Drying of Heterogeneous Hydrogels Formed with Various Water Contents: A Photon Transmission Study

SELIM KARA,[1] ÖNDER PEKCAN[2]

[1] Department of Physics, Trakya University, 22030 Edirne, Turkey

[2] Department of Physics, Istanbul Technical University, Maslak 80626 Istanbul, Turkey

ABSTRACT: Drying of acrylamide (AAm) gels was monitored by using a photon transmission technique. These hydrogels are formed from AAm and N,N'-methylenebis(acrylamide) (Bis) with various water contents by the free-radical crosslinking copolymerization (FCC). The transmitted light intensity, I_{tr}, increased continuously as AAm gels were dried. The 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. A decrease in I_{sc} was modeled by using Rayleigh's equation where drying times with various exponents were found to be proportional to the size of the holes. It was observed that the radius of holes, ξ_c, decreased in various powers of the drying time depending on water content used during FCC. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1944–1951, 2001

Key words: frozen blobs; drying; transmitted light

INTRODUCTION

The swelling and drying kinetics of gels are very important in various fields of industry: in the pharmaceutical industry in designing slow-release devices for drugs; in the agricultural industry for producing storable foods; and in medical industry in developing artificial organs.

The swelling and shrinking kinetics were first predicted by Li and Tanaka by considering the osmotic pressure versus the restraining force[1] in chemically crosslinked gels. The total free energy of a chemical gel was described by bulk and shear energies in the swollen state. However, very little is known for the drying kinetics of chemical and physical gels. It was shown that the drying rate of thin-gelatin gel films in dry air increased with time[2] instead of a slow-down process expected in the gel-shrinking theory developed by Li and Tanaka.[1] These unexpected drying kinetics was attributed to the differences between the drying and shrinking processes and/or to the nature of gelatin gel formation.

The imperfections in the gel structures were known to influence the solvent permeability, the diffusion of small and large molecules, and more indirectly the swelling properties of gels. In the swollen state, these imperfections manifest themselves in a nonuniformity of polymer concentration. Considerable work was done on the characterization of the gel inhomogeneities. It was shown that high permeability of acrylamide gels is related to the inhomogeneous crosslink distribution.[3] The effect of inhomogeneities of the polymer network on the swollen state of acrylamide gels and on the diffusion of water molecules within the gels were examined.[4]

When an ionized acrylamide 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.[5] If acrylamide gels are swollen

in acetone–water mixture, gel-aging time plays an important role during collapse of the network.[6] The kinetics of swelling of acrylamide gels were studied by light scattering and the cooperative diffusion coefficient of the network was measured.[7,8] Small-angle X-ray and dynamic light scattering were used to study the swelling properties and mechanical behavior of acrylamide gels.[9,10] Photon transmission technique was used to study the existence of frozen blob clusters in acrylamide gels, which caused strong light scattering during swelling.[11] The same technique was recently used to study gelation processes of acrylamide where light scattering intensity increased during gel formation.[12–14]

In this article, *in situ* photon transmission experiments were reported during the drying of acrylamide (AAm) gels formed with various water 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 because of spatial inhomogeneities that disappear during the drying processes. I_{tr} intensities were measured by UV–visible (UV–Vis) spectrometric technique. Drying of AAm gels were monitored in real time by using the time-drive mode of the UV–Vis spectrometer. The decrease in I_{sc} against time was modeled by using Rayleigh's equation[15] and the frozen blob model.[16,17] It is observed that volume, ν, of holes shrink in time with various exponents depending on water contents used during FCC. The changes in I_{sc} were found to be inversely proportional to various powers of wavelength, λ, of incident light.

LIGHT SCATTERING

Light is scattered only when a light wavelength, λ, is greater than the size of a particle of the dispersed phase. If λ is much smaller than the particle diameter, light is reflected. If the intensity of incident 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[15]:

$$I_{sc} = I_o b v^2 \lambda^{-\eta} \tag{1}$$

Here $b = kc$, where k is related the indices of refraction of the dispersed phase and the dispersion medium. In other words, k is the measure of refractive index increment. This equation is valid for spherical particles which do not conduct electric current and are small in comparison with the wavelength, λ, of the incident light. ν presents the volume of a single particle and c is the numerical concentration of the scattered centers of the medium. Rayleigh's equation can be used for particles the size of which is not > 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 λ ($\eta = 4$). However, for larger particles, I_{sc} changes in inverse proportion to a smaller power of λ.

When the size of the particles in the dispersed medium becomes much greater than λ, light is no more scattered but reflected, regardless of the wavelength of the incident light. If the particles are too large in size (>70 nm), reflection of light from them increases, which causes the reduction of the intensity of scattered light. At the same time, as seen from eq. (1), the intensity of light scattering decreases as the particle size decreases. Therefore, dispersed medium scatters light to the greatest extent. In conclusion, Rayleigh's equation provides the following important information to be used: For a given concentration and wavelength, the intensity of scattered light is directly proportional to the volume of a particle. This principle can be used to determine the variation of the size of the dispersed phase by measuring I_{sc} in the system. However, because multiple scattering occurs at very high concentrations, precautions must be taken. At a given concentration and particle size, the variation in $\log \lambda$ against $\log I_{sc}$ can produce the exponent η, which can be used to predict the particle size.

FROZEN BLOB CLUSTERS

A gel can be describe as a 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.[18,19] In the swollen state of a gel, these crosslinks cannot move apart from each other, because 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. The random crosslinking of chains can be de-

(a)

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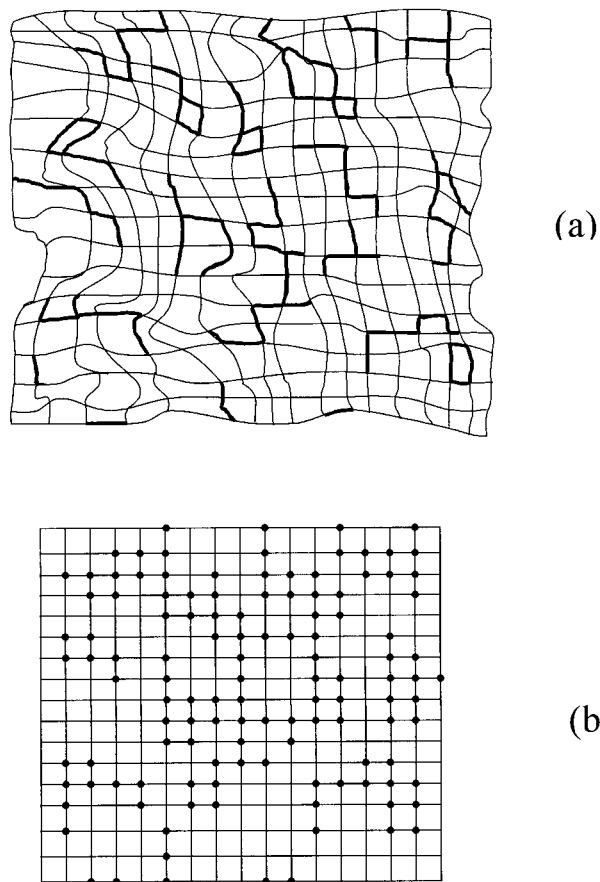
Figure 1 Schematic representation of a two-dimensional gel. (a) Swollen in good solvent. The clusters of first-neighbor junctions (frozen blobs), which do not swell, are represented by thick solid lines. (b) In dried state. Black dots represent the interchain crosslinks.

scribed as a site percolation on a blob lattice (i.e., the problem can be regarded as a site percolation on a lattice with a site having the blob size). 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 is randomized as the gel dries and shrinks. Figure 1(a,b) presents 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, ξ_c, is the typical size of clusters that are not entangled with smaller ones. In other words, ξ_c is the typical size of holes which are created as

a part of the interstitial medium. Shrinkage process during drying does resemble a random packing and rearrangement of Russian dols.[19] Because of polydispersity of clusters, one would expect a very strong dependence of ξ_c on shrinkage. The increase in scattering of light comes from the contrast between frozen blob clusters and holes created by dilution during swelling (i.e., the partial separation of frozen blob clusters during the dilution process leads to a strong increase in scattering intensity). However, during drying, the scattered light intensity decreases because of the decrease in contrast between frozen blob clusters and holes. The similar excess light scattering was observed during the stretching of a gel where the frozen blob clusters are diluted upon stretching, because they are expected to deform less than the interstitial medium.[16] In short, the change of concentration fluctuations cause an increase and/or a decrease in light scattering during the swelling and/or drying processes.

EXPERIMENTAL

Each gel was prepared by using 2.5 g of AAm and 40 mg of ammonium persulfate (APS) as an initiator by dissolving them in water into which 10 μL tetramethyl ethylenediamin was added as an accelerator. Methylenebis(acrylamide) (Bis) (150 mg) was used as a crosslinking agent. Six different gels were obtained by adding 15, 20, 25, 30, 35, and 45 mL water into the each of the samples prepared with the above procedure. Free-radical crosslinking copolymerization (FCC) was performed (for each sample) at room temperature in 1×1 cm quartz cells. Drying of gels was monitored in real time and *in situ* photon transmission measurements were performed by using a Perkin–Elmer UV–Vis spectrometer. Photon transmission intensities, I_{tr}, were measured by using the time-drive mode of the spectrometer during drying of gels at five different wavelengths (440, 500, 550, 600, and 690 nm). Typical I_{tr} curves against drying time are given in Figure 2 for the experiments made at 550-nm wavelength for six different water-content samples. In Figure 3, I_{tr} curves at various wavelengths are compared for 30-ml water-content sample. 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 25-mL water-content samples, gels present high-lattice heterogeneities that disappear due to dry-
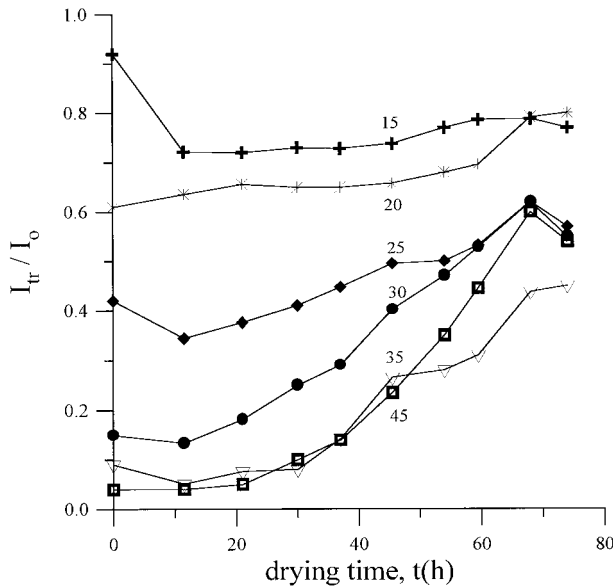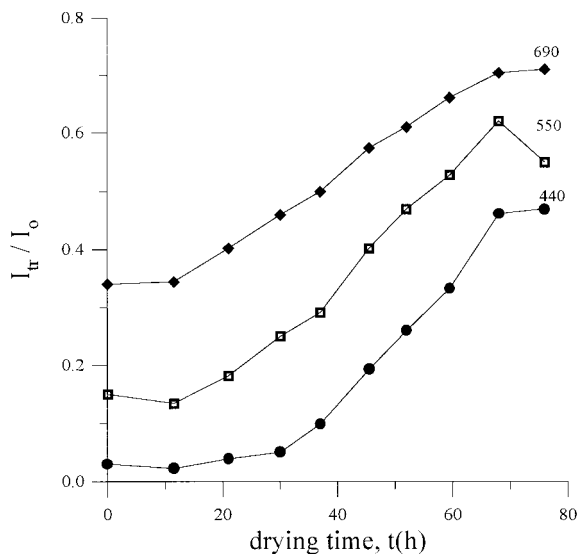
Figure 2 Variation in transmitted photon intensities, I_{tr}, versus drying time, t, during *in situ* drying experiments in six different water contents for 550-nm wavelength. Numbers on each curve present the water content in milliliters.

ing process; however, 15- and 20-mL water-content gels present no lattice heterogeneities.

RESULTS AND DISCUSSION

The results in Figures 2 and 3 can be interpreted by employing eq. (1), where it can be assumed

Figure 3 Variation in transmitted photon intensities, I_{tr}, versus drying time, t, during *in situ* drying experiments at different wavelengths for 30-mL water-content sample. Numbers on each curve indicate the wavelength of the transmitted light.
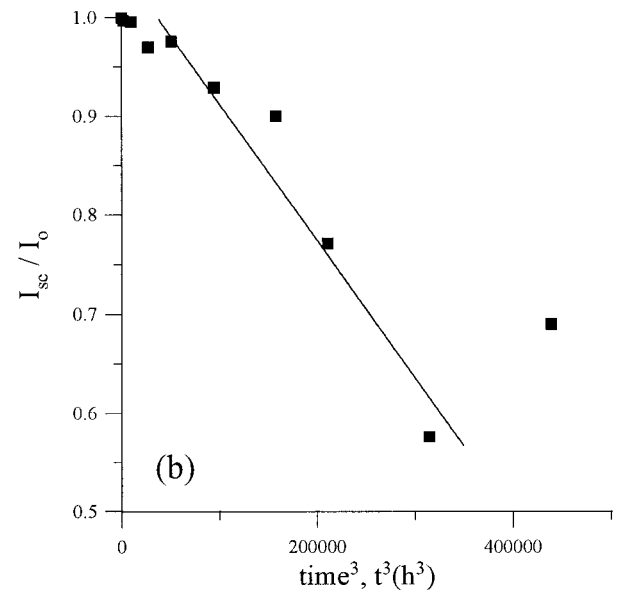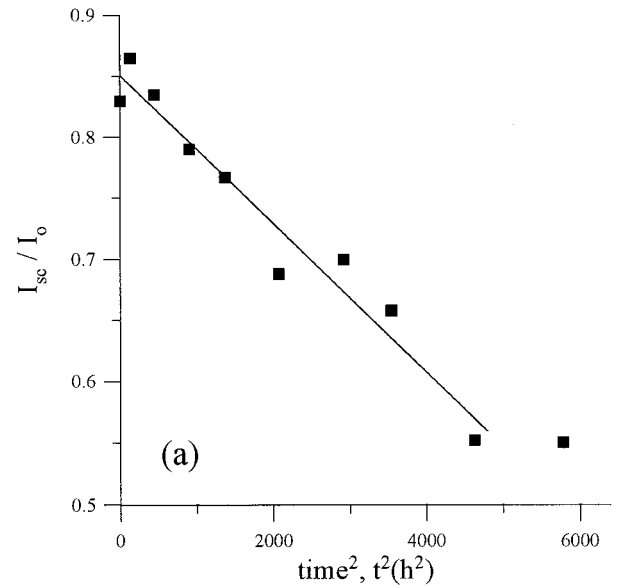
Figure 4 Variation in the scattered light intensity, I_{sc}, at 440 nm versus t^2 and t^3 during *in situ* drying experiments for (a) 25- and (b) 35-mL water-content samples, respectively.

that the increase in I_{tr} during drying solely originates from the decrease in scattering intensity, I_{sc}. In Figure 4(a,b) normalized $I_{sc} = (I - I_{tr})$ intensities are plotted versus t^2 and t^3 at the 440-nm wavelength drying experiments for the samples prepared with 25- and 35-mL water contents, respectively. It is seen in Figure 4 that I_{sc} presents a nice linear decrease by indicating that the hydrogel system scatters less light by presenting less turbidity during drying. These results can

Table I   Decrease in Correlation Length, ξ_c, of Various Gels Made in Different Water Contents

Water (cc)	15	20	25	30	35	45
ξ_c	$t^{1/6}$	$t^{1/6}$	$t^{1/3}$	$t^{1/2}$	$t^{1/2}$	$t^{1/2}$

be modeled by knowing that the randomness of the frozen blob clusters increases as the gel dries (i.e., when the gel dries, it presents more homogeneous structure and scatters less light).

If the holes are assumed to be spherical in volume with

$$v = \frac{4\pi}{3}\,\xi_c^3 \tag{2}$$

then eq. (1) becomes

$$I_{sc} = I_o a (\xi_c^3)^2 \tag{3}$$

where $a = b\lambda^{-\eta}(4\pi/3)^2$. Decrease in I_{sc} in Figure 4 predicts that ξ_c shrinks during drying with a certain exponent of time. Other gels present similar behavior dependent on the water content used to prepare the gel sample. For example, samples prepared with 25- and 35-mL water contents dry in time with $t^{1/3}$ and $t^{1/2}$. Similar plots are made for other samples and produced results are listed in Table I, according to following relation

$$\xi_c = bt^{n/6} \tag{4}$$

where b is the related constant and $n = 1, 2, 3$. It is seen in Table I that in the samples prepared with lower and higher water content, gels dry with different powers of time. The power of t may present a model for drying; for instance, gels prepared with 30-, 35-, and 45-mL water contents dry as in Fickian type of diffusion; then b in eq. (4) should be related to the self-diffusion coefficient, D for the frozen blob clusters. In other words, the correlation length, ξ_c, shrinks with the following law:

$$\xi_c = (Dt)^{1/2} \tag{5}$$

for the high water content gels. These gels present lower concentration fluctuations upon drying (i.e., lattice heterogeneities disappear during drying of these gels). On the other hand, gels

prepared with low water content (15 and 20 mL) dry with one-sixth the power of time and present almost no change in lattice inhomogeneities. Most probably these gels have quite homogeneous lattice structures, which present no concentration fluctuations during drying process. The gel prepared with 25-mL water content dries with one-third the power of time and presents intermediate-level heterogeneities in its lattice structure. Here, it is interesting to note that gels prepared with low water content dry much slower than high water gels (i.e., densely formed gels dry much slower than loosely formed gels, which is expected). Because dense gels can keep the water droplets inside the gel for larger times, as a result, slow drying of dense gels follow non-Fickian behavior. However, loose gels dry faster by obeying Fickian law.

Figure 5 presents the log I_{sc} versus log λ plot for 25-mL water-content sample at a drying time of 11 h, where the slope of the linear relation produces an η value from eq. (1). Similar plots are obtained at other drying times and for various water-content samples. The observed η values for all gel samples are listed in Table II, where it is seen that exponent η is much lower than 4, which predicts that the radius of the holes, (ξ_c), are much larger than 70 nm, which is the upper limit to use the Rayleigh equation.

Here, as a control experiment, the gel samples are weighed during the drying processes. The
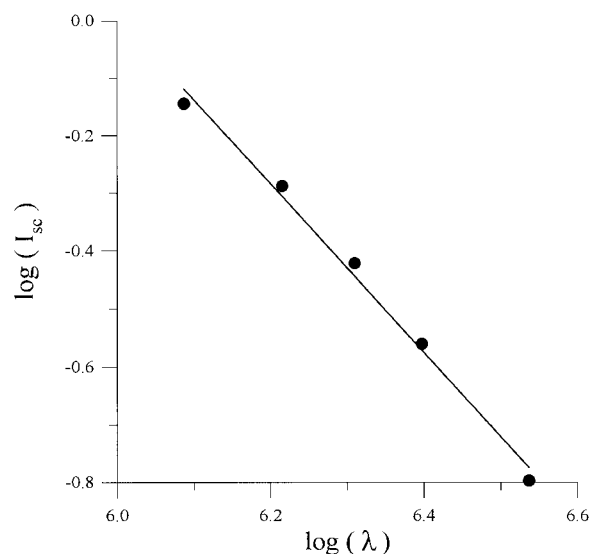
Figure 5   log–log plots of I_{sc} versus λ for 25-mL water-content sample at the drying time of 11 h. Slope of the curve produces η value.

Table II   Experimentally Produced η Values at Different Drying Times for Various Gels Made in Different Water Contents

| Water Content (cc)	η Values for Different Drying Times (h)									
	0	11	21	30	37	45	52	59	68	76
15	2.28	1.18	1.35	1.49	1.36	1.20	1.08	1.14	0.74	0.97
20	1.63	1.41	1.58	1.54	1.39	1.37	1.38	1.41	1.35	0.93
25	2.04	1.45	1.47	1.47	1.55	1.49	1.43	1.45	1.54	1.44
30	0.88	0.88	1.05	1.28	1.31	1.42	1.42	1.50	1.31	1.20
35	0.50	0.43	0.50	0.62	0.91	1.04	1.46	1.53	1.47	1.30
45	0.55	0.48	0.64	0.64	0.73	0.91	0.96	0.89	0.80	1.18

plots of weights versus drying times for the gel samples are shown in Figure 6, where it is seen that all samples dry in a similar way. This behavior of drying predicts that water loss of gels obeys a different law than the shrinkage of frozen blob clusters. In other words, variation in lattice heterogeneities can be detected by using the transmitted light intensity from the drying gels; on the other hand, simple weight measurements can only determine water loss of drying gels.
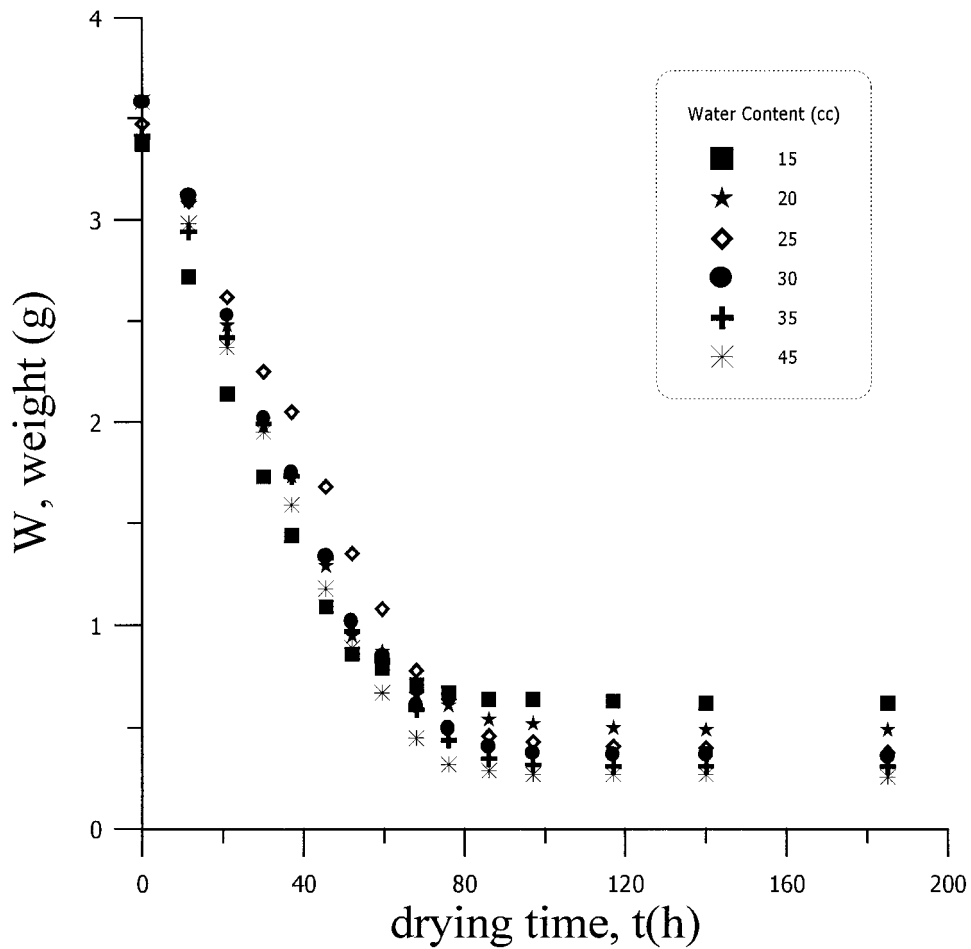
Figure 6   The plots of W, weights versus drying times for 15-, 20-, 25-, 30-, 35-, and 45-mL water-content gel samples.
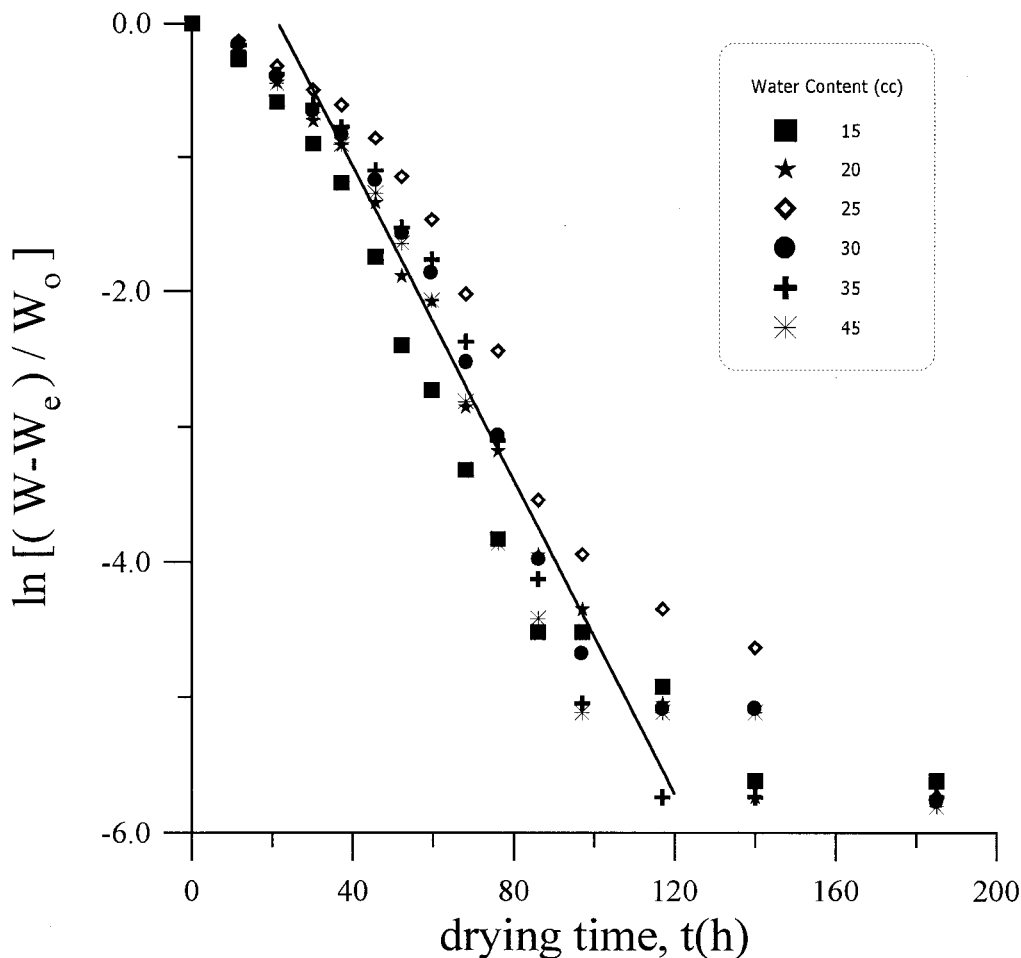
Figure 7   The fit of the data to eq. (6) for 30-mL water-content gel sample. Slope of the curve produces the τ value.

The data in Figure 6 are fitted to the following equation

$$W = W_e + W_o e^{-t/\tau} \qquad (6)$$

where W and $W_e + W_0$ are the weight of the gel at time t and at time zero. W_e is the weight of gel after the drying process is completed and W_0 is the water uptake by the gel. Here one can argue that eq. (6) is the reverse of the solvent uptake equation of Li and Tanaka.[1] Now τ can be named as the time constant for the drying process. Here the nature of drying is much different from the swelling processes; however, eq. (6) may predict that elasticity (shear modulus) is also the critical parameter for the drying process. The fit of the data for the gel prepared with 30-mL water content to eq. (6) is shown in Figure 7, where the slope of the linear relation produces the τ value.

Similar fits are done for the other gel samples and the results are listed in Table III for the gels prepared with different water contents. Table III shows that all gels regardless of water content dry with same rate. Here one may compare the eqs. (4) and (6) and can make a statement that gels with different lattice heterogeneities can dry at the same time. By using the estimated values of ξ_c (200 nm) and the measured time constant, τ (35 h), the self-diffusion coefficient, D, for the frozen blob cluster can be calculated and found to

Table III   Drying Time Constants, τ, of Various Gels Made in Different Water Contents

Water (cc)	15	20	25	30	35	45
τ (h)	15.9	16.0	15.1	14.4	14.5	13.7

be around 10^{-15} cm^2 s^{-1}. The estimated value of D predicts that holes show very slow shrinkage during the drying process. In other words, motion of lattice point in a drying gel is as slow as diffusing of a chain in bulk above the glass transition.[20,21] Most probably when the gel dries, it goes through its glass transition point.

CONCLUSION

This article presented interesting data and a different point of view for the drying processes in acrylamide gels. Variation in I_{tr} from the gels prepared with 25-, 30-, 35-, and 45-mL water contents presented strong evidence for the existence of lattice inhomogeneities, which result in the change in concentration fluctuations during the drying processes. Inclusion of 25-, 30-, 35-, and 45-mL water during FCC produced more lattice inhomogeneities because of high dilution than the gels that contain 15 and 25 mL water, which presented quite homogeneous lattice structure. High and low water contents used to prepare gels affect drying (i.e., different powers of times were measured during drying of densely and loosely formed gels). Here the exponents are important to predict the rate of shrinkage of holes in the lattice. The size (ξ_c) and the shrinkage rate (D) of the holes are estimated.

REFERENCES

1. Li, Y.; Tanaka, T. J Chem Phys 1990, 92, 1365.
2. Wu, C.; Yang, C. Y. Macromolecules 1994, 27, 4516.
3. Weiss, N.; van Vliet, T.; Silberger, A. J Polym Sci, Polym Phys Ed 1974, 17, 2229.
4. Hsu, T. P.; Ma, D. S.; Cohen, C. Polymer 1983, 24, 1273.
5. Tanaka, T.; Sun, S. T.; Hirokawa, Y.; Katayama, S.; Kucera, J.; Hirose, Y.; Amiya, T. Nature 1987, 325, 796.
6. Tanaka, T. Phys Rev Lett 1978, 40, 820.
7. Tanaka, T.; Filmore, D. J Chem Phys 1979, 20, 1214.
8. Bastide, J.; Duoplessix, R.; Picot, C.; Candau, S. Macromolecules 1984, 17, 83.
9. Ilavsky, M. Macromolecules 1982, 15, 782.
10. Patel, S. K.; Rodriguez, F.; Cohen, C. Polymer 1989, 30, 2198.
11. Pekcan, Ö.; Çatalgil-Giz, H.; Çalışkan, M. Polymer 1998, 39, 4453.
12. Kara, S.; Pekcan, Ö. Polym Commun 2000, 41, 3093.
13. Kara, S.; Pekcan, Ö. Polymer 2001, 42, 7411.
14. Kara,S.; Pekcan, Ö. J Appl Polym Sci 2001, 80, 823.
15. Voyutsky, S. Colloid Chemistry; MIR: Moscow, 1978.
16. Bastide, J.; Leibler, L.; Prost, J. Macromolecules 1990, 1821, 23.
17. Doud, M.; Leibler, L. Macromolecules 1988, 21, 1497.
18. Bastide, J.; Leibler, L. Macromolecules 1988, 21, 2649.
19. Bastide, J.; Bove,F.; Busier, M. In Molecular Basis of Polymer Networks; Baumgartner, A.; Picot, C., Eds., Springer–Verlag: Berlin, 1989.
20. Pekcan, Ö. Trends Polym Sci 1994, 2, 237.
21. Canpolat, M.; Pekcan, Ö. Polymer 1997, 38, 2595.