Rheology of Guar and HPG Cross-Linked by Borate

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ABSTRACT: Measurements have been conducted on the linear viscoelastic properties of guar and (hydroxypropyl)guar (HPG) polymer solutions cross-linked with borate ions to form gels. Chemical equilibria involving boric acid, borate ions, and borate ions associated with *cis*-diol sites on the polysaccharide chains determine the number of cross-links. These equilibria are functions of temperature and pH, and thus the rheology of the borate gels depends on temperature and pH. Measurements on 0.48 wt % polymer solutions were performed over the temperature range from 15 to 65 °C and the pH range from 6.35 to 9.5. The storage and loss moduli obey time–temperature superposition so that master curves can be constructed over 6 decades in frequency. The shift factors along the time axis follow a single-exponential Arrhenius form at pH values above 8 with activation energies that vary from 90 to 115 kJ/mol. The activation energies for guar and HPG are identical, which is consistent with the *cis*-diols on each polymer being the active site for cross-linking. Also, the data at different pH values can be superimposed by "time–pH" shifting to produce master curves from which the temperature and pH sensitivity of the gel rheology can be determined. Leibler et al. have recently proposed a theory for the rheology of associating polymer systems. Following this theory, we have subtracted the solution moduli from the gel moduli, and the resulting reduced moduli data follow a single time constant Maxwell model, where the time constant reflects the relaxation time of borate/*cis*-diol interactions in the network.

Water-soluble polymers can be cross-linked to form water-swellable gels using a number of cross-linking chemistries. Examples include covalently cross-linked gels used in controlled drug release or as soft contact lenses,[1-6] gels formed by hydrogen bonding such as photographic gelatins,[7] gelatin foods,[8] or agarose gels for electrophoresis,[9] gels formed by hydrophobic interactions,[10,11] or gels formed using inorganic metal ions[12,13] as the cross-linking species. The latter category, gels formed with inorganic cross-linkers, are used in the oil and gas industries to block flow channels through underground rock formations[14,15] (called permeability modification) and to create high-viscosity fluids to transport sand in artificially created underground fractures around a wellbore[16] (called hydraulic fracturing). This is by far the largest volumetric use of cross-linked water-soluble polymers. A single hydraulic fracturing operation may involve 1 million gallons of 1/2% by weight cross-linked polymer solution. Understanding the relationship between rheology, chemistry, and molecular gel structure is crucial for the proper formulation and application of these cross-linked gels. We have previously reported on the gelation of polyacrylamides with chromium ions[12] and the gelation of (hydroxypropyl)guar (HPG) with titanates.[13] In this paper we present a study of the gelation of (hydroxypropyl)guar and guar polymers by borate ions. The surprising result is that the borate "gels" obey the laws of time–temperature superposition just like linear polymer melts or solutions. The shift factors show an Arrhenius dependence on pH and temperature which is in accord with the borate ion equilibria that governs cross-linking.

Guar is a naturally occurring polysaccharide which is composed of a linear backbone of (1–4)-β-linked D-mannose units with (1–5)-α-linked D-galactose units randomly attached as side chains.[17] The molecular weight of guar is about 2×10^6. Guar is derivatized to form (hydroxypropyl)guar (HPG) or (carboxymethyl)(hydroxypropyl)guar (CMHPG) because the propylation step reduces the amount of insoluble cell debris in the final solutions. The structure of the repeating unit of guar and its derivatives is shown in Figure 1.

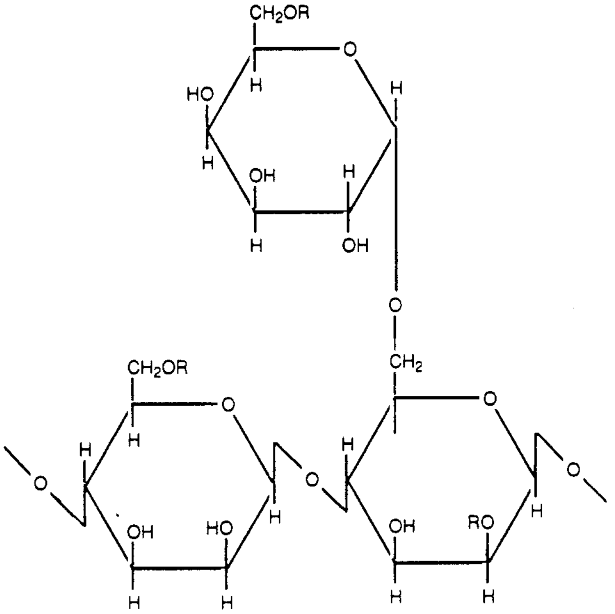

Figure 1. Structure of the repeating unit of guar and its derivatives. R = H for guar and R = $CH_2CH_2CH_2OH$ for (hydroxypropyl)guar.

Guar and (hydroxypropyl)guar are cross-linked by borax to form borate-cross-linked guar and HPG gels, respectively. The borate ion ($B(OH)_4^-$) is the effective species in cross-linking, and its concentration is a function of the pH, temperature, and concentration of borax in the solution.

The equilibrium reactions for borate ions in aqueous solution have been studied[18,19] previously. Sodium borate (borax) dissociates completely to form boric acid, $B(OH)_3$, and borate ions, $B(OH)_4^-$

$$B_4O_7^{2-} + 7H_2O \rightarrow 2B(OH)_3 + 2B(OH)_4^- \qquad (1)$$

and an acid–base equilibrium is established between boric acid and monoborate ions[18]

$$B(OH)_3 + H_2O \overset{K_A}{\rightleftarrows} B(OH)_4^- + H^+ \qquad pK_A = 9.0\text{–}9.2 \qquad (2)$$

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The monoborate ions react with the *cis*-hydroxyl groups in guar or HPG to form cross-links. The binding constant of the monoborate ion to a single hydroxyl group is much weaker than the binding constant to *cis*-hydroxyls and can be neglected in the following mass-action calculations. In order to study the complexation chemistry, most of the studies in the literature[18-22] were performed with simple polyols like pentanol[18] and 1,2-propanediol[20] and with model sugars like methyl α-D-galactopyrannoside and methyl α-D-mannopyrannoside.[19] Since galactopyrannoside and mannopyrannoside are the repeating units in guar, similar reactions are expected to occur between the borate ions and the hydroxyl groups on guar. The reactions of the borate ions with polyols (cis-hydroxyls) are

$$A + B^- \overset{K_1}{\rightleftarrows} AB^- \qquad (3)$$

$$2A + B^- \overset{K_2}{\rightleftarrows} A_2B^- \qquad (4)$$

where A refers to the polyol, B^- refers to $B(OH)_4^-$, and AB^- and A_2B^- are the 1:1 and 2:1 complex structures formed by the reaction of a polyol with a borate ion and two polyols with a borate ion, respectively.

The rheological properties of the borate-cross-linked gels depend strongly on the number of effective cross-links, i.e., the concentration of A_2B^-. They exhibit fluid-like behavior at low pH (about pH 7.0) and solid-like behavior at high pH (about pH 9–9.5), and a similar transition from fluid-like to solid-like behavior is seen as the temperature is decreased from 65 to 15 °C. The pH and temperature effects arise from the boric acid equilibria (eq 2) and the Arrhenius dependence of the equilibrium constants on temperature.[18-22]

Experimental Protocol. Solutions are prepared by mixing guar (Dowell Schlumberger, Inc., Tulsa, OK) or HPG (Hi Tek Polymers, Inc., Louisville, KY, Lot No. 39-18-014T) with deionized water, borax (Fisher Scientific, Lot No. 794671), sodium diacetate (Celanese Plastics and Specialities Co., Jefferstown, KY, WSP-OS-1015-02), and glutaraldehyde (Eastman Kodak, Lot No. E11A) in a blender for approximately 2–3 min, followed by further mixing in a roller mixer for about 20–24 h. The composition of the solution is

material	amount
deionized water	500.0 g
guar or HPG	2.4 g
sodium diacetate	0.6 g
borax	0.6 g
25% glutaraldehyde solution in water	0.125 mL

Sodium diacetate is used to buffer the solution to about pH 6 to permit dissolution and mixing of the polymer and borate; because of the equilibrium between boric acid and borate ions, appreciable association of the polymer and borate ions occurs only above pH 8. Glutaraldehyde is a bacteriacide. The pH of the solution is increased by adding small quantities of 1 N NaOH solution. The solution immediately gels due to the formation of borate cross-links. A uniform gel is produced by heating (to "melt") the gel to about 65 °C for about 15 min and subsequently cooling the solution. The solution is stirred when it is hot, and this process is repeated several times (from 2–5 times depending on the pH of the gel) to produce the homogeneous gel.

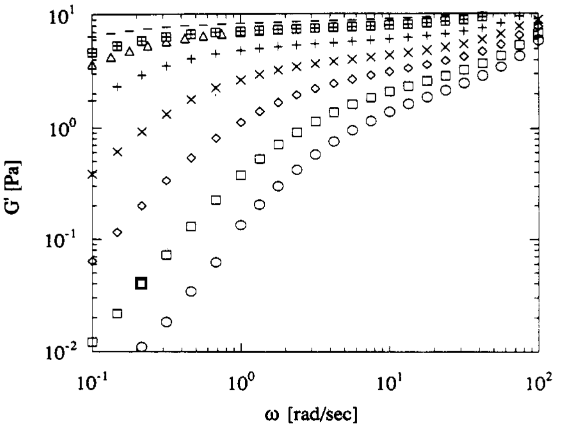

Figure 2. Storage modulus (G') of 0.48% by weight HPG cross-linked by 0.12% by weight borax from 10 to 65 °C at pH 9.15. Symbols: (○) 65 °C, (□) 55 °C, (◇) 45 °C, (×) 35 °C, (+) 25 °C, (△) 20 °C, (⊞) 15 °C, (- -) 10 °C.

Rheological measurements were performed on a Rheometrics Fluids Spectrometer II (Rheometrics, Inc., Piscataway, NJ) using a Couette geometry whose inner bob and outer cup radii are 16 and 16.925 mm, respectively, and length is 33.3 mm. The solution is loaded into the rheometer, and sufficient time (about 10–15 min) is allowed for the stresses to relax and to attain thermal equilibrium. Mineral oil (immiscible with water) is added on top of the solution to prevent evaporation. Then the solution is subjected to a series of dynamic oscillatory tests at various temperatures. At high pH, 0.48% guar gel cross-linked by borate phase separates at a temperature below 15 °C.[23] In order to maintain a homogeneous gel at all temperatures, the tests were conducted in the order of decreasing temperatures. Sufficient time (15 min) was allowed between tests so that the sample attains the test temperature. Tests were performed in the pH range 6.5–9.5 and in the temperature range 15–65 °C at intervals of 10 °C.

Strain sweep experiments were initially performed on the sample to determine the linear viscoelastic region, where the modulus is independent of strain, and subsequent measurements were performed within the linear region. To generate optimum torque values within the range of the transducer, two sets of experiments were performed at each temperature to cover the frequency region from 0.1 to 100 rad/s: one experiment covering high frequency (from 100 to 1 rad/s) at low strain and the other covering low frequencies (from 10 to 0.1 rad/s) at high strain. Strain values between 5 and 50% were used depending on the strength of the gel.

Time–Temperature Superposition (TTS). The storage modulus (G') and loss modulus (G'') were monitored as a function of frequency. The behavior of G' and G'' at various temperatures in shown in Figures 2 and 3, respectively, for 0.48% by weight HPG cross-linked by 0.12% by weight borax at a pH of 9.15. Because reactions 1–4 have positive activation energies, the number of cross-links decreases as the temperature increases. This results in the transition from gel-like behavior to solution-like behavior as temperature increases. Traditionally, the loss in intermolecular association, and the resulting loss in viscosity, has been the major limitation in the use of borate gels in high-temperature applications. Since the cross-links or association sites are temporary, the gel exhibits a terminal region like a polymer solution rather than a permanently cross-linked network.

Time–temperature superposition[24,25] involves superimposing data obtained at various temperatures by shifting the data in the vertical and horizontal directions. It is based on the principle that all of the relaxation modes of the polymer system scale with temperature in the same

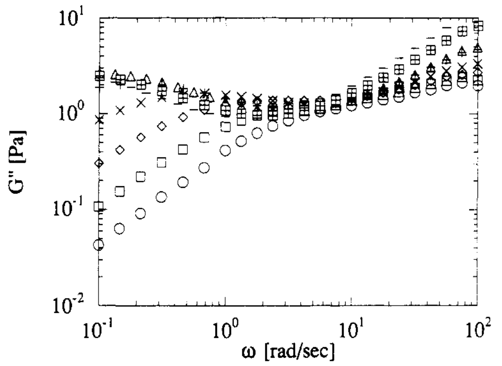

Figure 3. Loss modulus (G'') of 0.48% by weight HPG cross-linked by 0.12% by weight borax from 15 to 65 °C at pH 9.15. Symbols: Same as Figure 2.

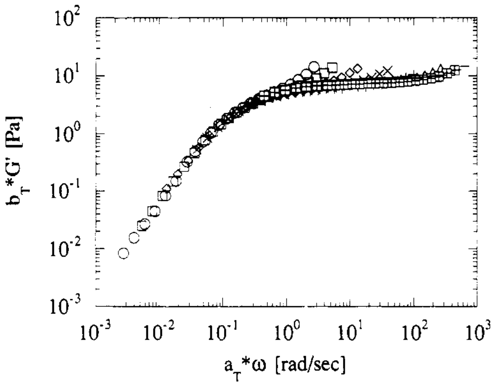

Figure 4. Master curve of the storage modulus (G') of 0.48% by weight HPG cross-linked by 0.12% by weight borax from 10 to 65 °C at pH 9.15. Symbols: Same as Figure 2.

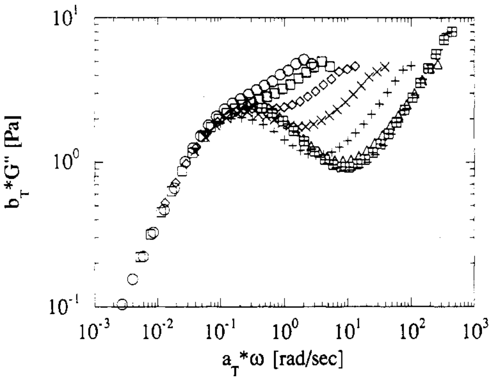

Figure 5. Master curve of the loss modulus (G'') of 0.48% by weight HPG cross-linked by 0.12% by weight borax from 10 to 65 °C at pH 9.15. Symbols: Same as Figure 2.

way. Because of instrument limitations and the long times required to do experiments at very low frequencies, the experimental range of frequencies is limited to about 4 decades. But by making use of the time–temperature superposition, a "master curve" of the relaxation response of the HPG–borate gel can be obtained over a range of 6 decades. The modulus at any temperature can be obtained from the master curve using the shift factors

$$b_T G'(\omega,T) = \frac{T}{T_{\text{ref}}} G'(\omega a_T, T_{\text{ref}}) \tag{5}$$

$$b_T G''(\omega,T) = \frac{T}{T_{\text{ref}}} G''(\omega a_T, T_{\text{ref}}) \tag{6}$$

where a_T and b_T are the horizontal and vertical shift factors and T_{ref} is the reference temperature.

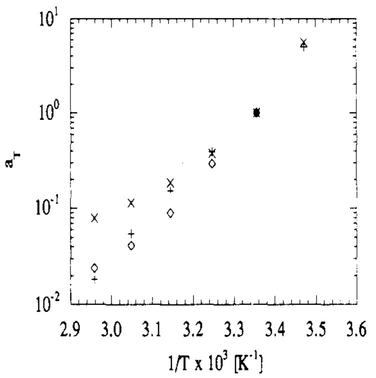

Figure 6. Horizontal shift factor (a_T) for 0.48% by weight guar cross-linked by 0.12% by weight borax at pH values of 7.86, 8.25, and 8.86. Symbols: (×) pH 7.86, (+) pH 8.25, (◇) pH 8.86.

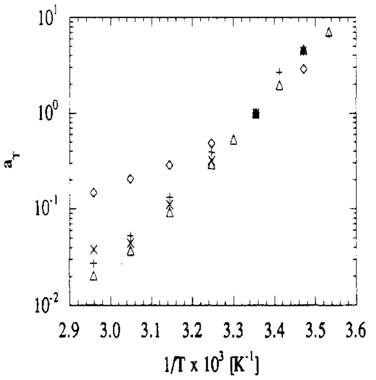

Figure 7. Horizontal shift factor (a_T) for 0.48% by weight HPG cross-linked by 0.12% by weight borax at pH values of 8.05, 8.68, 9.15, and 9.45. Symbols: (◇) pH 8.05, (×) pH 8.68, (+) pH 9.15, (△) pH 9.45.

Table I
Horizontal and Vertical Shift Factors for Guar Cross-Linked by Borax as a Function of pH and Temperature

	a_T			b_T		
T, °C	pH 7.86	pH 8.25	pH 8.86	pH 7.86	pH 8.25	pH 8.86
15	5.623	5.013		1.246	1.034	
25	1.000	1.000	1.000	1.000	1.000	1.000
35	0.377	0.394	0.292	0.968	1.230	1.195
45	0.185	0.151	0.089	1.001	1.416	1.556
55	0.114	0.054	0.041	1.035	1.536	1.876
65	0.079	0.018	0.024	1.083	1.562	1.713

TTS was used to obtain master curves by superimposing the storage modulus data at various temperatures from 15 to 65 °C and at pH values of 8.05, 8.68, 9.05, and 9.45. This was done by shifting the curves horizontally (along the frequency axis) and vertically so that all the curves could be combined into a single master curve at each pH with 25 °C as the reference temperature. The superposition was performed using the Rheometrics, Inc., software RHIOS. The data at temperatures closer to the reference temperature are shifted first, so that the overlapping region between the curve that is shifted and the reference curve is as large as possible. The program determines the vertical and horizontal shift factors at each temperature by minimizing the mean-square deviation of the data in the overlapping region between the curve that is shifted and the reference curve. The master curve for the pH value of 9.15 is shown in Figure 4. The loss modulus data are subsequently shifted using the shift factors obtained from the storage modulus, and the master curve is plotted in Figure 5. The same shift factors correctly shift the loss modulus (G'') data, which is an indication of the validity

Table II
Horizontal and Vertical Shift Factors for HPG Cross-Linked by Borax as a Function of pH and Temperature

	a_T				b_T			
T, °C	pH 8.05	pH 8.68	pH 9.15	pH 9.45	pH 8.05	pH 8.68	pH 9.15	pH 9.45
10			6.448	7.1315			0.9832	0.9497
15	2.8756	4.4193	4.4193	4.6476	1.1700	0.9665	0.9665	0.9665
20			2.6705	1.9739			0.9832	0.9832
25	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
30				0.5324				1.1088
35	0.4837	0.3180	0.3894	0.2920	1.0000	1.1200	1.3836	1.2297
45	0.2855	0.1110	0.1320	0.0928	1.0345	1.0876	1.7302	1.4520
55	0.2044	0.0443	0.0527	0.0371	1.0671	1.0672	2.0600	1.6228
65	0.1463	0.0380	0.0273	0.0204	1.100	1.1012	2.4347	1.7944

Table III
Activation Energies for the Horizontal Shift Factor (a_T) of HPG and Guar Cross-Linked by Borax Gels at Various pH Values and for the Reduced Data of HPG–Borax Gels Where E_a Is the Activation Energy Calculated from the Shift Factors of the Gel Moduli (G' and G'') and $[E_a]_r$ and $[E_b]_r$ Are the Reduced Activation Energies Calculated from the Shift Factors of the Reduced Gel Moduli (G'_r and G''_r)

			reduced activation energy	
sample	pH	activation energy E_a, kJ/mol	$[E_a]_r$, kJ/mol	$[E_b]_r$, kJ/mol
0.48% HPG cross-linked by 0.12% borax	8.68	105.5 ± 0.6		
	9.15	89.7 ± 3.0	77.5 ± 1.0	27.8 ± 0.6
	9.45	93.8 ± 2.1	81.5 ± 0.3	24.8 ± 0.6
0.48% guar cross-linked by 0.12% borax	8.25	114.7 ± 1.3		
	8.86	93.0 ± 1.7		

of the superposition. The shifting was done to superimpose data in the terminal zone, that is, shifting with respect to the longest relaxation time. Short-time relaxation processes of the chain backbone are unaffected by the widely-spaced borate cross-links. Therefore, as shown in Figures 4 and 5, higher frequency relaxation processes in the transition zone do not follow the same time–temperature superposition.

Most of the shifting was done in the horizontal direction (along the frequency axis), and only a small vertical shift was needed to obtain a good fit. The horizontal shift factor (a_T) for guar gels and HPG gels at various pH values are plotted in Figures 6 and 7. Tables I and II contain the horizontal and vertical shift factors for guar–borate gels and HPG–borate gels, respectively. The shift factors can be fitted using an Arrhenius equation

$$a_T = \exp\left(\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}}\right)\right) \tag{7}$$

$$b_T = \exp\left(-\frac{E_b}{R}\left(\frac{1}{T} - \frac{1}{T_{\mathrm{ref}}}\right)\right) \tag{8}$$

where E_a and E_b are the activation energies, which are tabulated for the various pH values in Table III. At high pH values, if the same reference temperature is used for all the pH values, the shift factor curves lie one over the other as is shown in Figure 7. This means that the response of the gel can be separated into a pH-dependent part and temperature-dependent part.

Both temperature and pH affect the dynamics of the gel by changing the borate association equilibria. Therefore, it is possible to shift the "isothermal" moduli data at various pH values using time–pH superposition to obtain the master curve shown in Figure 8. The pH horizontal shift factors are shown in Figure 9. The horizontal and vertical shift factors with pH are tabulated in Table IV.

The fact that there are only minor changes in the plateau modulus (i.e., only minor vertical shift factors are used) for the gels over a wide range in temperature and pH indicates that the borate association does not change the intrinsic "mesh" size or "correlation length" describing the chain–chain interactions. But it does change the time scales for these interactions. The shift factors that empirically produce the best "master curves" for the data show the striking result that, for pH values above pH = 8, a single Arrhenius activation energy (80 kJ/mol) describes the relaxation process over the range of temperatures studied. Over this range, the relaxation time shifts by 3 orders of magnitude. At lower pH values and higher temperatures the number of borate association sites are so few that the dynamics are governed by the polymer

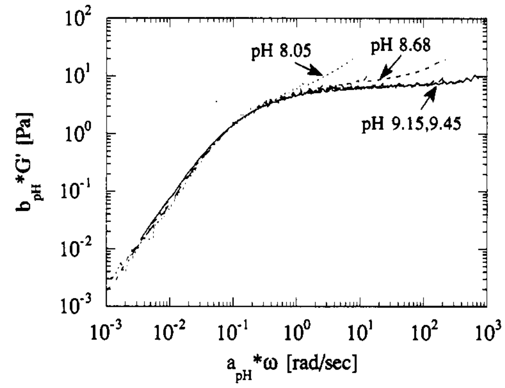

Figure 8. pH master curve obtained by superimposing the master curves at pH values of 8.05, 8.68, 9.15, and 9.45.

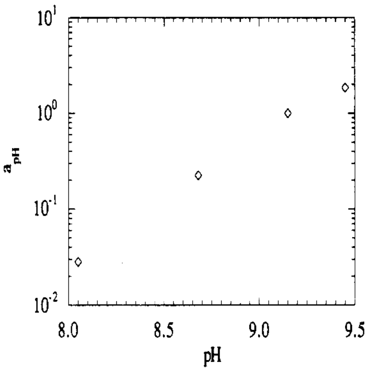

Figure 9. Horizontal shift factor (a_{pH}) for 0.48% by weight HPG cross-linked by 0.12% by weight borax.

Table IV
Horizontal and Vertical Shift Factors for Time–pH Superposition of HPG Cross-Linked by Borax Master Curves as a Function of pH

pH of sample	horizontal shift factor (a_{pH})	vertical shift factor (b_{pH})
8.05	0.0282	2.8200
8.68	0.2245	2.2600
9.15	1.0000	1.0000
9.45	1.8500	1.1800

solution behavior, and the shift factors deviate from the simple Arrhenius form having a single activation energy. It is also significant that both the HPG and guar solutions display similar activation energies. This is further evidence that the relaxation is governed by the borate–*cis*-diol equilibria because the association sites are identical on both polymers. Even though the HPG polymer will have fewer sites per chain, the energetics of association is the same in both cases.

Although the superimposed data (Figures 4 and 5) are similar to data for a series of different molecular weight linear polymers,[26] the underlying mechanism has recently been presented in a model by Leibler et al.[27]. In their model for the rheology of an associating polymer system, the behavior of the gel can be described in four regions. At very short times, $t < \tau_e$, where τ_e is the Rouse relaxation time of the entanglement strand, the behavior of the gel is similar to the behavior of an un-cross-linked solution. When $\tau_e < t < \tau$, where τ is the association time of a cross-link, a plateau in the modulus is attained and the contribution to the modulus is due to both the cross-links and the entanglements. At times, $\tau < t < \tau_d$, where τ_d is the terminal relaxation time of the gel, another plateau with a lower value for the plateau modulus is reached, whose contribution is due to entanglements only. At times longer than the terminal relaxation time, the gel relaxes like a polymer solution.

The model predicts that there are two plateau moduli for associating systems. We cannot obtain data at a high enough frequency to directly access the high-frequency plateau modulus for these semidilute polysaccharide solutions. But in an approximate manner, we can isolate the relaxation processes resulting from borate associations by subtracting the storage and loss moduli for the polymer solution from the data obtained for the borate gels. Since at short times the system responds like a nonassociating polymer solution, this has the effect of removing the short-time relaxation processes associated with local relaxation of the polymer chains which are associated with the transition zone[24]—this is the motivation for subtracting out the solution behavior from our data. These reduced moduli are defined by

$$G'_r(\omega) = G'(\omega) - G'_s(\omega) \tag{9}$$

$$G''_r(\omega) = G''(\omega) - G''_s(\omega) \tag{10}$$

where G' and G'' are the storage and loss moduli of the gel, respectively, G'_r and G''_r are the reduced storage and loss moduli, and G'_s and G''_s are the storage and loss moduli of the un-cross-linked solution. The data obtained at the lowest pH value (pH 6.35) are used as the response for the un-cross-linked solution. Since the number of cross-links decreases exponentially with pH due to reactions 1–4, three pH units away from the pK_a of boric acid, we would expect a reduction in the number of cross-links by e^{-3}—which for this system would produce fewer than one borate cross-link per chain.

The reduced moduli data at various temperatues and at pH 9.15 are shown in Figures 10 and 11. TTS was used to superimpose the data at various temperatures, and the superimposed curves are shown in Figure 12. As Leibler's model[27] suggests, the high-frequency dynamics of the polymer solution and the cross-linked gel should be the same. Therefore, the reduced moduli are obtained by subtracting the moduli of the un-cross-linked solution from the moduli of the gel. These reduced moduli superimpose over the entire frequency range for the samples tested.

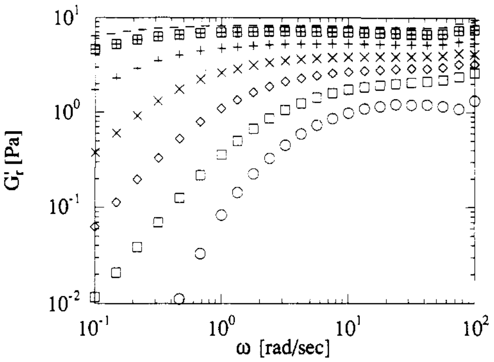

Figure 10. Reduced storage modulus (G'_r) of 0.48% by weight HPG cross-linked by 0.12% by weight borax gel at pH 9.15 and at temperatures from 10 to 65 °C. Symbols: Same as Figure 2.

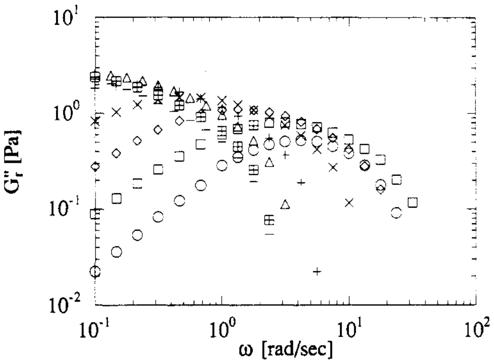

Figure 11. Reduced loss modulus (G''_r) of 0.48% by weight HPG cross-linked by 0.12% by weight borax gel at pH 9.15 and at temperatures from 10 to 65 °C. Symbols: Same as Figure 2.

The width (in time or frequency) of the plateau is related to the lifetime of individual associations and the number of association sites, but the height of the plateau is related only to the number of association sites. Once the faster modes associated with local chain relaxation have been subtracted, the resulting reduced moduli are found to fit a single time constant Maxwell model remarkably well. The Maxwell model equations for G' and G'' are given by eqs 11 and 12 where G is the plateau modulus and τ is the

$$G'(\omega) = \frac{G\omega^2\tau^2}{1 + \omega^2\tau^2} \tag{11}$$

$$G''(\omega) = \frac{G\omega\tau}{1 + \omega^2\tau^2} \tag{12}$$

relaxation time of the polymer chain. The values of G and τ are 5.213 Pa and 5.7 s at pH 9.15 and 4.46 Pa and 7.7 s at pH 9.45. The longest relaxation time at any pH and temperature can be estimated using eq 13.

$$\tau = \tau_{ref}{*}a_T{*}a_{pH} \tag{13}$$

The fact that a single time constant describes the data is attributable to the wide separation in time scales between the fast local modes of the polymer chain relaxation and the much slower kinetics of the association site exchanges. We know of no other polymer system which obeys a single time constant Maxwell model as well as these borate gels.

The curves were shifted in both the horizontal and vertical direction to obtain the master curve. The horizontal and the vertical shift factors at various pH values are plotted in Figure 13 and tabulated in Table V. The shift factors were fitted with an Arrhenius-type equation, and the reduced activation energies $[E_a]_r$ and $[E_b]_r$ are

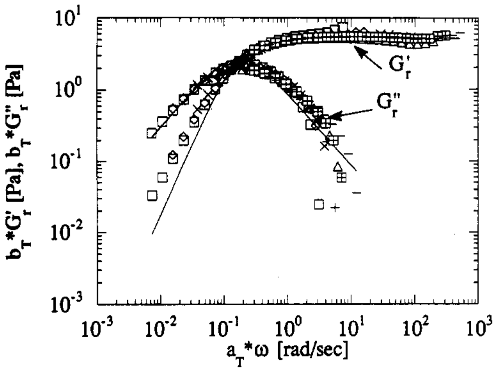

Figure 12. Master curve of the reduced storage and loss moduli at pH 9.15 with a single relaxation Maxwell model fit. Symbols: Same as Figure 2. The solid line is the fit of a Maxwell model to the data.

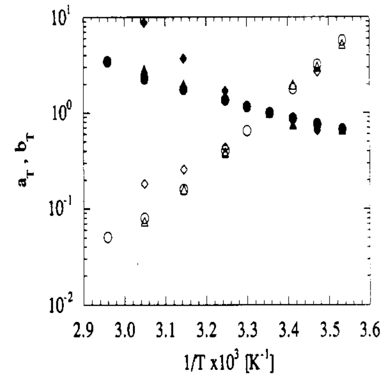

Figure 13. Horizontal (a_T) and vertical shift factors (b_T) for the reduced data of 0.48% by weight HPG cross-linked by borax. Open symbols: a_T. Closed symbols: b_T. (○) pH 9.45, (△) pH 9.15, (◇) pH 8.68.

Table V
Horizontal and Vertical Shift Factors for HPG Cross-Linked by Borax as a Function of pH and Temperature Using the Reduced Moduli Data

	a_T			b_T		
T, °C	pH 8.68	pH 9.15	pH 9.45	pH 8.68	pH 9.15	pH 9.45
10		5.205	5.7152		0.6611	0.6705
15	2.6799	3.032	3.1852	0.6476	0.7675	0.7637
20		1.9807	1.7786		0.7518	0.8726
25	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
30			0.6507			1.1608
35	0.4360	0.3859	0.4045	1.7000	1.4144	1.3652
45	0.2576	0.1587	0.1594	3.6940	1.9791	1.7665
55	0.1822	0.0739	0.0799	8.7500	2.8292	2.2800
65			0.0505			3.4542

tabulated in Table III. The shift factors are independent of pH, and hence the reduced data from the various pH values again can be shifted. The vertical shift factor, b_T, should be proportional to the number of borate cross-linking sites which is controlled by the equilibrium reactions given in eqs 1–4, and the horizontal shift factor is related to the change in the relaxation time of the polymer gel. If the equilibrium constants and activation energies for HPG cross-linking with borate are known, then they could be compared with the experimentally determined modulus and activation energy for the vertical shift factor. However, the exact equilibrium constants and activation energies for these guar and HPG cross-linked by borate are not known. The closest estimate is to look at the activation energies for the reactions using the basic repeating unit. Pezron et al.[19] have obtained the activation energies for methyl α-D-galactopyrannoside and methyl α-D-mannopyrannoside to be about 14 and 10 kJ/mol. These should be compared with the activation energies for the vertical shift factor, which correspond to an increase in the number of cross-links. The reduced activation energy $[E_b]_r$ from our experiments is about 25 kJ/mol. The higher activation energies may be due to steric interactions present in the long-chain molecule. Therefore, the activation energies from the experiments are reasonable.

Conclusions. Guar and (hydroxypropyl)guar (HPG) solutions which are cross-linked with borate ions to form gels change in consistency from dilute polymer solutions at high temperatures or low pH values to solid gels at low temperatures or high pH values. The linear viscoelastic response of these gels has been studied over the range of temperatures from 10 to 65 °C and pH values from 6.35 to 9.5. The surprising result is that the moduli obey time–temperature and time–pH superposition. Master curves can be obtained that look identical to master curves for linear polymer melts.[26] The temperature shift factors, a_T, obey a simple single-exponential Arrhenius relationship for pH values above 8.0. The master curves for various pH values can be superimposed by pH shifting. Following Leibler,[27] we have separated the contributions to stress from chain entanglements from those due to chain associations by subtracting the solution response from the gel data. The resulting reduced moduli data are shifted using time–temperature superposition. The master curves obtained from the reduced moduli data are fit extremely well by a Maxwell model with a single relaxation time. The simplicity of the rheological response for these HPG–borate gels suggests that they will be ideal candidates to test Leibler's theory of the rheology of associating polymer systems. Borate gels are especially attractive because boron NMR makes direct measurements of the borate–polymer interactions possible, and, therefore, model parameters can be obtained independently from the rheological data. Our future work is directed toward quantitatively relating the borate equilibria to the gel rheology using Leibler's model.

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