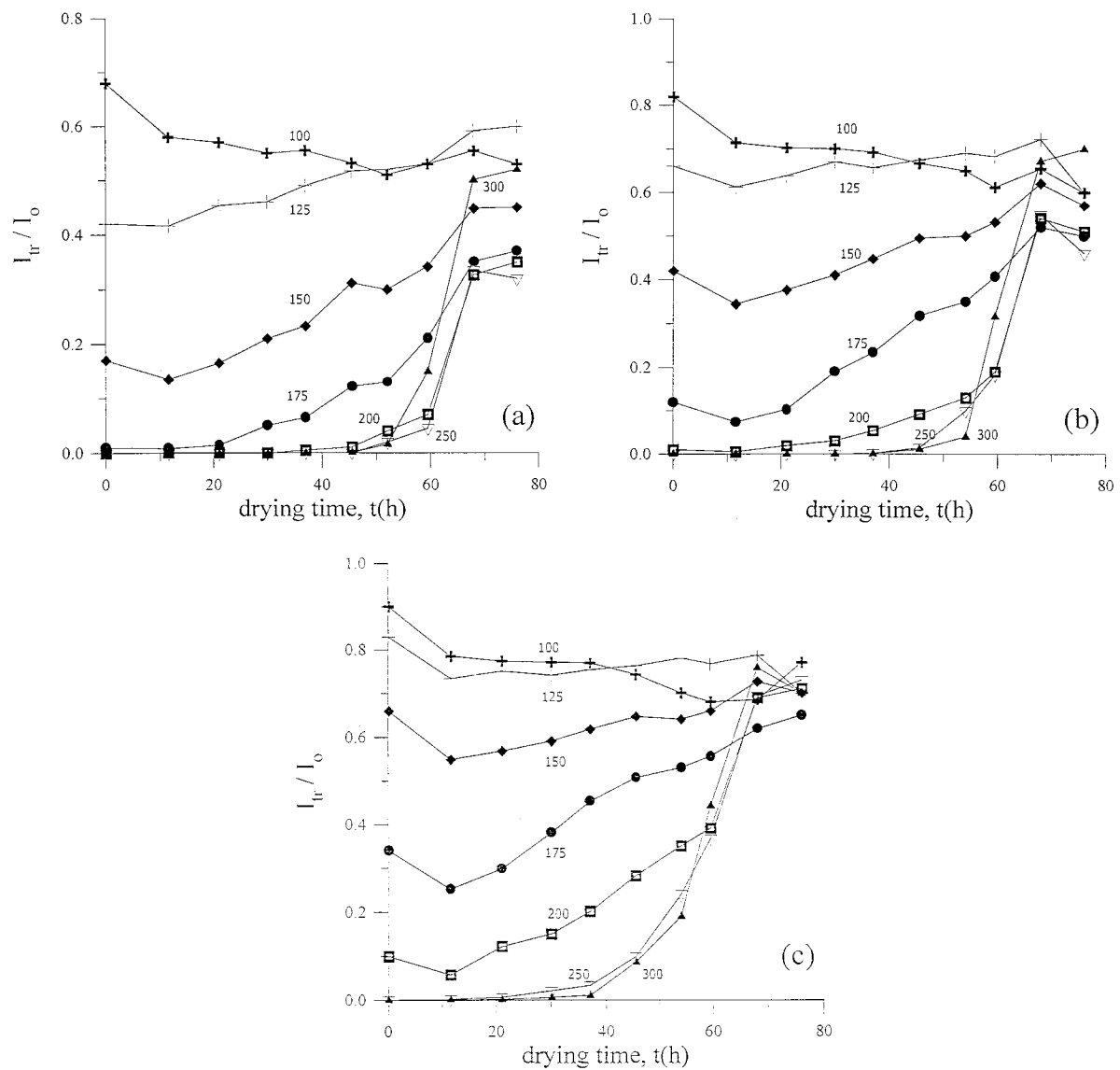


**Figure 1** Schematic representation of a two-dimensional gel (a) swollen in good solvent. The clusters of first neighbor junctions (frozen blobs), which do not swell, are represented by thick solid lines; (b) in the dried state. Block dots represent the interchain crosslinks.

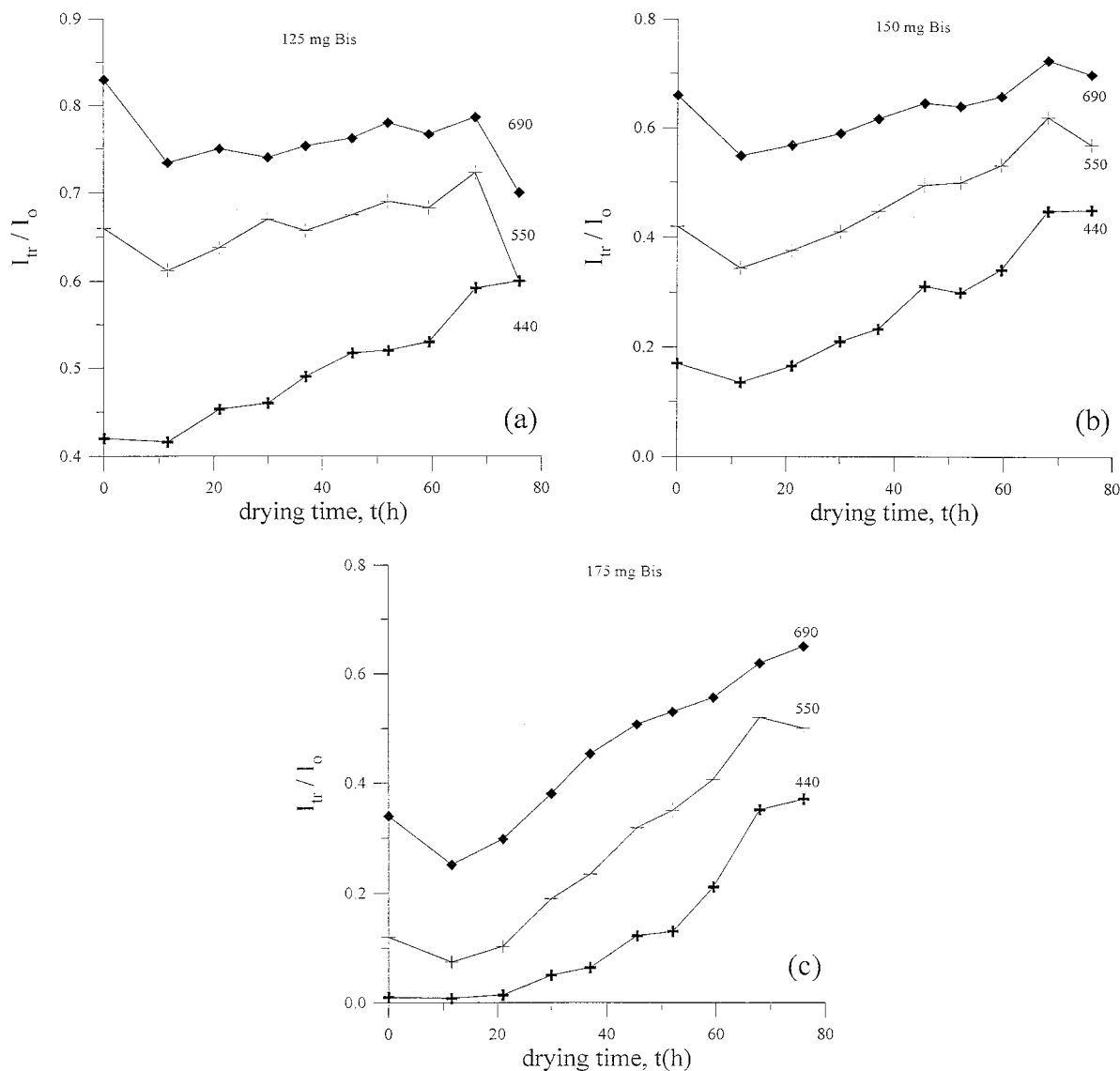
by UV-visible (UVV) spectrometric technique. Swelling in PAAm gels were monitored in real time by using the time drive mode of the UVV spectrometer. The decrease in  $I_{sc}$  against time was modeled using Rayleigh's equation<sup>32</sup> and the Frozen Blob model.<sup>31</sup> It is observed that volume  $\nu$ , of frozen blob clusters grow in time with various exponents, depending on Bis contents. The changes in  $I_{sc}$  were found to be inversely proportional to various powers of wavelength,  $\lambda$  of incident light.

## TURBIDITY AND LIGHT SCATTERING

It has been well known that light scattering causes turbidity when a light beam is passed through a solution. Light scattering is caused by density and concentration fluctuations, i.e., by deviation of density and concentration from their uniform values in a dispersed medium. Light is scattered only when a light wavelength,  $\lambda$ , is greater than the size of a particle of the dispersed phase. If  $\lambda$  is much smaller than the particle diameter, light is reflected. If the intensity of in-



**Figure 2** Variation in transmitted photon intensities,  $I_{tr}$  vs. drying time,  $t$  during *in situ* drying experiments in six different Bis content for (a) 440, (b) 550, (c) 690 nm wavelengths. Numbers on each curve present the Bis content in mg.



**Figure 3** Variation in transmitted photon intensities,  $I_{tr}$  vs. drying time,  $t$  during *in situ* drying experiments at different wavelengths for (a) 125, (b) 150, (c) 175 mg Bis content samples. Numbers on each curve indicate the wavelength of the transmitted light.

cident light is  $I_0$  and on passage of the light through a dispersed medium, the incident intensity is reduced to  $I_{sc}$  as a result of scattering. Rayleigh derived an equation by excluding the absorption of light by the medium, which connects  $I_0$  with  $I_{sc}$ , the intensity of light scattered per unit volume of a dilute system as follows<sup>32</sup>:

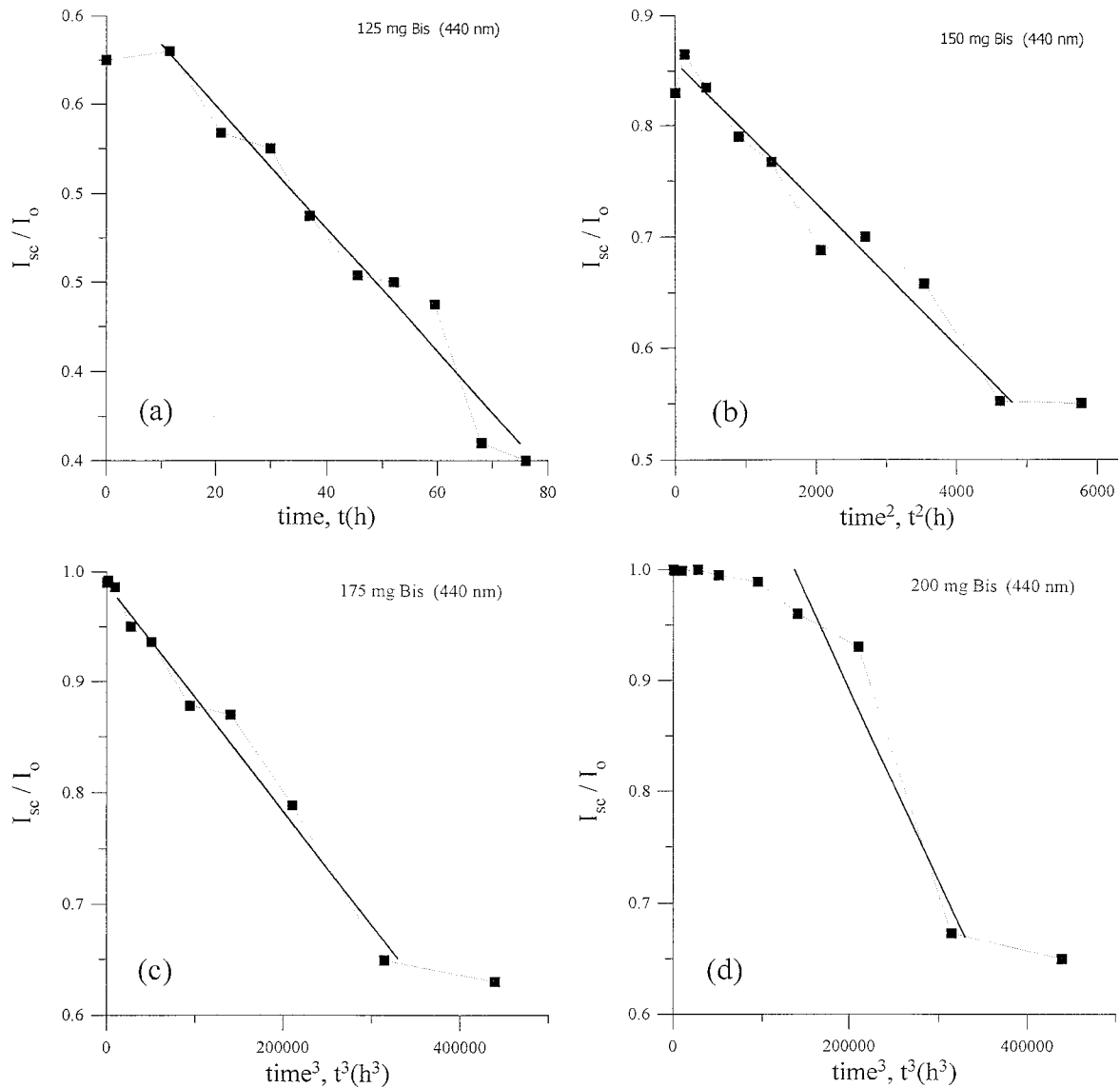
$$I_{sc} = I_0 k c v^2 \lambda^{-7} \quad (1)$$

This equation is valid for spherical particles, which do not conduct electric current and are

small in comparison with the wavelength,  $\lambda$ , of the incident light. In eq. (1)  $k$  is given by

$$k = 24 \pi^3 \left( \frac{n_1^2 - n_0^2}{n_1^2 + 2n_0^2} \right)^2 \quad (2)$$

where  $n_1$  and  $n_0$  are the indices of refraction of the dispersed phase and the dispersion medium respectively.  $v$  presents the volume of a single particle, and  $c$  is the numerical concentration, i.e., the number of particles in 1 cc of the system in eq.



**Figure 4** Variation in the scattered light intensity,  $I_{sc}$  at 440 nm versus  $t$ ,  $t^2$ ,  $t^3$ ,  $t^3$ , and  $t^3$  during *in situ* drying experiments for (a) 125, (b) 150, (c) 175, (d) 200, (e) 250, (f) 300 mg Bis content samples, respectively.

(1). Rayleigh's equation determines the turbidity of the medium, and can be used for particles whose size is not more than 0.1 of the wavelength of light, i.e., for particles of diameters from 40 to 70 nm. In this case  $I_{sc}$  changes in inverse proportion to the fourth power of  $\lambda$  ( $\eta = 4$ ). However, for larger particles,  $I_{sc}$  changes in inverse proportion to a smaller power of  $\lambda$ . The dependence of  $\eta$  on particle size was studied in monodispersed latex systems of polystyrene,<sup>32</sup> and it was observed that  $\eta$  decreased from 4 to 2.8.

When the size of particles in the dispersed medium becomes much greater than  $\lambda$ , light is no

more scattered but reflected, regardless of the wavelength of the incident light. If the particles are too large in size, reflection of light from them increases, which causes the reduction of the intensity of scattered light; however, in the meantime, the intensity of light scattering decreases as the particle size decreases. Therefore, dispersed medium scatter light to a greatest extent. In conclusion, Rayleigh's equation provides the following important information to be used: for particles of a given size, the intensity of scattered light is directly proportional to the numerical concentration. This principle can be used to determine the

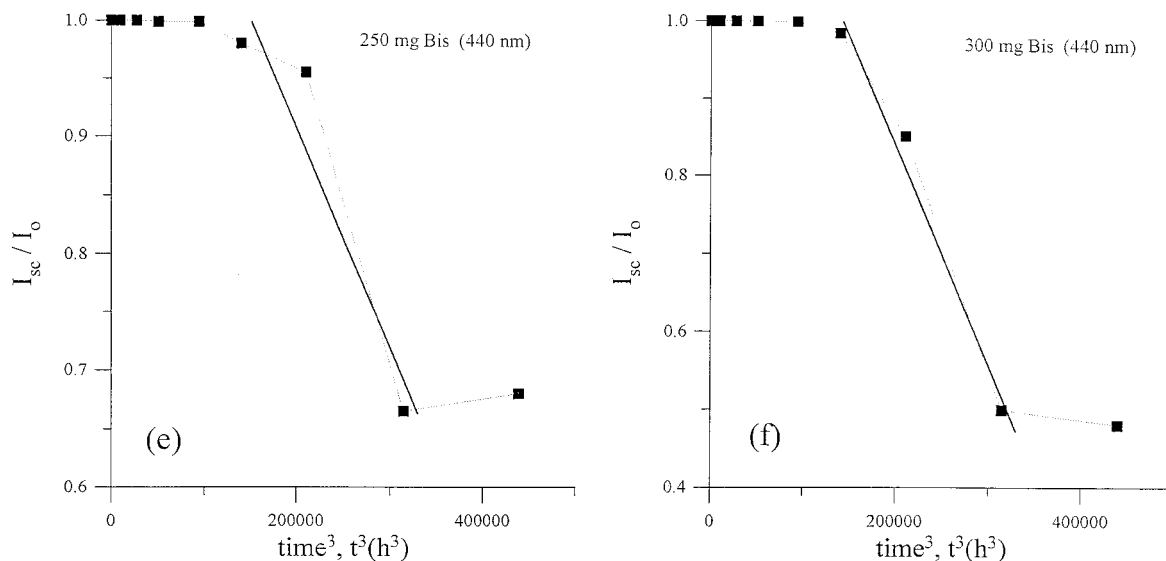


Figure 4 (Continued from the previous page)

concentration of the dispersed phase by measuring  $I_{sc}$  in the system. However, because multiple scattering occurs at very high concentrations, precaution has to be taken. At a given concentration and particle size, variation in  $\lambda$  against  $I_{sc}$  can produce the exponent  $\eta$ , which can be used to determine the particle size.

## FROZEN BLOBS

A gel can be describe as random distribution of crosslinks on a lattice formed by the interchain contact points. When two junctions are located on neighboring lattice sites, a “frozen blob” is formed. In the swollen state of a gel these crosslinks cannot move apart from each other, because they are chemically connected by a chain segment that is in an optimal excluded volume conformation. Frozen blobs are often connected, and form clusters of first topological neighbors. As a result, the random crosslinking 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. If the swollen gel is left in air for drying then the process can be represented as shrinkage of the clusters of frozen blobs accompanied by a partial inclusion of smaller clusters into the larger ones. In this case, the distribution of frozen blobs are randomized as the gel dries and shrinks. Figure 1(a) and (b) present the swollen and dried gel lattices, respectively.

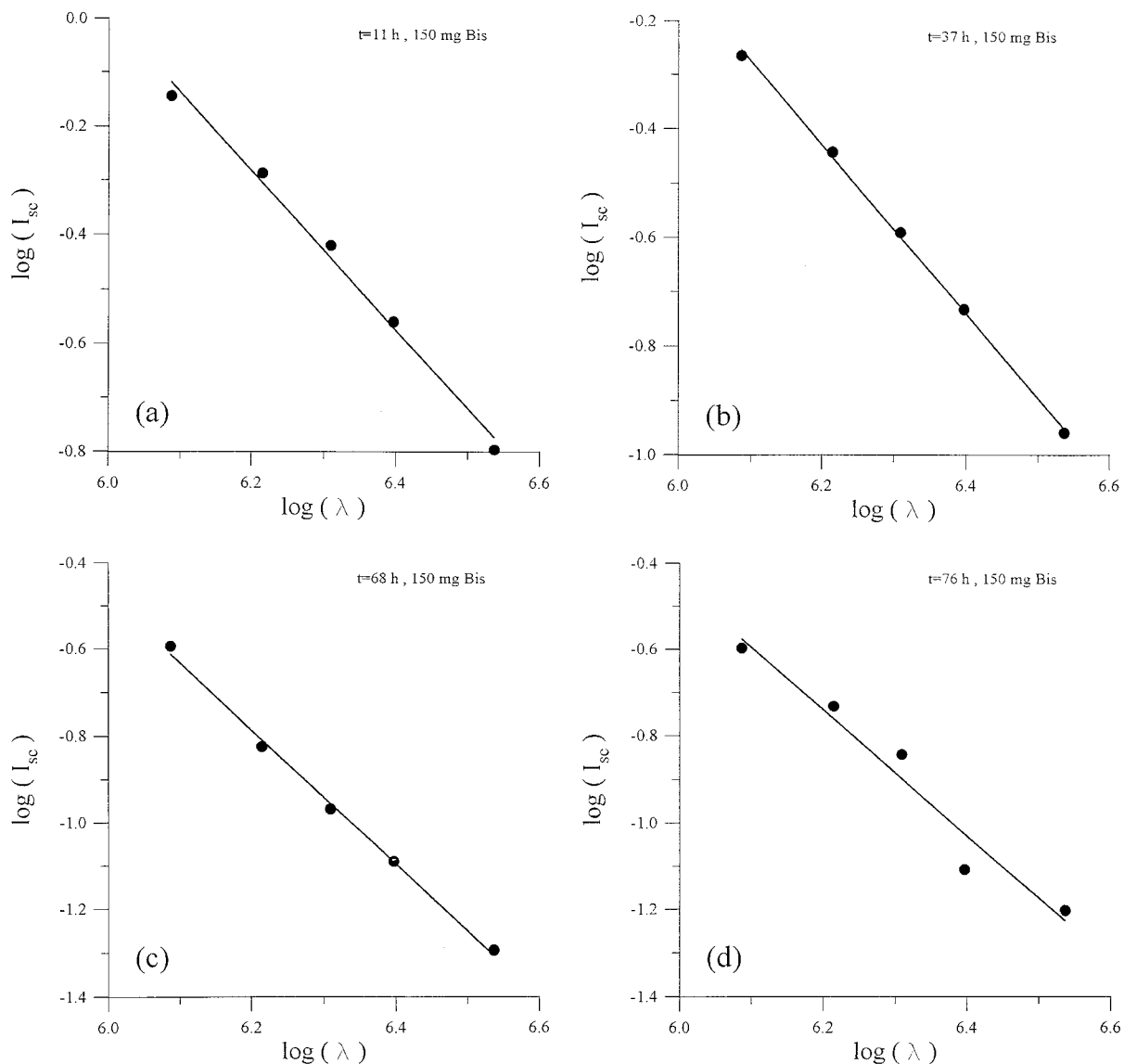
When the gel is in a swollen state, small clusters are expelled from bigger ones, creating regions of low concentration. Here, the correlation length,  $\xi_c$  is the typical size of clusters that are not entangled with smaller ones. In other words,  $\xi_c$  is the typical size of holes that are created as a part of the interstitial medium. Shrinkage process during drying does resembles a random packing and rearrangement of Russian dolls.<sup>28</sup> Because of polydispersity of clusters, one would expect a very strong dependence of  $\xi_c$  on shrinkage. The increase in scattering of light is caused from the contrast between frozen blob clusters and holes created by dilution during swelling. However, during drying, the scattered light intensity decreases due to the decrease in contrast between frozen blob clusters and holes.

Table I Time Dependence of Correlation Length,  $\xi_c$  for the Various Bis Content Samples

| Bis (mg) | 125       | 150       | 175       | 200       | 250       | 300       |
|----------|-----------|-----------|-----------|-----------|-----------|-----------|
| $\xi_c$  | $t^{1/6}$ | $t^{1/3}$ | $t^{1/2}$ | $t^{1/2}$ | $t^{1/2}$ | $t^{1/2}$ |

## EXPERIMENTAL

Each gel was prepared by using 2.5 g of AAm and 40 mg of ammonium persulfate (APS) as an initi-



**Figure 5** Log-log plots of  $I_{sc}$  vs.  $\lambda$  for 150 mg Bis content samples at the gelation times (a) 11, (b) 37, (c) 68, (d) 76 h. Slopes of the curves produces  $\eta$  values, which are listed in Table II.

ator by dissolving them in 25 cc of water in which 10  $\mu$ L of tetramethyl ethylenediamin was added as an accelerator. Eight different gels were obtained by adding 50, 100, 125, 150, 175, 200, 250, and 300 mg Bis into the each of the gels prepared above procedure. Gelations were performed at room temperature in  $1.0 \times 1.0$ -cm quartz cells. Drying of gels were monitor in real 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 drying of gels at five differ-

ent wavelengths (440, 500, 550, 600, and 690 nm). Typical  $I_{tr}^*$  curves against drying time are given in Figure 2(a), (b), and (c) for the experiments made at 440, 550, and 690 nm wavelengths at eight different Bis contents. In Figure 3(a), (b), and (c)  $I_{tr}$  curves at various wavelengths are compared for 125, 150, and 175 mg Bis content samples, respectively. In Figures 2 and 3 it is seen that  $I_{tr}$  intensity increased above a certain time by indicating that turbidity disappeared during drying. Here, one can predict that above 125 mg Bis content gels present lattice heterogeneities, which disappear due to drying process.

**Table II Experimentally Obtained  $\eta$  Values for Various Bis Content Samples at Different Times**

| Bis Content (mg) | $\eta$ Values for Different Times (h) |      |      |      |      |      |      |      |      |      |
|------------------|---------------------------------------|------|------|------|------|------|------|------|------|------|
|                  | 0                                     | 11   | 21   | 30   | 37   | 45   | 52   | 59   | 68   | 76   |
| 100              | 2.74                                  | 1.50 | 1.43 | 1.50 | 1.45 | 1.32 | 1.23 | 0.86 | 0.73 | 1.43 |
| 125              | 2.66                                  | 1.75 | 1.74 | 1.65 | 1.61 | 1.57 | 1.65 | 1.53 | 1.41 | 0.66 |
| 150              | 2.04                                  | 1.45 | 1.47 | 1.47 | 1.55 | 1.49 | 1.43 | 1.45 | 1.54 | 1.44 |
| 175              | 0.90                                  | 0.62 | 0.75 | 0.98 | 1.19 | 1.29 | 1.39 | 1.27 | 1.17 | 1.58 |
| 200              | 0.22                                  | 0.12 | 0.27 | 0.36 | 0.48 | 0.70 | 0.82 | 0.90 | 1.71 | 1.63 |
| 250              | 0.00                                  | 0.00 | 0.01 | 0.03 | 0.06 | 0.22 | 0.57 | 0.91 | 1.71 | 1.96 |
| 300              | 0.00                                  | 0.00 | 0.00 | 0.00 | 0.02 | 0.18 | 0.43 | 0.94 | 1.58 | 0.50 |

## RESULTS AND DISCUSSION

The results in Figures 2 and 3 can be interpreted by employing eq. (1), where it can be assumed that the increase in  $I_{tr}$  during drying solely originates from the decrease in scattering intensity,  $I_{sc}$ . In Figure 4(a)–(f) normalized  $I_{sc} = (1 - I_{tr})$  intensities are plotted vs.  $t$ ,  $t^2$ , and  $t^3$  at the 440 nm wavelength drying experiments for 125, 150, 175, 200, 250, and 300 mg Bis content samples, respectively. It is seen in Figure 4 that  $I_{sc}$  present a linear decrease by indicating that hydrogel system scatters less light by presenting a less turbidity during drying. These results can be modeled by knowing that the randomness of the frozen blob clusters increase as the gel dries, i.e., when the gel dries it becomes more homogeneous and scatters less light.

If the frozen blob cluster is assume to be spherical in volume with

$$v = \frac{4\pi}{3} \xi_c^3 \quad (3)$$

then eq. (1) becomes

$$I_{sc} = I_o \alpha (\xi_c^3)^2 \quad (4)$$

where  $a = kc\lambda^{-\eta}(4\pi/3)^2$ . Figure 4 predicts that  $\xi_c$  shrinks with various exponents in time, dependent on the Bis content of the gel sample during drying process. For example, 125 mg Bis content samples dries in time with  $t^{1/6}$ ; on the other hand, samples with 175 mg Bis content dry in time with  $t^{1/2}$ . Results in Figure 4 are listed in Table I according to following relation

$$\xi_c = bt^{n/6} \quad (5)$$

where  $b$  is the related constant and  $n = 1, 2, 3$ . It is seen in Table I that higher Bis content gels dry much faster than lower Bis content gels. The power of  $t$  presents the model of drying, for instance, 175 mg Bis content gel dries as a Fickian type of diffusion then  $b$  in eq. (5) is related to the diffusion coefficient of a frozen blob cluster.

Data in Figure 3(a), (b), and (c) are converted to the scattering light intensity,  $I_{sc}$  and fitted to eq. (1) for a given time. Figure 5(a), (b), (c), and (d) present the  $\log I_{sc}$  vs.  $\log \lambda$  plots for 150 mg Bis content sample a various drying times. Slope of these plots produce  $\eta$  values. Similar plots are obtained at other drying times and for various Bis content samples. The observed  $\eta$  values for all gel samples are listed in Table II, where it is seen that exponent  $\eta$  is much lower than 2.8, which predicts that the radius of the frozen blob clusters are much larger than 100 nm.

## REFERENCES

- Dušek, K.; Paterson, D. J Polym Sci 1968, A26, 1209.
- Tanaka, T. Phys Rev Lett 1980, 45, 1636.
- Tobolsky, A. V.; Goobel, J. C. Macromolecules 1970, 3, 556.
- Schild, H. G. Polym Sci 1992, 17, 163.
- Amiya, T.; Tanaka, T. Macromolecules 1987, 20, 1162.
- Li, Y.; Tanaka, T. J Chem Phys 1990, 92, 1365.
- Zrinyi, M.; Rosta, J.; Horkay, F. Macromolecules 1993, 26, 3097.
- Candau, S.; Baltide, J.; Delsanti, M. Adv Polym Sci 1982, 7, 44.
- Geissler, E.; Hecht, A. M. Macromolecules 1980, 13, 1276.
- Zrinyi, M.; Horkay, F. J Polym Sci Polym Ed 1982, 20, 815.
- Tanaka, T.; Filmore, D. J Chem Phys 1979, 20, 1214.



12. Bastide, J.; DuOplessix, R.; Picot, C.; Candau, S. *Macromolecules* 1984, 17, 83.
13. Peters, A.; Candau, S. J. *Macromolecules* 1988, 21, 2278.
14. Wu, C.; Yan, C.-Y. *Macromolecules* 1994, 27, 4516.
15. Pekcan, Ö.; Yilmaz, Y. *Prog Coll Polym Sci* 1996, 102, 89.
16. Pekcan, Ö.; Yilmaz, Y. *Polymer* 1998, 39, 5351.
17. Pekcan, Ö.; Yilmaz, Y.; Uğur, Ş. *Polymer Int* 1997, 44, 447.
18. Pekcan, Ö.; Yilmaz, Y. *Applied Fluorescence in Chemistry, Biology and Medicine*; Rettig, W.; Strehnel, B.; Schrader, S., Eds.; Springer-Verlag: Berlin, 1999, p 331.
19. Hirokawa, Y.; Tanaka, T. *J Chem Phys* 1984, 81, 6379.
20. Hu, Y.; Horie, K.; Ushiki, H. *Macromolecules* 1992, 25, 6040.
21. Tanaka, T.; Sun, S. T.; Hrokawa, Y.; Katayama, S.; Kucera, J.; Hirose, Y.; Amiya, T. *Nature* 1987, 325, 796.
22. Tanaka, T. *Phys Rev Lett* 1978, 40, 820.
23. Ilavsky, M. *Macromolecules* 1982, 15, 782.
24. Patel, S. K.; Rodriguez, F.; Cohen, C. *Polymer* 1989, 30, 2198.
25. Dušek, K.; Prius, W. *Adv Polym Sci* 1969, 1, 6.
26. Silberger, A. In *Biological and Synthetic Networks*; Kramer, O., Ed.; Elsevier Applied Science: Amsterdam, 1988.
27. Bastide, J.; Leibler, L. *Macromolecules* 1988, 21, 2649.
28. Bastide, J.; Bove, F.; Busier, M. In *Molecular Basis of Polymer Networks*; Baumgartner, A.; Picot, C., Eds.; Springer Verlag: Berlin, 1989.
29. Hsu, T. P.; Ma, D. S.; Cohen, C. *Polymer* 1983, 24, 1273.
30. Pekcan, Ö.; Çatalgil-Giz, H.; Çalıřkan, M. *Polymer* 1998, 39, 4453.
31. Bastide, J.; Leibler, L.; Prost, J. *Macromolecules* 1990, 1821, 23.
32. Voyutsky, S. *Colloid Chemistry*; MIR Publisher: Moscow, 1978.