BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 26, pp. 5057–5059, 1995

0032-3861/95/$10.00+0.00

polymer communications

Kinetics and equilibrium swelling of gelatine gels

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(Received 27 September 1994; revised 7 February 1995)

The swelling features of gelatine gels in water (good solvent) were studied as a function of thermodynamic conditions of sol–gel transition and ripening. It is shown that the degree of equilibrium swelling Q_e varies with the volume fraction of the polymer in a casting solution ϕ_o in accordance with the prediction of the classic theory: $Q_e \sim \phi_o^{-0.4}$. Q_e, as a function of the gelation temperature T_g, the ripening time t_r and ϕ_o, can be rescaled and described by the single empirical equation: $Q_e \sim T_g^{-x} t_r^{-y} \phi_o^{-0.4}$, where $x = 0.1$, $y = 0.15$ for wet gels and $x = -0.5$, $y = 0.04$ for dried gels. The kinetics of macroscopic swelling is described by the equation of Peters and Candau, with values of collective diffusion coefficients being in good agreement with values obtained by other workers via photon correlation spectroscopy.

(Keywords: gelatine gel; kinetics; swelling)

Gelatine gels are used extensively in a variety of technologies associated with photography and holography, and with medical, pharmaceutical and food industries. In many instances, the application of these gels includes their swelling in water or in a mixed solvent. In general, the swelling process depends significantly on the structure of the polymer network and is governed by collective diffusion of polymer and solvent molecules[1,2]. Being a product of collagent denaturation, gelatine can be regarded as a copolymer with a complex hierarchy of structures[3]. Moreover, the structure and properties of gelatine gels depend considerably on the conditions of their formation. In spite of their wide application, detailed investigations of swelling in gelatine gels are relatively few in number and the processes are not yet well understood[4–6]. In the present work we are concerned with the effect of gelation conditions and ripening of gelatine gels on kinetics and their degree of swelling in water.

Gel samples were prepared from gelatine of a photographic grade (Polymerphoto, Kazan, Russia). The viscosity of an aqueous gelatine solution with polymer volume fraction of 0.0625 at 40°C was 20 cP, its isoelectric point was 4.7, and pH was 6.2. Homogeneous aqueous gelatine solutions with different volume fractions of polymer ϕ_o were poured onto thin cover glass substrates at 45°C and quenched to various temperatures T_g at which gelation took place. The resulting gels, with thicknesses of less than 0.5 mm, were ripened during different times t_r. The magnitudes of parameters ϕ_o, T_g and t_r were varied in the ranges 0.021–0.1288, 4–22°C and 1–5 h, respectively. Some of the gels were thoroughly dried before swelling. Both wet and dried gels on glass substrates were inserted into a reservoir with bidistilled water at 22°C. The mass of each gel as a function of time $m(t)$ was determined gravimetrically.

The degree of swelling $Q(t)$, which we define as the ratio of the gel volume V at time t to the volume of the polymer alone $V_p(Q(t) \equiv V(t)/V_p)$, was calculated from experimental data of $m(t)$ through the equation:

$$Q(t) = 1 + \left[\frac{m(t)}{m_p} - 1\right]\frac{\rho_p}{\rho_s} \qquad (1)$$

where m_p is the mass of gelatine in a casting solution, ρ_p is the density of polymer (gelatine), taken as 1.465 g cm^{-3}, and ρ_s is the density of solvent (water). For the sake of clarity, however, it is more convenient to represent experimental data on swelling in terms of the swelling ratio $Q(t)/Q_o$, where $Q_o \equiv V_o/V_p$ (V_o is the initial volume of a gel after sol–gel transition or after drying). Thus, the value of $Q(t)/Q_o$ is the measure of the variation of gel volume during swelling with respect to its volume in unswollen (reference) conditions. Kinetic curves representing $Q(t)/Q_o$ as a function of time for two gels of different volume fraction are shown in *Figure 1*. It can be seen that the swelling proceeds rapidly during the first few hours and reaches saturation after about 24 h. After that the value of Q does not change, within experimental error, and can be taken as the degree of equilibrium swelling Q_e.

The kinetics of swelling of polymer gels with negligible ratio of gel thickness at equilibrium swelling h_e to its area $S(h_e/S \Rightarrow 0)$ in a good solvent can be described by the following equations[7]:

$$u(h,t)/u(h,0) \cong \frac{8}{\pi^2}\exp\left(-\frac{t}{\tau}\right) \qquad (2)$$

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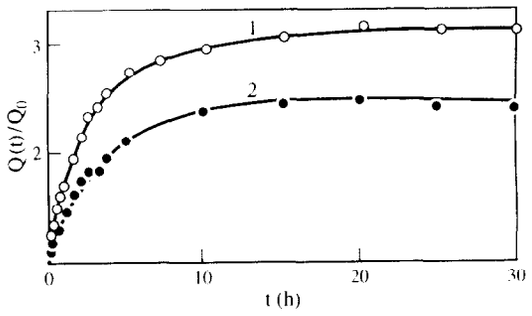

Figure 1 Kinetics of swelling for gelatine gels formed at gelation temperature $T_g = 22$ C after a ripening time t_r of 1 h. 1, $\phi_0 = 0.0625$; 2, $\phi_0 = 0.0308$

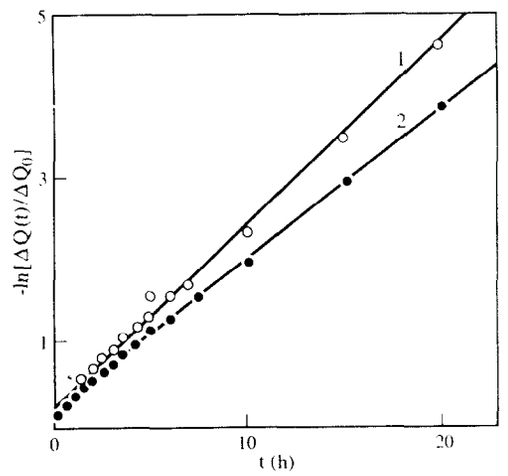

Figure 2 Kinetics of swelling in variables of equations (2) and (4). Notations are the same as in *Figure 1*

$$\tau = \frac{h_e^2}{\pi^2 D_c (1 + \mu/M_{os})} \tag{3}$$

where $u(h, t)$ and $u(h, 0)$ represent the displacement of a point in the network from its final location at the swelling equilibrium at time t and $t = 0$, respectively, τ is the relaxation time of swelling which is closely related to the collective diffusion coefficient D_c, and μ and M_{os} are the shear modulus and the osmotic longitudinal modulus of the gel, respectively. Equations (2) and (3) take into account the effect of the non-negligible shear modulus of swelling networks and were obtained by Peters and Candau[7] as a generalization of the theory previously developed by Tanaka and Fillmore[8] for kinetics of swelling under the assumption that $\mu/M_{os} \Rightarrow 0$. The value of $u(h, t)/u(t, 0)$ in equation (2) can be related to experimentally measured parameters through[9]:

$$u(h, t)/u(h, 0) = \frac{h_e - h(t)}{h_e - h_0} = \frac{Q_e - Q(t)}{Q_e \quad Q_0} \equiv \frac{\Delta Q(t)}{\Delta Q_0} \tag{4}$$

where h_0 and $h(t)$ are the thicknesses of gel in the reference state and at time t, respectively.

The data on kinetics of swelling were processed by equations (2)–(4) and results are presented in *Figure 2*. As indicated by the graph, the kinetics of swelling is adequately described by equation (2). The slope of straight lines in *Figure 2* corresponds to the characteristic time τ, the values of which are summarized in *Table 1*.

Table 1 Parameters of equations (2) and (4) used for calculation of collective diffusion coefficients

ϕ_0	h_e (mm)	C_0/C_e	M_{os}/μ	τ (h)	$D_c(10^{-7}$ cm^2 s$^{-1})$
0.0308	1.8	2.5	0.255	5.2	1.4
0.0625	1.9	3.2	0.264	4.4	1.8

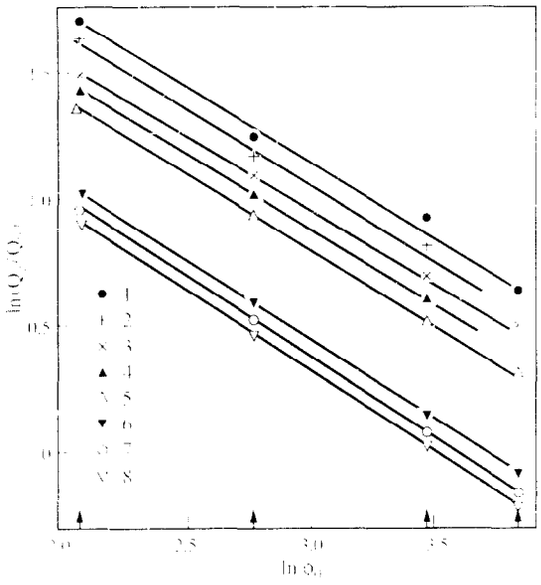

Figure 3 The relative degree of swelling for gelatine gels as a function of ϕ_0. Wet gels: 1, $T_g = 22$ C, $t_r = 1$ h; 2, $T_g = 22$ C, $t_r = 3$ h; 3, $T_g = 22$ C, $t_r = 5$ h; 4, $T_g = 4$ C, $t_r = 1$ h; 5, $T_g = 4$ C, $t_r = 5$ h. Dried gels: 6, $T_g = 22$ C, $t_r = 1$ h; 7, $T_g = 22$ C, $t_r = 3$ h; 8, $T_g = 22$ C, $t_r = 5$ h

Note that the gel with a higher concentration of polymer swells more rapidly, which is associated with faster collective diffusion in a denser polymer–solvent system[10]. Known magnitudes of the parameter τ make it possible to extract appropriate collective diffusion coefficients for each sample from equation (3) using calculated values of μ/M_{os} (ref. 11):

$$(\mu/M_{os})^{-1} = 2.25 + \left[1 + \frac{1}{2}(C_0/C_e)^{-2/3}\right] \div \left[1 - \frac{1}{2}(C_0/C_e)^{-2/3}\right] \tag{5}$$

where C_e and C_0 are the polymer concentrations (in g cm^{-3}) at the swelling equilibrium and in the reference unswollen state, respectively. It is remarkable that values of D_c obtained from the conducted *macroscopic* experiments are in good agreement with the results of *microscopic* measurements by photon correlation spectroscopy. Thus, Amis *et al.*[12] reported $D_c = 4.12 \times 10^{-7}$ cm^2 s^{-1} for 15 w% gelatine gel at $T = 20$ C, which is close to our observations presented in *Table 1*.

The values of the degree of equilibrium swelling for both wet and dried gelatine gels, with various volume fractions of polymer formed at different temperatures and ripening times, are shown in *Figure 3*. For the 'affine' network swollen in a good solvent, Flory's classic theory predicts the following relationship between parameters Q_e, ϕ_0 and the number of links N of the elementary chain of the network (i.e. chain between two first neighbour

junctions)[13]:

$$Q_e \sim \phi_0^{\nu} N^m \tag{6}$$

where $\nu = 2/5$, $m = 3/5$. The classic approach is based on the concept of affine deformation in the strain of both the locations of the junction points and the dimensions of elementary chains. More realistic models account for two additional problems of major importance, namely, the existence of pendent chains and topological changes involved in the swelling process. Wheres the former is expected to influence the swelling equilibrium only slightly[1], the latter can lead to pronounced changes in Q_e. As shown in ref. 14, the value of the exponent ν in equation (6) shifts to 0.1 if the effect of chain desinterspersion is taken into account. If, in addition, strong entanglements between macromolecules exist, the value of ν becomes 0.85. At the same time, the value of the exponent m in equation (6) proves to be invariant to both topological effects and remains equal to 3/4. Thus, the degree of equilibrium swelling is determined predominently by gel structure dictating the value of the exponent ν in equation (6).

The value of ν corresponding to the slope of the straight lines in *Figure 3* was found to equal 0.4 ± 0.1, irrespective of preparation conditions and prior drying. The whole set of data shown in *Figure 3* can be rescaled and described by the following empirical equation:

$$Q_e = A\Delta T^{-x} t_r^{-y} \phi_0^{-0.4} \tag{7}$$

where A is a constant, $\Delta T = T_m - T_g$ ($T_m = 36°C$ is the temperature of melting of gelatine gels). For wet samples $A = 24$, $x = 0.1$, $y = 0.15$ whereas for dried ones $A = 9.2$, $x = -0.5$, $y = 0.04$. Strong correlation between experimental and calculated values of the degree of equilibrium swelling is illustrated by *Figure 4*.

The value of $\nu \cong 0.4$ revealed in this study corresponds to the prediction of the classic theory, which is quite unexpected taking into account the complex structure of the investigated polymer networks. This value differs significantly from $\nu = 0.1$ and $\nu = 0.85$, inherent in networks of complex topology, and points to relatively weak topological effects and affine deformation of gelatine gels during swelling in water. This result can be attributed to the rather high rigidity of gelatine macromolecules at temperatures $T < T_m$ caused by their partial renaturation into collagen-like helices[15,16]. Appreciable rigidity can prevent the desinterspersion of chains as well as change in their overlapping degree on swelling. Furthermore, our results show that the degree of equilibrium swelling decreases with an increase in the ripening time; this is associated with a higher rigidity of more ripened networks owing to the number of renatured helices increasing with t_r. A more complex and ambiguous situation arises with variation of gelation temperature. It is well known that lower T_g promotes the formation of a greater number of collagen-like helices[15,16], resulting in higher rigidity of the polymer network and, therefore, in its lower swelling. However, if wet gels manifest the expected decrease in Q_e with decreasing T_g, the dried ones reveal just the opposite effect, namely $Q_e \sim T_g^{-0.5}$. Such behaviour can be understood from available X-ray data on changes in gelatine gel structure during drying and swelling. As was found in ref. 16, the polymer network of dried gelatine gel may contain up to 10 vol% of the microcrystalline phase, an appreciable amount of which is retained in the network during further swelling in water. The microcrystalline regions involve a much greater number of gelatine macromolecules than junction zones of wet gels (most likely two, but a maximum of three polymers[16]) and therefore impose significant additional restrictions on swelling. The amount of the microcrystalline phase formed on drying depends on the mobility (i.e. flexibility) of macromolecular chains, which decreases with gelation temperature. Thus, the gels formed at lower T_g become less crosslinked on drying owing to additional microcrystalline junctions which, in turn, results in a higher degree of equilibrium swelling.

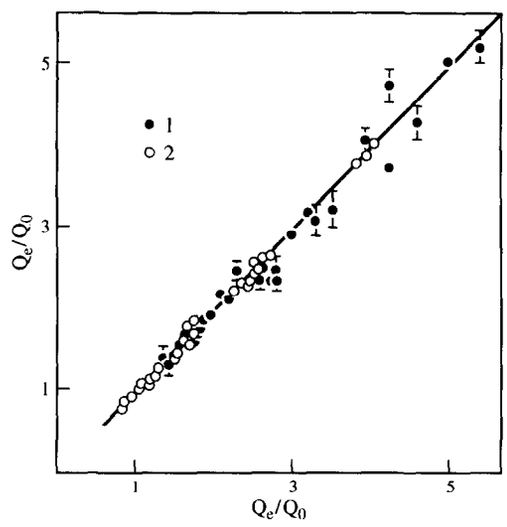

Figure 4 Correlation between values of Q_e/Q_0 from experiment (abscissa) and calculated from equation 7 (ordinate). 1, Wet gels; 2, dried gels

Acknowledgements

Financial support of Yu. M. by Alexander von Humboldt Stiftung and Max Planck Gesellschaft, Germany, is greatly acknowledged.

References

1 Bastide, J., Picot, C. and Candau, S. *J. Macromol. Sci.* 1981, **B19**, 13
2 Scherer, G. W. *J. Non-Cryst. Solids* 1987, **91**, 83
3 Djabourov, M. *Contemp. Phys.* 1988, **29**, 273
4 Robinson, J. D. *J. Photogr. Sci. Eng.* 1964, **8**, 220
5 Libicky, A. and Bermane, D. 'Photogr. Gel. Proc. Symp.' 1970, p.39
6 Ofner, C. M. and Schott, R. *J. Pharm. Sci.* 1986, **75**, 786
7 Peters, A. and Candau, S. J. *Macromolecules* 1988, **21**, 2278
8 Tanaka, T. and Fillmore, J. *J. Chem. Phys.* 1979, **70**, 1214
9 Klepko, V. and Mel'nichenko, Yu. *Vysokomol. Soedin.* 1994 (in Russian)
10 Gutsalyuk, V., Guly, J., Mel'nichenko, Yu. and Klepko, V. *Polym. Int.* 1994, **33**, 359
11 Hecht, A. M. and Geissler, E. *Polym. Commun.* 1983, **24**, 98
12 Amis, E. J., Janmey, P. A., Ferry, J. D. and Yu, H. *Macromolecules* 1983, **16**, 441
13 Flory, P. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, 1983
14 Handelsman, M. I. and Budtov, V. P. *Vysokomol. Soedin.* 1988, **B30**, 825 (in Russian)
15 Djabourov, M., Leblond, J. and Papon, P. *J. Phys. (Fr.)* 1988, **49**, 319
16 Mel'nichenko, Yu., Gomza, Yu., Shilov, V. and Osipov, S. *Polym. Int.* 1991, **25**, 153