Gels of poly(vinyl alcohol) from dimethyl sulphoxide/water solutions

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Sol–gel diagrams of atactic poly(vinyl alcohol) (at-PVA) in a mixture of dimethyl sulphoxide and water (60/40 vol/vol) have been investigated. The crosslinking points of the gels are crystallites of PVA. Gelation of seven samples of at-PVA having degrees of polymerization (P_n) ranging from 186 to 20 200 was observed at quenching temperatures (T_Qs) between -60°C and 80°C. Gelation time, which is defined as time required for gelation, decreases with decreasing T_Q. In a temperature range below ~ -20°C, the gels are transparent and the critical gelation concentrations (C^*s) are independent of T_Q for all the samples except the lowest P_n. Further, C^*s in this temperature range are proportional to $P_n^{-0.5}$, suggesting that C^* is determined by the polymer chain overlap concentration. On the other hand, gels formed above -20°C are not transparent, and the degree of transparency decreases with increasing T_Q. The lowest C^* which is lower than the overlap concentration for polymer chains with radius of gryration R_g is observed in the T_Q range of -20 to 40°C. This may be explained by the effect of liquid–liquid phase separation or spinodal decomposition, which is supported by T_Q and PVA concentration dependences of u.v. transmission.

(Keywords: poly(vinyl alcohol); sol–gel diagram; crystallites; polymer chain overlap concentration; phase separation; transparency)

INTRODUCTION

A polymer gel is a continuous network of chains crosslinked by chemical or physical junctions. Physical junctions in polymer gels may be classified into at least four types[1,2]: crystallites for crystalline polymers, double helical structure for biological polymers, nodules for block copolymers and polymer–solvent complexes. Gelations accompanying crystallization have been extensively studied for various polymer systems[3–5]. However, there remain a lot of unsolved problems in this field.

Poly(vinyl alcohol) (PVA) is a typical crystalline polymer, and many studies have been carried out on aqueous PVA gels, where the crosslinking points are thought to be crystallites. Shibatani[6] suggested from the macroscopic rigidity of the gel that the crosslinking points of the aqueous PVA gel would be syndiotactic sequences of six to eight monomer units. This is in accordance with the value estimated by Takahashi and Hiramitsu[7] from melting temperature measurements. Matsuzawa *et al.*[8,9] examined effects of syndiotacticity and found that aqueous gels of syndiotactic-rich PVA have higher melting temperatures and higher elastic moduli than those of atactic PVA (at-PVA) aqueous gels. Komatsu *et al.*[10] investigated the relationship between gelation and phase separation (spinodal decomposition) of the PVA–water system, concluding that spinodal decomposition is not necessary for gelation but has a significant effect on gelation.

Hyon *et al.*[11] have reported that the transparent and high elastic gel of PVA can be obtained from a solution of dimethyl sulphoxide (DMSO) and water when it is cooled below 0°C. The freezing temperature of the mixture depends on the fraction of DMSO[12], and a mixture with 60 vol% DMSO does not freeze down to -70°C. In order to understand the gelation mechanism of PVA, it is essential to carry out investigations over wide temperature and concentration ranges. Therefore, a mixture of DMSO and water, which does not freeze until very low temperatures, is suitable as a solvent for PVA.

In this work, we have investigated the gelation of at-PVA in a mixture of DMSO and water (60/40 vol/vol). As mentioned above, this system enables the gelation of PVA to be investigated over a wide temperature range (-60 to 80°C). We have experimentally determined the sol–gel diagrams and the degree of turbidity of the system as functions of temperature and PVA concentration. Based on these results, we discuss the critical gelation concentration of the system and the effect of phase separation upon gelation.

EXPERIMENTAL

Fully saponified at-PVAs with number-average degrees of polymerization (P_n) in the range of 186–20 200 (Unitika Chemical Co. and Kuraray Co. Ltd) were used. Molecular weights and their distributions were determined from g.p.c. measurements of a 0.25 wt% tetrahydrofuran solution of poly(vinyl acetate) which was obtained by acetylation of the corresponding parent PVA. For the calculation of the molecular weight, the equation proposed by Mori[13] was used. The triad tacticities *mm*, *mr* and *rr* of the at-PVA samples were determined from 400 MHz ^{1}H n.m.r. measurements in deuterated DMSO, based on the assignment of OH

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Table 1 Characteristics of the at-PVA samples

Sample	P_n [a]	M_w/M_n [b]	Fraction[c] *mm*	*mr*	*rr*	Lot no.
S1	186	2.04	0.20	0.49	0.32	U8002[d]
S2	590	1.61	0.21	0.49	0.30	G2117[d]
S3	1640	1.97	0.21	0.49	0.30	UV[d]
S4	5430	1.90	0.22	0.49	0.29	HMPVA3[e]
S5	10700	1.99	0.22	0.49	0.29	HMPVA4[e]
S6	11900	1.93	0.22	0.49	0.29	HMPVA1[e]
S7	20200	2.17	0.22	0.49	0.29	HMPVA2[e]

[a] Calculated from number-average molecular weight
[b] Measured by g.p.c.
[c] Measured by n.m.r.
[d] Supplied by Unitika Chemical Co.
[e] Supplied by Kuraray Co. Ltd

triplet signals[14]. No signal of the acetyl group at ~1.8 ppm was observed in the PVA samples, indicating that they were fully saponified. The characteristics obtained are given in *Table 1*. Sample solutions were prepared by the following procedure. A given amount of at-PVA was dissolved in a mixture of DMSO and water (60/40 vol/vol) at ~130°C in an autoclave to be homogenized, and solutions with different concentrations were prepared by adding a corresponding amount of solvent. For gelation experiments, the solution (2 ml) was heated at 95°C for 15 min in a test tube (10 mm diameter) to be homogenized and then quickly quenched in a bath kept at a given quenching temperature (T_Q) between −60°C and 80°C. After standing for 24 h, the test tube was tilted. When the solution flowed under its own weight, it was regarded as a sol. Transparency of the gel was evaluated by u.v. transmission in the wavelength range of 400–800 nm. The measurements were carried out by a double-beam spectrophotometer Hitachi-220. In this case, the PVA solutions were gelled in a quartz cell (10 mm × 10 mm × 50 mm). To avoid the surface of the cell becoming cloudy, the measurements were carried out under dry nitrogen atmosphere, immediately after the cell was removed from the bath.

RESULTS AND DISCUSSION

Figure 1 shows the sol–gel phase diagrams as functions of PVA concentration (C_p) and T_Q 24 h after quenching to T_Q for at-PVA samples with P_n values ranging from 186 to 20200 in a mixture of DMSO and water (60/40 vol/vol). Solid lines for the individual samples were drawn by eye. The time required for gelation (t_{gel}) depends on C_p, T_Q and P_n. Roughly speaking, t_{gel} increases with increasing T_Q, and decreasing C_p and P_n. This means that the sol–gel diagram depends on the standing time after quenching. It was, however, confirmed that gelation is almost completed within 24 h for the ranges of T_Q, C_p and P_n employed in this study, though above 40°C it took longer than 24 h. Even in the latter case, the phase diagram obtained is similar to that obtained for a standing time of 24 h. The sol–gel transition curves in *Figure 1* appear to be complicated, but the temperature dependence is almost identical for all the samples. Some distinct features are seen dependent on the range of T_Q: (1) below ~−20°C the critical gelation concentration (C^*) is independent of T_Q except for the lowest molecular weight sample S1; (2) between ~−20°C and ~40°C the lowest C^* is lower than that below −20°C; and (3) above ~40°C, C^* increases rapidly with increasing T_Q, and above ~75°C gelation was not observed.

We first consider the sol–gel transition curves below −20°C. In *Figure 2*, the average C^* for various T_Qs is plotted against P_n in double logarithmic expression. The slope of the straight line is −0.5 and the following relationship is obtained:

$$C^* = K(P_n)^{-0.5} \quad (1)$$

where K is a constant. This relationship implies that C^* is determined by the overlap threshold of Gaussian chains. As will be shown later, the gels formed below −20°C are transparent, suggesting that gelation occurs homogeneously. When an infinite network is formed over the whole system in the homogeneous solution, polymer chains should overlap. The homogeneous solution lower than the overlap concentration cannot become a gel

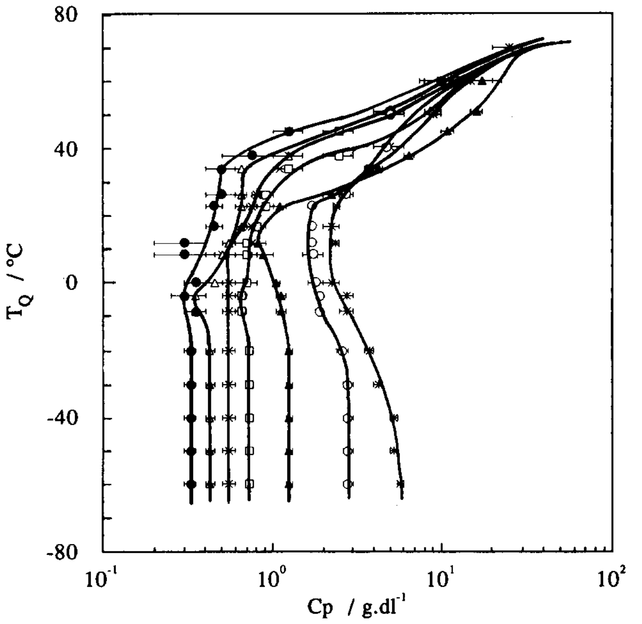

Figure 1 Sol–gel transition diagrams of at-PVA in a mixture of DMSO and water (60/40 vol/vol) for the samples listed in *Table 1*: (✱) S1; (○) S2; (▲) S3; (□) S4; (×) S5; (△) S6; (●) S7

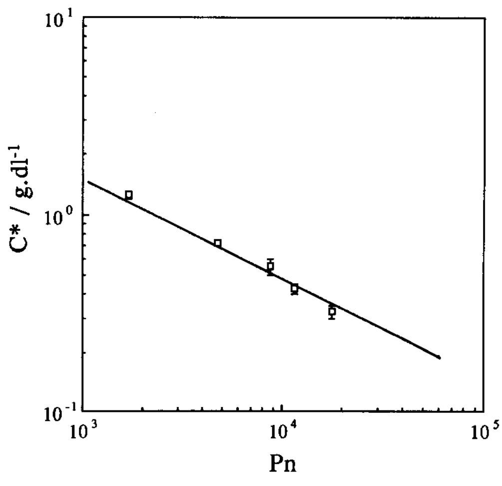

Figure 2 Critical gelation concentration C^* as a function of the degree of polymerization P_n of PVA in the temperature range between −20°C and −60°C

Table 2 Comparison of C^* and $C^*_{R_g}$ calculated from equation (4)

Sample	$C^*_{R_g}$ (g dl^{-1})	C^* (g dl^{-1})
S1	3.43	5.25 ± 0.25[a]
S2	2.49	2.80 ± 0.20
S3	1.19	1.25 ± 0.05
S4	0.684	0.725 ± 0.025
S5	0.465	0.550 ± 0.050
S6	0.454	0.425 ± 0.025
S7	0.310	0.325 ± 0.025

[a] Value at −50°C

because crosslinking points do not connect over the system. Therefore chain overlap is necessary for gelation from the homogeneous solution. The overlap concentration $C^*_{R_g}$ for polymer chains with radius of gyration R_g is given by:

$$C^*_{R_g} = \frac{M_w}{(4/3)\pi\langle R_g^2\rangle^{3/2}} \tag{2}$$

where M_w is the weight-average molecular weight and $\langle R_g^2\rangle$ is the mean square radius of gyration of the polymer chain. $\langle R_g^2\rangle$ is given by equation (3) under the Gaussian chain approximation with molecular weight distribution $U = M_w/M_n - 1$ (ref. 15):

$$\langle R_g^2\rangle = \frac{bL(2U+1)}{3(U+1)} \tag{3}$$

where b is the persistence length and L is the contour length. Equations (2) and (3) give the relationship:

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

where m and l_0 are the molecular weight and the length of the PVA monomer unit, respectively. The dependence of $C^*_{R_g}$ on P_n agrees with the experimental result [see equation (1)]. We also calculated $C^*_{R_g}$ from equation (4) assuming a persistence length b. The measurement of the persistence length at low temperatures is very difficult because gelation or aggregation occurs very easily. Therefore, it was estimated from the literature. In reference 16 the end-to-end distance (r_0) as a function of molecular weight (M) is given as $r_0 = 950 \times 10^{-4}M^{1/2}$ for a PVA/water system at 30°C. Using the worm-like chain model, we obtain $b = 8$ Å. However, we adopted a value of 7 Å as the most reasonable value because it provides the best agreement between calculated $C^*_{R_g}$ and the observed C^*. The molecular weight distributions were taken from *Table 1*. The results are summarized in *Table 2*, where C^* values are also listed. The agreement between C^* and $C^*_{R_g}$ is very good except for sample S1 which has the lowest molecular weight.

As shown above, it seems natural to regard the chain overlap concentration as a critical gelation concentration. This concept has been successfully applied to the gelation of atactic polystyrene (at-PS) in carbon disulphide (CS_2)[17,18] where the crosslinking points were thought[2] to be a complex between at-PS and CS_2. To our knowledge, however, the gelation of PVA in DMSO/water below −20°C is the first crystallite system for which the chain overlap concept can be applied. In the study of gelation of linear polyethylenes in toluene or *p*-xylene[5] where the crosslinking points are crystallites, it was reported that the chain overlap concept was invalid. This may be due to the large crystallites of polyethylene. It is therefore considered that the chain overlap concept cannot be applied to gelation from a heterogeneous system caused by phase separation or to gelation accompanying large crystallite formation.

In the temperature range between −20°C and 40°C, each sample has C^* values lower than $C^*_{R_g}$; the temperature range for sample S6 is between −15°C and 0°C. If the solution is homogeneous, it is considered difficult to form a gel at a concentration lower than $C^*_{R_g}$ because all the polymer chains cannot connect. It is therefore suggested that gelation in this temperature range occurs in the heterogeneous solution. By analogy of aqueous gels of PVA[10], the origin of the heterogeneity may be caused by liquid–liquid phase separation or spinodal decomposition. This is supported by the fact that the gels in this temperature range are translucent or opaque as will be shown later. The structure of solutions after spinodal decomposition has been reported[18,19]; it consists of concentrated and dilute phases, and the concentrated phase is continuous like a network over the whole system. When the concentration of at-PVA in the concentrated phase is larger than $C^*_{R_g}$, gelation can occur and the connectivity of the concentrated phase makes it possible to consider the whole system as a gel even though the macroscopic average concentration is lower than the overlap concentration. This is the reason why between −20°C and 40°C C^* is lower than $C^*_{R_g}$. Thus, the sol–gel curves above −20°C may be considered as those obtained by shifting the sol–gel curves which would be obtained without phase separation, to lower concentration.

Above the temperature corresponding to the lowest C^*, C^* increases with increasing T_Q. This is explained by taking into account that the crosslinking points in the PVA gel are crystallites[20]. From the crystallization point of view, at-PVA is regarded as a copolymer of different stereoisomers only the syndiotactic-rich sequences of which are available for crystallization[6,7]. According to the theory of crystallization in copolymers by Flory[21], the sequences longer than the minimum stable crystallite length at equilibrium, which increases with increasing temperature, can be converted to crystallites. The number of syndiotactic sequences longer than the minimum length per chain or the number of crystallites therefore decreases with increasing temperature. Consequently, C^* increases with increasing temperature. The level-off of the sol–gel curves is observed at 70–75°C for all the at-PVA samples. The equilibrium dissolution temperature of the PVA crystals in the DMSO/water solution is above 75°C.

We have been discussing the sol–gel diagrams assuming liquid–liquid phase separation in the solution. In order to confirm this assumption, we measured the u.v. transmission of the gels and sols. *Figure 3* shows the dependence of u.v. transmission on T_Q for sample S3 at a concentration of 6 g dl^{-1}. The measurements were started 24 h after quenching to T_Q under the same conditions as those employed for obtaining the sol–gel diagram. The transmission of the gel prepared below −20°C is >85%, suggesting that phase separation does not occur and the gel is formed from the homogeneous solution. The transmission begins to decrease above −20°C, indicating that phase separation occurs above ~ −20°C. This result supports the observation of C^* being lower than $C^*_{R_g}$ as being due to phase separation.

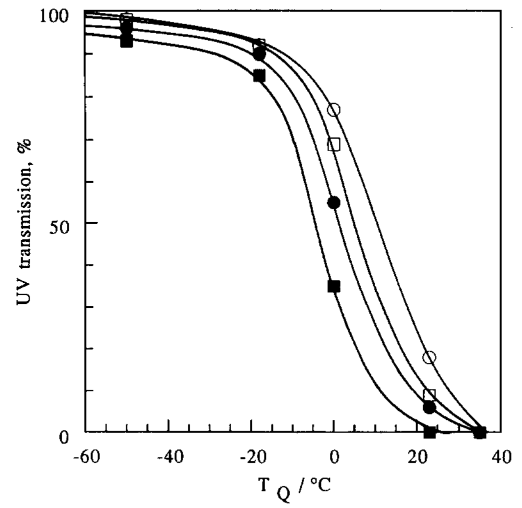

Figure 3 U.v. transmission for the S3 gels as a function of quenching temperature T_Q. The measurements were performed 24 h after quenching. $C_p = 6\ \mathrm{g\ dl^{-1}}$. U.v. wavelength: (○) 800; (□) 700; (●) 600; (■) 500 nm

The transmission at 35°C is almost zero. Though the solution with $C_p = 6\ \mathrm{g\ dl^{-1}}$ does not gel above 40°C in 24 h, the solution with higher C_p can gel at higher T_Q in 24 h as shown in *Figure 1.* It was confirmed that u.v. transmission can be hardly detected for gels of higher C_p formed above 40°C. Therefore, even if the gelation occurs in a given concentration above 40°C, it will be after phase separation is almost completed. There is another possibility for the origin of the turbidity of gels; the existence of large crystals or superstructure such as spherulites makes the system turbid. We, however, discarded this possibility because we cannot explain the fact that C^* is lower than $C^*_{R_g}$ in the temperature range between −20°C and 40°C.

It is noted from *Figure 3* that the u.v. transmission for the S3 gels decreases with decreasing wavelength. The wavelength dependence may be related to the structure of the phase separation. For a detailed study, however, light scattering experiments, currently in progress, are essential.

The PVA solution does not become turbid above 75°C (not shown in *Figure 3*). This means that the solution has an upper critical solution temperature (*UCST*) at ~75–80°C. However, the gels formed below −20°C are also transparent as shown in *Figure 3.* Does this mean that the solution has a lower critical solution temperature (*LCST*), too? As shown below, the solution may not have a *LCST. Figure 4* shows the time evolution of the u.v. transmission of the S3 solution with $C_p = 6\ \mathrm{g\ dl^{-1}}$ after quenching to −40, 23 and 45°C. The t_{gel} at each T_Q is represented by a downward arrow in the figure. The t_{gel} decreases with decreasing T_Q. The transmissions at t_{gel} are 95, 70 and 20% at −40, 23 and 45°C, respectively. At 23°C and 45°C, the solution first becomes turbid, and then gelation occurs to form opaque gel. In other words, phase separation occurs before gelation. This agrees well with the picture discussed above to explain that in the temperature range between −20°C and 40°C C^* is lower than $C^*_{R_g}$ below −20°C. On the other hand, at −40°C gelation occurs within a few minutes to form transparent gel and the transmission after gelation decreases very slowly. This may be because the rate of gelation at −40°C is so fast that it occurs before phase separation, and the homogeneous gel structure formed at such low temperatures is so rigid that phase separation is greatly obstructed. It is noted, however, that the transmission of the formed gels decreases slowly with time, suggesting that phase separation occurs even in the gel phase. When we consider turbidity of gels due to phase separation, two types of phase separation should be distinguished; one is liquid–liquid phase separation before gelation and the other is phase separation in the network structure after gelation. In *Figure 4*, the curve for 45°C corresponds to the former and that for −40°C to the latter. In the case of gelation at 23°C the transmission immediately after gelation is 70% and decreases with time, approaching zero ~1000 min after quenching. It seems that the gel structure is formed mainly in the concentrated phase produced by phase separation since gelation occurs as phase separation proceeds. The phase separation proceeds even after macroscopic gelation at 23°C. This may be because many polymer segments not taking part in constructing the gel structure at the macroscopic gelation point proceed phase separation. This is in contrast to the gel formed at −40°C. In recent years, the problem of phase separation in the network has been of great interest and has been discussed on the basis of elasticity of gels[22]. We, however, do not discuss this problem as it is beyond the scope of this paper.

Finally, we measured the u.v. transmission of the at-PVA gels as a function of C_p (*Figure 5*). The measurements were performed 24 h after quenching to 23°C. The transmission first decreases with increasing C_p, but it increases again through a minimum around a C_p of $8\ \mathrm{g\ dl^{-1}}$. In the low C_p range, the degree of turbidity due to phase separation may be determined from the amount of the concentrated phase in the system as judged by the phase diagram with *UCST.* Therefore unless gelation occurs, the turbidity of the system would increase with increasing C_p. This explanation is valid for C_p below $4\ \mathrm{g\ dl^{-1}}$ in *Figure 5* because t_{gel} below $4\ \mathrm{g\ dl^{-1}}$ is much longer than that at higher C_p as shown in *Figure 6* and it is considered that phase separation may occur before gelation in the low concentration range. On the other hand, t_{gel} decreases with increasing C_p. In the higher concentration range above $8\ \mathrm{g\ dl^{-1}}$, gelation occurs during or before phase separation. This may be because above $C^*_{R_g}$ the rate of phase separation becomes slower with increasing C_p. Since gel formation makes phase

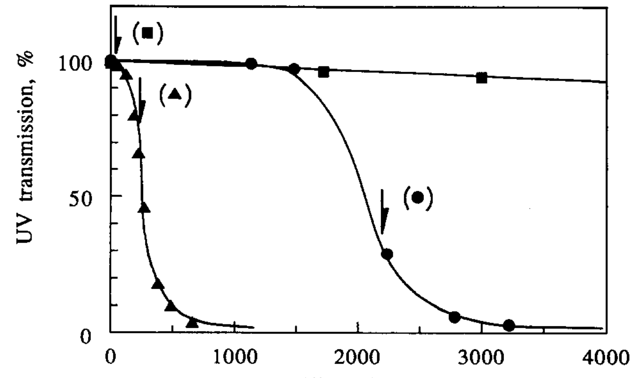

Figure 4 Time evolution of u.v. transmission for S3 after quenching to various T_Q. Downward arrows indicate the gelation time. The u.v. wavelength used is 500 nm. $C_p = 6\ \mathrm{g\ dl^{-1}}$. T_Q: (■) −40; (▲) 23; (●) 45°C

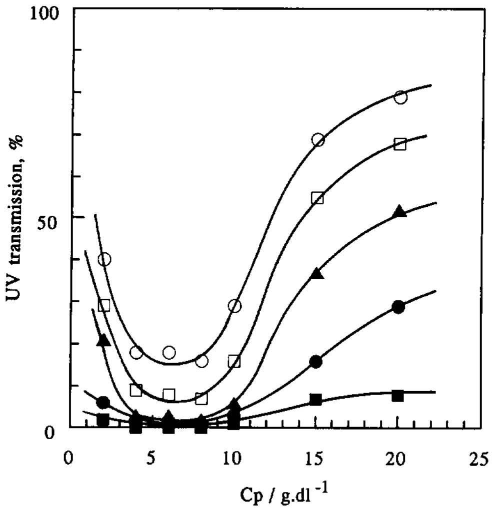

Figure 5 U.v. transmission for the S3 gels as a function of PVA concentration C_p. The measurements were performed 24 h after quenching to 23°C. U.v. wavelength: (○) 800; (□) 700; (▲) 600; (●) 500; (■) 400 nm

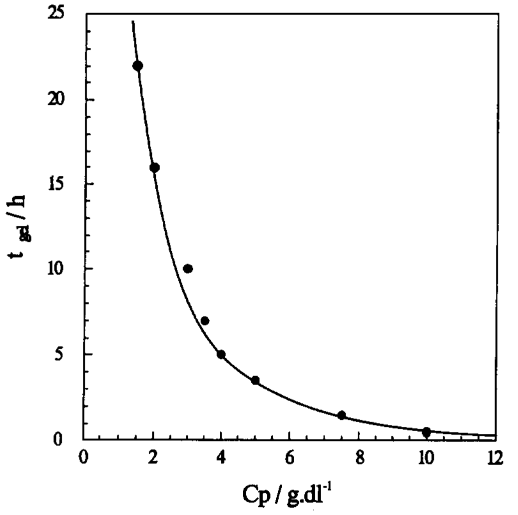

Figure 6 Gelation time t_{gel} for S3 at 23°C as a function of PVA concentration C_p

separation difficult and the gel structure becomes stronger with increasing C_p, the transmission increases with C_p.

In this paper, we have determined the sol–gel diagrams of at-PVA in a mixture of DMSO and water (60/40 vol/vol) and explained the results by the concept of competition between crystallization resulting in crystallites as crosslinking points and phase separation. At T_Q values below −20°C, gelation occurs very rapidly to interrupt the development of phase separation. In this temperature range, C^* corresponds to $C^*_{R_g}$. The lowest C^* of each sol–gel diagram is observed in a T_Q range from −20 to 40°C, where gels are translucent or opaque. This result is well explained by taking into account liquid–liquid phase separation or spinodal decomposition.

REFERENCES

1 de Gennes, P. G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, 1979
2 François, J., Gan, Y. S., Sarazin, D. and Guenet, J. M. *Polymer* 1988, **29**, 898
3 Keller, A. 'Structure–Property Relationships of Polymeric Solids' (Ed. by A. Hiltner), Plenum, New York, 1983, p. 25
4 Mandelkern, L., Edwards, C. O., Domszy, R. C. and Davidson, M. W. 'Microdomains in Polymer Solution' (Ed. P. Dubin), Plenum, New York, 1985, p. 121
5 Domszy, R. C., Alamo, R., Edwards, C. O. and Mandelkern, L. *Macromolecules* 1986, **19**, 310
6 Shibatani, K. *Polym. J.* 1970, **1**, 348
7 Takahashi, A. and Hiramitsu, S. *Polym. J.* 1974, **6**, 103
8 Ogasawara, A., Nakajima, T., Yamaura, K. and Matumoto, S. *Progr. Colloid. Polym. Sci.* 1975, **57**, 145
9 Yamaura, K., Takahashi, T., Tanigami, T. and Matsuzawa, S. *J. Appl. Polym. Sci.* 1987, **33**, 1983
10 Komatsu, M., Inoue, T. and Miyasaka, K. *J. Polym. Sci., Polym. Phys. Edn* 1986, **24**, 303
11 Hyon, S.-H., Cha, W.-I. and Ikada, Y. *Polym. Bull.* 1989, **22**, 119
12 Rasmussen, D. H. and MacKenzie, A. P. *Nature* 1968, **220**, 1315
13 Mori, S. *J. Chromatogr.* 1978, **157**, 75
14 Hu, S., Horii, F. and Odani, H. *Bull. Inst. Chem. Res., Kyoto Univ.* 1990, **67**, 239
15 Oberthür, R. C. *Makromol. Chem.* 1978, **179**, 2693
16 Brandrup, J. and Immergut, E. H. (Eds) 'Polymer Handbook', 3rd Edn, Wiley Interscience, New York, 1989, p. VII–36
17 Tan, H.-M., Moet, A., Hiltner, A. and Baer, E. *Macromolecules* 1983, **16**, 28
18 Callister, S., Keller, A. and Hikmet, R. M. *Makromol. Chem.* 1990, **39**, 19
19 van Aartsen, J. J. *Eur. Polym. J.* 1970, **6**, 919
20 Kanaya, T., Ohkura, M. and Kaji, K. *Polym. Prepr. Jpn* 1990, **39**, 2171
21 Flory, P. J. *Trans. Faraday Soc.* 1955, **51**, 848
22 Sekimoto, K. and Kawasaki, K. *Phys. Rev.* 1989, **A39**, 4912