^{11}B n.m.r. study on the reaction of poly(vinyl alcohol) with boric acid

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The crosslinking mechanism of an aqueous alkaline solution of poly(vinyl alcohol) (PVA) in the presence of boric acid was investigated by means of ^{11}B nuclear magnetic resonance (n.m.r.). 2-Propanol and 2,4-pentanediol were chosen as monomeric and dimeric model samples of PVA, respectively. In the case of 2-propanol, only one strong signal was observed, which was the same as in the case without alcohol. By contrast, 2,4-pentanediol and PVA had two distinct signals, one of which was unique to 1,3-diols, i.e. pentanediol and PVA. It is concluded that monohydroxyl alcohol does not react with boric acid, whereas di- and polyhydroxyl alcohols having the structure of 1,3-diol do. The temperature dependence of the chemical shift of the signals shows that the product is a so-called monodiol type but not a didiol type, which is not consistent with the conventional concept of PVA and boric acid reaction.

(Keywords: poly(vinyl alcohol); ^{11}B n.m.r.; monodiol complex; didiol complex; crosslinking spinning)

INTRODUCTION

Attention has been focused on poly(vinyl alcohol) (PVA) for more than 30 years because of its unique chemical and physical properties as well as its industrial applications[1]. Some of the unique properties come from the large number of hydroxy groups which react chemically with many kinds of functional groups. The hydrogen bond related to the hydroxy group also plays an important role in the physical properties of PVA, e.g. high water solubility, wide range of crystallinity and high crystal modulus.

Studies on the production of ultra-high strength fibres have been accelerated by the development of gel spinning of ultra-high molecular weight polyethylene[2,3]. This technique is now applied to other kinds of polymer. PVA is one of the candidates because the crystal modulus of PVA is even higher than that of polyethylene. It is necessary, however, to reduce the strong inter- and intramolecular interactions, such as hydrogen bonding, for gel spinning of PVA. Crosslinking spinning of PVA may be an alternative way to produce ultra-high strength fibres, where use is made of the unique properties of PVA. Crosslinking of PVA can be easily attained by adding alkaline reagent. Boric[4-6], cupric[7] and titanic[8] reagents also crosslink PVA. In this case, the amount of alkaline reagent can be greatly reduced. Although crosslinking spinning with boric acid has been applied for more than 20 years[9-10], the precise mechanism of crosslinking has not been fully understood. There are at least two kinds of proposed structure of PVA and boric acid reaction, i.e. the monodiol type and the didiol type (shown in *Figure 1*). Since the monodiol-type reaction does not seem to lead to gelation of PVA, the didiol type reaction has long been accepted[1,4]. Recently, Ochiai *et al.*[11] and Matsuzawa *et al.*[12] investigated the complex formation of PVA and sodium tetraborate and concluded that the didiol-type complex was dominant. However, most of the studies on PVA and boric acid reaction were carried out with titration techniques and little attention was paid to the characterization of the chemical species involved in the reaction.

In this paper we examine the reaction of PVA, and its model samples, with boric acid by ^{11}B nuclear magnetic resonance (n.m.r.) spectroscopy as a function of temperature and pH and propose a crosslinking mechanism of PVA in the presence of boric acid.

EXPERIMENTAL

Materials

PVA with degree of polymerization $P=120$ was provided by Unitika Kasei Ltd, Japan. The PVA provided was re-saponified in an aqueous NaOH solution and purified by dialysis. The final saponification value was determined to be over 99.6 mol% by titration[1]. Two reference samples, 2-propanol (PNL) and 2,4-pentanediol (PDL), were commercially provided and were used as received.

Samples for n.m.r. measurement

Prescribed amounts of alcohol sample (PVA, PDL or PNL) and boric acid were dissolved in deuterated water

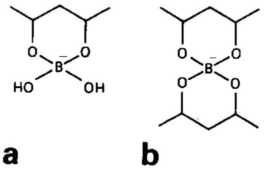

Figure 1 Chemical structure of monodiol complex (a) and didiol complex (b)

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Table 1 Details of n.m.r. samples

Run no.	Sample code	Concentration ($mol\,l^{-1}$) Hydroxy group	$B(OH)_3$	pH
1	PVA	1.304	0.111	5
2	PVA	1.304	0.111	11
3	PDL	2.378	0.101	5
4	PDL	2.378	0.101	11
5	PNL	1.881	0.100	5
6	PNL	1.881	0.100	11

and the pH was adjusted with aqueous sodium hydroxide. The details are listed in *Table 1*. For investigation of concentration dependence, the concentration of hydroxy groups was reduced stepwise without changing that of boric acid.

^{11}B *n.m.r.*

^{11}B n.m.r. spectroscopy was carried out on a Varian FT-80 Fourier transform n.m.r. spectrometer at 25.517 MHz; i.e. more than 1000 scans, 2.5 μs pulses with no delay and 4000 Hz sweep width for 4K data points after transformation. Temperature was controlled within $\pm 3°C$. The chemical shift was referenced to the external standard, boron trifluoride diethyl etherate ($Et_2O:BF_3$).

RESULTS AND DISCUSSION

Temperature dependence

Figures 2a–d show the temperature-dependent ^{11}B n.m.r. spectra of borate ions produced in the presence of PVA, 2,4-pentanediol (PDL), 2-propanol (PNL) and boric acid D_2O solution, respectively, at pH 11. As can be seen, the PVA and PDL systems have two distinct signals, whereas PNL and the boric acid D_2O solution have only one. The changes in their chemical shift with temperature are plotted in *Figure 3*. The signals of Type I which appear at higher chemical shift in all runs are regarded as the signal of the borate ion itself, i.e. free borate ions with little chemical interaction with the alcohol. On the other hand, signals with lower chemical shift of Type II are characteristic in the cases where 1,3-diol-type alcohols exist. They should be assigned to a new species resulting from the reaction between borate ions and 1,3-diols. It should be noted here that PVA and PDL have almost the same effect on the signal changes, although the signals of PVA are broader. The signals due to the new species were not accurately detected by ^1H n.m.r. spectra of these solutions because of their complexity.

The chemical shifts are temperature dependent, i.e. the higher the temperature, the higher is the chemical shift. This may be due to desolvation of borate ions at higher temperature. The difference in the slopes of the two lines is related to the degree of hydration of the corresponding species. The Type II species have a relatively small number of solvated molecules due to the coordination of 1,3-diol and result in lower temperature dependence of the chemical shift. These spectra, however, were reproducible with temperature. In addition, a reversible sol–gel transition with temperature was observed. Therefore the systems studied were considered to be in chemical equilibrium.

As shown in *Figure 2a*, there was no distinct broadening of the signals in the PVA system on

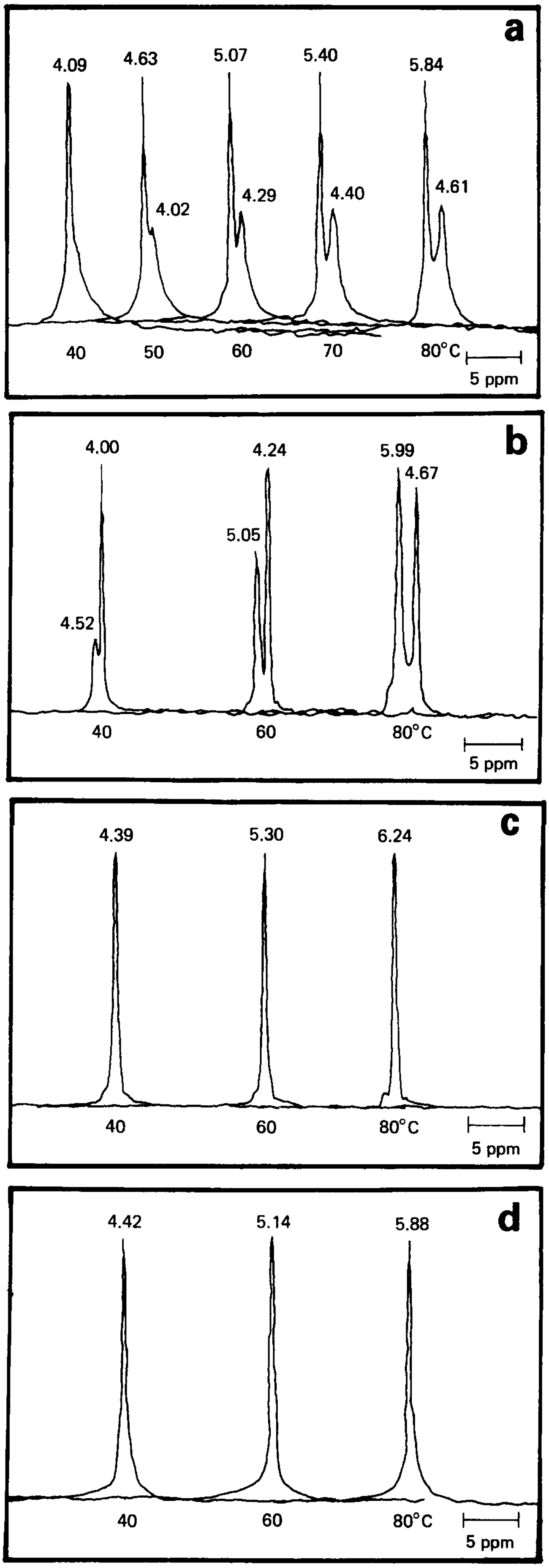


Figure 2 ^{11}B n.m.r. spectra of borate ion in the presence of PVA (a), PDL (b), PNL (c) and boric acid D_2O solution (d) at several temperatures

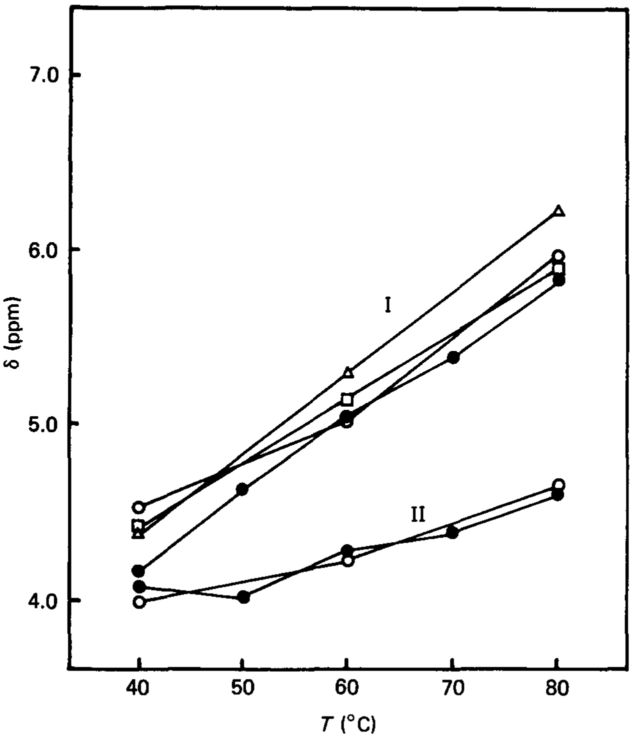


Figure 3 Temperature dependence of the chemical shifts of borate ions in the presence of PVA (●), PDL (○), PNL (△) and boric acid D_2O solution (□) at pH = 11

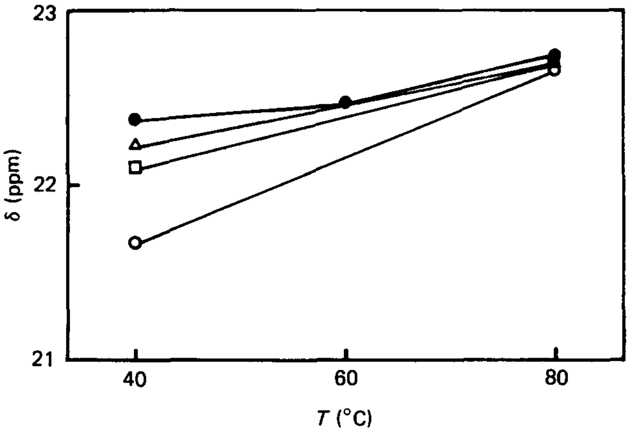


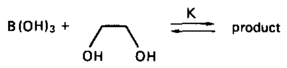
Figure 4 Temperature dependence of the chemical shifts of borate ions in the presence of PVA(●), PDL (○), PNL (△) and boric acid D_2O solution (□) at pH = 5

decreasing the temperature below 60°C, at which temperature the system became gel. This suggests that borate ions are still mobile even after their participation in gelation. The details will be discussed later.

Under acidic conditions (pH = 5), only one distinct signal appeared, around $\delta = 22$ ppm, in the four systems, as shown in *Figure 4*. The down-field shift of the signal in comparison with basic conditions is due to the decreasing electron shield in the acidic form. These results indicate that there is little interaction or reaction between boric acid and hydroxy groups other than hydrogen bonding or dipole–dipole interaction.

Concentration dependence

Concentration dependence of the signals was examined to specify the chemical shift of Type II. Suppose boric acid reacts with 1,3-diol (in this case PDL and PVA) and attains chemical equilibrium as follows:



One can estimate the chemical equilibrium constant K from the following equation:

$$K = \frac{x}{(a-x)(b-x)} \tag{1}$$

where a, b and x are the initial molar concentrations of boric acid and the diol (with respect to the diol unit) and the product at reaction equilibrium, respectively. The molar concentration of the product concentration x is related to the peak ratio R of the signals of Types II and I as

$$R = A_{\mathrm{II}}/A_{\mathrm{I}} = x/(a-x) \tag{2}$$

where A_i is the integral value of the signal of type i. A_{I} is, therefore, proportional to the content of free borate ions and A_{II} is proportional to that of the product. Substituting equation (2) into equation (1) gives

$$R = K[b - aR/(1+R)] \tag{3}$$

Therefore, by plotting R as a function of $b - aR/(1+R)$ one gets K from the slope, as shown in *Figures 5* and *6* for the PVA and PDL systems, respectively. If one assumes that two moles of diol react with one mole of boric acid to yield didiol type products, for example, equation (3) has to be modified to

$$R = K[b - 2aR/(1+R)]^2 \tag{4}$$

Figures 7 and *8* show plots of R *versus* $[b - 2aR/(1+R)]^2$. Although the data points are scattered, particularly for the PVA system, the linearity of the plots in *Figures 5* and *6* is much better than that of the plots in *Figures 7* and *8*, indicating that the reaction between borate and diol occurs in a stoichiometric manner. The scattering of the

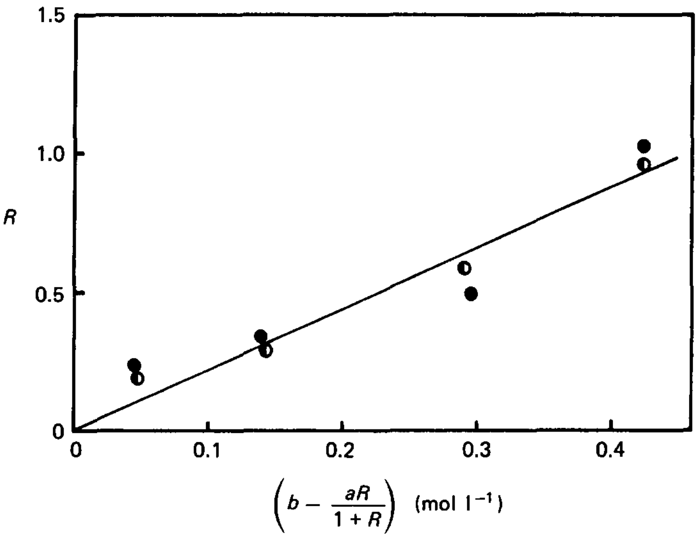


Figure 5 Peak ratio R as a function of equilibrium diol concentration for the PVA system: (●) 80°C; (◐) 60°C; $K = 2.16$ l mol^{-1}

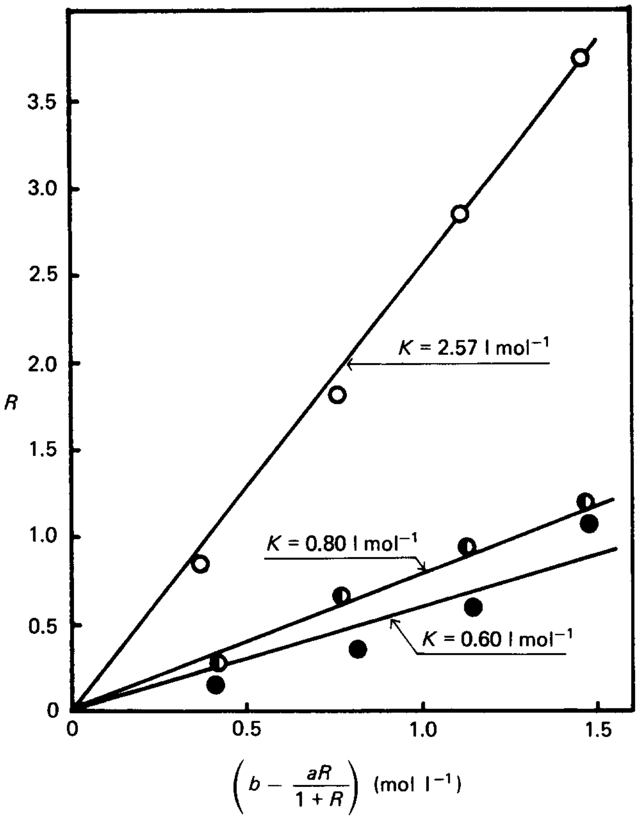


Figure 6 Peak ratio R as a function of equilibrium diol concentration for the PDL system: (●) 80°C; (◐) 60°C; (○) 40°C

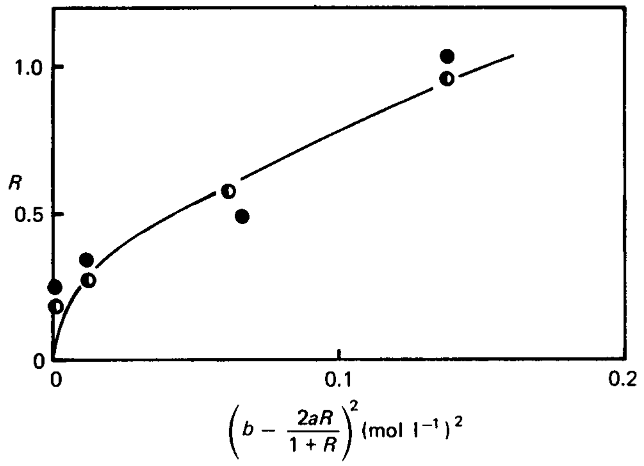


Figure 7 Peak ratio R as a function of the square of equilibrium diol concentration for the PVA system: (●) 80°C; (◐) 60°C

data points for the PVA system is mainly due to the fact that the resolution of the apparatus is not great enough to estimate quantitatively the n.m.r. signals, as seen in *Figure 2a*.

Values of the reaction equilibrium constant K were estimated from the plots in *Figures 5* and *6* and are listed in *Table 2*. The value of K for PVA at 40°C could not be obtained because of superposition of the signals of Types I and II. As seen in *Table 2*, the constant K for PVA is about three times that for PDL, both at 60°C and at 80°C, in spite of the lower initial concentration of diol units in the former. This may be because the PVA–borate product is stabilized by anchimeric assistance of the hydroxy group of the PVA chain. This is one of the positive polymeric effects. For PDL, K decreases with increasing temperature. However, the temperature dependence of K for PVA is not clear. This may suggest that the PVA–borate interaction is not directly related to the temperature-induced sol–gel transition of aqueous PVA solution in the presence of borate ions.

Crosslinking mechanism of PVA

Based on the above results the following facts are disclosed in conjunction with the scheme of reaction of PVA with borate ions shown in *Figure 9*.

1 There was no indication of a reaction occurring between PNL (2-propanol) and borate ions. This denies the possibility of independent reaction of borate ions with the single hydroxy group of PVA and PDL. Therefore, crosslinking of the type in *Figure 9a* is less probable.

2 Equilibrium reaction occurred between PDL and borate ions in a stoichiometric manner to yield a 1:1 product with covalent bonds. This reaction simulates the PVA–borate ion reaction reasonably. Therefore, borate

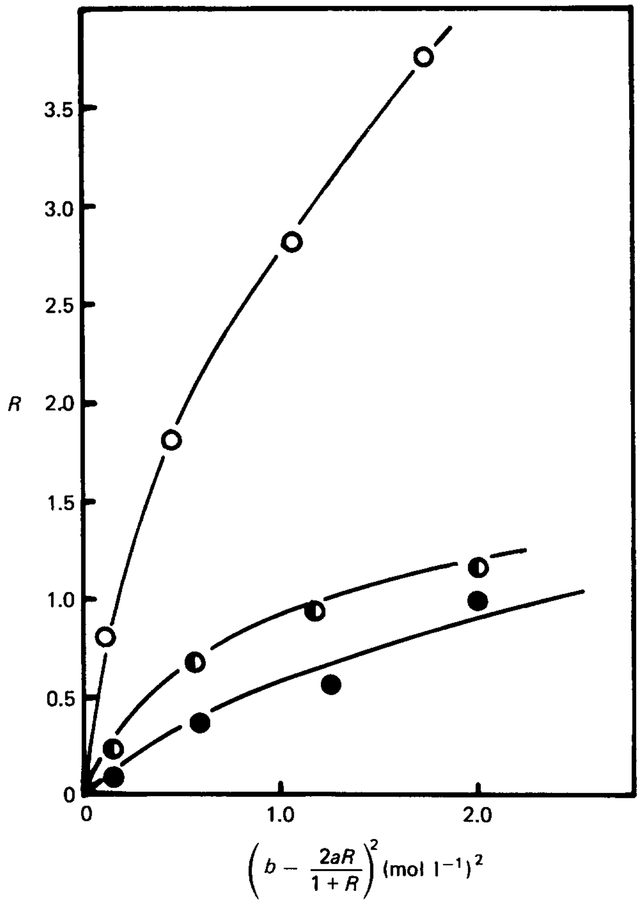


Figure 8 Peak ratio R as a function of the square of equilibrium diol concentration for the PDL system: (●) 80°C; (◐) 60°C; (○) 40°C

Table 2 Chemical equilibrium constant K for borate ion reactions with PVA and PDL

	K (l mol^{-1})	
Temp. (°C)	PVA	PDL
40	–	2.57
60	2.16	0.80
80	2.16	0.60

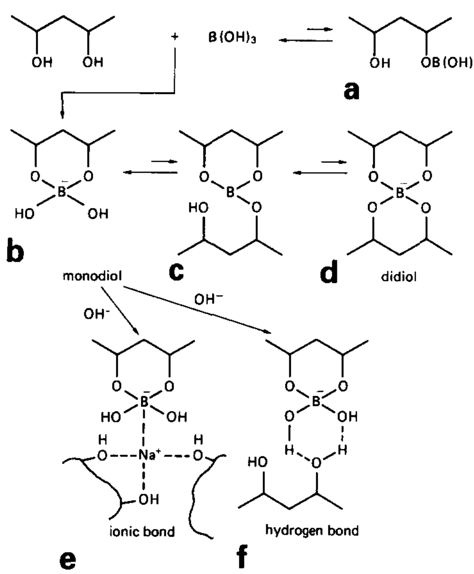


Figure 9 Schematic diagram of the chemical reactions between PVA or PDL and boric acid

ions are to be bound on 1,3-diol units of a PVA chain to form the 1,3,2-dioxaborinane rings (*Figure 9b*) as pendants, whereas covalent crosslinking like *Figures 9c* and *d* does not seem to occur. In particular, the presence of the didiol-type structure of *Figure 9d* is hardly believed. These findings are in conflict with the results of Ochiai *et al.*[11] and Matsuzawa *et al.*[12] One possible reason for the discrepancy is experimental temperature difference: our experiments were at higher temperatures (40–80°C) than those of Ochiai *et al.* (10–35°C). According to their results, the didiol complex is dominant at low temperature, e.g. 10°C. But it should be noted that ^{11}B n.m.r. spectroscopy employed in this study did not show any distinct proof of a didiol complex even at the lowest temperature (40°C).

3 A positive polymeric effect was observed for the formation of the product.

4 As previously reported[1,4,6], alkaline aqueous PVA solution containing a small amount of boric acid tends strongly to gel at room temperature. When heated above 60°C, it turns to sol. This sol–gel transition is thermally reversible although it certainly depends upon the molecular weight of PVA, concentration, pH etc.

Because of the absence of the didiol-type structure in the PVA gel network, one must introduce a different crosslinking mechanism. We propose here a 'borate-ion-aided crosslinking' between PVA molecules as shown in *Figure 9e*. In basic condition, the diol units form borate monodiol ions (*Figure 9b*), as verified above, which strongly interact with sodium counter ions that are in coordination with PVA chains. In this model, the crosslinkage is formed by ionic bonding between the PVA-bound borate ion and the PVA-chelated sodium ion. The cationic centres of *Figure 9e* have been considered as the crosslinking species of PVA in the presence of concentrated sodium hydroxide only[1]. They are probably able to associate with the anionic centres of *Figure 9e* to form a semi-tight crosslink of PVA chains. This is compatible with the relatively high mobility of the borate ion group, which was indicated by the smallest broadening of the signals after gelation. However, the ionic bond, occurring in aqueous solution, should be dissociated at higher temperature. In addition, the chelation of PVA units to sodium ions should be released. These dissociation processes lead to a gel–sol transition at higher temperature. The bond breakage of PVA–borate ion is not directly responsible for the dissolution of gel since the monodiol-type ion remains in considerably high quantities even after the transition occurs.

The same ionic crosslinking mechanism is found in so-called ionomers[13], which also have a reversible crosslinking phenomenon or sol–gel transition by heating. The state of chelation of sodium ions is similar to the binding of sodium ions in crown ethers and their open chain analogues[14]. Crosslinking is also possible by hydrogen bonding between the diol complex and PVA chains such as *Figure 9f*, although its bonding force is weak and its participation will be minor.

Under acidic conditions, on the other hand, no characteristic change in chemical shift was observed, indicating no specific interaction between the diol and boric acid. The aqueous PVA solution is stable some time after preparation but becomes an opaque gel if it is left for a long time, e.g. a couple of weeks at ambient temperature. This phenomenon is due to crystallization of PVA in aqueous solution[15,16], which needs further investigation.

CONCLUSION

^{11}B n.m.r. was carried out to investigate poly(vinyl alcohol) and boric acid reaction. It turns out that polyols having a 1,3-diol unit (i.e. poly(vinyl alcohol) and 2,4-pentanediol) react with boric acid under basic conditions in a stoichiometric manner and form a monodiol complex. No didiol-type complex was detected. A borate-ion-aided crosslinking mechanism based on the monodiol complex, i.e. an ionic bonding between the PVA-bound borate ion and the PVA-chelated sodium ion, is then proposed to account for the gelation phenomenon of polyvinyl alcohol.

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