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SYNTHESIS AND CHARACTERIZATION OF 2, 3-DIHYDROXYPROPYLCELLULOSE

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ABSTRACT

Water-soluble 2,3-dihydroxypropylcellulose (DHPC) was successfully synthesized by the reaction of 3-chloro-1,2-propanediol with alkali cellulose in dioxane, or with glycidol in acetone. DHPC from the glycidol reaction was shown to have better solubility and yield. DHPC made from cotton wool and glycidol possesses the highest intrinsic visocisty (up to 4.05 dL/g). Quantitative ^{13}C-NMR analysis was utilized to estimate the molar substitution and degree of substitution of the resulting DHPC. Since the ratios of molar substitution to degree of substitution were found to be 2 or less, the substituents on the cellulose probably consist of monomer, dimer, or trimer of the alkylation agents used. Above the critical concentration of DHPC, the solution viscosity was found to be increased tremendously upon treating with boric acid under basic conditions.

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INTRODUCTION

Much research has been carried out on the grafting of synthetic macromolecules onto cellulose to produce materials with new properties intermediate between those of cellulose and those of synthetic polymers [1, 2]. Since cellulose is insoluble in water, the direct grafting of cellulose with water-soluble monomers such as acrylamide does not generally result in completely water-soluble graft copolymers. In order to obtain cellulose-based water-soluble graft copolymers, the synthesis of water-soluble cellulose derivatives suitable for grafting is desirable. These considerations have prompted us to investigate in some detail the synthesis and characterization of 2,3-dihydroxypropylcellulose (DHPC). This polymer possesses a 1,2-diol structure that is expected to confer water solubility on cellulose. Also this group has been shown to be suitable as a substrate for grafting [3]. DHPC can be synthesized by reaction of 3-chloro-1,2-propanediol with alkali cellulose or of glycidol with cellulose by base catalysis. Little has been reported so far on the synthesis and characterization of DHPC [4-7]. This paper reports a comprehensive study of the synthesis of DHPC, involving reaction conditions such as effects of solvent, temperature, etc., and the correlation with properties of the resulting DHPC.

EXPERIMENTAL

General Information

All the temperatures are uncorrected and are reported in degrees centigrade. The viscosities of the DHPC-borate complexes were measured by Brookfield viscometry at room temperature. Intrinsic viscosities were measured by standard procedures using a Cannon-Ubbelohde viscometer (dilution viscometer). IR spectra were recorded on a Perkin-Elmer 281 infrared spectrophotometer. The observed frequencies are expressed in wavenumber (cm^{-1}) with the 1601 cm^{-1} line of polystyrene film as a standard. Proton nuclear magnetic resonance (NMR) spectra (60 MHz) were recorded on a Varian EM-360L spectrometer. Carbon-13 (50.3 MHz) spectra were obtained on a Varian XL-200 high resolution NMR spectrometer. Chemical shifts are given in parts per million (ppm) on a δ scale, using as an internal reference the methyl protons of sodium 2,2-dimethylsilapentane-5-sulfonate (DSS) or the ^{13}C absorption of 50% aqueous NaSCN (133.0 ppm). A Waters size-exclusion chromatography (SEC) system, consisting of a Model 590 pump and a U6K injector, was used in combination with a Perkin-Elmer LC-25 RI detector and a Kratos Spectroflow 757 variable-wavelength UV-VIS detector. The TSK-gel-GMPW SEC col-

umn (MW range, 500-2 X 10^6, made by Toyo Soda) was purchased from Bio-Rad Labs. The mobile phase (0.2 *M* Na_2SO_4) was filtered through a 0.45-μm Millipore membrane under vacuum prior to use. The velocity of the mobile phase was 0.8 mL/min. The universal calibration curve was made with the use of polydisperse polyacrylamide standards, which were purchased from American Polymer Standards Co. A computer program, GPCVIS, incorporating the universal calibration concept [8, 9] was used to calculate number- and weight-average molecular weights of DHPC.

Reagents and Solvents

50-μm Cellulose was obtained from Scientific Polymer Products. Cotton linter powder and spruce powder were purchased from Fluka. 3-Chloro-1,2-propanediol and glycidol were obtained from Aldrich Chemical Co. and were purified by vacuum distillation before use. All solvents used for general application were of reagent grade or ACS grade quality.

Synthesis of DHPC Derived from 3-Chloro-1,2-propanediol

Procedure 1. Into a three-necked round-bottomed flask equipped with condenser, gas inlet/outlet, and mechanical stirrer were charged 5.0 g cellulose powder and 150 mL dioxane under nitrogen or argon. After stirring for 45 min at room temperature, 12.4 mL of a 50% sodium hydroxide aqueous solution was added dropwise during a 15-min period. After heating to 60°C and stirring for 2 h, 3-chloro-1,2-propanediol was added dropwise during a 30-min period. The reaction was continued for another 4 h at 60°C.

Procedure 2. The cellulose was treated with sodium hydroxide aqueous solution according to Procedure 1, except that the liquid portion was decanted after treatment. To the solid portion was then added fresh dioxane, and to the resulting mixture was added dropwise 3-chloro-1,2-propanediol. The mixture was kept stirring at room temperature for 2 h and at 60°C for another 4 h.

Procedure 3. The reaction was carried out like Procedure 1, but at room temperature. The resulting material was reacted again following the same procedure from one to three times in order to increase the degree of substitution of cellulose.

DHPC Derived from Glycidol

A three-necked round-bottomed flask, equipped with condenser, gas inlet/outlet, and mechanical stirrer, was charged with 5.0 g cellulose and 150 mL acetone under nitrogen or argon. After stirring for 45 min at room temperature, a 15% sodium hydroxide aqueous solution was added dropwise during a 15-min period. A glycidol/acetone solution was then added over a period of 2 h, and the mixture was then stirred at 50°C for 6 h.

Purification of DHPC

In the preparation of DHPC from both glycidol and 1-chloro-2,3-propanediol, the resulting products were purified by the following steps: The reaction mixture was filtered and then washed with dioxane several times. To the solid portion was added a suitable amount of deionized water, and the mixture was then transferred into Spectra/por 1 (MWCO 6-8000) dialysis tubing and dialyzed against water for 3 d. The water-insoluble portion was removed from the water by filtration or centrifugation. The water was removed from the filtrate by a rotatory evaporator *in vacuo*. Both water-soluble and water-insoluble polymers were dried at 60°C under vacuum.

RESULTS AND DISCUSSION

1. Synthesis of DHPC from 3-Chloro-1,2-propanediol (CPD)

The alkylation of alkali cellulose with 3-chloro-1,2-propanediol was carried out in an organic solvent under heterogeneous conditions. Several solvents were examined as reaction media. The results are shown in Table 1.

Water-soluble DHPC was only obtained when the reaction medium was dioxane or pyridine. However, more side products were isolated when pyridine was used, so that dioxane was selected as the reaction solvent. The effect of the molar excess of CPD and the general reaction conditions described in the Experimental section are shown in Table 2 and Fig. 1.

It is apparent that both the [CPD]/[AGU] molar ratio and the reaction temperature are most important in determining the yields and properties of DHPC. In Procedures 1 and 2, the CPD/AGU molar ratios were varied between 1.32 and 9.98. Curves I and II (Fig. 1) show that the optimum yield and solubility are obtained for CPD/AGU molar ratios between 2.5 and 4.0. The yields, solubilities, and intrinsic viscosities of DHPC prepared according to Procedure 2 are higher than those of Procedure 1. This could be attributed to the re-

TABLE 1. Water Solubility of DHPC Prepared at 60°C in Various Solvents

Solvent	Base	Polymer solubility	Procedure no.
n-Butanol	NaOH	Water insoluble	1
DMSO	NaOH	" "	1
DMF	KOH	" "	1
Acetone	NaOH	" "	1
THF	NaOH	" "	1
NMP	NaOH	" "	1
DME	NaOH	" "	1
Diglyme	NaOH	" "	1
Xylene	NaOH	" "	1
Pyridine/dioxane (v/v = 1/1)	NaOH	30% water soluble	1
Dioxane	NaOH	98% water soluble	1
Pyridine	NaOH	100% water soluble	1

moval of excess sodium hydroxide after base treatment of cellulose in Procedure 2. During the alkylation process, the excess sodium hydroxide tends to compete with alkali cellulose for CPD. On the basis of the synthetic method used for the preparation of methylcellulose of a high degree of substitution in Procedure 3, a multiple-step substitution reaction of CPD with alkali cellulose was utilized to increase the degree of substitution of DHPC. The water solubility of the resulting polymers is excellent. Also, the degree of substitution and molar substitution of the resulting DHPC sample are much higher than those prepared according to Procedure 1 and 2. The decrease of the intrinsic viscosity of DHPC with the number of steps (Procedure 3) indicates that progressive degradation of the cellulose backbone is occurring under these basic conditions at all temperatures.

2. Synthesis of DHPC from Glycidol

The synthesis of DHPC was also carried out by the reaction of alkali cellulose with glycidol instead of 3-chloro-1,2-propanediol. The reaction conditions

TABLE 2. Reaction Conditions for Synthesis of DHPC from 3-Chloro-1,2-propanediol and Properties of Resulting Polymers[a]

Code no.	Molar ratio [CPD]/[AGU]	w_1,[b] g	w_2,[b] g	Yield,[c] g	Solubility,[d] %	$[\eta]$,[e] w_1	$[\eta]$,[e] w_2	$[\eta]$,[f] w_2	MS[g]	DS[g]
					Procedure 1					
3D	1.32	0.321	0.037	4.76	10	1.51	0.90	1.00		
3A	2.55	0.040	0.370	6.23	90	1.45	1.41	1.70		
3F	3.93	0.030	0.283	5.92	91	2.03	1.23	1.40	1.63	1.24
3B	4.99	0.316	0.082	5.42	21	1.81	0.76	1.20	3.18	2.02
3C	9.98	0.327	0.018	4.62	5	1.85	0.34	0.62		
					Procedure 2					
4E	1.32	0.300	0.094	5.36	24	2.22	0.98	1.01	1.00	0.87
4D	2.55	0.080	0.356	6.87	82	1.12	1.48	1.60	1.47	1.10
4B	3.93	0.004	0.396	8.49	99	1.61	1.40	1.47	2.90	1.42

4A	4.99	0.127	0.450	6.53	72	2.32	1.11	1.20	1.40	1.21
4C	9.98	0.350	0.023	4.89	6	1.17	0.69	0.81		
					Procedure 3					
5A	3.93 (0)[h]	0.176	0.270	6.49	61	1.65	1.30	1.25		
5B	3.93 (1)[h]	0	0.310	7.84	100		1.24	1.65	3.08	2.28
5C	3.93 (2)[h]	0	0.200	9.20	100		1.31	1.10	4.04	2.64
5D	3.93 (3)[h]	0	0.161	9.77	100		0.79	0.83	5.74	2.84

[a]Mixture of 5 g cellulose in 150 mL dioxane was treated with 6.2 g NaOH in 12.4 mL deionized water for 15 min.
[b]Water-insoluble polymer (w_1) and water-soluble polymer (w_2) recovered by dialysis from 1 g crude product.
[c]Weight of dialyzed polymer (water-soluble and insoluble portion).
[d]Percentage of water-soluble DHPC.
[e]Intrinsic viscosities of w_1 and w_2 measured in 33% NaSCN aqueous solution at 30°C, in dL/g.
[f]Intrinsic viscosity of w_2 in H_2O at 30°C, in dL/g.
[g]Molar substitution (MS): number of moles of substituent per anhydroglucose unit. Degree of substitution (DS): average number of hydroxyl groups substituted per anhydroglucose unit. Determined by ^{13}C NMR.
[h]Number of repeated reactions.

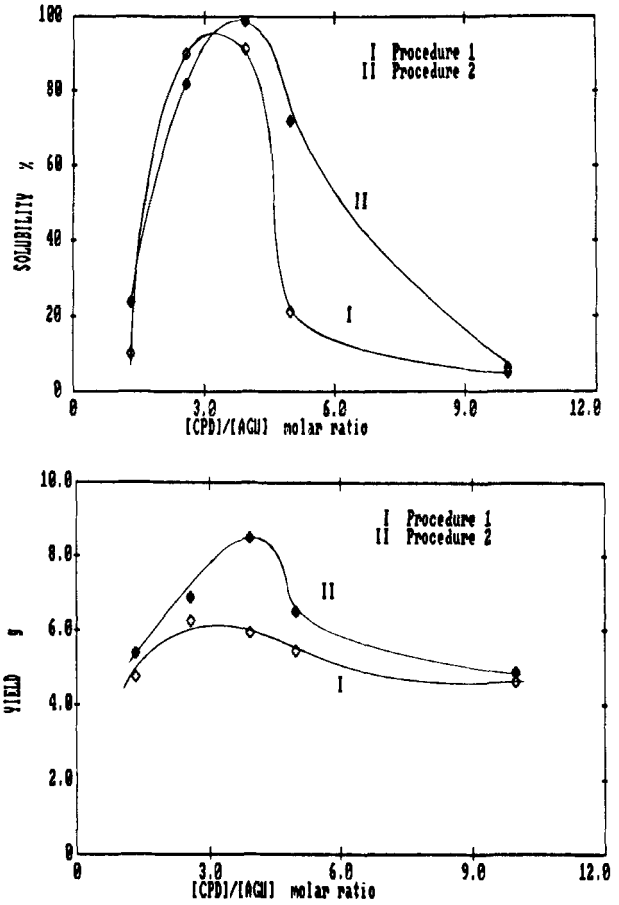


FIG. 1. The effect of the molar excess of CPD on the solubility and yield of the resulting DHPC.

and results are listed in Table 3. Cellulose samples with various ranges of molecular weight were used. DHPC prepared from both 50-μm cellulose and cotton linter have an excellent water solubility, but the water solubility of the cotton wool derivative is lower. From Tables 2 and 3 it is clear that the solubility and yield of DHPC derived from glycidol is much better than that derived from CPD. The resulting water-soluble DHPC samples were characterized by aqueous size-exclusion chromatography. Number- and weight-average molecular weights are shown in Table 4.

3. Determination of Molar Substitution (MS) and Degree of Substitution (DS) of DHPC by ^{13}C NMR

Quantitative ^{13}C-NMR spectra can be obtained when nuclear Overhauser enhancement effects are suppressed by a gated decoupling technique in which the acquisition of data is made only when the decoupler is on, but off during a delay of at least five times the longest T_1 (spin-lattice relaxation time) of the resonance observed. Due to the high viscosity of the resulting polymer solutions, it proved necessary to increase the temperature of the solution, leading to a narrower line width. However, at high temperature, T_1 is increased due to enhanced molecular motions, so that a longer pulse delay was required.

The ^{13}C-NMR spectra with a width of 5000 Hz were obtained at 60°C on a Varian XL-200 high-resolution NMR spectrometer operating at 50.3 MHz with a standard 5-mm probe. The parameters for running the DHPC spectra based on the T_1 values for hydroxyethylcellulose [9] were estimated. The flip angle, acquisition time, and time delay were 90°, 0.8 s, and 1.0 s, respectively. The samples were dissolved in a 50% NaSCN/D_2O solution. The carbon peak of NaSCN was used as internal standard (133 ppm from TMS). The intensities of signals of these spectra were determined by using the integration routine of the NMR program. The spectrum of DHPC is shown in Fig. 2.

The interpretation of the spectrum is facilitated by comparison with the spectra of oligoglycidol [10], hydroxyethylcellulose [9], and 2-hydroxypropylcellulose [11, 12]. Due to the high mobility of the substituents relative to that of the cellulosic matrix, their ^{13}C nuclei produce resonances narrower than those of the anhydroglucose unit.

The peak at 101.9 ppm is assigned to the C-1 carbon. The average number of carbon atoms per anhydroglucose unit was determined from the ratio of the ratio of the intensity of all carbons observed to the intensity of the C-1 carbon. Since each unsubstituted anhydroglucose unit (AGU) has six carbons and each substituent will contribute three carbons to the substituted AGU, the number of substituents per AGU (MS) can be easily calculated. On the basis of the assignment of the ^{13}C spectra of oligoglycidol, the signal at 62.5 ppm corresponds to that of the terminal carbon (C-9 in Fig. 2) regardless of branching. The adsorption of this carbon to that of C-1 is therefore equal to the number of chains per AGU (DS). The MS and DS values are reported in Tables 2 and 3.

4. Structures of DHPC, Its Side Chains and Side Products

The three hydroxyl groups of the AGU have been demonstrated to have different reaction rates in alkylation reactions [13]. Since the C-2 hydroxyl group is the most acidic, it has the greatest tendency toward deprotonation. The C-6 hydroxyl is the least sterically hindered, and the C5–C6 covalent bond

TABLE 3. Reaction Conditions of Synthesis of DHPC from Glycidol (GLY) and the Properties of Resulting Polymers[a]

Code no.	Molar ratio [GLY]/[AGU]	w_1,[b] g	w_2,[b] g	Yield,[c] g	Solubility,[d] %	$[\eta]$,[e] w_2	MS[f]	DS[f]
				50 μm Cellulose				
8B	1.31	0	0.717	6.02	100	1.45		
8C	2.62	0	0.699	6.78	100	1.01	1.88	1.53
8D	3.93	0	0.680	8.45	100	1.01	3.91	2.76
8E	5.24	0	0.673	10.16	100	0.92	4.60	2.96
				Cotton Linter				
7A	1.31	0	0.800	6.48	100	1.91		
7B	2.62	0	0.717	7.88	100	2.42		

7C	3.93	0	0.769	10.09	100	1.78		
7D	5.24	0	0.778	12.29	100	1.73		
				Cotton Wool				
9C	2.62	0.124	0.439	3.20	78	4.05	2.54	1.98
9D	3.93	0.017	0.644	4.40	97	3.84		
9E	5.24	0.011	0.668	5.86	98	3.11	4.02	2.60
9F	7.86	0.089	0.537	6.43	86	2.80	4.82	2.82

[a]The mixture of cellulose (5 g of 50 μm, or 5 g cotton linter, or 2.5 g cotton wool) in 150 mL acetone treated with 1.5 g of NaOH in 10 mL deionized water.

[b]Water-insoluble polymer (w_1) and water-soluble polymer (w_2) recovered by dialysis from 1 g crude product.

[c]Weight of dialyzed polymer (water-soluble and insoluble portion).

[d]Percentage of water-soluble DHPC.

[e]Intrinsic viscodity of w_2 by H_2O at 30°C, in dL/g.

[f]Molar substitution (MS): number of moles of substituent per anhydroglucose unit. Degree of substitution (DS): average number of hydroxyl groups substituted per anhydroglucose unit. Determined by ^{13}C NMR.

TABLE 4. The Number- and Weight-Average Molecular Weights of Water-Soluble DHPC

Code no.	Cellulose substrate	$\bar{M}_n \times 10^{-5}$ [c]	$\bar{M}_w \times 10^{-5}$ [c]	$[\eta]$ in 0.2 M Na_2SO_4, dL/g
9D[a]	Cotton wool	2.22	8.30	3.69
9B[a]	Spruce	0.33	2.51	1.89
9A[a]	Cotton linter	0.68	2.44	2.29
5C[b]	50-μm Cellulose	0.24	0.58	1.05

[a]Reaction carried out at 23°C.
[b]Reaction conditions: see Table 2 or Table 3.
[c]SEC characterization: see Experimental Section.

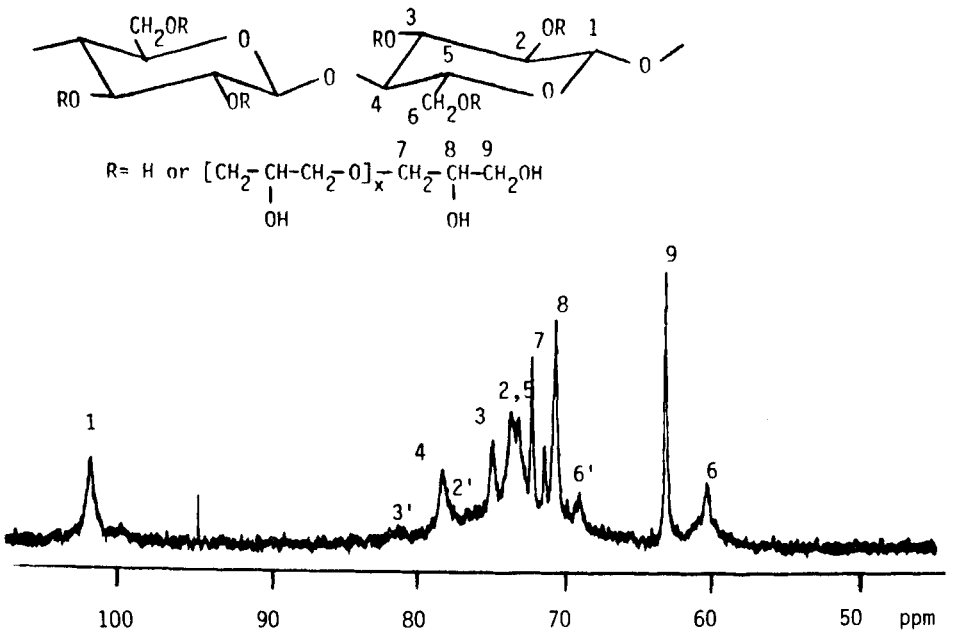


FIG. 2. ^1H Gated-decoupling ^{13}C-NMR (50.3 MHz) spectrum of DHPC (4E-4) in 50% NaSCN/D_2O at 60°C.

can freely rotate, providing accessibility in the etherification reaction. On the basis of these factors, the substitution should occur predominantly at the C2 and C6 positions. This prediction is in a good agreement with the ^{13}C spectra of the resulting DHPC.

During the preparation of DHPC, the alkylation agent may react not only with the hydroxyl groups of the AGU, but also with the newly formed hydroxyl groups of the hydroxyalkyl substituents, resulting in the formation of poly(glycidol) side chains. The maximum value of the DS is 3, while there is no theoretical maximum limit of MS. The average degree of polymerization of side chains was found to be 2 or less. The DHPC samples derived from CPD and from glycidol are found to have similar ^{13}C spectra.

After the preparation of DHPC from both CPD and glycidol, substantial amounts of dioxane-soluble side products were isolated. Characterization of these products by NMR proved to be complicated, their NMR spectra being consistent with linear or branched oligomers of glycidol.

5. Effects of Boric Acid Addition

DHPC was shown to have the ability to undergo a reversible gelation with boric acid [6]. The results of this study are summarized in Figs. 3 and 4, and Table 5.

The critical concentration (C^*) at which all of the available volume is approximately fully occupied by the DHPC coils may be estimated by Eq. (1) [14]. These values for Sample 9E ($[\eta]$ = 3.11 dL/g and 8D ($[\eta]$ = 1.01 dL/g) are about 0.8 and 2.5 g/dL, respectively.

$$C^* = 2.5/[\eta]. \tag{1}$$

At or below these concentrations, there was little increase in viscosity due to complex formation but a dramatic increase is seen above the critical DHPC concentration (Fig. 3 and Table 5) due to intermolecular complex formation.

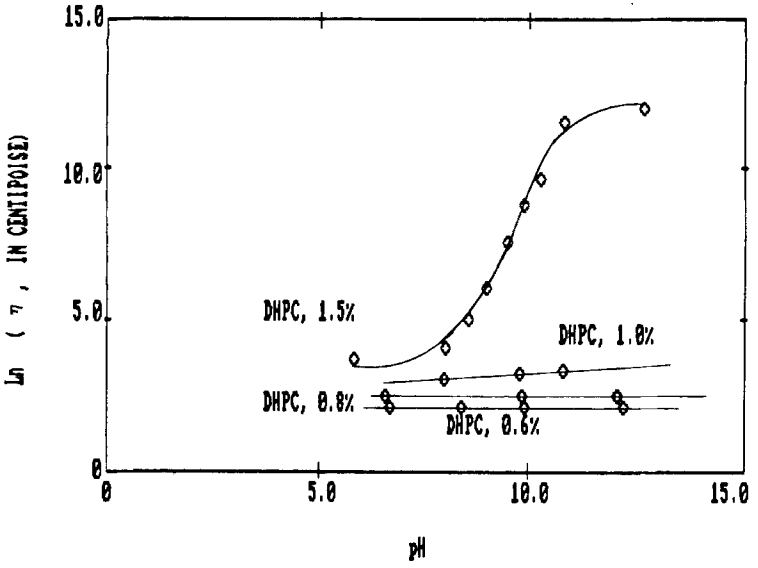


FIG. 3. Effect of pH on the viscosity of a H_3BO_3-borate complex solution at room temperature.

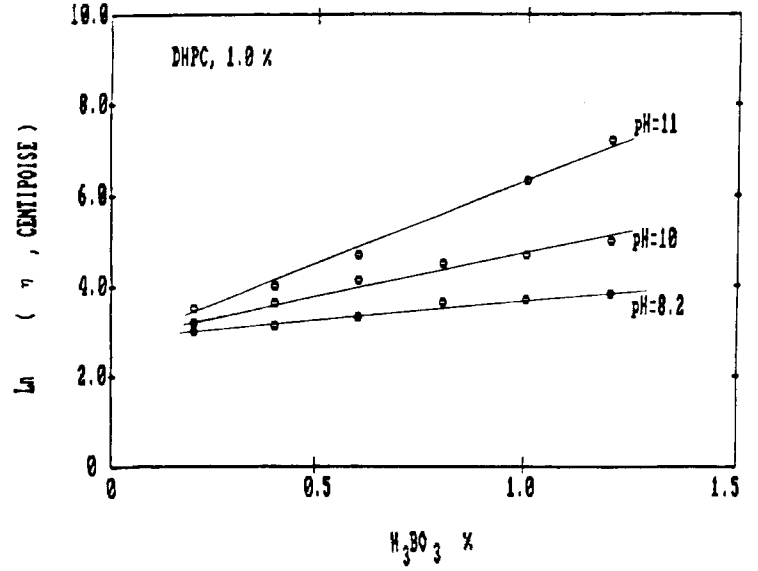
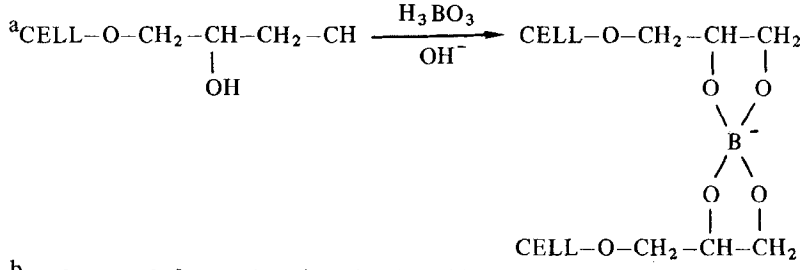


FIG. 4. Effect of boric acid concentration on the viscosity of H_3BO_3-DHPC solution at room temperature.

TABLE 5. Reversible Gelation[a] of DHPC-Borate Complex[b]

DHPC, wt%	pH	Viscosity, cP
1.6	9.2	14
	10.4	15
	11.2	16
2.0	9.4	23
	10.9	30
2.4	9.3	33
	9.6	73
	10.6	280
2.8	8.7	28
	9.7	162
	11.5	8880
3.2	8.6	49
	9.5	267
	10.6	4640
4.0	8.9	131
	9.6	4670



[b]DHPC, 8D, $[\eta]$ = 1.01 dL/g, C^* = 2.5 g/dL.

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