Mechanical Properties of Borate Crosslinked Poly(vinyl Alcohol) Gels*

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Synopsis

Boric acid does not introduce crosslinks in poly(vinyl alcohol) solutions, but gelation does occur in the presence of cations. In this experimental study, the dynamic mechanical properties of these gels were determined using test-tube torsion pendulums and an air-bearing torsion pendulum. The modulus at a fixed concentration of polymer and boric acid increases with increasing sodium ion concentration up to the point where the atom ratio of sodium to boron reaches 1. Higher sodium concentrations do not increase the modulus. The log decrement, on the other hand, decreases with increasing sodium concentration continuously without reaching a plateau at the equal atom ratio. Log decrements as low as 0.02 can be measured. The storage modulus depends on the logarithm of borate concentration and on the 4.7 power of poly(vinyl alcohol) concentration. Only a very small portion of the borates in solution take part in effective crosslinks. The activation energy for breaking individual bonds is a function of temperature and the cation to boron ratios. At a fixed cation concentration, this activation energy is more negative with increasing amount of boron ions due to a transformation of monomeric crosslinks into polymeric crosslinks, so that the storage modulus which measures crosslink density decreases as a temperature rises.

INTRODUCTION

A number of workers have reported on the gelation of poly(vinyl alcohol) by borates.[1–9] Schultz and Myers[5] used a dynamic test to characterize the dynamic modulus and viscosity of gels made using sodium metaborate. The present work extends the study to other borates and to other cations. The torsion pendulum used does not have as broad a frequency range as used by Schultz and Myers, but it does overlap the range they used. The term gel is used here to mean a moderately dilute, crosslinked polymer solution.

The properties of borates alone in aqueous solution or in the presence of hydroxyl-bearing organic molecules have also been reported.[10–13] Borates and boric acid polymerize at low pH. Although tetraborates, pentaborates, and hexaborates have rather complex ionic structures in the solid state, they all depolymerize to $B(OH)_4^-$ ions in alkaline solutions.[11] Typical condensed (polyborate) forms are

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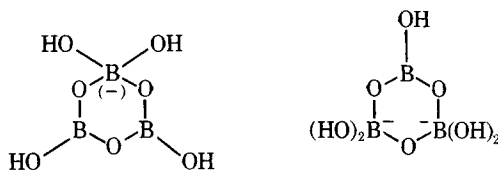
* Presented at the 73rd Annual Meeting of the American Institute of Chemical Engineers, Chicago, Illinois, November 1980.

These two ring structures are considered to be more stable than the rings with only three hydroxyls or with six hydroxyls[11] and, therefore, more likely to persist in solutions at low pH.

EXPERIMENTAL APPARATUS AND PROCEDURE

Most of the work reported here was done using a single grade of poly(vinyl alcohol): Vinol-65 (Air Products and Chemicals, Inc.), 99.7+% hydrolyzed; intrinsic viscosity (water, 30°C), 1.0 g/dL. Three other grades (Table I) were used to ascertain the effects of molecular weight and acetate content. The salts used were reagent grade (Table I).

The torsion pendulums have been described previously. The air-bearing model was used with cone-plate geometry for modulus and damping measurements.[14] Simple test-tube pendulums in which a concentric-cylinder geometry obtains were adequate for replicate testing of modulus only.[15,16] In the cone-plate model, the modulus G' is given by

$$G' = \frac{3I\phi\omega^2}{2\pi R^3}\left(1 + \frac{\Delta^2}{4\pi^2}\right) \qquad (1)$$

where I is the moment of inertia (typically 6,240 g·cm^2), ϕ is the cone angle (0.0873 rad), R is the radius (2.20 cm), and ω is the angular velocity (rad/s). The log decrement Δ is derived from a plot of maximum oscillation amplitudes (A) at successive cycles (n):

$$\Delta = \ln_e (A_n/A_{n+1}) \qquad (2)$$

Within the range of 3–10 Hz, the long decrement was found to decrease with frequency raised to the 0.77 power. In the torsion pendulums, the frequency depends on the modulus and the moment of inertia. It was not always convenient to alter the moment of inertia to get the same frequency, and so the original log decrement data were always corrected to a reference frequency of 7.96 Hz (50 rad/s). In the frequency range used, no correction was necessary for modulus, although, over a lower range, correction would be needed.[5]

### TABLE I
Materials Used in Gelation Studies

Polymers	Intrinsic viscosity, water, 30°C (g/dL)	% Hydrolysis (mfgrs.' data)
Vinol 165 (Air Products and Chem.)	1.00	99.7+
Vinol 125 (Air Products and Chem.)	0.65	99.7+
Elvanol 70-05 (du Pont)	0.40	98.5+
Lemol 75-98 (Borden)	1.20	98

Boron Compounds	Formula
Boric acid	H_3BO_3
Sodium perborate	$NaBO_2 \cdot 4H_2O$
Sodium metaborate	$Na_2B_2O_4 \cdot 8H_2O$
Sodium tetraborate (borax)	$Na_2B_4O_7 \cdot 10H_2O$

RESULTS AND DISCUSSIONS

Boric acid alone does not crosslink poly(vinyl alcohol) solutions, but gelation does occur when cations are present. The crosslinking reaction of the borates and poly(vinyl alcohol) occurs rapidly on mixing the two solutions together. Generally, the gels have a self-healing character, although gels with a high cation content will not deform too far on stressing before they break into small pieces. At the beginning of the crosslinking reaction, "fiberlike" structures forming a network can be observed in most of the gels. Gels of this structure (especially pronounced in stronger gels) have poor adhesion to metal and glass. Nevertheless, this fiberlike structure will disappear in an hour or so after gelation. Truly stable gels are not formed until 10–20 h. After this time, modulus and loss do not change as long as water does not evaporate.

A.   Sodium to Boron Ratio

From the previous work of Ingri,[17] it is known that the concentration of the polyborate anion depends on the pH of the solution. In order to see the effects of polyborate anion in a crosslinking mechanism, storage moduli of gels at fixed boric acid concentration and at various sodium hydroxide concentrations were determined. At 25°C the storage modulus of the poly(vinyl alcohol)–borate gels increases with sodium hydroxide concentration (Fig. 1). This shows that more and more orthoboric acid, which forms monodiol and which does not induce crosslinks,[1] is converted into tetraboric acid. The tetraboric acid, which is a crosslinking agent, then reacts with poly(vinyl alcohol), forming didiol.[4] A plateau value is reached when the molar concentration of sodium ion about equals that of boric acid (for the lower concentrations of boric acid in Fig. 1). The plateau value suggests that the crosslinking mechanism should be
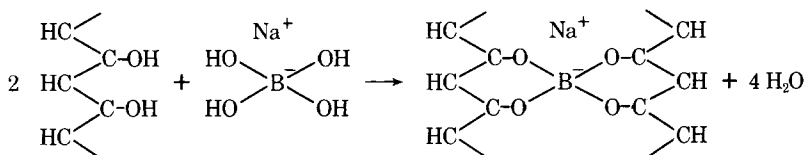
This crosslinking mechanism predicts that the plateau value has to be at the 1:1 sodium to boron ratio since all boric acid would be in didiol form and no further crosslinking would be possible with the addition of sodium hydroxide.
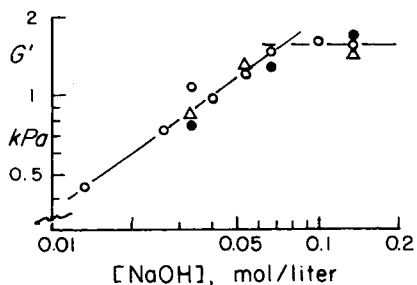

Fig. 1. Modulus of gels with 0.0283 g/cm^3 polymer at 25°C and boric acid concentration of (●) 0.0832, (○) 0.0693, and (△) 0.0559 mol/L.

As shown in Figure 1, a gel with higher boric acid concentration has a slightly higher plateau value of storage moduli than one with a lower boric acid concentration.

A more remarkable effect of sodium to boron ratio on gel properties can be seen from the log decrement measurements. The dependence of log decrement on sodium hydroxide concentration, at fixed boric acid concentration and at 30°C, is shown in Figure 2(a). All data have been reduced to 50 rad/sec. The ionic crosslinks of the poly(vinyl alcohol)–borate gel can be broken under stress and reformed again. The log decrement is a measure of the dimensional stability of the gel. In addition, it measures the ability of the gel to interchange crosslinks, which is an intensive property of the gel and is independent of the crosslink density. With increasing sodium hydroxide, the log decrement decreases continuously. As the ratio becomes greater than 1, the log decrement continues to decrease, even though the storage modulus reaches a plateau value. This behavior suggests that the gel changes properties by two different mechanisms as sodium ion concentration increases. The initial slope, where the sodium hydroxide concentration is lower than that of boric acid, may be due to a change of trimeric crosslinks into monomeric crosslinks. The decrease of log decrement is probably due to the fact that monomeric crosslinks are more rigid and more difficult to rotate than the six-member ring of the trimeric crosslinks and that the trimer also contains a larger amount of B–O bonds which are substantially weaker than the C–O bonds and have a higher probability for crosslinks to interchange. The further decrease in log decrement, where the sodium to boron ratio is greater than 1, may be due to a polar or electrostatic effect from the presence of a large amount of cation that further increases the ionic bond strength of the monomeric crosslinks, even though there is no further increase in crosslink density. The effect of polyborate formation can also be seen in Figure 2(b), in which a small amount of boric acid greatly increases the log decrement of the gel, or, in other words, highly increases the probability of breaking and reforming the crosslinks due to larger amount of B–O bonds being present. The figure also
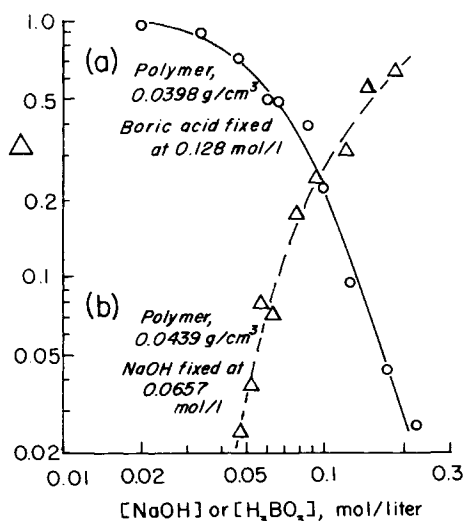

Fig. 2. Log decrement (at 7.96 Hz) with one reagent fixed and the other varied.

shows that no plateau value is observed for gels with sodium to boron ratios less than 1.

As the log decrement further decreases with increasing sodium hydroxide concentration, a limiting value can be reached at which the gel becomes so stiff that the gel actually pulls away from the side wall, precipitates, exudes water, and forms a plasticlike white material. At this stage, the electrostatic force from the cations is sufficiently large to cause polymer segments to be drawn so closely together that the breaking of crosslinks of deforming of gels becomes extremely difficult. This plasticlike material can retain its own shape for weeks and is insoluble in aqueous alkaline solutions. On the other hand, the log decrement does not change with borax or metaborate concentration when the sodium to boron ratio is held constant. For salt concentrations of 0.003 to 0.04 mol/L, the log decrement at 30°C for 0.0439 g/cm^3 polymer solution is 0.096 for metaborate and 0.42 for borax.

Gels with sodium to boron ratios higher than 1 are not practical since stability tests show that most of these gels actually degrade and form white precipitates in a matter of days. Both boric acid and sodium hydroxide have a lower concentration limit below which a wall-to-wall gel cannot be formed. The boric acid has the solubility limit as its upper concentration boundary, and the sodium hydroxide concentration has to be kept low enough so that no precipitation of poly(vinyl alcohol)–borate gels results.

B. Poly(vinyl Alcohol) and Borate Concentrations

The storage modulus of the gels depends only on the sodium to boron ratio of the poly(vinyl alcohol)–borate gel and is independent of the kind of borate solution the gel started with, e.g., at a sodium to boron ratio of 1:2 and corresponding ionic concentrations, the borax ($Na_2B_4O_7 \cdot 10H_2O$) solution gives the same storage modulus as a mixed solution of sodium hydroxide and boric acid in reacting with poly(vinyl alcohol). Since purified borate salts are easily available, borate salts were used in preparing the poly(vinyl alcohol)–borate gels. Borax was chosen for detailed concentration-dependence experiments because the borax–poly(vinyl alcohol) gel is easy to work with. Its self-healing character leads to more reproducibility than the gels prepared from sodium metaborate ($Na_2B_2O_4 \cdot 8H_2O$) or perborate ($NaBO_2 \cdot 4H_2O$).

Generally, the efficiency of crosslinking decreases as the concentration of the borax and poly(vinyl alcohol) increases. Both the borax and the poly(vinyl alcohol) have lower concentration limits for them to have a continuous network and upper concentration limits for them to be soluble. In borax crosslinked poly(vinyl alcohol) gel, a maximum is not observed, because borax concentrations higher than 0.05 mol/L cannot be reached. For borax crosslinked poly(vinyl alcohol) the storage modulus was plotted (Fig. 3) vs. the logarithm of borax concentration. Since all the lines with different poly(vinyl alcohol) concentrations have the same intercept and only the slope changes with the poly(vinyl alcohol) concentration,

$$G' = K_p \cdot \log(b/b_0) \qquad (3)$$

where G' is the storage moduli, b is the borax concentration, b_0 is the minimum borax concentration for a wall-to-wall gel to form (0.00167 m/L) and K_p is a
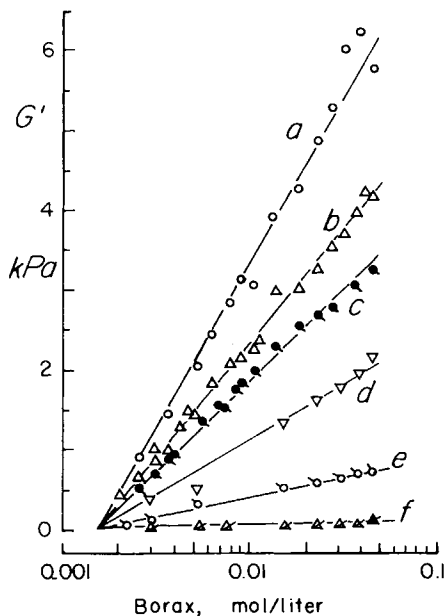
Fig. 3. Plots of eq. (3) for polymer concentrations of (a) 0.0405, (b) 0.0368, (c) 0.0350, (d) 0.0323, (e) 0.0258, and (f) 0.0181 g/cm³, 25°C.

function of polymer concentration and is independent of borax concentration. Schultz and Myers[5] reported that the storage modulus is directly proportional to sodium metaborate concentration above a minimum concentration. That would seem to be true only for the lowest concentrations used in the present work.

An equation which expresses storage modulus as an experimental function of polymer concentration and takes into account the minimum concentration for gelation gives a somewhat better fit to the data than a simple power form. However, a power dependence is adequate (Fig. 4) in the form

$$K_p = 5.36 \times 10^7 [P]^{4.7} \tag{4}$$

where P is in g/cm³. Combining the two equations gives

$$G' = 5.36 \times 10^7 [P]^{4.7} \log (b/b_0) \tag{5}$$

The storage moduli of both metaborate and perborate gels of poly(vinyl alcohol) are only slightly higher than those for borax at the same sodium concentration (Fig. 5). Since the sodium to boron ratio in borax is only half that in the other salts, it is to be expected on the basis of Figure 1 that the moduli should be lower for borax. The data of Schultz and Myers also fall on the same line. Presumably their higher concentration compensates for a lower molecular weight so the agreement is no doubt fortuitous. The minimum concentration of salt for gel formation is the same as that for borax (on a sodium concentration basis).
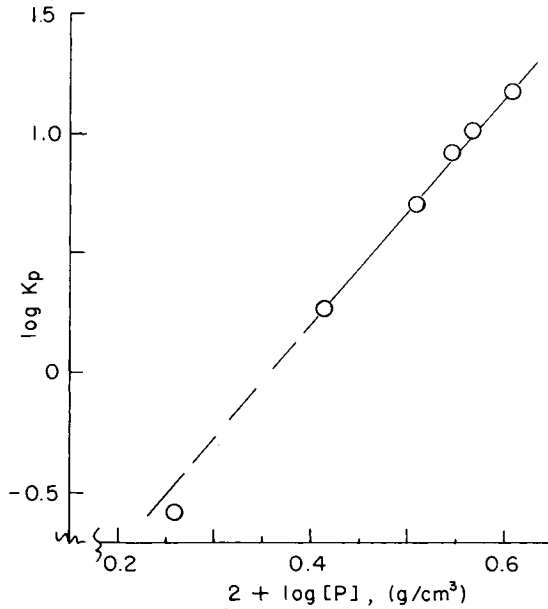
Fig. 4. Slopes of lines in Figure 3 as a function of polymer concentration, where K_P is in kPa and $[P]$ is in g/cm^3.

C. Crosslink Density

For an ideal rubber the dynamic storage modulus is related to the crosslink density by[18,19]

$$G'_m = NRT\upsilon_2 = (\rho_p/Z_eM_0)RT\upsilon_2 \qquad (6)$$

where $G'_m = G_{\max}$ = dynamic storage modulus, at maximum borate concentration at which steric hindrance occurs, in terms of energy per unit volume of gel; N = number of network chains per unit volume of dry crosslinked polymer ($N = 2$
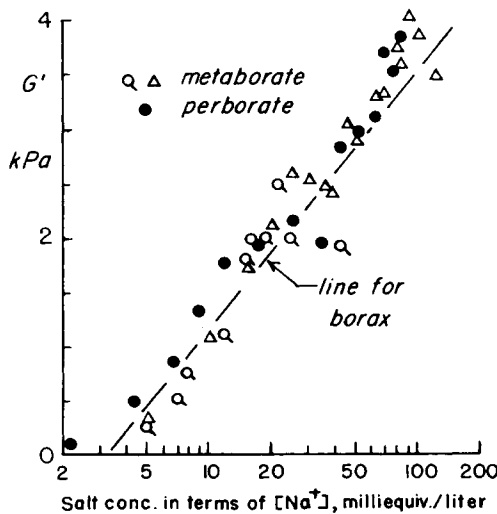

Fig. 5. Plots according to eq. (3) where (Q) are data of Schultz and Myers and dashed line is for borax (Fig. 3).

$\times$ crosslink density); ρ_p = density of the dry crosslinked polymer; v_2 = volume fraction of the dry crosslinked polymer to that of the gel; Z_e = average degree of polymerization between effective polymer chains; and M_0 = molecular weight of a monomer unit.

At this point, we have to distinguish between gels which are diluted first and then crosslinked and those which are cross-linked first and then swollen.[20] In the former, the network chains have their average random configuration in the unstrained state (except perhaps for gels linked at quite high dilution, where the polymer coils overlap each other's domains only to a limited extent). In the latter, however, the chains are all extended beyond their normal root-mean-square lengths, in proportion to the cube root of the swelling factor v_2. Since the borate crosslinked poly(vinyl alcohol) gel was crosslinked under dilute conditions, the flexible chain theories of viscoelastic behavior apply and little modification is required. Experimental evidence shows that the borate cross-linked poly(vinyl alcohol) gel follows the rubberlike elasticity model because the storage modulus of the gels was found to be independent of the frequency (in the range 3–10 Hz). At a G_{max} of 5×10^4 dynes/cm^2 for a metaborate-gelled PVA (0.035 g/cm^3), the crosslink density is calculated to be 2.54×10^{-3} chains per monomer unit and Z_e is 394 monomer units per network chain or 788 monomer units per crosslink. This value is very much different from the value that Schultz and Myers[5] reported. They calculated, at a G_{max} 2.5×10^4 dynes/cm^2, that one borate crosslink is present for each 150 monomer units in a 4.4% poly(vinyl alcohol) gel crosslinked by sodium metaborate. One reason that they obtained a lower G_{max} may be that they allowed a gelation time of only 1 h before the dynamic tests, and stability tests show that 1 h is insufficient for the borate cross-linked poly(vinyl alcohol) gel to achieve an equilibrium or pseudo-equilibrium condition at such a borate concentration.

The crosslink density, at the G_{max} of 5×10^4 dynes/cm^2, can be expressed as 1×10^{-6} mol of crosslinks per cm^3 of gel, with a sodium hydroxide concentration of 1.5×10^4 mol/cm^3 of gel. Therefore, there are 150 sodium ions per crosslink or the efficiency of crosslinking is only 0.7%. On the other hand, the threshold value of sodium ion concentration is found by extrapolating the curve in Figure 5 to zero storage modulus. For the 3.5% poly(vinyl alcohol) solution of original M_n of 9.2×10^4 g/mol, the threshold sodium ion concentration is 0.0034 mol/L, so there are nine sodium ions per crosslink and the efficiency of crosslinking at threshold concentration is 11%. Thus the crosslink density increases with borate concentration (until steric hindrance occurs), but the efficiency of crosslinking decreases with borate concentration.

D. Cation Effects

As discussed earlier, the storage modulus increases rapidly with sodium ion concentration at a given boric acid concentration, as long as the boron to sodium ratio is greater than 1. The question remaining is whether this increase in gel modulus (crosslink density) is due either to a pH effect or to the number of cations present, or due to both. In order to distinguish among these effects, a number of gels were prepared with the same number of moles of cations, but with differing pH's since different kinds of cations were used. The storage moduli of these gels are proportional to various cation (or OH$^-$) concentrations raised
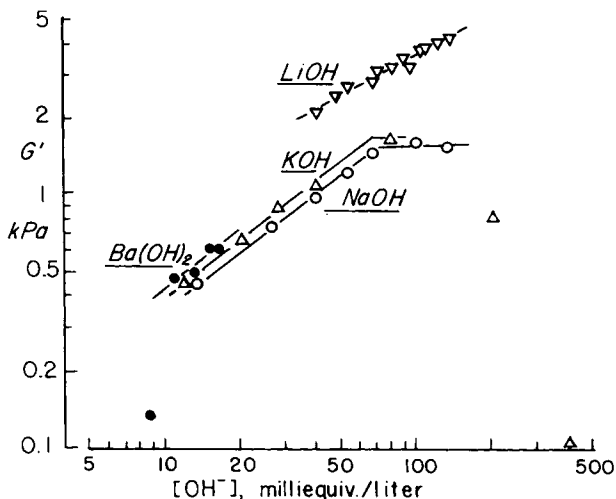
Fig. 6. Poly(vinyl alcohol gels) at 25°C with polymer concentration (g/cm³) and boric acid concentration (mol/L), respectively, of LiOH (0.035, 0.128), Ba(OH)₂ (0.0377, 0.0748), KOH (0.0283, 0.0832), and NaOH (0.0283, 0.0693).

to 0.8 power (or 0.5 power for LiOH) (Fig. 6). Preparation of a barium borate crosslinked poly(vinyl alcohol) gel is extremely difficult because the barium borate (obtained from mixing the barium hydroxide and boric acid) has very low solubility and also may precipitate from acid solution, e.g., from solution of large excess amount of boric acid. Table II shows some predicted values of storage modulus for the poly(vinyl alcohol) gels crosslinked by sodium borates and the actual data of gels crosslinked by other metallic borates tested under the corresponding conditions. The storage modulus of the lithium and potassium borate–poly(vinyl alcohol) gels is only very slightly higher than that predicted for the sodium borate–poly(vinyl alcohol) gels despite the fact that lithium and potassium hydroxides have significant higher dissociation constants than sodium hydroxide. The exceptional case of the barium borate-crosslinked poly(vinyl alcohol) gels can be explained by the efficiency of crosslinking rather than the pH effect. The efficiency of crosslinking of these gels is extremely low, mainly due to the steric hindrance and highly selective sites necessary for crosslinking (even at the threshold concentration), the efficiency is less than 10%). Most of the borons are either present as excess borons in polymeric crosslinks or bonded with free hydroxyl ions. Barium ion is bivalently charged, and each barium ion associates with two borons. It is not likely that both borons will take part in

TABLE II
Storage Modulus of Gels with Various Cations

Cation	OH^- (mol/L)	Boric acid concentration (mol/L)	Poly(vinyl alcohol) (g/cm³)	G' measured (kPa)	Ratio[a] to sodium G'
Sodium	0.010	0.0693	0.0283	0.58	1.0
Potassium	0.010	0.0832	0.0283	0.65	1.2
Lithium	0.100	0.128	0.0350	0.37	1.0
Barium	0.010	0.0748	0.0377	0.75	0.4

[a] Sodium G' calculated for same conditions of OH^- and polymer concentration.

crosslinking since sites available for crosslinking at close neighbors are limited. In addition, if both borons do take part in crosslinking, then this crosslinked group will be more bulky and have higher steric hindrance on the other crosslink sites. Another major difference between the barium and the monovalently charged cations in crosslinking reactions is that the storage modulus of the gel containing the latter cations reaches a plateau modulus when the normality of the cations is equal to that of the boric acid. On the other hand, the storage modulus of the gel containing barium ions reaches a limit when the normality of the barium hydroxide is less than one third of the molar concentration of the boric acid. The barium hydroxide actually starts to precipitate the poly(vinyl alcohol) at this concentration or higher. This shows that the bivalently charged cations do have the greater tendency to draw the crosslinked polymer chains closer to each other and to suffer more steric hinderance than the monovalently charged cations.

E. Temperature Dependence

The crosslinking reaction of the sodium metaborate-crosslinked poly(vinyl alcohol) gels is known to be thermally reversible.[5] The increase in storage modulus with temperature which one would expect from ideal rubber elasticity is negligible compared to the decrease in storage modulus due to changes in crosslink density. Further experiments showed that cross-linked reactions of other borate crosslinked poly(vinyl alcohol) gels are also thermally reversible. Assuming that the activation energy of crosslinking is of the Arrhenius type, the log of the storage modulus is plotted against the inverse of absolute temperature (Fig. 7). It appears that the corresponding activation energies are fairly constant (about 2.5 kcal/mol) at low temperatures and decrease as temperature rise. This deviation from Arrhenius type of behavior is especially pronounced in borax crosslinked poly(vinyl alcohol) gels. This difference appears also when gels of different sodium to boron ratios are used (Fig. 8). None of the activation energies of these gels is constant throughout the whole temperature range. The variability of the activation energy is also more evident for gels with lower sodium to boron ratios. Apparently, the excess borons change the gel structure and decrease the activation energy required for breaking individual crosslinks (or activation energy
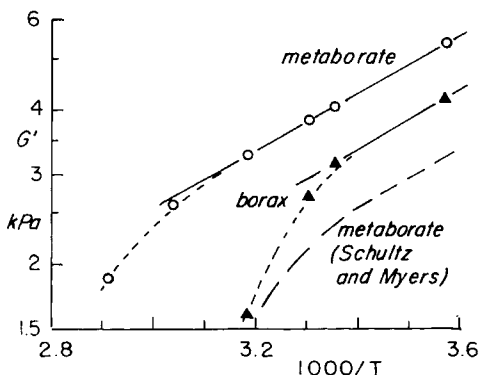

Fig. 7. Arrhenius plot for polymer concentration of 0.035 g/cm^3 and metaborate (0.0518 mol/L) or borax (0.0454 mol/L). Straight lines correspond to energy of activation around 2.5 kcal/mol. Results of Schultz and Myers estimated by extrapolation to 100 Hz.
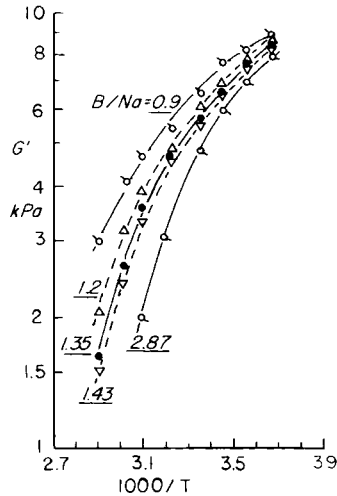
Fig. 8. Arrhenius plots for gels with polymer concentration of 0.0405 g/cm^3 and NaOH concentration of 0.0625 mol/L.

of crosslinking).   The apparent activation energy at 25°C decreases almost linearly with the boron to sodium ratio.   Addition of borons into the gels does have a consistent effect on the crosslinking system.

The dependence of apparent activation energy on temperature and sodium to boron ratio can be seen in a plot of storage modulus vs. boric acid concentration (Fig. 9).   The power dependence of the storage modulus on sodium to boron ratio changes continuously with temperature.   This behavior is best explained by the reason that gels of different sodium to boron ratio have different apparent activation energy of breaking crosslinks.   The values of the slopes increase rapidly with temperature; therefore, the temperature effect actually magnifies the sodium to boron dependence of the gels, especially at higher temperatures.   The dependence of apparent activation energy on the sodium to borate ratio leads to the conclusion that the excess borons alter the gel properties by forming polymeric crosslinks rather than changing the crosslink density.   The dependence of this activation energy on temperature is rather common in other types of dilute crosslinked gels.[19]
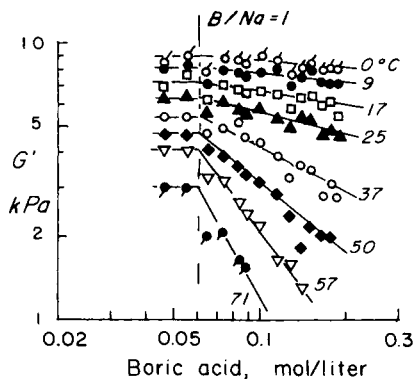

Fig. 9. Effect of boric acid concentration on temperature dependence of modulus for gels with 0.0405 g/cm^3 polymer and 0.0625 mol/L NaOH.

On the other hand, the activation energy is found to be constant in an Arrhenius plot of the log decrement, as shown in Figure 10. This activation energy is actually the activation energy of viscoelastic flow or the activation energy for bond interchanging. This activation energy of viscoelastic flow appears to be relatively indifferent to the sodium to boron ratio, regardless of the fact that excess boron increases the possibility of crosslink interchange. The gels with boron to sodium ratio of 2 and of 1 give the activation energies of 5.5 and 6.5 kcal/mol, respectively. These values are lower than the 10 kcal/mol reported by Schultz and Myers,[5] but their method of calculating the activation energy assumed a time-temperature superposition not used here.

F. Molecular Weight Dependence

Generally, the gel strength increases with original poly(vinyl alcohol) molecular weight (Fig. 11). The 98% hydrolyzed poly(vinyl alcohol) has the highest in-
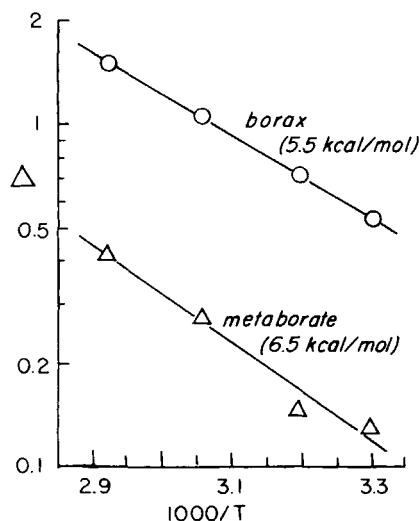
Fig. 10. Arrhenius plot for log decrement (Δ) with 0.0398 g/cm^3 polymer and 0.0438 mol/L of borate salt.
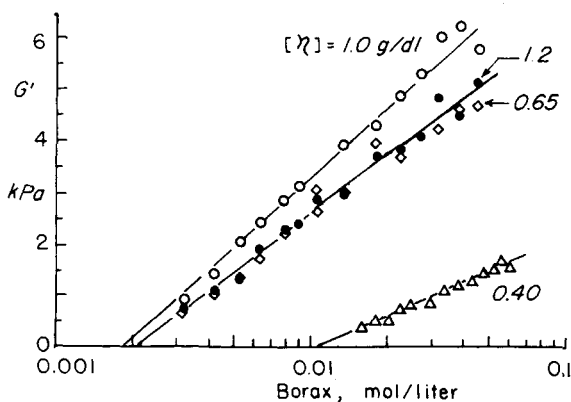
Fig. 11. Effect of molecular size on modulus for borax crosslinked gels at 25°C. Polymer concentration (g/cm^3) is 0.041 ± 0.001. The polymer with the highest intrinsic viscosity is 98% hydrolyzed while the rest are reported to be more completely hydrolyzed.

trinsic velocity among the polymers tested; yet the storage moduli of gels with original polymer intrinsic velocity of 1.20 are only comparable to the 100% hydrolyzed poly(vinyl alcohol) gels with original polymer intrinsic viscosity of 0.65 at the corresponding borax concentrations. The acetate side groups must have a major part in hindering the crosslinking process. The storage moduli of these borax crosslinked poly(vinyl alcohol) gels with various molecular weights are also found to be proportional to the logarithmic function of the borax concentration. The straight lines drawn for gels of individual original molecular weights have different x-intercepts. This means the borax crosslinked poly(vinyl alcohol) gels with lower original molecular weights have higher minimum borax concentrations.

CONCLUSIONS

The properties of the borate crosslinked poly(vinyl alcohol) gels are dependent on six variables: the cation to boron ratios; borate and poly(vinyl alcohol) concentrations; temperature; molecular weight; and acetate content of the polymer. The origin of the borates (e.g., borate salts of mixture of boric acid and alkaline solutions) and pH effect do not have a significant impact on the gel properties.

Boric acid does not introduce crosslinks in poly(vinyl alcohol) solutions, but gelation occurs in the presence of cations. At low cation to boron ratios, the excess borons react with poly(vinyl alcohol) as monodiol, which does not induce crosslinks or take part in the crosslinking reaction in a polymeric form. At these ratios, the monomeric crosslinks occupy only a negligible fraction. These gels are weaker and have larger values of log decrement than the gels with higher cation contents. As the cation to boron ratio increases, both the monodiol and the polymeric crosslinks are converted into didiols (monomeric crosslinks). Evidence of these changes are the increase of storage modulus (an external property), the decrease of log decrement (an internal property), and the increase of activation energy for breaking individual crosslinks. At a cation to boron ratio of 1, the storage modulus reaches a plateau value at which the crosslinks are in monomeric form only, but the cation effect is continuous because the log decrement continues to decrease with cation concentration until the gel precipitates.

The crosslink density increases with both borate and poly(vinyl alcohol) concentrations. The storage modulus is found to be dependent on the logarithmic function of borate concentration and a power function of poly(vinyl alcohol) concentration. Only a very small portion of the borates in solution take part in effective crosslinks.

The activation energy for breaking individual bonds is a function of temperature and the cation to boron ratios. At a fixed cation concentration, this activation energy is more negative with increasing amount of boron ions due to a transformation of monomeric crosslinks into polymeric crosslinks, so the storage modulus which measures crosslink density decreases as a temperature rises.

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