Studies on the Swelling and Shrinking Kinetics of Chemically Cross-Linked Disk-Shaped Poly(vinyl acetate) Gels

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ABSTRACT: The kinetics of swelling and shrinking of disk-shaped poly(vinyl acetate) networks swollen in isopropyl alcohol is measured at different temperatures. The cooperative diffusion coefficient and the ratio of the shear modulus over the longitudinal osmotic modulus have been determined by using a theory developed by Li and Tanaka. The macroscopic swelling and deswelling experiments show good agreement with other experimental results as well as with the theoretical predictions.

Introduction

The elastic and swelling properties of permanent networks can be understood by considering two opposing effects, the osmotic pressure and the restraining force.[1,2] In general, the total free energy of a chemically cross-linked 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_{os}, defined as

$$K_{os} = \Phi\left(\frac{\partial \omega}{\partial \Phi}\right)_T \qquad (1)$$

where Φ is the volume fraction of the polymer in the gel, ω is the swelling pressure, and T stands for the temperature.

The other important energy, the shear energy, keeps the gel in shape by minimizing the nonisotropic deformation. The characteristic coefficient of these forces is the shear modulus, G, which can be most directly evaluated by stress–strain measurements.[1,2]

The longitudinal osmotic modulus, M_{os}, is a combination of shear and osmotic bulk moduli:[2–6]

$$M_{os} = K_{os} + {}^4/_3 G \qquad (2)$$

Light scattering probes longitudinal modes which involve changes in local concentration of the network. This process is controlled by the longitudinal osmotic modulus; thus M_{os} can be obtained by quasielastic light scattering experiments.[2,6,7]

It is useful to introduce the ratio of the shear and the longitudinal osmotic modulus:

$$R = G/M_{os} \qquad (3)$$

Since both G and K_{os} scale with the equilibrium concentration, Φ_e, in the same way ($G \sim \Phi_e^m$, $K_{os} \sim \Phi_e^m$, where the quantity m is determined by the excluded volume exponent only[2–6]), the ratio R does not depend on the equilibrium concentration. According to theory, R is independent of molecular details and is determined by the quality of the swelling agent only.[8–10] Besides mechanical, swelling pressure, and light scattering measurements, it is possible to obtain R from the kinetics of the volume change of gels.[11–14]

In this article an attempt is made to determine the cooperative diffusion coefficient of the network chains as well as the value of R by measuring the kinetics of both swelling and shrinking. The effect of solvent quality—altered by changing the temperature—is the main subject of this work. The results are discussed on the basis of thermodynamics of swelling.

Kinetics of Swelling and Shrinking

The theory of kinetics of swelling of a cross-linked polymeric network was first derived by Tanaka and Fillmore for spherical gel samples.[11] They assumed that the shear modulus is negligible compared to the osmotic compressional modulus. This is the case for polymer melts, where $G/K_{os} \sim 10^{-4}$. However, several studies have shown that the shear modulus is the same order of magnitude as the osmotic compressional modulus.[4,10] Peters and Candau developed a model with nonnegligible shear modulus to characterize the kinetics of swelling of spheres, cylinders, and disks made of polymer gels.[12] Recently, Li and Tanaka proposed a two-process mechanism based on the assumption that neither gel swelling nor shrinking is a pure diffusion process.[13] The shear modulus plays an important role: it keeps the system in shape due to coupling of any change in different directions. As a result of this, the geometry of the gel plays an important role.

The equation for swelling and shrinking of a gel disk as expressed by Li and Tanaka is given by

$$\frac{u(r,t)}{u(r,0)} = \sum_n B_n \exp[-t/\tau_n] \qquad (4)$$

where t denotes the time and $u(r,t)$ is the displacement vector of a point in the network from its final equilibrium location after the gel is fully swollen ($u = 0$ at $t = \infty$). The displacement vector is expressed as a decomposition into components, each of them decaying exponentially with a time constant τ_n. In eq 4 B_n is predicted to be a function of R only. The series given by eq 4 is convergent. The first term of the expansion is dominant at large t, that is, at the last stage of swelling. Therefore kinetics of swelling or shrinking experiments in the limit of large t allows us to determine the parameters B_1 and τ_1. By considering the movement of the surface, that is, setting $r = a$ (a is the radius of the gel disk) in eq 4, one obtains the long-time deformation of the free surfaces:

$$\ln \frac{u(a,t)}{u(a,0)} = \ln B_1 - t/\tau_1 \qquad (5)$$

Thus eq 5 can be used for the determination of B_1 from the short-time linear extrapolation of the logarithmic plot (intercept) and τ_1 from the slope of the dependence. Once

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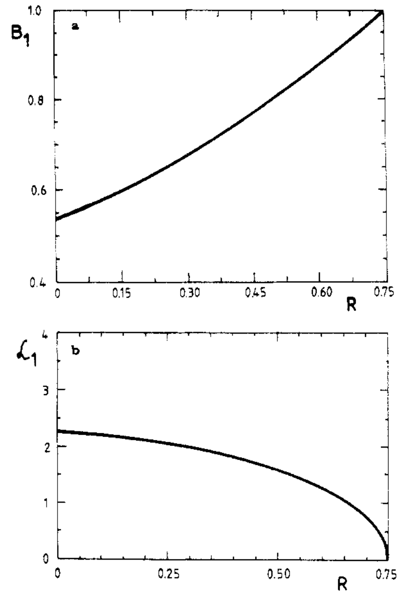

Figure 1. Theoretically predicted dependence of B_1 (a) and α_1 (b) on R for gel disks. These graphs were taken from ref 13.

the value of B_1 has been established, one can obtain the value of R, since the dependence of B_1 on R on sphere, cylinder, and disk can be found in the literature. Figure 1a shows the dependence of B_1 on R for disk-shaped gels as taken from ref 13. It is important to mention that the effective cooperative diffusion coefficient, D_c, of a gel disk at the surface is

$$D_c = \frac{3a_\infty^2}{\tau_1 \alpha_1^2} = M_{os}/f \qquad (6)$$

where α_1 is a function of R only as shown in Figure 1b, f denotes the coefficient of friction between the network polymer and the gel fluid, and a_∞ stands for the half-thickness of the gel in the final equilibrium state. Once the quantities τ_1 and B_1 are known, R, α_1, and D_c can be calculated as well.

Experimental Section

Network Preparation. Poly(vinyl acetate) (PVAc) gels swollen in isopropyl alcohol (i-PrOH) have been investigated in the form of cylindrical films (gel disks). The gel disks were 1-2 cm in diameter and 1-1.3 mm in height in the initial swollen state. The PVAc networks were obtained by acetylation of poly(vinyl alcohol) (PVA) gels in a pyridine-acetic anhydride-acetic acid mixture at 90 °C for 8 h, whereafter the mixture was exchanged with acetone and finally with iPrOH.[16,17] The PVA gels were prepared by cross-linking a commerical product (PVA-420, Kuraray Poval, Japan) with glutaraldehyde in aqueous solution at pH = 1.5. Prior to the cross-linking reaction, the acetate content (18-20 wt %) of the commercial polymer was reduced by alkali hydrolysis in a 20:80 (v/v) methanol-water mixture below 1%. The homogeneity with respect to molecular mass was increased by fractionation with a mixture of acetone and n-heptane. Several series of the PVAc gels were prepared, varying both the cross-linking density, L, and the initial PVA concentration, c, at which the cross-links had been introduced. L is the average number of cross-links on a primary chain having an average polymerization degree of 2000. The gel samples are identified by the c/L figures; e.g., "6/40" means c = 6 wt % and L = 40.

Swelling and Shrinking Kinetics. Since i-PrOH is a poor solvent for PVAc at room temperature and becomes a good solvent above 60 °C, the dependence of swelling degree on the temperature is very significant. Thus swelling can be induced by increasing the temperature and shrinking by decreasing the temperature.

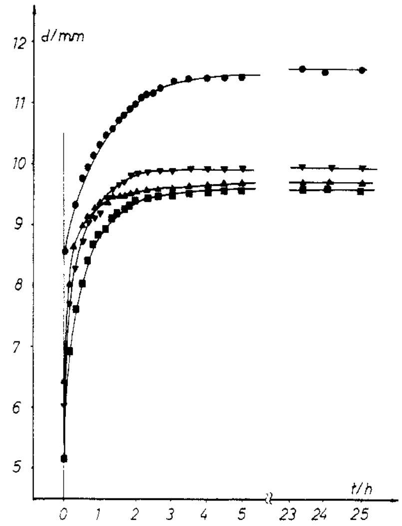

Figure 2. Swelling kinetics for disk-shaped gel films. d is the diameter of the disks. Swelling was induced by heating from 40 to 60 °C. Gels: (○) c/L = 7/10; (▼) c/L = 7/20; (▲) c/L = 7/30; (■) c/L = 7/40.

The kinetics of swelling and shrinking was demonstrated by measuring the unidirectional deformation, i.e., changes of the diameter of the gel disks as a function of time at constant temperature. The gel disks were placed in a glass cell, the mantle of which could be connected with each of two thermostats of the initial and the final temperature. Before the experiments started, the samples were stored for 24 h in i-PrOH to attain the swelling equilibrium. After equilibrium at the initial temperature was reached, the water circulation was switched over to the other thermostat of the final temperature. This time was taken to be zero (t = 0). The diameter of the gel disks was determined using a cathetometer with a translational stage graduated down to 0.01 mm. The aspect ratio of the gel disks (diameter/thickness) exceeded 15 in every case.

Two temperature programs were used to study the swelling and shrinking kinetics of PVAc/i-PrOH gels. For swelling, the initial temperature was 25 and 40 °C, respectively, whereas the final temperature was 60 °C. For shrinking, 60 °C was the initial temperature and 25 and 40 °C, respectively, were the final temperatures.

Experimental Results

Kinetics of Swelling. For some representative gel samples the diameter of the gel disks as a function of time was measured, and this dependence is shown in Figure 2. Due to different cross-linking densities, both the initial and the final diameters of the gel disks are different. According to eq 5, B_1 and τ_1 can be determined experimentally from the short-time linear extrapolation of the function

$$y = \ln \frac{u(a,t)}{u(a,0)} \qquad (7)$$

versus time. Now the quantity $u(a,t)$ denotes $d(t=\infty)-d(t)$, where d is the diameter of the gel disk. Such replots of swelling kinetics measurements are shown in Figure 3.

It is evident, that the long-time behavior of swelling can be well described with the aid of eq 5. Deviation from the straight lines occurs only in the limit of small time. A linear regression of the y versus time dependence provides us with B_1 and τ_1. Given these data, one can also determine R and D_c. We have summarized our results for B_1, τ_1, and D_c in Table I. Since B_1 has been predicted to depend on the geometry as well as on the R value, taking into account the B_1-R dependence for disks given by Figure 1a, it is possible to obtain R. The mean value for B_1 was found to be B_1 = 0.71, which gives R = 0.34. Having established

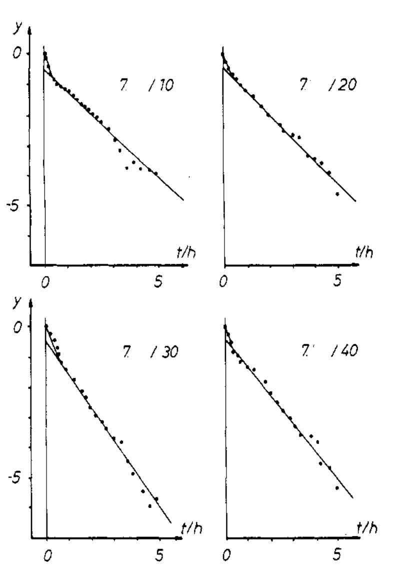

Figure 3. Time dependence of y for different gel disks. The numbers indicate the c/L characteristics of the gels. Swelling was induced by increasing the temperature from 40 to 60 °C.

Table I. Kinetic Behavior of Different Gel Disks[a]

c/L	a_∞ (mm)	$10^2\Phi$	B_1	$10^{-3}\tau$ (s)	$10^{11}D_c$ (m²/s)
7/10	0.280	6.89	0.75	4.78	0.39
7/20	0.290	9.34	0.71	4.52	0.39
7/30	0.306	11.62	0.81	3.11	0.62
7/40	0.349	16.66	0.78	3.57	0.71
9/10	0.348	8.54	0.90	4.52	0.55
9/20	0.300	9.52	0.57	2.96	0.63
9/30	0.289	11.90	0.60	2.70	0.64
9/40	0.341	18.82	0.56	3.21	0.75

[a] Temperature program: 40 → 60 °C.

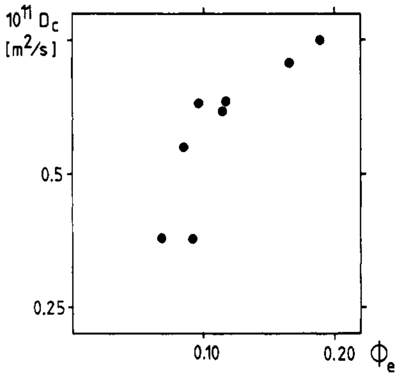

Figure 4. Cooperative diffusion coefficient of PVAc network chains against the volume fraction of polymer in the gel in swelling equilibrium with i-PrOH at 60 °C.

the value for R, one can obtain α_1 with the aid of Figure 1b. It was found that $\alpha_1 = 1.9$. On the basis of eq 6 one can determine the cooperative diffusion coefficient of the network in the gel liquid. These data are also presented in Table I. In contradiction with B_1, D_c depends on the concentration. One can conclude that the measured D_c increases with increasing polymer volume fraction as seen in Figure 4.

Effect of Gel Size and Extent of Swelling on the Relaxation Time and on the Cooperative Diffusion Coefficient. Two temperature programs were used to determine the relaxation time and the cooperative diffusion coefficient. In addition to the initial temperatures, the gel size was also varied. It is well known that the relaxation time is in proportion to the square of the linear size; therefore it strongly depends on the radius of the gel disk. This dependence can be seen in Figure 5, where the

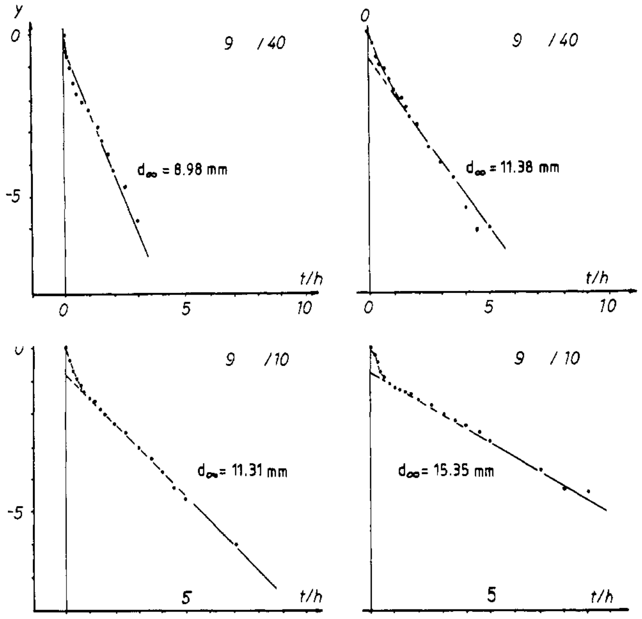

Figure 5. Dependence of y on time for different disk-shaped networks. The numbers indicate the c/L characteristics and the diameter, d_∞ of gels in equilibrium at 60 °C. The swelling was induced by increasing the temperature from 20 to 60 °C.

Table II. Kinetic Characteristics of Gel Disks

c/L	temp prog	$2a_\infty$ (mm)	$10^{-3}\tau$ (s)	$10^{11}D_c$ (m²/s)
7/20	40 → 60 °C	0.289	4.52	0.38
7/20	25 → 60 °C	0.315	5.85	0.35
7/20	25 → 60 °C	0.405	9.24	0.37
9/10	40 → 60 °C	0.347	4.52	0.55
9/10	25 → 60 °C	0.341	4.68	0.51
9/10	25 → 60 °C	0.462	8.21	0.54
9/40	25 → 60 °C	0.270	1.90	0.79
9/40	25 → 60 °C	0.343	3.30	0.74

kinetics of swelling is presented for several gel disks. Besides the size, the cross-linking density was also varied. We do not know exactly how strong the influence of cross-linking density on the diffusion coefficient is. In our experiments the equilibrium swelling degree is altered by changing the temperature. Since the equilibrium swelling degree is uniquely determined by the cross-linking density, we cannot compare two different networks at the same equilibrium concentration. This means that on the basis of our experiments the influence of cross-linking density cannot be studied. With increasing equilibrium concentration (with increasing cross-linking density) the relaxation time decreases; as a result of this, the cooperative diffusion coefficient increases. This effect is much more clearly seen in Table II, where kinetic characteristics of some disk-shaped gels are presented. It can be concluded that neither the temperature program nor the size of the gel disks influences the value of the cooperative diffusion coefficient significantly. The value of D_c remains the same within the experimental accuracy. This is not the case if the cross-linking density is varied. A definite increase can be observed with increasing polymer concentration.

Kinetics of Shrinking. When the temperature decreases, the PVAc/i-PrOH gels begin to shrink. The kinetics of shrinkage can also be measured as shown in Figure 6. This figure shows the decrease of diameter as a function of time. The shrinking, or deswelling, was induced by decreasing the temperature from 60 to 40 °C.

Comparing the swelling and shrinking kinetics shown in Figures 2 and 6, one can arrive at the conclusion that swelling and deswelling are not symmetrical processes. The shrinking takes much longer than the swelling. This

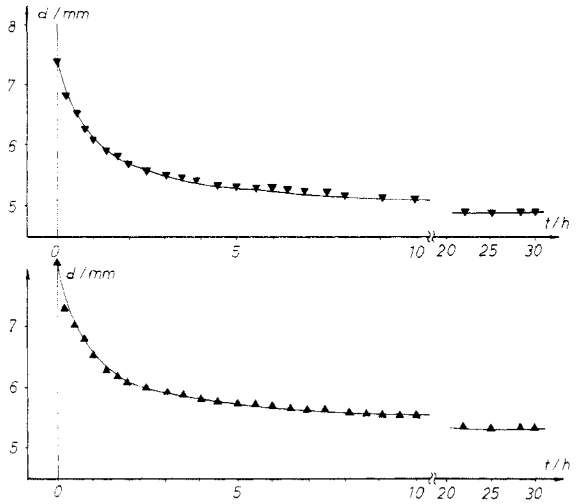

Figure 6. Kinetics of deswelling (shrinking) of gel disks as a result of changing the temperature from 60 to 40 °C. Gels: (▼) c/L = 7/30; (▲) c/L = 7/40.

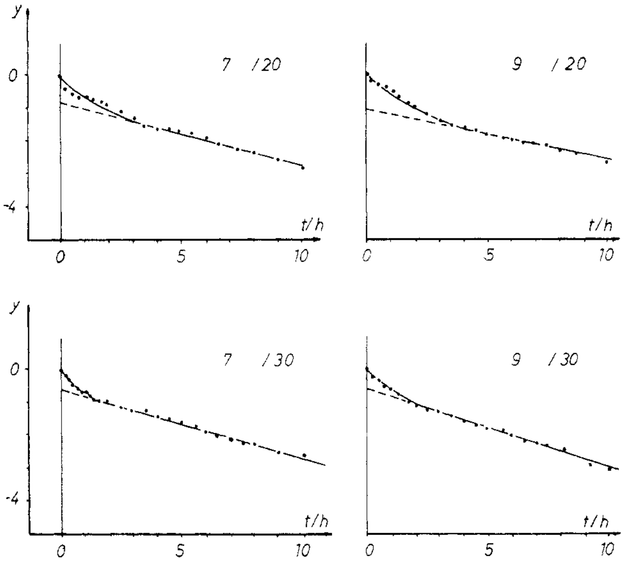

Figure 7. y versus t dependence for gel disks upon cooling the system from 60 to 40 °C.

difference is due to microsyneresis, that is, polymer–diluent incompatibility on a microscale. As a consequence of microsyneresis, upon cooling, all the gels exhibit optical, and many of them also structural, changes that can be observed by the naked eye. The originally transparent PVAc/i-PrOH gels became turbid, the extent of turbidity and its variation with time being different for gels of various cross-linking density.[18,19] The rate of attaining the new equilibrium upon cooling is smaller by 1 or 2 orders of magnitude than that for swelling.

The Li–Tanaka equation can be applied to describe the shrinking process in time as demonstrated by Figure 7. On the basis of Figure 7 one can say that not only the long-time swelling but also the long-time shrinking kinetics can be well described by eq 5. The parameters of this equation for shrinking can be found in Table III.

The relaxation times cannot be directly compared with those shown in Tables I and II due to the large difference in final size.

For the B_1 parameter an average of B_1 = 0.48 was obtained. Taking into account the dependence of B_1 on R (see Figure 1a), one obtains $R=0$ and for α_1 (see Figure 1b) α_1 = 2.3 was found.

With the aid of eq 6 it was possible to determine the cooperative diffusion coefficient of network chains, too.

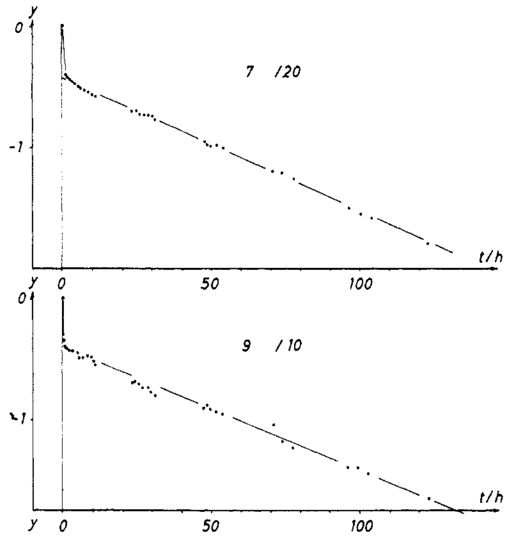

Figure 8. Dependence of y on time for two gel disks. The shrinking was induced by cooling the systems from 60 to 25 °C.

Table III. Kinetic Parameters of Gel Disks upon Cooling from 60 to 40 °C

c/L	$2a_\infty$ (mm)	$10^{-3}\tau$ (s)	B_1	$10^{13}D_c$ (m^2/s)
7/20	0.147	19.8	0.42	1.54
7/30	0.148	16.5	0.46	1.89
7/40	0.161	19.0	0.39	1.93
9/20	0.191	24.1	0.35	2.14
9/30	0.175	14.9	0.56	0.29
9/40	0.181	12.8	0.69	0.36

The surprising result is that the value of D_c is much smaller upon cooling than upon heating.

The deviation between swelling and shrinking kinetics is much more pronounced when temperature program cooling from 60 to 25 °C is investigated. At lower temperatures the deswelling needs much more time than at higher temperatures. This is supported when the plots for the 7/20 gel in Figures 7 and 8 are compared. The slowdown at 25 °C is probably due to microheterogeneities which cause the turbidity. Very often, the gel disks contain visible pores and bubbles distributed rather uniformly over the film as can be seen in Figure 9.

In Table IV, the kinetic characteristics upon cooling from 60 to 25 °C are summarized. Comparing the results given in Tables III and IV, it is obvious that a decrease in temperature results in a huge decrease in the value of the cooperative diffusion coefficient.

Discussion

Let us briefly summarize our main results.

(a) The Li–Tanaka equation can be applied to describe both swelling and shrinking kinetics of disk-shaped gels.

(b) Within the experimental accuracy the cooperative diffusion coefficient does not depend on the gel size and on the extent of swelling realized by temperature jumps of different magnitude.

(c) The cross-linking density, which determines the equilibrium swelling degree, makes its strong influence felt on the cooperative diffusion coefficient. D_c increases with increasing volume fraction of polymer in the network.

(d) The cooperative diffusion coefficient strongly depends on the temperature when turning from the good solvent condition to poor solvent. D_c decreases more than 2 orders of magnitude when the gel is cooled below the Θ temperature.

(e) All the gel systems studied were capable of undergoing a continuous phase transition which results in the

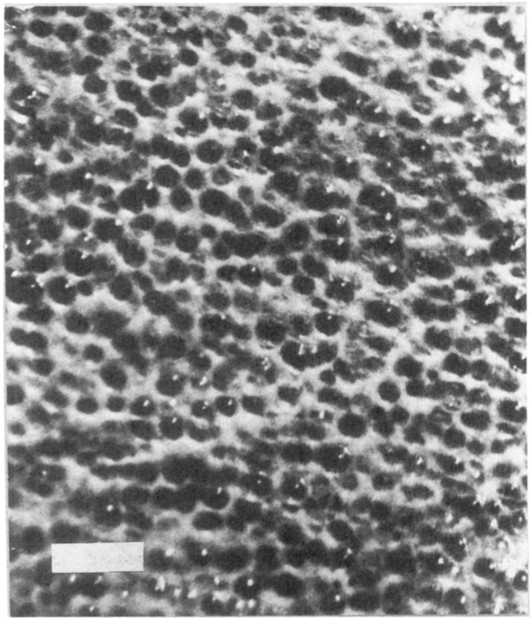

Figure 9. Porous structure of a gel film at 25 °C. The bar corresponds to 1 cm.

Table IV. Kinetic Parameters of Shrinking upon Cooling from 60 to 25 °C

c/L	$2a_\infty$ (mm)	$10^{-3}\tau$ (s)	$10^{14}D_c$ (m^2/s)
7/20	0.210	322	1.93
9/10	0.225	250	2.86

development of turbidity. This phase transition has a very pronounced effect on the kinetics of shrinking.

(f) Within the experimental accuracy the ratio of shear modulus to the longitudinal modulus, R, was found to be independent of cross-linking density. At the good solvent condition $R = 0.34$ was obtained. At the poor solvent condition $R = 0$ was found.

Regarding the scaling properties of gels, de Gennes has shown that a swollen gel is very similar to a solution at the overlap concentration (C^* theorem).[2,20] This analogy is also present in certain dynamic properties. The cooperative diffusion coefficient has been predicted to vary as

$$D_c \sim \Phi^{3/4} \quad \text{in good solvent} \tag{8a}$$

$$D_c \sim \Phi \quad \text{in } \Theta \text{ solvent} \tag{8b}$$

A rough estimation on the basis of experimental data shown in Figure 4 gives an exponent 0.6, which is slightly smaller than 0.75 predicted for the good solvent condition. This corresponds to the situation when the gels were rapidly heated. In this case the quality of solvent increases and as a result the good solvent conditions thought to be realized. When the gels are cooled, a significant decrease in the quality of swelling agent takes place. If T is decreased to a certain spinodal temperature, an instability occurs. As a consequence the gels become turbid. Very little is known about the region below the spinodal temperatures. We expect domains which can coalescence and segregate. Not only the optical but also the kinetic properties are strongly influenced by the spinodal decomposition. For gels Tanaka has shown that the cooperative diffusion coefficient becomes vanishing small when we get down to the spinodal.[8,21,22]

Similar results were obtained for solutions of polystyrenes in cyclohexane at the spinodal temperature.[25] We suppose that practically the same phenomenon was observed by us. Since the PVAc/i-PrOH gels have a Θ = 52 °C, the spinodal temperatures are below 52 °C. For the 7/20 gel $D_c = 0.39 \times 10^{-11}$ m^2/s was found at 60 °C. However, D_c sharply decreases when the kinetics of shrinking is studied at 40 °C, $D_c = 1.54 \times 10^{-13}$ m^2/s. At 25 °C $D_c = 1.93 \times 10^{-14}$ m^2/s was found. It must be mentioned that it is not possible to study the temperature dependence of D_c on the basis of the data presented here, because not only the temperature but also the concentration of gels are different.

Table V. Predicted and Experimentally Determined Values for R

quality of solvent	ν	σ_{os}	R_σ	R_t	R_{exp}^{kin}
good	$^3/_5$	$^1/_4$	$^1/_3$	$^4/_{13}$	0.34
Θ	$^1/_2$	$^1/_3$	$^1/_4$	$^1/_4$	
poor	$^1/_3$	$^1/_2$	0	0	0.0

Our other result was in connection with the ratio of shear modulus over the longitudinal osmotic modulus. This quantity can be related to the osmotic Poisson ratio σ_{os} of the polymer coils composing the network:[9,10]

$$R = \frac{1 - 2\sigma_{os}}{2(1 - \sigma_{os})} \tag{9}$$

Equation 9 was derived on the basis of the C^* theorem of gels. Table V contains the predicted value for σ_{os} as well as for R.

We can also adopt a thermodynamic theory to express the value of R. An equation of state of swollen networks can be written as follows:[16]

$$\omega(\Phi) = G(\Phi)\left[\left(\frac{\Phi}{\Phi_e}\right)^t - 1\right] \tag{10}$$

where Φ_e is the equilibrium volume fraction of polymer in pure solvent. The exponent t can be related to the excluded volume exponent, ν, according to the following relation:

$$t = \frac{1}{3\nu\text{-}1} + \frac{2}{3} \tag{11}$$

The validity of eq 10 is strongly supported by experimental results.[16,17,23] By using eq 10, one can derive the osmotic bulk modulus:[24]

$$K_{os} = \Phi\frac{\partial G(\Phi)}{\partial \Phi}\left[\left(\frac{\Phi}{\Phi_e}\right)^t - 1\right] + tG(\Phi)\left(\frac{\Phi}{\Phi_e}\right)^t \tag{12}$$

In equilibrium with pure solvent $\Phi = \Phi_e$, one can write

$$K_{os}(\Phi_e) = tG(\Phi_e) \tag{13}$$

With the aid of eqs 11 and 13 we get

$$R = \frac{1}{t + {}^4/_3} = \frac{3\nu\text{-}1}{1+2(3\nu\text{-}1)} \tag{14}$$

This relation says that R is determined by the solvent quality via the excluded volume exponent only. It is independent of swelling degree, which means that both the shear and the longitudinal osmotic moduli vary with the concentration in equal measure, in agreement with our previous results.[4,6] In Table V we present the value for R obtained by different methods including theoretical analysis as well as experimental data. For the sake of distinction the following notation is used. R_σ denotes the ratio calculated by eq 9. R_t represents the ratio obtained by eq 14. R_{exp}^{kin} means the experimental data determined from swelling kinetics. One can conclude that eqs 9 and 14 give the same result for poor and Θ conditions; however, a slight deviation occurs at the good solvent condition. It is also seen that the experimental results support the predicted R values.

It is worth mentioning that for polyacrylamide–water gel samples (good solvent) $R = 0.31$ was obtained by osmotic and shear modulus measurements.[6] Peters and Candau found $R = 0.307$ by swelling kinetics for the same kind of system.[28]

For PVAc/i-PrOH gels at the Θ temperature $R = 0.25$ was found.[26] Based on uniaxial deswelling for PVAc/toluene (good solvent) gels $R = 0.32$, and for PVAc/i-PrOH $R = 0.25$ was obtained.[27]

Conclusion

The results presented in this paper show that the kinetics of swelling and shrinking of disk-shaped gels is satisfactorily described by the Li–Tanaka theory. It has been demonstrated that the cooperative diffusion coefficient of network chains increases with increasing polymer concentration and drastically decreases below the Θ temperature. The ratio of the shear modulus over the longitudinal osmotic modulus obtained from the kinetics of swelling agrees within the experimental accuracy with previous experiments as well as with theoretical results.

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