Reversible Gelation of Short-Chain *O*-(2,3-Dihydroxypropyl)cellulose/Borax Solutions. 2. Sol–Gel Transition

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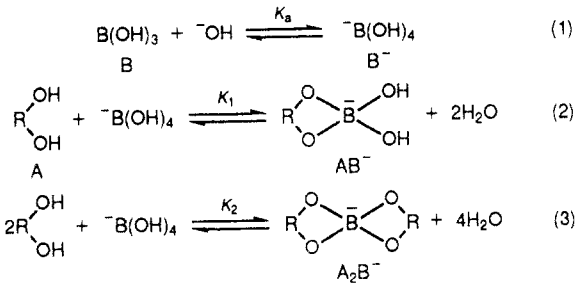
ABSTRACT: The thermoreversible gelation of aqueous *O*-(2,3-dihydroxypropyl)cellulose solutions induced by addition of borax was studied. The sol–gel transition thresholds were determined as a function of borax concentration, polymer molecular weight and concentration, and temperature. On the basis of ^{11}B-NMR analyses, the number of cross-links L per chain was determined at each point of the sol–gel phase diagrams. At a constant temperature, the plot of $L(M_w/M_n)$ vs C/C^* gave a master phase diagram independent of polymer samples, where M_w/M_n is the polydispersity index and C^* is the overlap concentration. The value of L at the sol–gel transition point was fairly large for small values of C/C^*, but it decreased with increasing polymer concentration, seemingly approaching a constant value close to the Flory–Stockmayer theoretical value, for sufficiently large concentrations (say $C/C^* > 10$).

Introduction

O-(2,3-Dihydroxypropyl)cellulose (DHPC), a novel polyhydroxyl polymer that can have more than three hydroxyl groups per anhydroglucose unit,[1,2] forms a thermoreversible gel in the presence of borate anion. The cross-linking points of the gel are known to be a borate chelate ion formed between borate anion and a pair of 1,2-diol sites. The complexation reactions proceed according to[3]



We will abbreviate $B(OH)_3$, $^-B(OH)_4$, free diol, and diol/monoborate complexes with 1:1 and 2:1 stoichiometry as B, B^-, A, AB^-, and A_2B^-, respectively.

In a previous paper,[3] we have investigated the complexation of DHPC with borate anion ($^-B(OH)_4$) by means of ^{11}B-NMR. At low polymer and borax concentrations, diol–borate 1:1 complex (AB^-) was mainly formed. With increasing polymer and borax concentrations, the fraction of didiol–borate 2:1 complex (A_2B^-) increased. These equilibrium reactions were followed by ^{11}B-NMR, and the equilibrium constants and thermodynamic parameters for the complexation were determined.

When the polymer concentration increases further, the solution gels. This DHPC–borax aqueous solution is a very simple system for studying the gelation mechanism. Unlike conventional cellulose derivatives[4–6] such as methylcellulose and ethylcellulose, DHPC forms no gel (hydrogel) in the absence of borax.[7] That is, the polymer chains are cross-linked solely by the 2:1 complex (A_2B^-). It forms a clear gel without demixing and clouding, and the number of cross-linking points' can be quantitatively evaluated by ^{11}B-NMR. Moreover, since we use short-chain DHPC's, the complexity arising from the formation of intrachain loops should be minimum. We thus are able to test the classical gelation theories[8,9] in a rather direct fashion, which has not been the topic of many previous papers. In what follows, we report results of such a study.

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Experimental Section

Materials. Three samples of *O*-(2,3-dihydroxypropyl)cellulose (DHPC) were prepared by reaction of cellulose with 2,3-epoxy-1-propanol (glycidol) in a 10 wt % LiCl–dimethylacetamide (DMAc) *homogeneous* solution, as described previously.[1,2] These samples will be designated P1, P2, and P3 in order of increasing molecular weight. As starting cellulose materials, an Avicel PH-101 powder (Asahi Chemical Industry) and a commercial bleach craft pulp from hardwood were used for preparing samples P2 and P3, respectively. Sample P1 was obtained from the cellulose powder (Avicel PH-101) depolymerized by boiling in LiCl–DMAc at 150 °C for 5 h. All DHPC samples were purified by dialysis against water, freeze-dried, and then thoroughly dried at 105 °C under vacuum for 24 h before use.

A gel permeation chromatographic (GPC) analysis was performed at 25 °C with a TOSOH HLC-803C high-speed liquid chromatograph equipped with a Model RI-8 differential refractometer. Hitachi GL-W530 and GL-W540 columns were used with a 0.5% acetic acid solution as eluent. The weight-average molecular weight M_w and the polydispersity index M_w/M_n were estimated on the basis of the calibration curve established with TOSOH standard poly(ethylene oxide)s. To check the molecular weights estimated by GPC, sedimentation equilibrium experiments[10] were carried out on a Hitachi Model A-1 analytical ultracentrifuge. The M_w of sample P2 was found to be 4.08×10^4, in good agreement with the GPC value of 3.91×10^4.

The degree of substitution (DS), the molar substitution (MS), and the average number (DE) per anhydroglucose unit of 1,2-diol sites located at the end of oligo(dihydroxypropyl) side chains were estimated by ^{13}C-NMR spectra obtained with a JEOL GX-400 spectrometer (100.8 MHz) as described previously.[2,3]

The intrinsic viscosity $[\eta]$ in aqueous solution was measured with a Ubbelohde dilution viscometer. The overlap concentration C^* was estimated by using the relation $C^*[\eta] \cong 1.4$ obtained for galactomannan by Pezron et al.[11] To test the applicability of this relation to our system, the viscosity of a borax-free aqueous solution of sample P2 was measured as a function of concentration by use of a Ubbelohde dilution viscometer. The result is given in Figure 1, which shows a change in the slope of the specific viscosity η_{sp} vs $C[\eta]$ plot at $C[\eta] = 1.42$. Thus, the value of C^* suggested by this measurement is virtually the same as that estimated by the above-noted relation. The molecular characteristics of the DHPC samples are summarized in Table I.

Sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$) of analytical grade and deionized-distilled water were used for all experiments.

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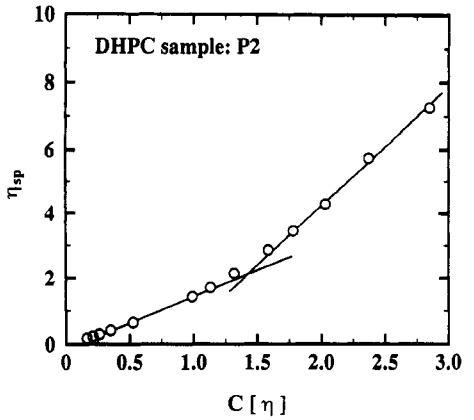

Figure 1. Plot of specific viscosity η_{sp} vs $C[\eta]$ for the aqueous solution of sample P2 ($[\eta]$ = 0.53 dL/g).

Table I
Molecular Characteristics of DHPC Samples

code	MS	DS	DE	M_n[a]	M_w/M_n[a]	$[\eta]$ (dL/g)	C^* [b]
P1	4.4	1.2	1.5	8000	2.0	0.48	29.0
P2[c]	4.4	1.3	1.4	17000	2.3	0.53	26.1
P3	2.2	1.2	1.3	22000	2.3	0.83	16.7

[a] Estimated by poly(ethylene oxide)-calibrated GPC. [b] $C^* = 1.4/[\eta]$ (g/L). [c] The M_w of this sample evaluated with a sedimentation equilibrium ultracentrifuge is 40 800.

Sol–Gel Transition. Phase diagram data were obtained at 15 °C. A DHPC sample was dissolved in water with stirring at room temperature, to which borax solution was added at 90 °C. The solution was cooled and kept in a sealed glass tube with a diameter of 10 mm at 15 °C for 24 h. Judgment of the sol or gel state was performed by the tube-inverting method:[12-14] the sealed sample tube was placed upside down in a water bath. If the solution flowed, it was defined as a sol, and if it did not flow, it was defined as a gel. This method has been confirmed to provide the same results as those provided by the ball-drop method.[15,16]

The melting point of a gel, T_m^{gel}, is defined as the temperature at which the gel begins to flow. The T_m^{gel} was determined by the tube-inverting method with the water bath temperature raised at an interval of 1 °C. The gel-containing tube was allowed to stand for 30 min at each temperature prior to the tube-inverting experiment.

^{11}B-NMR Measurement. ^{11}B-NMR spectra were recorded with a JEOL GSX-270 Fourier transform spectrometer operating at 86.55 MHz for ^{11}B nuclei. Before the measurement, the sample solution was kept for 30 min at the measurement temperature regulated to ±1 °C. The individual concentrations of boron species, B, B^-, AB^-, and A_2B^-, were estimated from the combined chemical shift due to free borons (B and B^-) and the relative signal intensities. The details were described previously.[3]

Results and Discussion

Phase Diagrams. The phase diagrams observed for the three DHPC samples at 15 °C are given in Figure 2, in which the filled and open circles represent the gel and sol states, respectively, and the filled triangles indicate that the solution is just close to the sol–gel transition point. In each solution, there seems to exist a critical polymer concentration below which gelation does not occur even in the presence of excess borax. This critical concentration C_{gel} becomes lower as the polymer molecular weight increases. There seems to exist a correlation between C_{gel} and the overlap concentration C^* indicated by the arrowhead in the figure. At concentrations above C_{gel}, the total boron concentration at the sol–gel transition point decreases with increasing polymer concentration. Presumably, this reflects the degree of homogeneity of the spatial distribution of polymer segments and hence of diol sites in solution. At low polymer concentrations, cross-links would be easier to form between the pairs of polymers that have already been cross-linked than between un-cross-linked pairs. Therefore the number of cross-links per chain necessary to gel the whole solution would be larger at low concentrations than at higher concentrations, which would result in the observed concentration dependence.

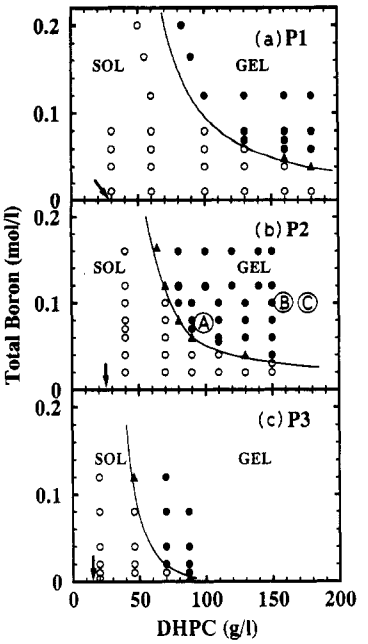

Figure 2. Phase diagrams of DHPC–borax aqueous solutions at 15 °C.

To examine this problem more closely, we have estimated the number of cross-links per polymer chain, L, which is defined by

$$L = \frac{\text{[cross-link density]}}{\text{[polymer number density]}} \tag{4a}$$

$$= \frac{[A_2B^-]}{C/M_n} \tag{4}$$

In this system, the cross-linking point is a 2:1 complex (A_2B^-), and the formation of the intramolecular 2:1 complex may be ignored owing to the short- and rigid-chain nature of the employed polymers.[3] The concentration of the 2:1 complexes, $[A_2B^-]$, at each point of the phase diagrams can be evaluated by solving the following equilibrium equations that follow from eqs 1–3:

$$K_a = [B^-]/([B][OH^-]) \tag{5}$$

$$K_1 = [AB^-]/([B^-][A]) \tag{6}$$

$$K_2 = [A_2B^-]/([B^-][A]^2) \tag{7}$$

The mass balance equations are

$$[A_T] = [A] + [AB^-] + 2[A_2B^-] \tag{8}$$

$$[B_T] = [B] + [B^-] + [AB^-] + [A_2B^-] \tag{9}$$

$$[Na^+] = [B_T]/2 \tag{10}$$

where $[A_T]$ and $[B_T]$ are total concentrations of diol compounds and boron species, respectively, which are constants and equal to the feed concentrations. Equation 10 is relevant to the dissociation of borax. The ion balance equation is

$$[Na^+] + [H^+] = [OH^-] + [B^-] + [AB^-] + [A_2B^-] \tag{11}$$

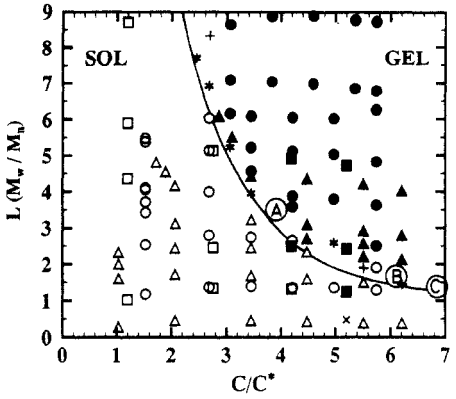

Figure 3. Master phase diagram of DHPC–borax aqueous solutions.

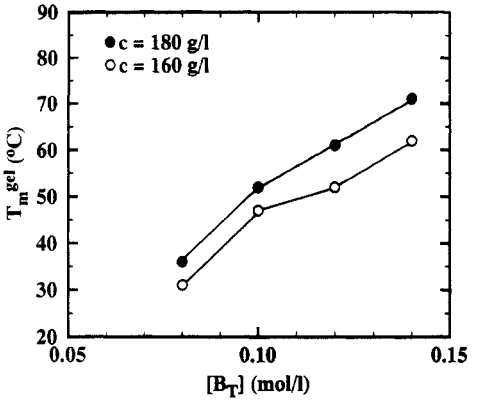

Figure 4. Dependence of gel melting temperature T_m^{gel} on total boron concentration $[B_T]$ for sample P2.

and the dissociation equation of water is

$$K_W = [H^+][OH^-] \quad (12)$$

On the basis of the previously reported data,[3] the values of K_1 and K_2 at 15 °C are estimated to be 11.3 M^{-1} and 28.8 M^{-2}, respectively. The values of K_w and K_a were taken from the literature ($K_w = 4.51 \times 10^{-15}$ and $K_a = 1 \times 10^{-9.27}$).[17,18]

The eight simultaneous equations 5–12 were numerically solved for $[A_2B^-]$ using a computer. Figure 3 shows the phase diagram in which the number of cross-links L per polymer chain is plotted against the polymer concentration normalized by the overlap concentration (C^*). To account for the differences among the polydispersities of the three samples, the ordinate scale has been multiplied by M_w/M_n (see below). It can be seen in the figure that the threshold of the sol–gel transition is represented by a single master curve.

The values of L given in Figure 3 were estimated on the basis of the ^{11}B-NMR data obtained for the DHPC/borax solutions in a sol range, i.e., below C_{gel}.[3] To confirm these results, supplementary ^{11}B-NMR experiments were made to directly determine L at the sol–gel transition. For this purpose, three solutions (A, B, and C) of sample P2, which are in the gel state at 15 °C and whose compositions are marked in Figure 2b, were prepared and their melting temperatures, T_m^{gel}, were determined. Each solution was then subjected to a ^{11}B-NMR analysis at the temperature T_m^{gel} to determine the concentration of A_2B^- at the sol–gel transition point. The values of L (L_{gel}) directly determined in this way are marked A, B, and C in Figure 3. These data points closely fall on the master curve obtained above.

According to the Flory–Stockmayer gelation theory, the threshold of the sol–gel transition is represented by

$$L_{gel}(M_w/M_n) = 0.5 \quad (13)$$

irrespectively of the molecular weight distribution of the polymer.[8,9] The present data for high concentrations ($C/C^* \geq 6$) show that $L_{gel}(M_w/M_n) \cong 1$, which is surprisingly close to the theoretical value. (Figure 3 does imply that the agreement of theory and experiment becomes even better at higher concentrations, where unfortunately we had some experimental difficulties in obtaining data points.) Previously reported values of L_{gel} are mostly very much different from (often larger by an order of magnitude than) the theoretical value.[19] To our knowledge, this is the first report in which such a close agreement between theory and experiment was obtained. The essential absence of intramolecular cross-links in this system[3] may be one of the main reasons for the good agreement of theory and experiment. We also note that rigorously solving all of the equilibrium equations (eqs 5–12) is primarily important to obtain meaningful results.

Table II
Number of Cross-Links per Polymer Chain (L_{gel}) at the Melting Temperature (T_m^{gel}) Determined for Sample P2 by ^{11}B-NMR

soln	10^2C (g/mL)	$[B_T]$ (M)	T_m^{gel} (°C)	$[A_2B^-]_{gel}$[a] (10^2M)	L_{gel}
A	10.1	0.075	23	0.90	1.5
B	16.0	0.1	47	0.67	0.7
C	18.0	0.1	52	0.67	0.6

[a] Concentration of diol/borate anion 2:1 complex at T_m^{gel}, calculated from the ^{11}B-NMR relative peak intensity.

Melting Point of Gel and Enthalpy of Gelation. Figure 4 shows the boron concentration dependence of the gel melting point T_m^{gel} observed for sample P2 at two polymer concentrations. The melting point increases with increasing polymer concentration and also with increasing total boron concentration. According to Eldridge and Ferry,[12] the melting point is determined by the critical concentration of cross-links, which corresponds to the critical concentration of 2:1 complexes $[A_2B^-]_{gel}$, in this system. Rearrangement of eq 4 gives

$$[A_2B^-]_{gel} = L_{gel}(C/M_n) \quad (14)$$

Equilibrium constant K_2 for the dicomplexation, defined by eq 7, is related to the enthalpy change according to the van't Hoff theory.

$$K_2 = \exp(\Delta S/R)\exp(-\Delta H/RT) \quad (15)$$

where R is the gas constant and ΔS and ΔH are the entropy and enthalpy changes, respectively. The diol concentration is proportional to the polymer concentration

$$[A] = kC \quad (k = \text{constant}) \quad (16)$$

Equations 14–16 give the following relation showing the temperature dependence of the gelation threshold:

$$\log (C[B^-]/L_{gel}) = \Delta H/RT + \text{constant} \quad (17)$$

The right hand side of eq 17 includes the factor L_{gel}^{-1}, which in the Eldridge–Ferry equation is assumed to be a constant independent of concentration. As already suggested, this constancy is perhaps realized at sufficiently high concentrations (say, $C/C^* > 10$), but it is necessary to retain this factor when experimental data for not high enough concentrations, like those presented in this work, are analyzed.

As described previously,[3] the concentration of the free borate anion B^- can be estimated by the ^{11}B-NMR method. We have carried out a NMR analysis at the gel melting

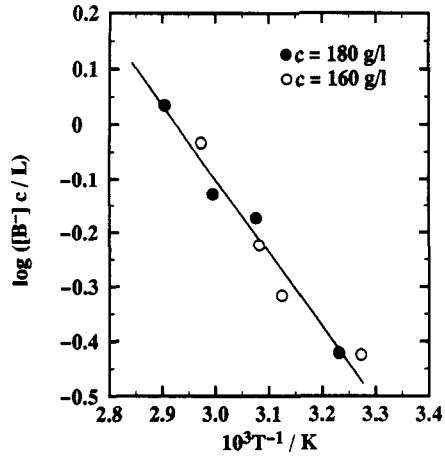

Figure 5. Plot of log ([B$^-$]C/L) vs inverse gel melting temperature.

point to estimate [B$^-$]. We have already found above that $L_{gel} \simeq 0.6$ and 0.7 for C = 180 and 160 g/L, respectively (see Figure 3 and Table II). On the basis of these data, we have constructed a plot according to eq 17, which is shown in Figure 5. The data points for the two concentrations roughly fall on a single curve. From the slope, the enthalpy change (ΔH) for the sol–gel transition was estimated to be −26 kJ/mol, which is reasonably close to the value of enthalpy change of dicomplexation (ΔH = −22 kJ/mol) estimated by the ^{11}B-NMR method.[3] This confirms that the polymer chains are cross-linked by the 2:1 complex and also indicates that the value of L_{gel} is in fact independent of temperature.

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Registry No. DHPC, 57608-21-6; (DHPC)($Na_2B_5O_7$) (copolymer), 143369-94-2; sodium tetraborate, 1330-43-4.