Sol–gel transition of poly(vinyl alcohol)–borate complex

Mitsuhiro Shibayama, Hiroyuki Yoshizawa, Hidenobu Kurokawa, Hiroshi Fujiwara and Shunji Nomura

Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Kyoto 606, Japan

The gel–sol transition of poly(vinyl alcohol) (PVA)–borate aqueous solutions was investigated as a function of polymer concentration, molecular weight, boric acid concentration and pH. By employing a modified Eldridge–Ferry theory for thermoreversible gels, we found that the gel melting temperature vs. gel melting concentration curves could be superimposed with respect to the molecular weight of PVA and boric acid concentration. The enthalpy of crosslink formation was estimated to be around -7 kcal mol^{-1} of junctions, which is consistent with literature values. The critical gelation concentration above which the solution is capable of gelation was also estimated as a function of the degree of polymerization.

(Keywords: poly(vinyl alcohol); gel; sol–gel transition; borate ion)

INTRODUCTION

Studies on thermoreversible gels have been extensive in the past decade since the discovery of the possibility of gelation in non-crystallizable polymers, e.g. a-polystyrene[1-6] and poly(vinyl chloride)[7,8]. The gel–sol transition curve (the gel melting temperature) in a plot of temperature vs. polymer concentration is studied in the light of the phase diagram for gels proposed by Coniglio et al.[9] The gel melting temperature and the enthalpy of crosslink formation are discussed in terms of theories of gel melting proposed by Eldridge and Ferry[10] and Park et al.[11], from which the mechanism of gelation is deduced.

Poly(vinyl alcohol) (PVA) aqueous solutions are well known to be capable of gel formation[12]. Prins et al.[13] studied a PVA gel in a mixture of ethylene glycol and water by quasi-elastic light scattering. The gel was prepared by temperature quenching. They observed that a resonance maximum related to coupled cooperative motions disappeared upon ageing. They concluded that this disappearance was due to the crystallization of PVA. Pines[14] reported that PVA gels were formed via initial liquid–liquid nucleated phase separation followed by syneresis caused by the formation of small crystallites in the polymer-rich regions. Komatsu et al.[15] studied the kinetic aspects of PVA gels via light scattering. They concluded that PVA–water had an upper critical solution temperature (UCST) and the spinodal curve crossed the sol–gel transition curve.

It is also well known that PVA reacts with borate ions and becomes a gel[16-19]. The thermal, optical and mechanical properties of PVA–borate gels (hereafter we call these alkaline gels) are very different from those of borate-free gels (so-called hydrogels). The former are thermoreversible[19], mostly clear and elastic, whereas the latter are not[14,15]. Since most work has been done on hydrogels, the origins of the difference in optical and mechanical properties are not well understood. Although the motivation of this work originated from the above question, we mainly discuss the gel melting behaviour of thermoreversible PVA–borate gels as a function of the degree of polymerization, polymer concentration, boric acid concentration and pH.

EXPERIMENTAL

Sample preparation

Resaponified atactic PVA powders were supplied by Unitika Kasei Co. Ltd, Japan. *Table 1* shows the sample characteristics. The triad tacticity was determined to be 21.6% iso, 48.9% hetero and 29.5% syndio by ^{1}H n.m.r.[20] The molecular weight was determined by viscometry.

The prescribed PVA powders were dissolved in distilled water by heating. After homogenization, boric acid solution and sodium hydroxide solution were added with a microsyringe. The microsyringe was calibrated with distilled water by measuring the weight at room temperature.

Gel melting temperature measurements

The gel melting temperature was measured as follows: A sample test tube was kept in a temperature-regulated water bath. Then the test tube was turned upside down and the meniscus checked. When the gel started to flow, the

Table 1 Sample characteristics

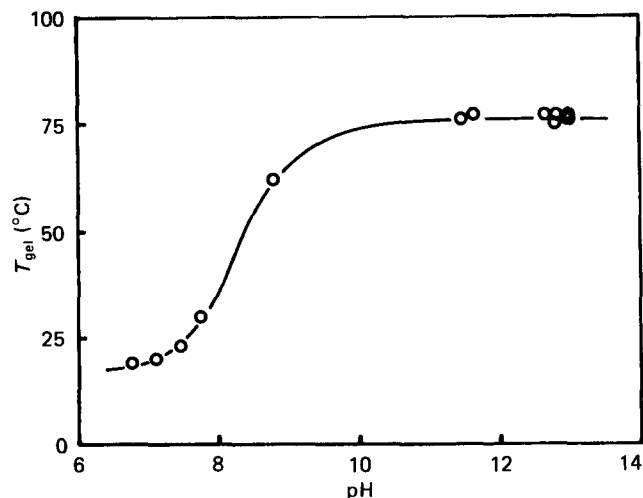| Sample code	Degree of polymerization, P	Degree of saponification (mol%)
PVA120	120	99.87
PVA300	300	99.87
PVA1790	1790	99.91
PVA2570	2570	99.08
PVA3230	3230	>99.5

Figure 1 pH dependence of the gel melting temperature of PVA300–boric acid aqueous solutions. The boric acid concentration b is $2.5 \times 10^{-2}\,\text{mol}\,\text{l}^{-1}$
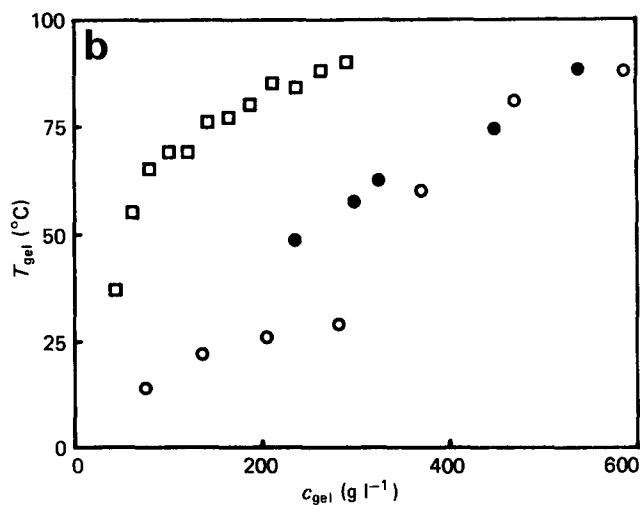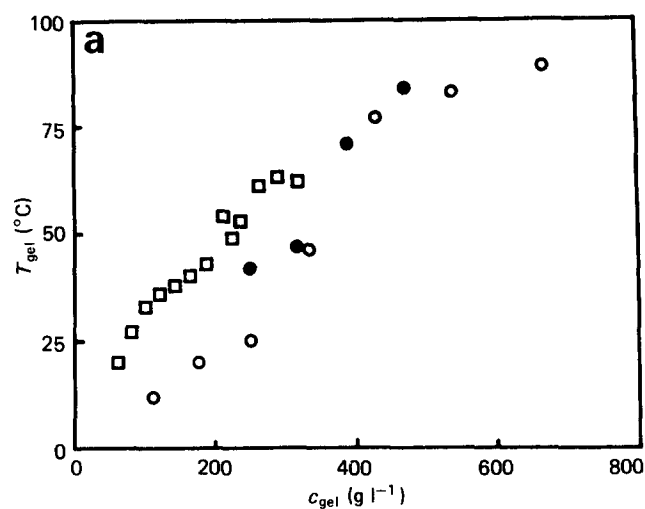

Figure 2 Gel melting temperatures of hydrogels chilled at 0°C (O), hydrogels chilled at 20°C (●) and alkaline gels (□) as functions of (a) PVA120 and (b) PVA300 concentrations $(b=2.5 \times 10^{-2}\,\text{mol}\,\text{l}^{-1}$; $[\text{NaOH}]=0.167\,\text{mol}\,\text{l}^{-1})$

temperature was recorded as the gel melting temperature. The same experiment was repeated several times. It was found that the transition temperature was reproducible and reversible with an error of ±2°C if the pH of the system was higher than pH ~ 10. It was also found that

the gel melting temperature determined by this method was identical to that determined by the ball-drop method[2,21].

RESULTS

The pH dependence of the gel melting temperature

Figure 1 shows the pH dependence of the gel melting temperature T_{gel} of PVA300–boric acid aqueous solution. The boric acid concentration was $2.5 \times 10^{-2}\,\text{mol}\,\text{l}^{-1}$. The gel melting temperature increases dramatically around pH 8.2. However, the gel melting temperature is not pH-dependent when the pH is higher than 10. Therefore, we fixed the pH to be higher than 10 in the following experiments to avoid any influence due to slight changes in pH and NaOH concentration.

Hydrogels and alkaline gels

Figures 2a and 2b show the gel melting temperatures of hydrogels and alkaline gels of PVA120 and PVA300, respectively, as functions of PVA gel melting concentration c_{gel}. The open and full circles in the figures show T_{gel} values of the hydrogels chilled at 20°C for 24 h and those chilled at 0°C for a week. The T_{gel} for alkaline gels (pH 11) is shown as open squares. In the case of the hydrogel, T_{gel} was found to be dependent on the chilling temperature, as discussed in the literature[12,15]. In contrast to the hydrogels, the alkaline gels were found to have a thermoreversible sol–gel transition at T_{gel} and to be independent of chilling temperature. Since the gel melting temperature T_{gel} was found to be identical to the gelation temperature for alkaline gels, both characteristic temperatures are commonly denoted as T_{gel} in this paper. The T_{gel} values for the alkaline gels are somewhat higher than those for the hydrogels at a given concentration, particularly in the case of PVA120.

PVA concentration, molecular weight and boric acid concentration dependence

The gel melting temperature was measured by changing the PVA gel melting concentration c_{gel}, the degree of polymerization P of PVA and the boric acid concentration b. Figure 3 shows plots of the gel melting

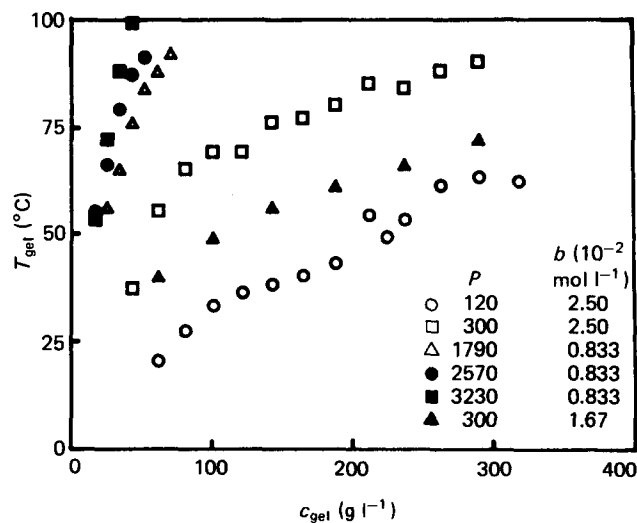|	P	b (10^{-2} mol l^{-1})
O	120	2.50
□	300	2.50
△	1790	0.833
●	2570	0.833
■	3230	0.833
▲	300	1.67

Figure 3 Effects of molecular weight and boric acid concentration on the gel melting temperature (T_{gel}) versus PVA gel melting concentration c_{gel} $([\text{NaOH}]=0.167\,\text{mol}\,\text{l}^{-1})$
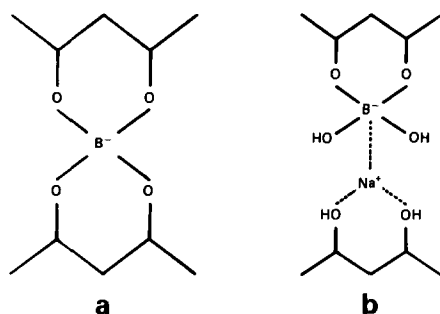
Figure 4 Models of the PVA–borate ion complex: (a) the di-diol type and (b) the ionic bonding type

temperature T_{gel} vs. the gel melting concentration c_{gel} for systems having different PVA molecular weights and boric acid concentrations. It was found that the higher the concentration, the higher was the gel melting temperature. In addition, the degree of polymerization and boric acid concentration dependence were also observed.

DISCUSSION

As shown in the previous subsection, it was found that the gel melting temperature was dependent on the PVA concentration, the molecular weight of PVA and the boric acid concentration. According to the modified Eldridge–Ferry theory of gel melting, as discussed in the Appendix, the gel melting concentration c_{gel} scales with respect to boric acid concentration b and degree of polymerization P, and is given by:

$$\ln(c_{gel}Pb) = \text{constant} + \Delta H/RT_{gel} + \ln\{([H^+] + K_a)/K_a\} \tag{1}$$

where ΔH and K_a are, respectively, the enthalpy of crosslink formation and the ionization constant of boric acid; and R, T and $[H^+]$ are the gas constant, absolute temperature and proton concentration, respectively. Since $pK_a = -\log K_a$ is around 9.0, a significant change in c_{gel} around pH 9 is expected from equation (1). This was confirmed experimentally, as shown in *Figure 1*. When $[H^+] \ll K_a$, equation (1) is written as:

$$\ln(c_{gel}Pb) = \text{constant} + \Delta H/RT_{gel} \tag{1a}$$

This condition is attained when pH > 10.

The basic assumptions in the derivation of equation (1) are as follows:

(1) There is no ring formation or a constant ratio of ring formation on gelation independent of the degree of polymerization of the original linear polymer.

(2) The Stockmayer theory[22] of gelation is applicable to this system.

(3) Two moles of PVA diol units are crosslinked with the aid of one mole of borate ions.

Assumptions (1) and (2) were originally used in the Eldridge–Ferry theory. Assumption (3) is introduced here. The crosslinking mechanism was up to now believed to be di-diol formation, as shown in *Figure 4a*. However, we propose a different mechanism[19], i.e. ionic bonding between the PVA-bound borate ion and the PVA-

chelated sodium ion, as shown in *Figure 4b*. Both models, however, support a two-to-one reaction between diols and borate ions.

In the following subsections, we discuss the gel melting behaviour of PVA alkaline gels in terms of equation (1) and examine the validity of the assumptions.

Concentration dependence

When the degree of polymerization P, boric acid concentration b and pH are kept constant, equation (1) is written as:

$$\ln c_{gel} = \text{constant} + \Delta H/RT_{gel} \tag{2}$$

which is equivalent to equation (7) of ref. 10 and equation (2) of ref. 11. *Figure 5* shows the reciprocal gel melting temperature, $1/T_{gel}$, dependence of $\ln c_{gel}$ for PVA120, PVA300, PVA1790, PVA2570 and PVA3230. Full lines are drawn using a least-squares method and the estimated ΔH for each sample is listed in *Table 2*. Sinton[17] obtained $-8.3\,\text{kcal mol}^{-1}$ for the enthalpy of formation of an atactic PVA–borate complex using [11]B n.m.r., and Schultz and Myers[23] reported $-6\,\text{kcal mol}^{-1}$ using a shear modulus measurement. Although the estimated values for the enthalpy of crosslinking are scattered, ΔH is in the range between -5 and $-8\,\text{kcal mol}^{-1}$, except for PVA300 and PVA3230, and is consistent with those reported by Sinton and by Shultz et al. The molecular-weight dependence of ΔH is not clear from this
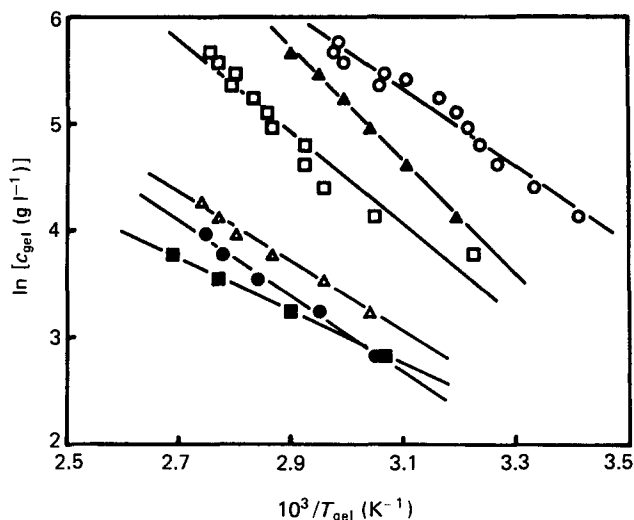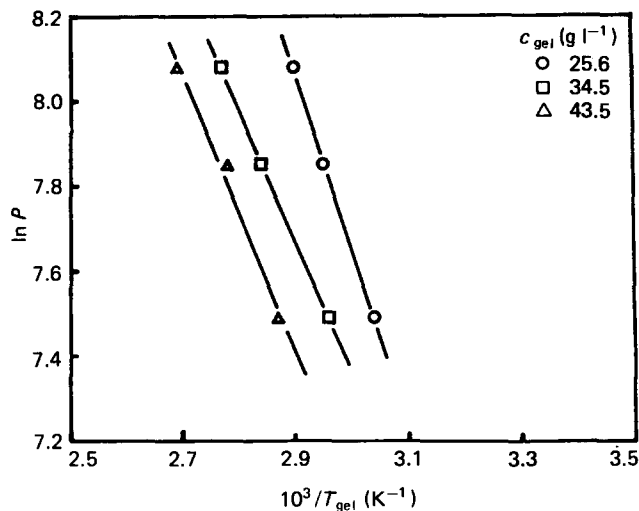

Figure 5 Dependence of the reciprocal gel melting temperature $(1/T_{gel})$ on $\ln c_{gel}$ for various molecular weights and boric acid concentrations. Symbols are the same as in *Figure 3*

Table 2 Enthalpy of formation of a mole of junction points, ΔH, estimated from equation (2)

| Sample | Concentrations (mol l^{-1}) | | ΔH (kcal mol^{-1}) |
	B(OH)$_3$	NaOH	
PVA120	2.50×10^{-2}	0.167	-7.16
PVA300	2.50×10^{-2}	0.167	-8.55
PVA300	1.67×10^{-2}	0.167	-10.6
PVA1790	0.83×10^{-2}	0.167	-6.47
PVA2570	0.83×10^{-2}	0.167	-7.08
PVA3230	0.83×10^{-2}	0.167	-4.86

Table 3 Enthalpy of formation of a mole of junction points, ΔH, estimated from equation (3)

c_{gel} (g l^{-1})	ΔH (kcal mol^{-1})
25.6	−8.32
34.5	−6.15
43.5	−6.51

Figure 6 Dependence of the reciprocal gel melting temperature $(1/T_{gel})$ on $\ln P$ at $b=2.5 \times 10^{-2}$ mol l^{-1} and [NaOH]$=0.167$ mol l^{-1}

experiment since the observed ΔH does not undergo a systematic change with the degree of polymerization.

Degree of polymerization dependence

If one keeps the gel melting concentration c_{gel}, boric acid concentration b and pH constant, equation (1) can be written as:

$$\ln P = \text{constant} + \Delta H/RT_{gel} \qquad (3)$$

which is equivalent to equation (16) of ref. 10 and equation (3) of ref. 11. *Figure 6* shows the reciprocal gel melting temperature dependence of $\ln P$ for different c_{gel} values, i.e. 25.6, 34.5 and 43.5 g l^{-1}. Each set of experimental points roughly falls onto a straight line. From the slopes of the lines, ΔH is again estimated and is listed in *Table 3*. The value of ΔH is almost the same as estimated from the c_{gel} dependence (see *Table 2*), which supports the validity of assumption (3). If n moles of di-diol units take part in a crosslink, the ΔH value estimated from the degree of polymerization dependence should be $(n-1)$ times bigger than that from the c_{gel} dependence, as discussed by Harrison *et al.*[11]

Boric acid concentration dependence

The boric acid concentration dependence is easily estimated from equation (1) for constant P and pH, which is given by:

$$\ln(c_{gel}b) = \text{constant} + \Delta H/RT_{gel} \qquad (4)$$

Figure 7 shows the reciprocal gelation temperature dependence of $\ln(c_{gel}b)$ for PVA300. The boric acid concentration dependence is taken into account by

multiplying b and c_{gel} in the ordinate. The two sets of data are superimposed on each other, although some deviations are still seen.

The master curve relationship between c_{gel}, T_{gel}, P and b

Figure 8 shows the master curve for the gel melting concentration and temperature. The ordinate is scaled by the degree of polymerization P and boric acid concentration b. Although the data points are quite scattered, they still fall onto a straight line. The discrepancy from the straight line results from experimental error, the molecular-weight dependence of the enthalpy of crosslink formation (if it exists) and the molecular-weight dependence of the ratio of ring formation on gelation. If c_{gel} is much higher than the critical concentration c^* at which each polymer chain begins to overlap, the ratio of ring formation might be constant. The concentration range in this study, however, goes below and above c^*, as will be discussed in the following subsection, and assumption (1) may break down. Therefore, the ring formation ratio might change
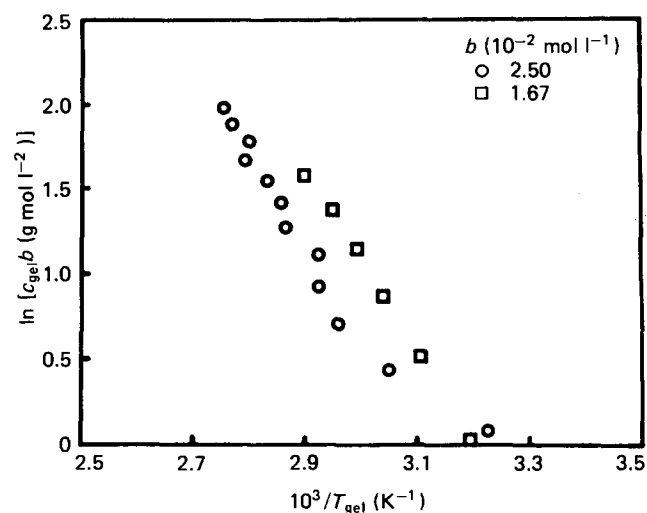
Figure 7 Boric acid concentration dependence of gel melting temperature for PVA300 ([NaOH]$=0.167$ mol l^{-1})
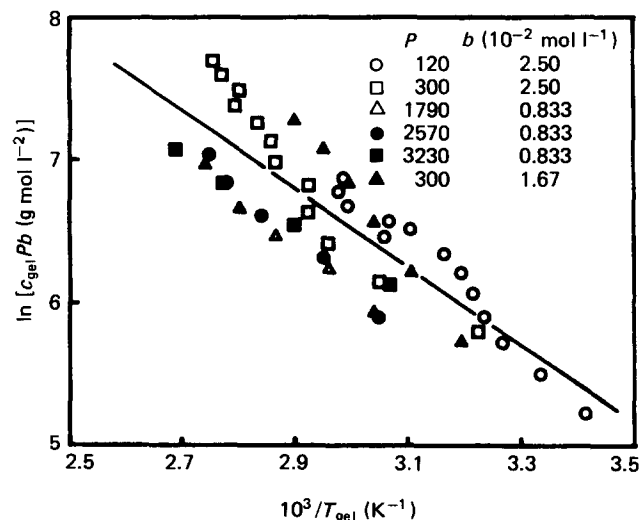
Figure 8 Master curve relationship among the gel melting temperature T_{gel}, gel melting concentration c_{gel}, boric acid concentration b and degree of polymerization P ([NaOH]$=0.167$ mol l^{-1})

with PVA concentration and/or with the degree of polymerization, resulting in the deviation of the data points from the straight line, as shown in *Figure 8*. The estimated ΔH value from a least-squares method on the data in *Figure 8* is -5.4 kcal mol^{-1}, which is consistent with the literature values discussed above.

The critical gelation concentration

Here we discuss the degree of polymerization dependence of the critical gelation concentration (*CGC*) and compare it with the critical concentration for chain overlap (*c**). The *CGC* was obtained by carefully measuring T_{gel} for diluted PVA–borate aqueous solutions. Only the PVA concentration was reduced, and the boric acid and sodium hydroxide concentrations were kept constant.

It seems that *CGC* has to be higher than the critical concentration for chain overlap *c**. Otherwise intrachain crosslink formation becomes dominant and precipitation of PVA occurs. Here *c** is estimated as the concentration[24] at which balls of PVA chains having a radius of R_g (the radius of gyration) start to overlap with increasing concentration. The PVA chains are assumed to be in an unperturbed condition:

$$c^* = Pm/(4\pi N_A R_g^3/3) \qquad (5)$$

and

$$R_g = (\sigma^2 P/6)^{1/2} \qquad (6)$$

where m, N_A and σ are the monomer molecular weight of PVA, Avogadro's number and the statistical segment length of PVA. The latter (σ) is given by the ratio of the end-to-end distance and the square root of the degree of polymerization, and $\sigma = 6.3$ Å[25]. The estimated c^* is calculated by assuming that the molecular-weight distribution of the PVAs is monodisperse.

The critical gelation concentrations (*CGC*) for the alkaline gels as well as the critical concentrations for chain overlap (*c**) are plotted as functions of the degree of polymerization in *Figures 9a* and *9b*. The concentrations of boric acid and sodium hydroxide were kept constant ($b = 2.5 \times 10^{-2}$ mol l^{-1}, [NaOH] $= 0.167$ mol l^{-1}). From *Figure 9b* the degree of polymerization dependence of *CGC* is estimated as:

$$CGC = \text{constant} \times P^{-0.45} \qquad (7)$$

On the other hand, c^* is definitely given by:

$$c^* = \text{constant} \times P^{-0.5} \qquad (8)$$

from equation (5). The observed exponent is a little bit smaller in magnitude than the value of 0.5 predicted from equation (8) and that reported by Tan *et al.*[2] for atactic polystyrene gels; however, this still means that the PVA in the system is close to the unperturbed state. This seems to be reasonable since water is not a good solvent for PVA. The reason why we obtained a smaller value of the exponent is not clear at this stage.

The *CGC* estimated here was about half of the corresponding c^* irrespective of the degree of polymerization, as shown in *Figure 9a*. Taking account of the fact that the estimation of c^* is very coarse and has only the meaning of an order estimate, one may conclude that the *CGC* is close to c^*.

CONCLUSIONS

The gel melting temperature and concentration of the PVA–borate complex are investigated as functions of the degree of polymerization P, boric acid concentration b and pH. The master relationship among these parameters is found, and is predicted theoretically by a modification of the Eldridge–Ferry theory of gel melting. The enthalpy of crosslink formation is estimated to be between -5 and -8 kcal mol^{-1}, which is consistent with the literature values estimated using [11]B n.m.r. and a rheological measurement. The gel formation mechanism of the PVA–borate complex is found to be a two-to-one complex formation of PVA diol units and borate ions using the estimate of the enthalpy of crosslink formation. The critical gelation concentration *CGC* was found to be proportional to $P^{-0.45}$ and close to the critical concentration for chain overlap.
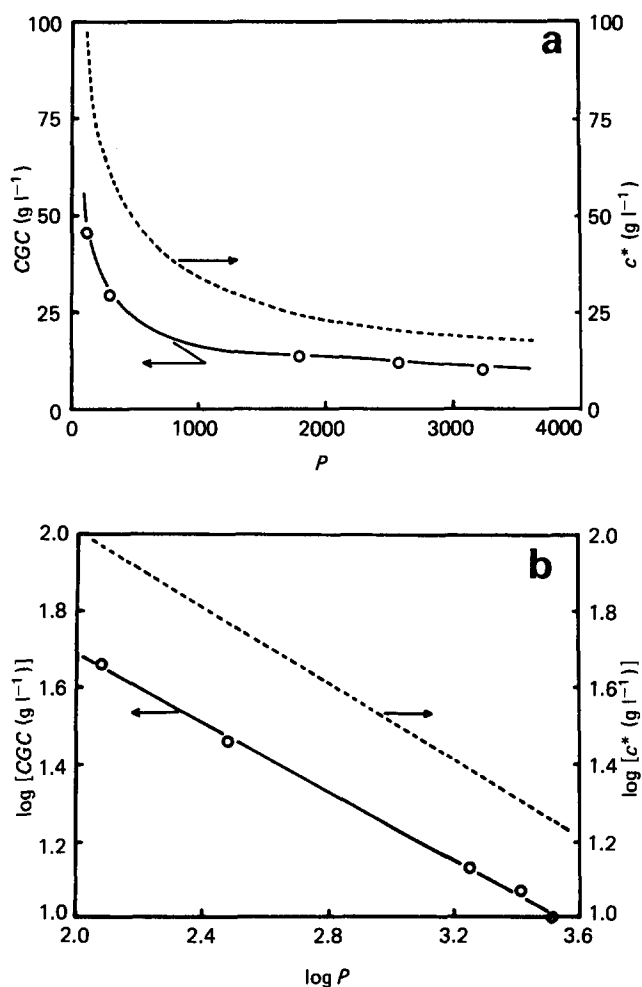
Figure 9 Dependence of the critical gelation concentration *CGC* (full curve) and the critical concentration, c^* (broken curve) on the degree of polymerization: (a) linear plot and (b) double logarithmic plot. The slopes in *Figure 9b* are -0.45 for *CGC* and -0.50 for c^*

APPENDIX

According to the Eldridge–Ferry theory, the gel melting point is determined by both the critical concentration of crosslinks $[N]_{gel}$ and the chemical equilibrium constant for crosslink formation. The critical crosslink concentration is given by:

$$[N]_{gel} = c_{gel}/M \qquad (A1)$$

if two potential junction points capable of being crosslinked take part in crosslinking of a junction. Here c_{gel} and M denote the polymer concentration (g l^{-1}) at gel melting and the polymer molecular weight, respectively. Equation (A1) can be understood by using the degree of polymerization P and the monomer molecular weight m of the polymer as:

$$[N]_{gel} = c_{gel}/mP \qquad (A2)$$

The chemical equilibrium constant K for crosslink formation is given by:

$$K = [N]/[J_p]^2 \qquad (A3)$$

$[J_p]$ is the concentration of potential junction points and can be assumed to be proportional to the polymer concentration if the tacticity is the same. Therefore $[J_p]$ is proportional to c_{gel}, i.e.

$$[J_p] = kc_{gel} \qquad (A4)$$

where k is a constant. According to the van't Hoff equation on chemical reactions, K is given by:

$$K = A \exp(-\Delta H/RT) \qquad (A5)$$

where ΔH, R and T are the enthalpy of formation of a mole of junction points, the gas constant and the absolute temperature, respectively. A is a constant. By combining equations (A2) to (A5), one gets the following equation at the gel melting point:

$$c_{gel} = (2mAk^2)^{-1}P^{-1}\exp(\Delta H/RT_{gel}) \qquad (A6)$$

Then

$$\ln(c_{gel}P) = \text{constant} + \Delta H/RT_{gel} \qquad (A7)$$

In the case of the PVA–borate system, a crosslink is formed with the aid of a borate ion, i.e.
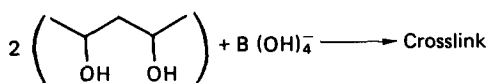
Since crosslinking is a third-order chemical reaction, one has to modify equation (A3) to:

$$K = [N]/[J_p]^2[B(OH)_4^-] \qquad (A8)$$

The borate ion concentration $[B(OH)_4^-]$ is given by:

$$[B(OH_4^-)] = bK_a/([H^+] + K_a) \qquad (A9)$$

where b and K_a are the boric acid concentration after addition into the system and the ionization constant of boric acid, respectively. Therefore, one obtains the following equation at the gel melting point:

$$\ln(c_{gel}Pb) = \text{constant} + \Delta H/RT_{gel} + \ln\{([H^+] + K_a)/K_a\} \qquad (A10)$$

REFERENCES

1 Wellinghoff, S., Shaw, J. and Baer, E. *Macromolecules* 1979, **12**, 932
2 Tan, H., Moet, A., Hiltner, A. and Baer, E. *Macromolecules* 1983, **16**, 28
3 Boyer, R. F., Baer, E. and Hiltner, A. *Macromolecules* 1985, **18**, 427
4 Gan, J. Y. S., Francios, J. and Guenet, J. M. *Makromol. Chem., Rapid Commun.* 1985, **6**, 225
5 Gan, J. Y. S., Francios, J. and Guenet, J. M. *Macromolecules* 1986, **19**, 173
6 Guenet, J. M., Willmott, N. F. F. and Ellsmore, P. A. *Polym. Commun.* 1983, **24**, 230
7 Takahashi, A., Nakamura, T. and Kagawa, I. *Polym. J.* 1972, **3**, 207
8 Gerth, C. and Myers, H. H. *Angew. Makromol. Chem.* 1978, **74**, 81
9 Coniglio, A., Stanley, H. E. and Klein, W. *Phys. Rev. Lett.* 1979, **42**, 518
10 Eldridge, J. E. and Ferry, J. D. *J. Phys. Chem.* 1954, **58**, 992
11 Harrison, M. A., Morgan, P. A. and Park, G. S. *Eur. Polym. J.* 1972, **8**, 1361
12 Hirai, N. in 'Polyvinyl Alcohol', (Ed. I. Sakurada), Society of Polymer Science, Japan, 1955
13 Prins, W., Rimai, L. and Chompff, A. J. *Macromolecules* 1972, **5**, 104
14 Pines, E. and Prins, W. *Macromolecules* 1973, **6**, 888
15 Komatsu, M., Inoue, T. and Miyasaka, K. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 303
16 Deuel, H., and Neukom, H. *Makromol. Chem.* 1949, **3**, 13
17 Maerker, J. M. and Sinton, S. W. *J. Rheol.* 1986, **30**, 77
18 Sinton, S. W. *Macromolecules* 1987, **20**, 2430
19 Shibayama, M., Sato, M., Kimura, Y., Fujiwara, H. and Nomura, S. *Polymer* 1988, **29**, 336
20 Moritani, K., Kuruma, I., Shibatani, K. and Fujiwara, Y. *Macromolecules* 1972, **5**, 577
21 Takahashi, A., Sakai, M. and Kato, T. *Polym. J.* 1980, **12**, 335
22 Stockmayer, W. H. *J. Chem. Phys.* 1943, **11**, 45; 1944, **12**, 125
23 Schultz, R. K. and Myers, R. R. *Macromolecules* 1969, **2**, 281
24 de Gennes, P. G., 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, NY, 1979, Ch. 3
25 Brandrup, J. and Immergut, E. H. (Eds.), 'Polymer Handbook', Wiley, New York, 1975, Ch. IV-4