The Chemorheology of Poly(vinyl alcohol)-Borate Gels

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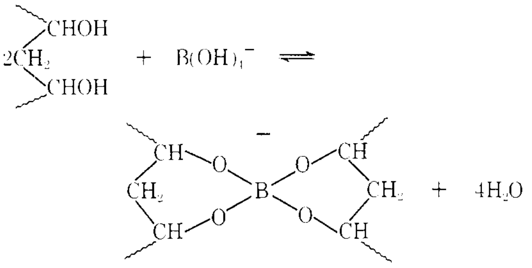
ABSTRACT: The reversible, exothermic reaction between borate ion and polyol leads to an inverse temperature dependence of cross-link density in borate-cross-linked poly(vinyl alcohol) gels. The decrease in the equilibrium constant of the cross-linking reaction with temperature necessitates a vertical shift in order to reduce dynamic rigidities and viscosities to master curves. The magnitude of the vertical shift factor is directly related to the enthalpy of the cross-linking reaction. From the dynamic mechanical behavior of the PVA–borate system one can calculate the enthalpy of the cross-linking reaction, the energy to break individual cross-links, the activation energy for viscoelastic flow, and the chemical relaxation time of the material. The enthalpy for the cross-linking reaction, ascertained from the vertical shift, was of the order of −5 kcal/mol. The activation energy for breaking individual cross-links was 6 kcal/mol. The activation energy for viscoelastic flow, ascertained from the horizontal shift, was 10 kcal/mol. The chemical relaxation time at room temperature was 0.33 sec.

Considerable effort[2,3] has been spent to elucidate relationships between the chemical constitution and mechanical and physical properties of bulk polymers, polymer melts, and polymer solutions. With gels these efforts have been particularly frustrating because the cross-links often are of uncertain nature and their concentration and properties change with time.

The results of an investigation of the dynamic mechanical behavior of a poly(vinyl alcohol) (PVA) solution gelled by the addition of borate ions are reported here. These gels are particularly intriguing because, unlike gelatin or Congo red cross-linked PVA gels, they are viscid in nature (*i.e.*, self-healing) and form instantaneously on mixing two fluid solutions. The gel cross-links are known to be borate chelate ions formed between borate ions and hydroxyl pairs on adjacent polymer strands.[4-6] The cross-linking reaction is



(I)

Furthermore, for this system the cross-links are precisely defined, their concentrations are readily controlled, and their properties are independent of time.

Because of the gel-like nature of the material, one cannot acquire meaningful data using rotational viscometry. On the other hand, static measurements of rigidity are impossible to obtain because the material flows markedly over extended periods of time. In this study, measurements of both the dynamic rigidity and viscosity were obtained using an oscillating cup rheometer. Data were obtained in the frequency range from 0.01 to 20 Hz as a function of cross-link concentration and temperature. From the change of mechanical properties with temperature and cross-link concentration the thermodynamic and kinetic properties of the cross-links were evaluated.

Experimental Section

A. Materials. An 8.8% by weight solution of a commercial grade ("Elvanol" grade 71–30 manufactured by E. I. DuPont de Nemours & Co.) poly(vinyl alcohol) (PVA) was prepared. The manufacturer reported the degree of hydrolysis to be 99–100 mol % and the weight-average and number-average molecular weights of the polymer to be 112,000 and 50,000, respectively. Residual salts were removed by a 48-hr dialysis. The cross-linking agent was a commercially supplied purified sodium metaborate which was used without further purification.

Samples were prepared by diluting the proper amount of the PVA solution with the required amount of distilled water, and then adding a calculated amount of 4.35×10^{-2} *M* sodium metaborate solution. With sufficient concentrations of the ingredients, gels formed immediately. The gels were puttylike masses from which lumps of stiff gel, which formed due to the heterogeneity of the mixing process, were dispersed by working the sample manually with a broad metal spatula until the gel appeared homogeneous; they were then transferred to the cup and held at constant temperature for at least 0.5 hr before obtaining data.

B. Apparatus. The equipment used for the dynamic measurements was of the type described by Markovitz.[7] The sample was contained in a cup which was oscillated mechanically at a known amplitude and frequency. A cylindrical bob, attached to the shaft of a rotary variable differential transformer (RVDT), was suspended coaxially in the sample. The stainless steel bob was 7.63 cm long, 2.54 cm in diameter, and had a moment of inertia of 258 g cm^2. The cup was 9.00 cm long and 3.49 cm in diameter. This gave a 1.37-cm clearance at the bottom of the bob and an annulus of 0.47 cm; with these dimensions end effects were shown to be negligible.

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(2) (a) T. Alfrey, Jr., "Mechanical Behavior of High Polymers," Interscience Publishers, New York, N. Y., 1948; (b) F. Bueche, "Physical Properties of Polymers," Interscience Publishers, New York, N. Y., 1962.

(3) J. D. Ferry, "Viscoelastic Properties of Polymers," John Wiley & Sons, Inc., New York, N. Y., 1961.

(4) H. Deuel and H. Neukom, *Makromol. Chem.*, **3**, 13 (1949).

(5) R. E. Schachat and L. Z. Raymond, Advances in Chemistry Series, No. 25, American Chemical Society, Washington, D. C., 1960.

(6) G. L. Roy, A. L. Laferriere, and J. O. Edwards, *J. Inorg. Nucl. Chem.*, **4**, 106 (1957).

(7) H. Markovitz, P. M. Yavorsky, R. C. Harper, L. J. Zapas, and T. W. DeWitt, *Rev. Sci. Instr.*, **23**, 430 (1952).

Table I
Dimensions of the Bob and Cup Assembly

Part	Height, cm	Radius, cm	Moment of inertia, g cm^2
Cup	9.00	1.745	
Bob	7.63	1.27	258
Collar		3.81	629
Inertia disks		3.81	1440

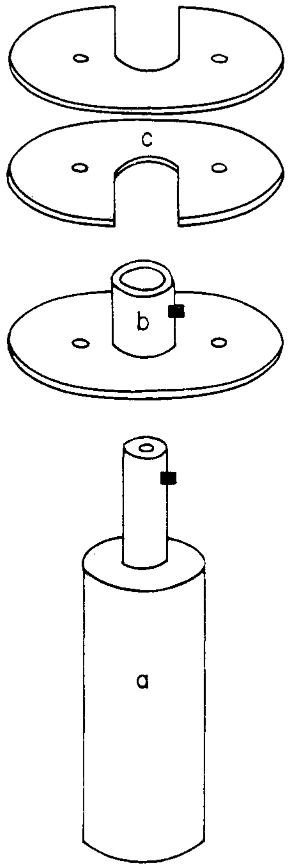

Figure 1. Bob and assembly for increasing inertia: a, bob; b, collar; c, pair of inertia rings.

The electrical signals obtained from the RVDT attached to the bob and a similar RVDT attached to the cup were detected on an oscilloscope. By comparing these two signals, the amplitude ratio (m) of the bob to the cup, and the phase angle (ϕ) between the bob and cup could be computed with an accuracy of 5% in amplitude and ±0.5 deg in phase difference. As the frequency is increased m increases from unity through a maximum at resonance and then decrease toward zero. Simultaneously ϕ increases from zero, passes rapidly through 90° near resonance, and approaches 180° at higher frequencies. In order to make the sample resonance fall in the frequency range of the instrument, the moment of inertia of the bob could be increased by adding a collar to which various rings could be added without disturbing the sample (see Figure 1 and Table I). This latitude was necessary when the temperature was varied over a wide range.

C. Calculations. Dynamic rigidity (G') and the dynamic viscosity (η') of the sample were computed on a GE 225 digital computer from the amplitude ratio and phase angle data. The basic equation for the rigorous treatment including the moment of inertia of the sample is a converging power series in the reciprocal complex viscosity.[8a] This equation was rearranged so that the data could be handled by the computer.[8b] Only the first-order term of the expansion was needed because the results differ by only 5% from the results including the second-order term, and the reproducibility between similar gels was of the order of 10%.

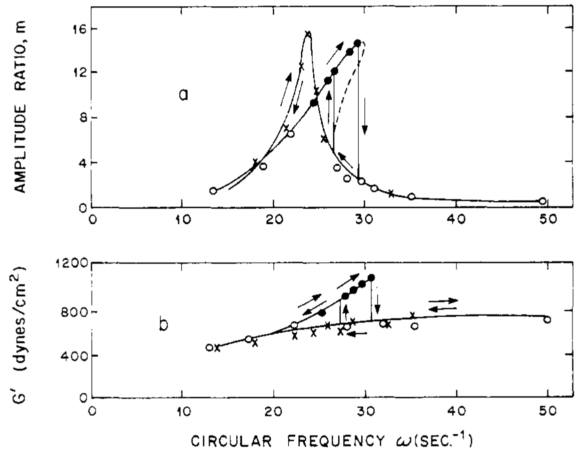

Figure 2. Nonlinear response at high strain amplitude; amplitude of cup oscillation: ×, 0.27 deg; ○, 0.64 deg and not near resonance; ●, 0.64 deg near resonance frequency.

The constants in the equation were calculated from the known dimensions of the bob and cup. These calculated constants were verified by using standard viscosity oils as well as a fully characterized viscoelastic sample of polyisobutylene in decalin.[9] The calibration procedure demonstrated that an anomaly in the bearing assembly of the RVDT became dominant at low frequencies; consequently, all data reported on the gel samples were taken at frequencies sufficiently high where the anomaly was absent.

Results and Discussion

A. Linearity of Mechanical Properties. The amplitude of oscillation of the cup was varied between 0.25 and 6 deg in a preliminary experiment to ascertain that G' and η' were independent of the magnitude of strain. At frequencies near resonance and cup amplitudes above 0.5 deg the sample behavior deviated from the linear behavior required by the Markowitz equations. This nonlinearity was immediately obvious because data obtained with the frequency increasing did not coincide with data obtained with the frequency decreasing. This hysteresis, shown in Figure 2a, was such that the resonance peak was skewed to the right. Since the skew was toward higher frequencies, G' increases when one exceeds the linear strain limit. This trend was confirmed by the results shown in Figure 2b which were obtained by calculating G' from the data shown in Figure 2a. Hence, the gel structure was not broken at the higher amplitude; the polymer strands merely were stretched beyond their Hookean limit of conformational elasticity and required a greater than linear increase in force to be stretched further. The increase in G' at high amplitudes also suggests that no slippage was present between the sample and the walls

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(8) (a) H. Markovitz, *J. Appl. Phys.*, **23**, 1070 (1952); (b) R. K. Schultz, Ph.D. Dissertation, Lehigh University, 1965, Appendix I & II.

(9) Obtained from and characterized by H. Markowitz and L. Zapas of Mellon Institute, Pittsburgh, Pa.

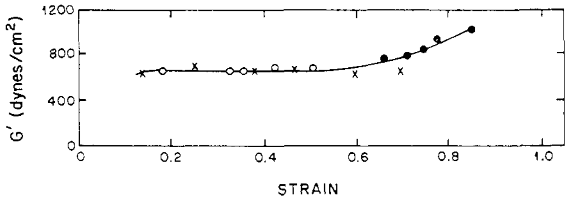

Figure 3. Increase of shear modulus at large sample strains; amplitude of cup oscillation: ×, 0.27 deg; ○, 0.64 deg and not near resonance; ●, 0.64 deg near resonance frequency.

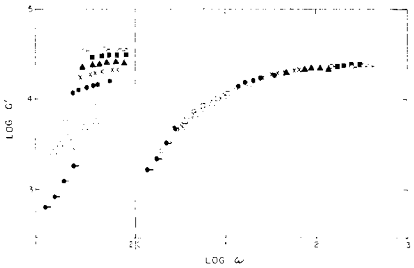

Figure 4. Variation of the dynamic shear rigidity with temperature for a borate gel. The gel contained 7% PVA and was 8.7×10^{-3} M in total borate ion. Curve on the right is the master curve at a reference temperature of 25°. Temperatures were as follows: ○-, 0°; ■, 8.5°; ▲, 17°; ×, 25°; ●, 36°; □, 47°; △, 57°; ○, 65°; ●-, 74°.

TABLE II

HORIZONTAL AND VERTICAL SHIFT FACTORS REQUIRED TO OBTAIN THE MASTER CURVES IN FIGURE 5

Temp, °C	Horizontal shift, log a_T		Vertical shift, log b_T	
	G'	η'	G'	η'
4	0.60	0.58	−0.34	−0.29
16	0.26	0.28	−0.23	−0.17
28[a]	0	0	0	0
43	−0.43	−0.41	0.26	0.26

[a] Reference temperature.

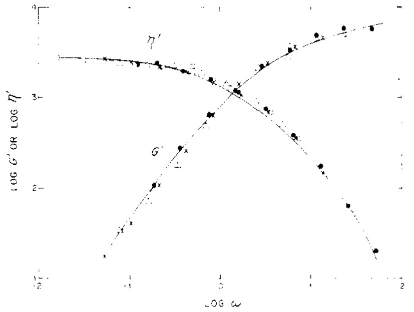

Figure 5. Master curve for dynamic viscosity and dynamic rigidity for a borate gel that contained 4.4% PVA and was 8.7×10^{-3} *M* in total borate ion. Data were reduced to 28°. Temperatures were as follows: ●, 4°; ○, 16°; ×, 28°; △, 43°; □, 62°.

of the cup or bob. Such slippage would be expected to lower the apparent G' at high cup amplitudes. Slippage was probably responsible for the large decrease in G' with increasing amplitudes reported on flour doughs.[10]

These results demonstrate that with dynamic rheometers designed to operate through resonance frequency the linear range cannot be specified, as often is done, by the cup amplitude alone. The limit of linearity is established by the shear strain on the sample which can be calculated for the bob and cup geometry by using an equation derived by one of the authors.[8b] When the apparatus is in oscillation near resonance, the amplitude ratio may rise to a value as high as 16; this large amplitude ratio produces a shear strain on the sample of 0.91 when the cup amplitude is 1 deg. Figure 3 shows that a shear strain above 0.6 produces nonlinear behavior in the PVA–borate gel samples. This is the upper limit of the linear range for these samples. All data reported below were obtained with such a low cup amplitude that the shear strain always remained below 0.6 even at resonance.

B. Temperature Effects. Reduction of Dynamic Data. The effective frequency range was extended by changing temperatures and shifting the data to a reference temperature of 25° in the manner proposed by Williams, Landel, and Ferry.[11] The results on a 7% PVA gel (1.6 *M* in alcohol groups) containing 8.7×10^{-3} *M* metaborate are shown in Figure 4. The master curve can be obtained only after applying a vertical shift in excess of that introduced by the temperature ratios. A vertical shift had been used previously with samples whose degree of crystallinity was temperature dependent,[12] and with nonaqueous dispersions.[13] It occurs in this case because the number of cross-links in the system decreases with increasing temperature; that is, reaction I is exothermic.

In order to determine the horizontal and vertical shift factors with better accuracy than could be realized from our limited frequency range, data were also obtained at lower frequencies (0.01–2 Hz) on a different torsional rheometer.[14] Over this range of frequencies the G' and η' values change considerably, so that the accuracy of the calculated shift factors is improved. The master curve is shown in Figure 5. Table 2 shows that the same horizontal and vertical shifts are required to transform both G' and η' values to the master curves. Such agreement confirms that the sample obeys the time–temperature superposition principle.

From the slope of a plot of log a_T *vs.* the reciprocal of absolute temperature one can calculate the activation energy, ΔH_a, required for the relaxation.[15a] ΔH_a is 10 kcal/mol for the borated PVA gel described in Figure 5. This energy, which is considerably lower than the 42 kcal/mol reported[15b] for the gelatinlike Congo red cross-linked PVA gel, accounts for the puttylike behavior of the borated system.

Stress Relaxation Calculations. In order to calculate the energy barrier involved to move individual

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(10) J. R. Van Wazer, J. W. Lyons, K. Y. Kim, and R. E. Colwell, "Viscosity and Flow Measurement," Interscience Publishers, New York, N. Y., 1963, p 376.

(11) M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Amer. Chem. Soc.*, 77, 3701 (1955).

(12) K. Nagamatsu, *Z. Kolloid*, **172**, 141 (1960).

(13) R. D. Hoffman and R. R. Myers, *Proc. Intern. Congr. Rheol., 4th, Providence, 1963*, 693 (1965).

(14) The authors are indebted to Dr. Ray D. Hoffman, W. R. Grace & Co., Clarksville, Md., for these measurements.

(15) (a) Reference 3, p 225; (b) K. Arakawa, *Bull. Chem. Soc. Jap.*, **32**, 1248 (1959).

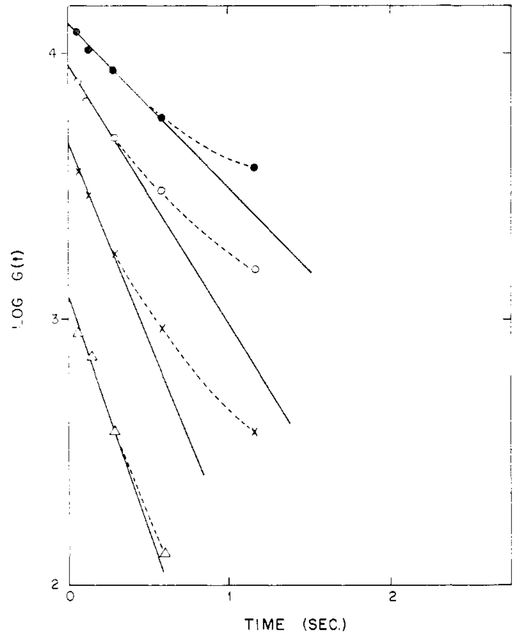

Figure 6. Decay of the stress relaxation modulus with time for the gel reported in Figure 5: ●, 4°; ○, 16.5°; ×, 28°; △, 43°.

cross-links, the above data were converted into stress relaxation data. These data were calculated from the dynamic shear moduli master curves reduced to different temperatures using the approximation of Ninomiya and Ferry[16] (eq 1), where $\omega = 1/t$. Here $G(t)$ is the

$$G(t) = G'(\omega) - 0.40G''(0.40\omega) + 0.014G''(10\omega) \quad (1)$$

stress relaxation modulus and G' and G'' are the dynamic shear rigidity and dynamic loss modulus, respectively. The last term in the approximation proved to be insignificant in the calculation.

The stress relaxation curves, Figure 6, are linear only over a small initial time period. The cross-links are broken during the relaxation process, but reform continually in the strained gel. Since the PVA molecules are somewhat oriented when the cross-links reform during the stress relaxation process, the probability is increased of finding two cross-links between two given parallel strands. The onset of this condition decreases the rate of stress relaxation because cooperative breaking of two cross-links is needed in order for further relaxation to occur.

The activation energy for bond migration was determined by plotting the initial decay rates of Figure 6 *vs.* $1/T$. The result is 5.8 kcal/mol. This activation energy can be regarded as the energy required to move an isolated cross-link across a potential barrier. It is not very different from the 7 kcal/mol reported[17] as the activation energy to break a single cross-link in the Congo red cross-linked PVA gel.

The chemical relaxation time is the time required for the stress to decay to $1/e$ of its original value.[18] For the PVA gel described in Figure 5 this relaxation time at room temperature is about 0.33. This short relaxation time is consistent with the putty-like properties of the PVA–borate gels.

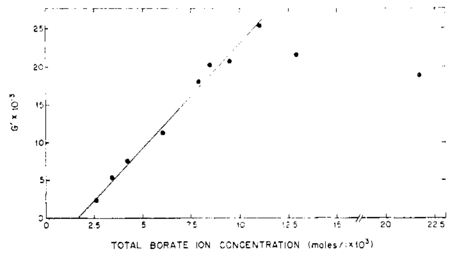

Figure 7. Effect of borate ion concentration on G' at high frequencies where cross-links do not have time to relax during a cycle. All gels contained 4.4% PVA and were measured at 25°.

C. Cross-link Concentration Effects. The constant value of G' reached at a level of about 3×10^4 dyn/cm^2 at higher frequencies (Figure 4) corresponds to the rubbery state of the cross-linked PVA. These frequencies do not permit significant relaxation during a cycle. At low frequencies this level drops off toward $G' = 0$ because the continuous breakage of borate cross-links permits the molecular chains to rearrange during each cycle. If the cross-links were not labile, the plateau region of Figure 4 would remain constant down to the lowest frequencies, and G' would equal the static shear modulus, G. For an ideal rubber, the static (and low frequency) modulus of rigidity, G, relates to the cross-link concentration, c, by eq 2, where n is the

$$G = 2cRT = nkT = \frac{\rho}{\bar{M}_c}RT \quad (2)$$

number of network chains per cubic centimeter, ρ is the density, and $\bar{M}_c$ is the number average molecular weight between cross-links. The equation will also be applicable to real rubbers if $\bar{M}_c$ is replaced by $\bar{M}_{ce}$, defined as the number average molecular weight between effective cross-links. By an effective cross-link is meant one that has at least three complete network strands leading from it. Because the borate cross-linked PVA is not an ideal rubber, eq 2 applies only if the plateau value of G' is used in place of the static G value, and $\bar{M}_c$ is replaced by $\bar{M}_{ce}$.

A plot of borate concentration *vs.* the G' value of the plateau should, however, be linear because the gel acts like an ideal rubber above a circular frequency of 100. Results of such a plot are shown in Figure 7. The intercept, according to Flory,[19] occurs when the concentration of cross-links in the solution equals the concentration, based on the number average molecular weight, of polymer molecules in solution. The polymer $\bar{M}_n$ was approximately 50,000, corresponding to a polymer concentration of 9×10^{-4} *M*. Using the equilibrium constants at room temperature for the formation of the 1:1 and 2:1 polyol–borate complexes,[6] the ionization constant of boric acid, the pH, and the conservation of mass equation, one can calculate algebraically by solving four simultaneous equations that 61% of the total boron is present as 2:1 cross-links. Hence a total borate concentration of 1.5×10^{-3} *M*

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(16) Reference 3, p 72.

(17) K. Arakawa, *Bull. Chem. Soc. Jap.*, **35**, 309 (1962).

(18) A. V. Tobolsky, "Properties and Structure of Polymers," John Wiley & Sons, Inc., New York, N. Y., 1960, p 239.

(19) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

is needed for gel formation to begin. This figure agrees favorably with the experimental concentration intercept of 1.7×10^{-3} *M* (a higher experimental value is expected due to free chain ends in the gel).

At high concentrations of borate the linear relationship between G' and borate concentration no longer holds, probably due to a salt effect. G' passes through a maximum near a total borate concentration of 1.1×10^{-2} *M*. At $G'_{\max}$ one borate cross-link is present for each 150 monomer units. At this point the bound borate ions probably cause enough electrostatic repulsion of the borate ions in solution to retard further complexing. Hence, above a critical concentration of borate the equilibrium constant for reaction I is no longer independent of concentration.

For gels eq 2 can be written

$$G = \frac{\rho RT}{\bar{M}_{ce}} \nu_c \qquad (3)$$

where ν_c is the volume fraction of polymer in the sample. The value calculated for $\bar{M}_{ce}$ at the lowest experimental cross-link concentration is four times the mass of the original polymer chains. Such results also have been reported for gelatin gels.[20] In this case the large $\bar{M}_{ce}$ values can be explained by assuming that borate links the smaller chains together to form an effective network strand that is longer than the initial polymer chain.

According to eq 2 the slope of the straight line in Figure 7 should equal $2RT$. The calculated value for the slope is 5×10^{10} ergs/mol compared to the experimental slope of 5×10^{9} ergs/mol. Such large deviations are often encountered for various cross-linked systems,[21] and the deviations are accounted for by incorporating a form factor into the equation. The form factor of 0.1 required for the borated gel reported in Figure 7 agrees exactly with the factor reported for a PVA solution of the same concentration cross-linked in solution with terephthalaldehyde and measured under static conditions.[21] This agreement indicates that the microstructure of the borated gel containing labile negatively charged cross-links is identical with that in the PVA gel containing permanent covalent cross-links.

For these PVA gels a form factor of 0.1 indicates that only one-tenth of the cross-links are effective cross-links. Since $\bar{M}_{ce}$ is up to four times the molecular weight of the original polymer, and since the 2:1 complexes linking these strands together are attached at random sites along the chain, many of these links are needed to form one effective strand. Hence, only a fraction of the 2:1 complexes form network junctions even though most of them join two different polymer chains together.

D. Reaction Energies from Vertical Shift Factors. G' decreases with increased temperature because the exothermic nature of reaction I lowers the cross-link concentration more than the entropic nature of elasticity causes G' to increase with increasing temperature. For a gel whose total borate concentration falls in the linear portion of Figure 7, the change in G' with temperature can be considered a direct consequence of a change of cross-link concentration with temperature. The vertical shift factor, log b_T, results from this change.

The equilibrium constant for reaction I can be written

$$K = \frac{[\mathrm{BP_2}^-]}{[\mathrm{B}^-][\mathrm{P}]^2} \qquad (4)$$

where $[\mathrm{BP_2}^-]$ represents the molar concentration of 2:1 complexes, $[\mathrm{B}^-]$ represents the borate concentration, and [P] represents the concentration of polymer in terms of moles of hydroxyl groups per liter. For the gel described in Figure 5, [P] = 1.0. Inasmuch as the concentration of borate $[\mathrm{B}^-]$ is of the order of 10^{-2} *M*, the concentration of polymer will remain within 4% of 1.0 regardless of temperature, and can be ignored. If $[\mathrm{B}^-]$, the $\mathrm{B(OH)_4}^-$ concentration, could also be held constant with changing temperature, the equilibrium constant would be directly proportional to the cross-link concentration, and hence would depend directly on K.

If these considerations apply, a plot of log b_T *vs.* $1/T$ would yield the enthalpy of the complexing reaction. When log b_T for the borated PVA was plotted against $1/T$, a straight line resulted with a slope corresponding to an energy of -5.0 kcal/mol. This energy agrees favorably with the enthalpy change of -5.2 kcal/mol reported[22] for the borate–diethyl tartrate complex in which the bonding is virtually identical with the PVA complex. Hence the approximation that G' is proportional to the equilibrium constant appears valid, and the enthalpy change of a chemical reaction can in this case be calculated from the change in a mechanical property with temperature.

Acknowledgments. The authors are pleased to acknowledge the assistance of Dr. T. R. Meeker and Dr. R. D. Hoffman. The work was supported by a grant from the Corn Industries Research Foundation.

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