Gelation rates of poly(vinyl alcohol) solution

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Apparent gelation rates t_{gel}^{-1}, defined as the reciprocal of the gelation time, are measured for poly(vinyl alcohol) solutions as functions of polymer concentration, C_{p}, and quenching temperature, T_{Q}. Here the measurements are limited to the case of homogeneous gelation where T_{Q} is below 0°C. The critical gelation concentration, $C^*_{t=\infty}$, extrapolated to $t_{\mathrm{gel}}^{-1}=0$ is independent of T_{Q}, and is identical to the polymer chain overlap concentration, C^*_{Rg}. In order to represent the degree of polymer chain overlap a reduced concentration, $\phi=(C_{\mathrm{p}}-C^*_{\mathrm{Rg}})/C^*_{\mathrm{Rg}}$, is introduced. An experimental relation, $t_{\mathrm{gel}}^{-1}=A(T_{\mathrm{Q}})\ \phi^2$, is obtained where $A(T_{\mathrm{Q}})$ is the temperature factor. The ϕ dependence of the equation can be explained using the chain overlap concept for gelation and random bond percolation theory, and the temperature factor $A(T_{\mathrm{Q}})$ is analysed by the crystal nucleation theory.

(Keywords: gelation rate; poly(vinyl alcohol); crystallite formation; chain overlap concentration)

INTRODUCTION

Gelation time, which is the time required for a polymer solution to gel, is one of the most important aspects in understanding the mechanism of gelation. In studying the formation of gel structure, two subjects may be considered: the formation of gel network structure and the formation of cross-linking points in gels. The former has been studied using theoretical models such as the classical tree model[1] and lattice percolation models[2]. The latter depends on the kind of polymer in the gelation system. When cross-linking points are crystallites of polymers, the gelation rate should be connected with the rates of nucleation and crystallization. It is known that gelation rate based on crystallization increases with decreasing temperature, and with increasing polymer concentration of the solution and molecular weight[3–5]. However, there has been no quantitative analysis for this as far as we know.

In a previous paper[5], we determined the sol–gel transition diagrams of atactic poly(vinyl alcohol) (at-PVA) in a mixture of dimethyl sulphoxide (DMSO) and water (60/40 vol/vol) and explained the results by the concept of competition between the rates of gelation and phase separation. We also confirmed that the gelation time of the PVA solution decreases with decreasing quenching temperature, T_{Q}, and with increasing polymer concentration, C_{p}, and degree of polymerization, P_{n}. These tendencies of gelation are valid for a whole T_{Q} range between about 70°C and −60°C. However, quantitative investigation of the gelation rate is made difficult by phase separation, because phase separation itself accelerates gelation. Below about 0°C gelation occurs very quickly to form a transparent gel, and phase separation may be considered to be inhibited. In this paper, gelation time is measured below 0°C where phase separation has almost no effect on gelation, and the gelation rate, defined as the reciprocal of gelation time, is studied quantitatively as a function of C_{p}, T_{Q} and P_{n}.

EXPERIMENTAL

Samples

Fully saponified at-PVA samples with P_{n} values of 1640 and 590 (Unitika Chemical Co. Ltd) were used in this study. The samples with $P_{\mathrm{n}}=1640$ and $P_{\mathrm{n}}=590$ are referred to as samples S3 and S2, respectively. Their characteristics are given in *Table 1*. A given amount of at-PVA was dissolved in a mixture of DMSO and water (60/40 vol/vol) at about 130°C, to give PVA concentrations, C_{p}, of 2.0, 5.0 or 10.0 g dl^{-1}, and kept there for about 30 min to ensure homogenization. In order to prepare the sample solutions of $C_{\mathrm{p}}\leqslant 2.0\,\mathrm{g\,dl^{-1}}$, $2.0<C_{\mathrm{p}}\leqslant 5.0\,\mathrm{g\,dl^{-1}}$ and $5.0\leqslant C_{\mathrm{p}}\leqslant 10\,\mathrm{g\,dl^{-1}}$, these homogenized solutions were immediately diluted by adding the corresponding amount of the solvent at room temperature. Then the test tubes, including the samples, were thoroughly shaken in a vibrator and heated at 95°C for about 5 min.

Gelation time measurements

The gelation time, t_{gel}, was determined by the ball-dropping method. First, 0.3 ml of the PVA solution was put in a test tube (3.3 mm i.d. and 8 cm in height), heated at 95°C for about 10 min to ensure homogeneity, and then quickly quenched in a bath at constant temperature, T_{Q}, between −60°C and 0°C. The test tube was held vertically, and a steel ball (diameter 2 mm) was dropped gently from the rim of the test tube. When the steel ball became stationary at a level less than about 1.2 cm below the meniscus, gelation was judged to have occurred. The gelation time was defined as the time from the instant

Table 1 Characteristics of at-PVA samples

			Tacticity (triad)			
Sample	P_{n}	$M_{\mathrm{w}}/M_{\mathrm{n}}$	*mm*	*mr*	*rr*	Lot no.
S3	1640	1.97	0.21	0.49	0.30	UV
S2	590	1.61	0.21	0.49	0.30	G2117

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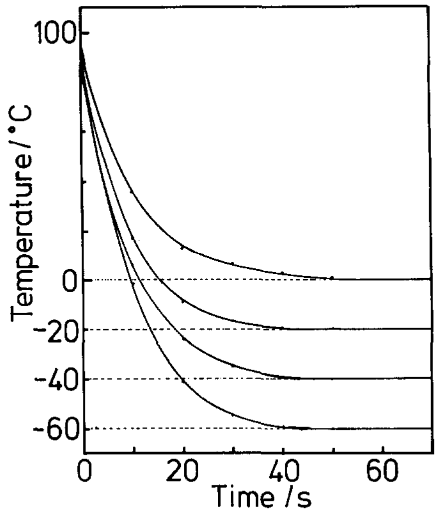

Figure 1 Temperature decay of PVA solution ($C_p = 2\,g\,dl^{-1}$) with time after quenching to T_Q. Dashed lines show corresponding T_Q

when the test tube was put into the bath to the gelation point. The measurements were repeated at least twice to determine the gelation time.

The i.d. of the test tube, volume of the sample and diameter of the steel ball were adjusted so that the time taken for the temperature of the sample solution to reach T_Q would be as short as possible. As the gels from S2 solutions and/or S3 solutions with lower C_p became more fragile, determination of gelation points was more difficult, therefore the t_{gel}^{-1} data for these were somewhat scattered.

Figure 1 shows the temperature change of the sample solution of $C_p = 2\,g\,dl^{-1}$ after the test tube was placed in the bath at T_Q; the temperature of each sample reaches T_Q within 40 or 50 s. When the measured gelation time, t_{gel}, was less than 60 s, the true value was considered to be less than the observed value and it was discarded for analysis. It was confirmed visually that each gel was completely transparent even after the measurement of t_{gel}. We therefore considered that phase separation did not occur during gelation in this study and all gels were formed from homogeneous solutions, except that gels formed at 0°C and/or −20°C became slightly translucent by phase separation of the formed gel networks if they were kept for more than several hours after gelation.

RESULTS

The reciprocal of gelation time, t_{gel}, of the PVA solution is referred to as the apparent gelation rate, t_{gel}^{-1}. *Figure 2a* shows t_{gel}^{-1} of sample S3 as a function of C_p at various values of T_Q. The t_{gel}^{-1} increases with increasing C_p and with decreasing T_Q. All curves in *Figure 2a* converge at $C_p = 1.30\,g\,dl^{-1}$ independent of T_Q when extrapolated to $t_{gel}^{-1} = 0$. This critical concentration at $t_{gel}^{-1} = 0$ is referred to as $C^*_{t=\infty}$, and its value is $1.30\,g\,dl^{-1}$ for S3. *Figure 2b* is a similar plot for sample S2, which shows the same characteristics as *Figure 2a*; $C^*_{t=\infty}$ for sample S2 is $2.65\,g\,dl^{-1}$. In the previous work[5], the sol–gel diagrams were drawn after 24 h for the same system. We found that the previously reported critical gelation concentrations, C^*, of PVA with P_n ranging from 590 to 20 200 were independent of T_Q below −20°C. This C^* was considered to be identical to the chain overlap threshold concentration or the concentration at the radius of gyration contact, $C^*_{R_g}$, since $C^*_{R_g}$ calculated by considering molecular weight distributions was identical to C^* for every sample. Values of $C^*_{t=\infty}$, $C^*_{R_g}$ and C^* for samples S3 and S2 are compared in *Table 2*. The three values are almost identical for each sample in the temperature range of −20 to −60°C. $C^* \cong C^*_{t=\infty}$ shows that a standing time of 24 h is enough, at least at low T_Q, to judge if the system is a gel. From $C^*_{t=\infty} \cong C^*_{R_g}$, the chain overlap concept for

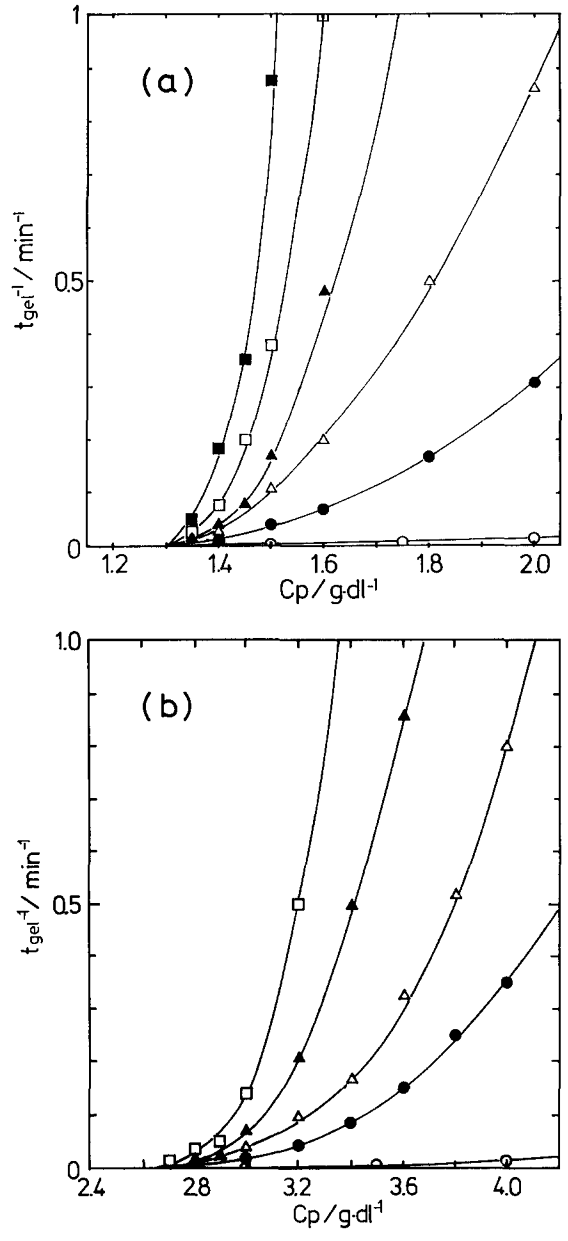

Figure 2 Apparent gelation rates, t_{gel}^{-1}, as a function of C_p for samples (a) S3 and (b) S2. T_Q: ○, 0°C; ●, −20°C; △, −30°C; ▲, −40°C; □, −50°C; ■, −60°C

Table 2 Comparison of $C^*_{t=\infty}$, $C^*_{R_g}$ and C^*

Sample	$C^*_{t=\infty}(g\,dl^{-1})^a$	$C^*_{R_g}(g\,dl^{-1})^b$	$C^*(g\,dl^{-1})^c$
S3	1.30	1.19	1.25±0.05
S2	2.65	2.49	2.80±0.20

[a] Obtained in this work by extrapolation to $t_{gel}^{-1} = 0$
[b] Chain overlap concentration calculated in the previous work[5]
[c] Critical gelation concentration measured in the previous work[5]

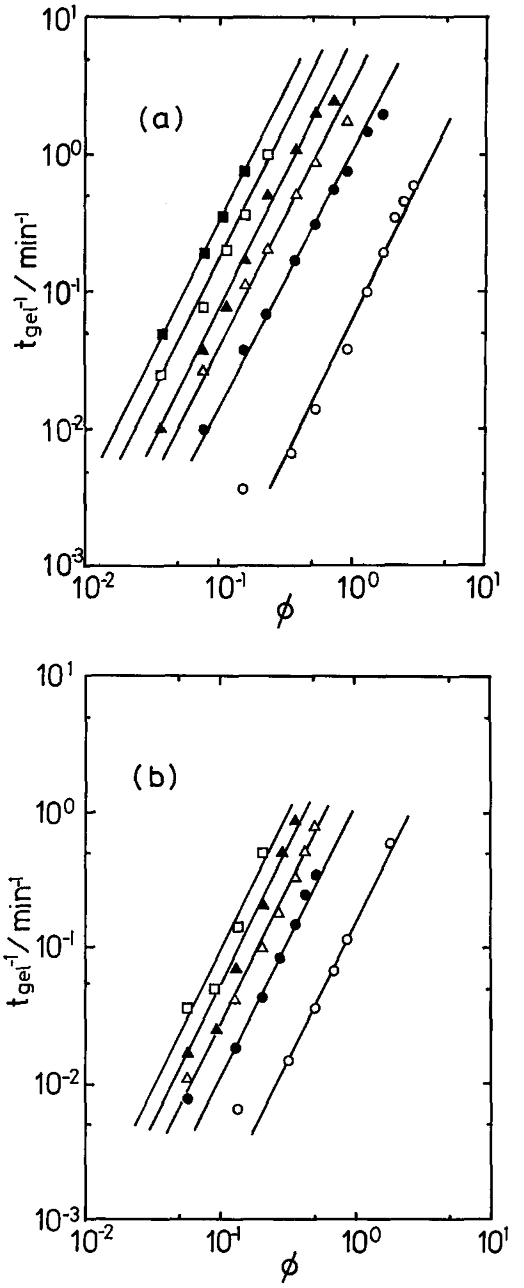

Figure 3 Double logarithmic plots of t_{gel}^{-1} against ϕ for samples (a) S3 and (b) S2. T_Q: ○, 0°C; ●, −20°C; △, −30°C; ▲, −40°C; □, −50°C; ■, −60°C

gelation is also supported; chain overlap should be necessary for gelation in the homogeneous solution. Analysis of t_{gel}^{-1} was therefore on the basis of this chain overlap concept.

Considering that cross-linking points are formed in the overlapping part of polymer chains, t_{gel}^{-1} should be related to the degree of overlap of polymer chains. In order to represent the degree of overlap, the reduced concentration, ϕ, is introduced:

$$\phi = (C_p - C_{Rg}^*)/C_{Rg}^* \qquad (1)$$

Values of ϕ were calculated using C_{Rg}^* values of 1.30 g dl^{-1} and 2.65 g dl^{-1} for samples S3 and S2, respectively. It is noted that C_{Rg}^* does not depend on T_Q in our experimental temperature range.

Figures 3a and *b* show double logarithmic plots of t_{gel}^{-1} as a function of ϕ for samples S3 and S2, respectively. In each figure, the observed points at each T_Q follow a good straight line with a slope of 2, independent of T_Q. Therefore, an interesting experimental relation is obtained:

$$t_{gel}^{-1} = A(T_Q)\phi^2 \qquad (2)$$

where $A(T_Q)$ is a constant depending on T_Q. This shows that the gelation rate can be separated into a concentration factor and a temperature factor.

DISCUSSION

Equation (2) suggests that the gelation process can be considered as the binary association of segments in the overlapping parts of polymer chains. The gelation process is discussed in order to explain equation (2) and analyse $A(T_Q)$.

Frequency of formation of the cross-linking points

Gelation from a homogeneous polymer solution is considered. When $C_p < C_{Rg}^*$ or $\phi < 0$, polymer chains hardly overlap one another, so that finite clusters of polymer chains will be formed. In the case of semidilute solutions near the chain overlap concentration, polymer chains start to overlap. The following discussion concerns the condition $0 \leqslant \phi \leqslant 1$, where ϕ denotes a volume fraction of the overlapping part to the whole volume. The average concentration of molecular segments belonging to the overlapping part is proportional to ϕC_{Rg}^*. Considering that the cross-linking points such as crystallites are constructed by segments of different polymers in the overlapping parts, the rate of cross-linking may be proportional to $(C_{Rg}^*\phi)^2$ based on the analogy of second-order reaction at the early stage of cross-linking reaction, i.e.

$$r_x = k(C_{Rg}^*\phi)^2 \qquad (3)$$

where r_x is the rate of formation of the cross-linking points per unit volume and k is a constant.

It has often been reported that the formation of cross-linking points in physical gel networks can be treated by binary association between chains[6–9]. Shibatani[6] considered that the rate of formation of cross-linking points was proportional to the square of the concentration of free cross-linking loci. We consider that in the case of semidilute solutions near the chain overlap concentration, the rate of formation of cross-linking points is proportional to the square of the reduced concentration ϕ instead of the square of polymer concentration C_p, which will be proportional to cross-linking loci.

Let us consider the gelation when crystallites of polymers are cross-linking points, as in the present system. The steady-state nucleation rate of crystallization per unit volume is proportional to:

$$\exp(-E_D/RT_Q - \Delta G^*/k_B T_Q)$$

where E_D is the energy of transport in the solid–liquid interface, ΔG^* is the Gibbs free energy of formation of a nucleus of critical size from a solution, R is the gas constant, k_B is Boltzmann's constant and T_Q is temperature[10]. When the nuclei and/or crystallites grown from them are cross-linking points, the rate of formation of cross-linking points, r_x may be regarded as proportional to the nucleation rate; that is, k in equation (3) is proportional to the steady-state nucleation rate $A'(T_Q)$:

$$k = k'A'(T_Q) \qquad (4)$$

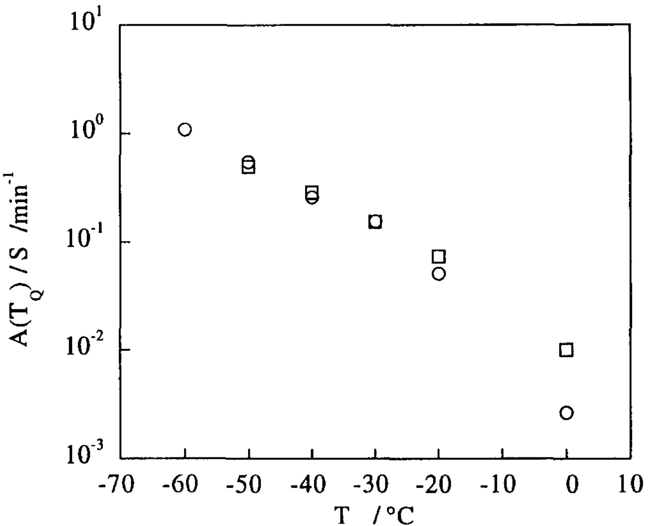

Figure 4 Temperature dependence of $A(T_Q)/S$. ○, sample S3; □, sample S2

where k' is a constant and

$$A'(T_Q) = \exp(-E_D/RT_Q - \Delta G^*/k_B T_Q) \tag{5}$$

Threshold of gelation

The gelation threshold of semidilute solution near C^*_{Rg} is determined using the bond percolation theory[2]. Considering that the centres of polymer chains occupy all sites of a periodic lattice with coordination number f and a bond is randomly formed between two nearest neighbours of lattice sites with probability p, the problem of gelation may be attributed to the random bond percolation because $0 \leqslant \phi \leqslant 1$. In this case it is assumed that the type of periodic lattice, such as a body-centred cubic lattice, does not change with C_p while the distance between sites decreases with increasing C_p. At a critical point, $p = p_c$, an infinite cluster starts to appear, where the system is regarded as a gel. The number of all possible bonds per unit volume is $Lf/2$, where L is the number of sites per unit volume. The molar concentration of cross-linking points or bonds at gelation point N^* is equal to $(p_c Lf)/2N_a$, where N_a is Avogadro's number. Using the relations $L = C_p N_a / mP_w$, where P_w and m are the weight average degree of polymerization and the molecular weight of the monomer of PVA, respectively, and $C_p = (\phi + 1)C^*_{Rg}$:

$$N^* = p_c Lf/2N_a = p_c f(\phi + 1)C^*_{Rg}/2mP_w \tag{6}$$

Gelation rate

Assuming that r_x is independent of time at the early stage of reaction, t_{gel}^{-1} can be approximated by:

$$t_{gel}^{-1} = r_x/N^* = KP_w C^*_{Rg}[\phi^2/(1+\phi)] \tag{7}$$

where $K = 2km/(p_c f)$. For $\phi \ll 1$, t_{gel}^{-1} is proportional to ϕ^2. From equations (4) and (7):

$$t_{gel}^{-1} = r_x/N^* = K'[\phi^2/(1+\phi)][P_w C^*_{Rg}]A'(T_Q) \tag{8}$$

where $K' = 2k'm/(p_c f)$.

In the previous paper, we showed that the Gaussian chain approximation is valid in the case of PVA solution. Assuming that PVA molecules are Gaussian chains in the present system, C^*_{Rg} is given by [11]:

$$C^*_{Rg} = \frac{M_w}{\frac{4}{3}\pi\langle R_g^2\rangle^{3/2}} = \frac{m(U+1)}{\frac{4}{3}\pi\left[\frac{(2U+1)bl_0}{3}\right]^{3/2}} P_n^{-1/2} \tag{9}$$

where $\langle R_g^2 \rangle$ is the mean square radius of gyration, b and l_0 are the persistence length of the polymer chain and the length of PVA monomer unit, respectively, U is the molecular weight distribution $(U = M_w/M_n - 1)$ and P_n is the number average degree of polymerization. Finally:

$$t_{gel}^{-1} = K''S[(\phi^2/(1+\phi)]A'(T_Q) \tag{10}$$

where

$$K'' = 3k'm^2/[2\pi p_c f(bl_0/3)^{3/2}]$$

and

$$S = [(1+U)^2/(1+2U)^{3/2}]P_n^{1/2}$$

because $P_w = (1+U)P_n$.

Analysis of t_{gel}^{-1}

Comparing the experimental equation (2) with equation (10), the experimental temperature factor $A(T_Q)$ can be rewritten as:

$$A(T_Q) = t_{gel}^{-1}/[\phi^2/(1+\phi)] \propto K''SA'(T_Q) \tag{11}$$

because $\phi^2/(1+\phi) \cong \phi^2$ in our experimental ϕ range, i.e. $\phi \ll 1$, except for $T_Q = 0$°C. K'' is assumed to be independent of T_Q. *Figure 4* shows a semilogarithmic plot of $A(T_Q)/S$ as a function of T_Q. Correction of $A(T_Q)$ by S is not large in our case ($S = 31.2$ and 19.0 for samples S3 and S2, respectively), but it is considered to be important when the difference in P_n or U is large. The data for samples S3 and S2 having different P_n and U agree well except at $T_Q = 0$°C. Equation (10) is a very rough approximation, but the analysis of the gelation rate on the basis of the concept of chain overlap seems to be valid. The disagreement at $T_Q = 0$°C may be due to phase separation, especially in the solution of sample S2.

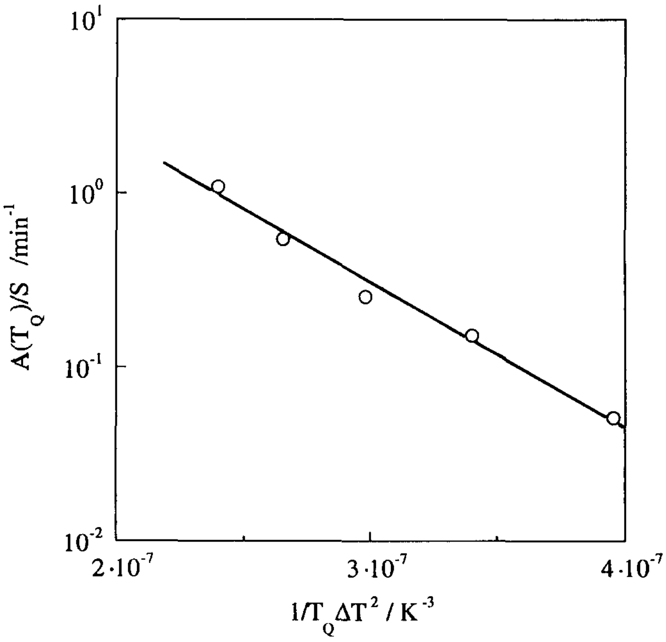

Figure 5 Semilogarithmic plot of $A(T_Q)/S$ as a function of $1/(T_Q \Delta T^2)$ for sample S3

Analysis of the T_Q dependence of gelation rate, i.e. analysis of $A'(T_Q)$, involves some assumptions. Considering that C^* is equal to $C^*_{R_g}$ and that $A'(T_Q)$ increases with decreasing T_Q, the effect of diffusion of segments on nucleation rate can be regarded as very small compared to the effect of the potential barrier of nucleation, i.e. $E_D/RT_Q \ll \Delta G^*/k_B T_Q$ in equation (5). In the case of nucleation from a polymer–diluent mixture the steady-state nucleation theory[12] gives:

$$\Delta G^* = \frac{B(T_Q)T_d^2}{(\Delta H \Delta T)^2} \qquad (12)$$

where

$$B(T_Q) = 8\pi\sigma_u^2\sigma_e - 4\pi R T_Q \sigma_u^2 \ln(v_2)$$

σ_u and σ_e are excess interfacial free energies for the side and end surfaces of a crystallite, respectively, $\Delta T = T_d - T_Q$ (T_d is the dissolution temperature of PVA crystallites), v_2 is the volume fraction of the polymer and ΔH is the heat of fusion. $T_d = 80°C$ is adopted from the previous work. *Figure 5* shows a semilogarithmic plot of $A(T_Q)/S$ as a function of $1/(T_Q \Delta T^2)$ for equation (11). The observed values are almost on a straight line showing that the steady-state nucleation theory may be applied to gelation from PVA solutions where $B(T_Q)$ can be regarded as independent of T_Q. Apparent ΔG^* can be calculated from the slope of $1.86 \times 10^7\,K^3\,min^{-1}$; e.g. $\Delta G^* = 2.6\,kcal\,mol^{-1}$ at $T_Q = -40°C$.

If we use a value of $A(T_Q)$ extrapolated to 23°C, gelation time is calculated to be about 120 h for the S3 solution, with $C_p = 2\,g\,dl^{-1}$ at 23°C, while the corresponding experimental value is about 20 h. The great difference between the calculated and the observed values may be explained by liquid–liquid phase separation, which will accelerate gelation, as discussed in the previous paper[5].

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