Swelling Activation Energy of κ-Carrageenan in Its Gel State: A Fluorescence Study

Ö. Tarı,[1] Ö. Pekcan[2]

[1]*Department of Physics, Istanbul Technical University, Maslak, 34469 Istanbul, Turkey*
[2]*Department of Physics, Işık University, Kumbaba, Şile, Istanbul, Turkey*

Received 11 January 2007; accepted 17 May 2007
DOI 10.1002/app.26980
Published online 7 September 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A steady-state fluorescence technique was employed to study the swelling of κ-carrageenan gels at various temperatures. Pyranine was used as a fluorescence probe. The fluorescence intensity of pyranine was measured during the *in situ* swelling process of κ-carrageenan gels. The fluorescence intensity increased exponentially as the swelling time increased. The increase in the fluorescence intensity was modeled with the Li–Tanaka equation, from which the swelling time constants and cooperative diffusion coefficients were determined. The swelling time constants decreased and the cooperative diffusion coefficients increased as the swelling temperature was increased. The swelling activation energies were measured to be 47.05 kJ/mol. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 4164–4168, 2007

Key words: activation energy; fluorescence; swelling

INTRODUCTION

The swelling, shrinking, and drying kinetics of physical and chemical gels are very important in many technological applications, especially in the pharmaceutical industry for the design of slow-release devices for oral drugs, in the agricultural industry for the production of storable foods; and in medical applications for the development of artificial organs. Understanding the mechanism of the swelling, shrinking, and drying kinetics is highly desirable for the use of cosmetics ingredients.

In cosmetic applications, preserving moisture in hand lotions is quite important for keeping skin softer. Because carrageenan is used as a filler in both drugs and foods, the slow-release and storage processes are strongly correlated with the swelling and drying mechanisms of these systems, respectively.

The elastic and swelling properties of permanent networks can be understood by the consideration of two opposing effects: the osmotic pressure and the restraining force.[1,2] The total free energy of a chemically crosslinked network can be separated into two terms: the bulk and shear energies.[3] In a swollen network, the bulk free energy can be characterized by the osmotic bulk modulus, which is defined in terms of the swelling pressure and the volume fraction of the polymer at a given temperature. On the other hand, the shear energy, which keeps the gel in shape, can be characterized by the shear modulus. Here the shear energy minimizes the nonisotropic deformations in the gel. The characteristic coefficient of these forces is the shear modulus, which can be most directly evaluated by stress–strain measurements.[1,2]

The theory of the kinetics of swelling for a spherical chemical gel was first developed by Tanaka and Fillmore.[4] They assumed that the shear modulus is negligible in comparison with the osmotic bulk modulus. However, several studies have shown that the shear modulus has the same order of magnitude as the osmotic bulk modulus.[5,6] Later, Peters and Candau[7] derived a model for the kinetics of swelling of spheres, cylinders, and disks made of polymer gels by assuming a nonnegligible shear modulus. Li and Tanaka[8] developed a model in which the shear modulus plays an important role, keeping the gel in shape because of the coupling of any change in different directions. This model predicts that the geometry of the gel is an important factor and that swelling is not a pure diffusion process.

Several experimental techniques have been employed to study the kinetics of swelling, shrinking, and drying for chemical and physical gels, such as neutron scattering,[9] quasielastic light scattering,[7] macroscopic experiments,[3] and *in situ* interferometric measurements.[10] The steady-state fluorescence technique has been used to study the drying and swelling kinetics of disc-shaped gels.[11–13] The modeling of swelling with a fast transient technique has already been reported by our group.[14,15]

In this work, we studied the swelling process of κ-carrageenan gels at various temperatures by using a steady-state fluorescence technique. The κ-carrageenan gels were completely dried and then swelled in water vapor. The Li–Tanaka equation was used to determine the swelling time constant (τ_c) and coopera-

Correspondence to: Ö. Pekcan (pekcan@isikun.edu.tr).

Journal of Applied Polymer Science, Vol. 106, 4164–4168 (2007)
©2007 Wiley Periodicals, Inc.

tive diffusion coefficient (D_c) for the swelling processes. τ_c decreased and D_c increased from 2.2 to 11.4 $\times 10^{-7}$ cm^2/s as the swelling temperature increased from 30 to 60°C. The activation energies were measured from the intensity measurements and found to be 47.05 kJ/mol. The swelling of the carrageenan gels in pure water and in a KCl solution was studied with a photon transmission technique. The collective diffusion coefficient was found to be around 10^{-5} cm^2/s.[16] The difference between the literature values and our findings most likely originated from the differences between the solvent and vapor penetration processes.

THEORETICAL

The equation for the swelling and shrinking of a gel disk, as expressed by Li and Tanaka,[8] is as follows:

$$\frac{u(r,t)}{u(r,0)} = \sum_n B_n \exp(-t/\tau_n) \quad (1)$$

where $u(r,0)$ is total change of radius, t is the time, $u(r,t)$ is the displacement vector of a point in the network from its final equilibrium location after the gel is fully swollen and B_n is pre-exponential factor. The displacement vector is expressed as decomposition into components, each of them decaying exponentially with a time constant (τ_n). The first term of the expansion is dominant at large t, that is, at the last stage of swelling. Equation (1) can also be written in terms of the solvent uptakes at time t and at equilibrium (W and W_∞, respectively) as follows:

$$\frac{W_\infty - W}{W_\infty} = \sum_{n=1}^{\infty} B_n \exp(-t/\tau_n) \quad (2)$$

In the limit of large t or if τ_1 is much greater than the rest of the τ_n values, all higher terms ($n \geq 2$) in eq. (2) can be omitted, so the swelling kinetics can be given by the following relation:

$$\left(1 - \frac{W}{W_\infty}\right) = B_1 \exp(-t/\tau_1) \quad (3)$$

where B_1 is related to the ratio of the shear modulus (G) to the longitudinal osmotic modulus [$M = (K + 4G/3)$, where K is the osmotic bulk modulus]. Once the value of B_1 is obtained, one can determine the value of $R = G/M$ because the dependence of B_1 and R for a disk can be found in ref. 8. τ_1 is related to D_c of a gel disk as follows:

$$D_c = \frac{3a_\infty^2}{\tau_1 \alpha_1^2} \quad (4)$$

where α_1 is a function of R only (given in ref. 17) and α_∞ is the half-thickness of the gel in the final equilibrium state. Once the quantities τ_1 and B_1 are obtained, R, α_1, and D_c can be calculated. Figure 1 shows the dependence of B_1 on R for disk-shaped gels according to ref. 8.

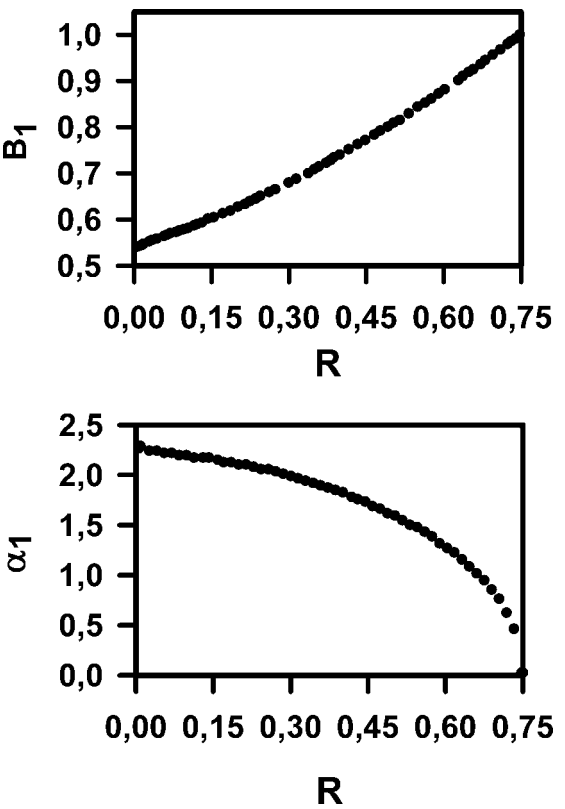

Figure 1 Relationships between B_1 and R and between α_1 and R. The plots are taken from ref. 8. (Reprinted with permission from Erdogan et al.[20] © 2002 Society Chemical Industry).

EXPERIMENTAL

Carrageenan (Sigma, St. Louis, MO) at a 3 wt % concentration and pyranine were dissolved in distilled water (pH 6.5) at the desired concentration by heating. The pyranine concentration was kept at $4 \times 10^{-4}M$, which was low enough to ensure that any excitation transfer effects were negligible. The heated carrageenan solution was held at 80°C and was continuously stirred with a magnetic stirrer. This solution was cooled to room temperature. These gels were completely dried at 30, 40, 50, and 60°C before the swelling measurements started. The swelling experiments of the κ-carrageenan gels were performed at 30, 40, 50, and 60°C.

The fluorescence intensity measurements were carried out with a PerkinElmer LS-50 model spectrometer (Beaconsfield, Buckinghamshire, England) equipped with a temperature controller. All measurements were made in the 90° position, and the slit widths were kept at 5 nm. Pyranine was excited at 460 nm during *in situ* experiments, and the emission intensities of pyranine were monitored at 515 nm as a function of the swelling time. At each temperature, the disc-shaped gel samples were placed in the wall of a 1 × 1 quartz cell saturated with vapor for the swelling experiments. The positions of the gel and the incident light beam

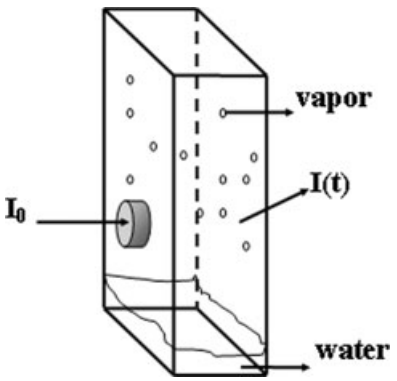

Figure 2 Position of the κ-carrageenan gel in the fluorescence cell during swelling in water vapor. I_0 and $I(t)$ are the excitation and emission intensities at 460 and 515 nm, respectively.

for the fluorescence measurements during the swelling in water vapor are shown in Figure 2.

RESULTS AND DISCUSSION

Typical fluorescence spectra from pyranine in carrageenan placed in vapor at various times are presented in Figure 3.

Figure 4 shows that the shape of the fluorescence spectra does not change during swelling; that is, no broadening or spectral shift can be observed. Here we can rule out the solvatochromic effect during the swelling process, which can be expected from the change in the local environment and its effect on the electronic, absorption, and emission spectra of pyranine during the vapor uptake process.[18]

Plots of the fluorescence intensity (I) and scattered light intensity (I_{sc}) versus time during the swelling of κ-carrageenan gels at various temperatures are presented in Figures 4 and 5, respectively. I increases but I_{sc} decreases during swelling. Because the transmitted light intensity ($I_{tr} = 1 - I_{sc}$) increases, the gel becomes transparent; as a result, I increases.

Here, because swelling occurs in the gel state of carrageenan, we have to assume that pyranine molecules

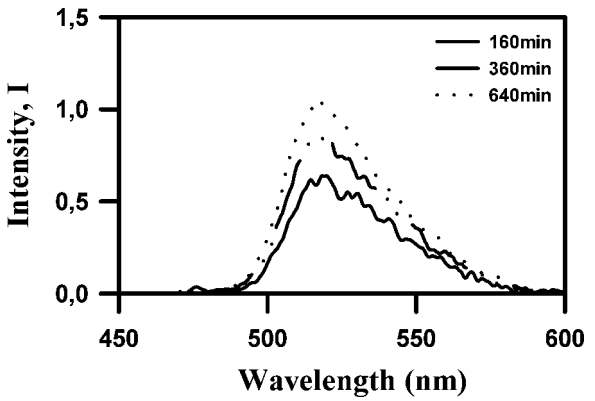

Figure 3 Fluorescence spectra of pyranine in carrageenan placed in vapor at 30°C.

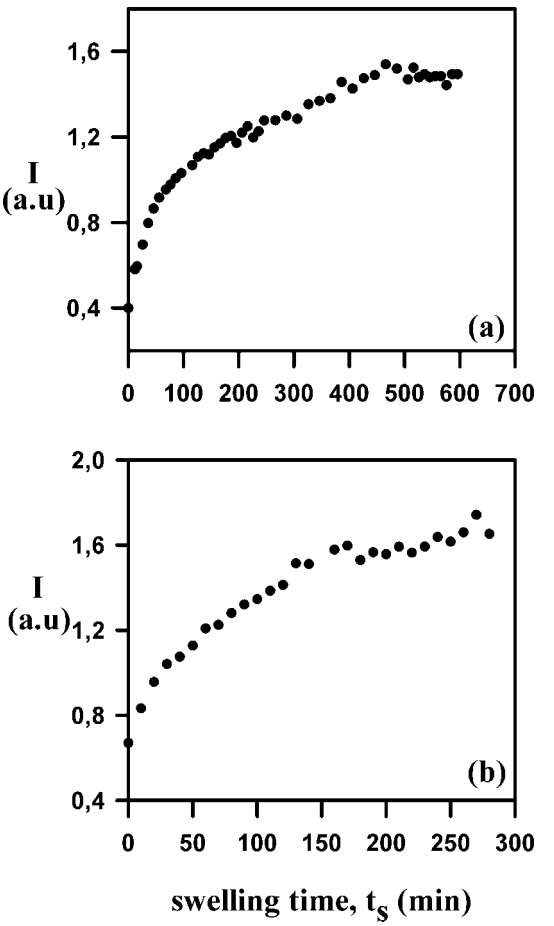

Figure 4 I for pyranine versus t_s at (a) 40 and (b) 50°C.

are embedded in the helices, so no quenching of fluorescence can take place.

In the equilibrium state of swelling, I reaches I_∞, at which the vapor uptake is W_∞. The relation between vapor uptake W and I is then given by

$$\frac{W}{W_\infty} = \frac{I}{I_\infty} \tag{5}$$

This relation predicts that as W increases, I will increase. Combining eq. (5) with eq. (3) and calculating their logarithm, we can obtain the following relation:

$$\ln\left(1 - \frac{I}{I_\infty}\right) = \ln B_1 - \frac{t_s}{\tau_1} \tag{6}$$

where $t = t_s$ is taken from eq. (3) to present the swelling time (t_s) in eq. (6). Logarithmic plots of $\left(1 - \frac{I}{I_\infty}\right)$ are presented in Figure 6. The linear regression of the curves in Figure 6 provides us with the B_1 and τ_1 values from eq. (6). Taking into account the dependence of B_1 on R, we can obtain R values, and from the α_1–R dependence, α_1 values can be produced[8] (see Fig. 1). Then, with eq. (4) D_c can be determined for these disc-shaped carrageenan gels. Experimentally obtained τ_1

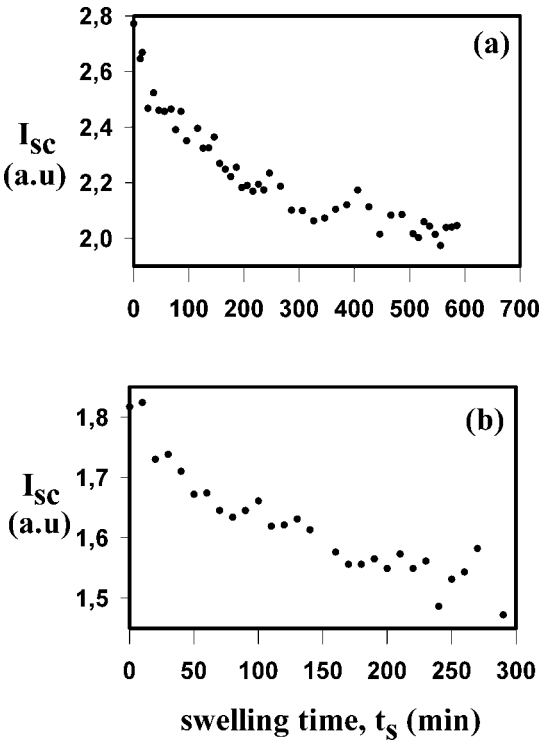

Figure 5 I_{sc} for pyranine versus t_s at (a) 40 and (b) 50°C.

and D_c values for κ-carrageenan gels at various temperatures are presented in Table I, where a_i and a_∞ are the half-thickness and m_i and m_∞ are the weights of

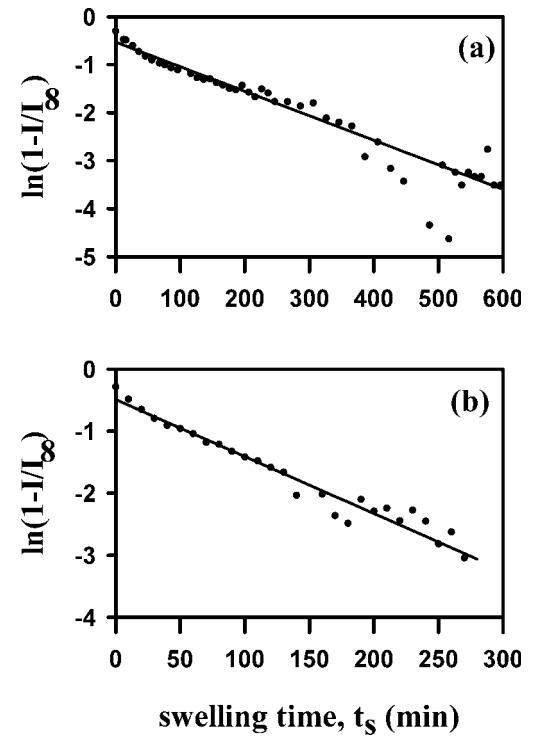

Figure 6 Logarithmic plots of normalized I according to eq. (6) for κ-carrageenan gels swelling in water vapor at (a) 40 and (b) 50°C.

TABLE I
Experimentally Determined Swelling Parameters of κ-Carrageenan Gels During Swelling in Vapor

	Temperature			
Gel property	30°C	40°C	50°C	60°C
a_i (mm)	0.23	0.35	0.4	0.45
a_∞ (mm)	0.8	0.8	0.85	0.95
$m_i \times 10^{-3}$ (g)	10.8	10.4	10.2	8.5
$m_\infty \times 10^{-3}$ (g)	30	32.7	33.2	56.2
τ_1 (min)	298	195	108	86
$D_c \times 10^{-7}$ (cm^2/s)	2.24	3.43	7.22	11.41

the gels before and after the swelling process, respectively. As the temperature is increased, τ_1 decreases, as expected; that is, the time for the network homogenization decreases as the temperature is increased. Here we note that a decrease in I_{sc} (an increase in I_{tr}) may correspond to homogenization of the gel network, which produces high transparency.

Plots of τ_1 and D_c versus temperature T are shown in Figure 7. The behavior of D_c versus T predicts that gel segments (helices) will move much faster at higher temperatures during vapor penetration. On the other hand, D_c increases as the temperature is increased, and this predicts that the D_c–T relation may obey the following Arrhenius law:

$$D_c = D_{co} \exp(-\Delta E/kT) \tag{7}$$

where ΔE is the activation energy of swelling, k is Boltzmann's constant, and D_{co} is the cooperative diffu-

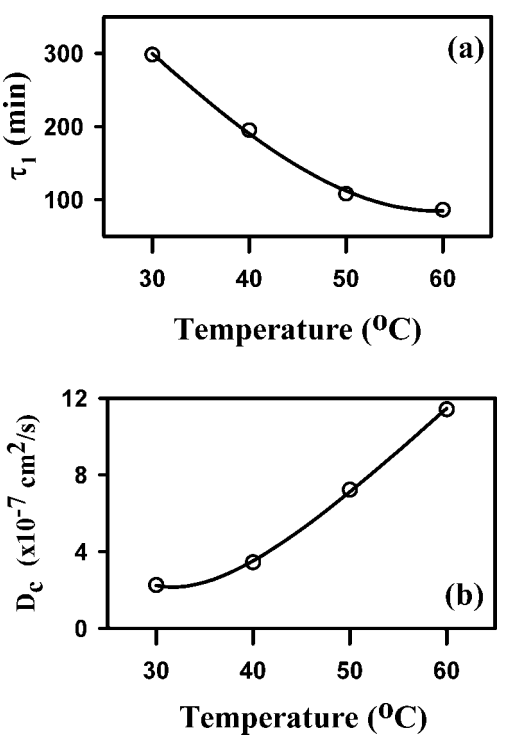

Figure 7 Plots of (a) τ_1 and (b) D_c versus the temperature.

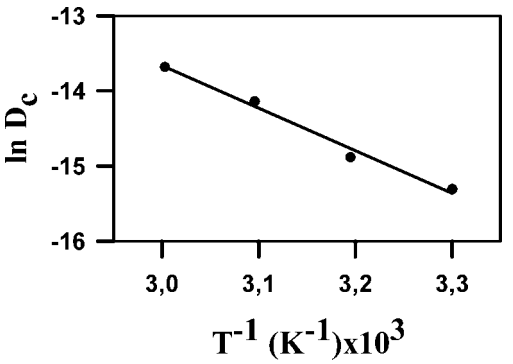

Figure 8 Logarithmic plot of D_c versus T^{-1} according to eq. (7). The slope of the linear relation produces ΔE for the swelling process.

sion coefficient at $T = \infty$. The logarithmic form of D_c is plotted versus t^{-1} in Figure 8, in which the slope of the linear relation produces $\Delta E = 47.05$ kJ/mol for the swelling gel. This value can be compared with our previous findings,[19] in which a polystyrene (PS) gel was swollen in chloroform vapor. The observed value (80 kJ/mol) was found to be two times larger than our recent observation. Here one could argue that the penetration of water molecules into a carrageenan gel needs much less energy than chloroform molecules penetrating a PS gel. Most likely, the elastic forces in the PS gel network oppose the penetrating chloroform molecules more strongly than they do in a carrageenan gel's helical network, which may have less resistance against water molecules.

CONCLUSIONS

The results presented in this article show that the fluorescence method can be used to measure τ_1 and D_c at a molecular level during the swelling of a carrageenan gel in vapor. The Li–Tanaka model has been used to measure these parameters. It has been observed that τ_1 decreases and D_c increases as the swelling temperature is increased.

References

1. Dusek, K.; Prins, W. Adv Polym Sci 1969, 6, 1.
2. Candau, S.; Bastide, J.; Delsanti, M. Adv Polym Sci 1982, 7, 44.
3. Zrinyi, M.; Rosta, J.; Horkay, F. Macromolecules 1993, 26, 3097.
4. Tanaka, T.; Fillmore, D. J Chem Phys 1979, 20, 1214.
5. Zrinyi, M.; Horkay, F. J Polym Sci Polym Phys Ed 1982, 20, 815.
6. Geissler, E.; Hecht, A.-M. Macromolecules 1981, 14, 185.
7. Peters, A.; Candau, S. J. Macromolecules 1988, 21, 2278.
8. Li, Y.; Tanaka, T. J Chem Phys 1990, 92, 1365.
9. Bastide, J.; Duoplessix, R.; Picot, C.; Candau, S. Macromolecules 1984, 17, 83.
10. Wu, C.; Yan, C. Y. Macromolecules 1994, 27, 4516.
11. Pekcan, Ö.; Yılmaz, Y. Prog Colloid Polym Sci 1996, 102, 89.
12. Pekcan, Ö.; Yılmaz, Y. Polymer 1998, 39, 5351.
13. Erdogan, M.; Pekcan, Ö. J Polym Sci Part B: Polym Phys 2000, 38, 739.
14. Pekcan, Ö.; Kaya, D.; Erdogan, M. Polymer 2000, 41, 1571.
15. Pekcan, Ö.; Kaya, D.; Erdogan, M. J Appl Polym Sci 2000, 76, 1494.
16. Kara, S.; Tamerler, C.; Pekcan, Ö. Biopolymers 2003, 70, 240.
17. Peters, A.; Candau, S. J. Macromolecules 1986, 19, 1952.
18. Shiftan, N. B.; Brauer, B.; Pines, E. J Phys Org Chem 1998, 11, 743.
19. Erdogan, M.; Pekcan, O. Polymer 2004, 45, 2551.
20. Erdogan, M.; Yonel, B.; Pekcan, O. Polym Int 2002, 51, 757.