Synthesis and Characterization of Cellulose Derivatives Prepared in NaOH/Urea Aqueous Solutions

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Received 10 January 2004; accepted 25 July 2004
DOI: 10.1002/pola.20431
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: We successfully synthesized hydroxypropylcellulose (HPC) and methylcellulose (MC) in high yields from cellulose in 6 wt % NaOH/4 wt % urea aqueous solutions at 25 °C. The cellulose derivatives were characterized with NMR, size exclusion chromatography/laser light scattering, gas chromatography (GC), ultraviolet, and solubility measurements in different solvents. According to the results of solution ^{13}C NMR and GC, the individual degree of substitution (DS; i.e., the average number of substituted hydroxyl groups in the monomer unit) at C-2 hydroxyl groups was slightly higher than the DS values at C-3 and C-6 hydroxyl groups for HPC and MC. In comparison with traditional systems, NaOH/urea aqueous solutions were proved to be a stable and more homogeneous reaction medium for preparing cellulose ether with a more uniform microstructure. The low limits for the average number of moles of the substituent groups per monomer unit and the DS value of water-soluble HPC were 1.03 and 0.85, respectively. MC (DS = 1.48) had good solubility in both water and organic solvents, and the precipitation point occurred at about 67 °C for a 2% (w/v) aqueous solution. In this way, we could provide a simple, pollution-free, and homogeneous aqueous solution system for synthesizing cellulose ethers. © 2004 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 42: 5911–5920, 2004

Keywords: synthesis; hydroxypropylcellulose; methylcellulose; NaOH/urea aqueous solutions; NMR

INTRODUCTION

Cellulose, the most abundant natural polymer, could be a primary chemical resource in the future because it is renewable, biodegradable, biocompatible, and derivatizable.[1] However, cellulose still has not reached its potential applications in many areas because it is difficult to process in normal solutions or in the melting state on account of its strong intermolecular and intramolecular hydrogen bonding. Chemical modification reactions continue to play a dominant role in improving the overall utilization of cellulose.[2] Nowadays, most commercial cellulose derivatives have been prepared with heterogeneous procedures with cellulose slurry. The discovery of novel solvents and solution complexes for cellulose in the past 3 decades has created opportunities for the application of significantly more diverse synthesis pathways and derivative types.[3] The *N*-methylmorpholine-*N*-oxide (NMMO) system, an important pollution-free cellulose solvent, has been commercially used for the fabrication of fi-

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 42, 5911–5920 (2004)

bers such as Tencel and Lyocell.[3,4] However, the modification reaction of cellulose in NMMO has been reported only for carboxymethylation.[2,5] LiCl/*N,N*-dimethylacetamide (DMAc) is a representative nonaqueous solvent system suitable for the homogeneous reaction of cellulose.[6,7] In particular, cellulose esters, carbamates, and sulfonates with a high and uniform degree of substitution have been prepared successfully with the LiCl/DMAc system.[8,9] However, the production of cellulose ethers in LiCl/DMAc does not appear to be better than conventional processes because of the low solubility of the metal hydroxide in LiCl/DMAc, the high reaction temperatures, and the long reaction time.[8] SO_2/diethylamine (DEA)/dimethyl sulfoxide (DMSO) has been reported to be a more suitable solvent for preparing highly substituted cellulose ethers.[10,11] Strictly, the etherification reactions in nonaqueous systems, such as LiCl/DMAc,[8,9] LiCl/1,3-dimethy-2-imidazolidinone (DMI),[12] and SO_2/DEA/DMSO,[10,11] are not completely homogeneous because cellulose precipitates from the reaction solution with the addition of powdered NaOH. The reaction in cellulose aqueous solution systems has been scarcely reported. Heinze et al.[2] reported the unconventional carboxymethylation of cellulose in Ni(tren)$(OH)_2$ [tren = tris(2-aminoethyl) amine] aqueous solutions and in melts of $LiClO_4 \cdot 3H_2O$; they showed that the distribution of functional groups on the level of the repeating unit and on the level of the polymer chain was comparable to that of products synthesized in a conventional slurry process with aqueous NaOH. The demands in research and industry stimulate us to search for a solvent that is appropriate for homogeneous phase reactions of cellulose.

In our previous work, NaOH/urea aqueous solutions were found to be a good solvent for cellulose,[13–15] and the molecular parameters of a cellulose solution as a direct solvent were obtained.[16] This new solvent system may be a suitable solvent for preparing cellulose ethers because the etherification of cellulose is usually produced under alkali conditions. In this work, we attempted to synthesize hydroxypropylcellulose (HPC) and methylcellulose (MC) in NaOH/urea aqueous solutions, and their structure and solubility were characterized. Moreover, the characteristics of this solvent system, as a new homogeneous aqueous reaction medium of cellulose, were examined.

EXPERIMENTAL

Materials and Preparation of the Cellulose Solutions

Whatman CF-11 fibrous cellulose powder was used as the starting cellulose; the weight-average molecular weight (M_w) was determined to be 3.46×10^4 by static laser light scattering.[16] Propylene oxide and dimethyl sulfate were analytical-grade and chemically pure, respectively, and all the chemical reagents were used without further purification.

An aqueous solution of 6 wt % NaOH and 4 wt % urea consisted of 60 g of NaOH, 40 g of urea, and 900 mL of dilute water, and the resulting solution was filtered with a G2 sand filter to be used as a solvent of cellulose. A cellulose solution was prepared according to our previous work[13]; that is, CF-11 (1 g) was dispersed in 49 g of the solvent with stirring for 5 min and then was stored in a refrigerator (−5 to −10 °C) for 12 h. The frozen solid was thawed and stirred extensively at room temperature to obtain a colorless and transparent cellulose solution.

Preparation of the Cellulose Derivatives

For the preparation of HPC, propylene oxide (4.0 mL, 56 mmol) was added to a 50-g cellulose solution (containing 1.0 g of cellulose), and the resulting mixture was stirred at 25 °C for a desired time. The reaction product was neutralized with acetic acid, dialyzed with water, and freeze-dried. By changing the molar ratio of the anhydroglucose unit (AGU) to propylene oxide from 1:3 to 1:6 and the reaction time from 4 to 72 h, we prepared four HPC samples coded HPC-1–HPC-4. The yields of HPC-1–HPC-4 were 1.08, 1.12, 1.15, and 1.15 g, respectively.

For the preparation of MC, dimethyl sulfate (7 g, 56 mmol) was added dropwise to the 50-g cellulose solution mentioned previously, and the mixture was stirred at 25 °C for 24 h. The reaction product was neutralized with acetic acid, dialyzed with water, and freeze-dried. The yield of the obtained MC was 1.08 g.

Measurements

^{13}C and ^{1}H NMR spectra of the samples were recorded on a Varian Inova 600 spectrometer in the proton noise-decoupling mode with a standard 5-mm probe and deuterated dimethyl sulfox-

ide (DMSO-d_6) as a solvent at 30 °C. The chemical shifts were referenced to the signals of DMSO-d_6 and tetramethylsilane (TMS). The quantitative-mode ^{13}C NMR measurement conditions for HPC and MC closely followed those in the structural analysis of the cellulose derivatives. The relative degree of substitution (DS; i.e., the average number of substituted hydroxyl groups in the monomer unit) at an individual hydroxyl group and the molar substitution (MS; i.e., the average number of moles of substitution groups per monomer unit) were estimated from the ratio between the peak areas. The peak areas were determined by the integration of each peak.

The acetylation of HPC-4 and MC was carried out before NMR analysis according to the improved characterization of the substitution distribution in HPC[17] and MC.[18] Acetylated HPC-4 and MC samples were dissolved in DMSO-d_6, and the NMR spectra were recorded at 75 °C.

Gas chromatography (GC) analysis of the substituent distribution of MC was performed according to the method described by Tezuka et al.[18] The acetylated hydrolyzates of MC were analyzed by the injection of 0.2 μL of a sample solution into an Agilent 6890N GC system equipped with a capillary split/splitless injector system and a flame ionization detector on an HP-5MS capillary column (25 m $\times$ 0.32 mm $\times$0.25 μm). The oven temperature was set at 150 °C and was increased by 2 °C/min to 220 °C. The detector temperature was set at 280 °C. Nitrogen was used as a carrier gas. HPCORE ChemStation (version A 09.01) software was used for instrument control and data analysis.

Size exclusion chromatography (SEC), combined with laser light scattering (LLS), was used to determine the molecular weight and its distribution of HPC and MC. The SEC–LLS measurements were performed on a multi-angle laser light scattering instrument (Dawn DSP, Wyatt Technology Co., United States) equipped with a He–Ne laser (λ = 632.8 nm) and combined with a p100 pump equipped with a TSK gel column (G4000 PWXL, 7.8 mm $\times$ 300 mm) and an Optilab refractometer (Wyatt Technology) at 25 °C. The fluent was a 0.2 mol/L NaCl aqueous solution at a flow rate of 1.0 mL/min. Astra software was used for data acquisition and analysis. The specific refractive-index increments of HPC and MC in 0.2 mol/L NaCl aqueous solutions were 0.127 and 0.135 cm^3/g, respectively; these were taken with an Optilab refractometer (Wyatt Technology) at 632.8 nm and 25 °C.

The solubility of HPC and MC samples in different solvents was measured at 25 °C, and the concentration was about 1% (w/v). The precipitation temperature (T_p) was evaluated for a 2% (w/v) aqueous solution of MC. A UV-240 spectrophotometer (Shimadzu, Japan) was used for the evaluation of T_p as follows. The transmittance at a 700-nm wavelength was measured as a function of temperature from the aqueous solution. The temperature was controlled with a Julabo temperature controller (Julabo Labrotechnik GmbH, Seelbach, Germany), and the heating rate was about 0.1 °C/min. T_p in this study is expressed in terms of the temperature at which 50% of the incident light is transmitted.[19]

RESULTS AND DISCUSSION

Structural Analysis

Figure 1(A) shows a typical ^{1}H NMR spectrum of an HPC sample in DMSO-d_6 at 30 °C; a strong peak at 1.0 ppm is assigned to methyl protons, whereas the broad peak from 2.8 to 5.8 ppm is attributed to methylene and methine of the hydroxypropyl substituents and all the protons of the cellulosic skeleton. The ^{13}C NMR spectra of samples HPC-1–HPC-4 in DMSO-d_6 at 30 °C are shown in Figure 2. According to the assignments in refs. 20 and 21, the peaks C_6 and C_{6s} are assigned to C-6 carbons bearing unsubstituted and substituted hydroxyl groups, respectively. There are no hydroxyl groups on the C-1 and C-4 carbons in the AGU units. For cellulose ether derivatives, however, the chemical shifts of C_1 and C_{1s} are due to C-1 carbons adjacent to C-2 bearing unsubstituted and substituted hydroxyl groups, respectively, whereas C_4 and C_{4s} are affected by adjacent C-3 carbons bearing unsubstituted and substituted hydroxyl groups, respectively. The DS values at individual hydroxyl groups can be estimated from the relative intensities of peaks C_1, C_{1s}, C_4, C_{4s}, C_6, and C_{6s} in Figure 2. The total DS has been obtained as the sum of the relative DS values at anhydroglucose positions 2, 3, and 6, and the MS value has been calculated from the ratio between the peak area of the —CH_3 signal and the total area of all C-1 (C_1 + C_{1s}) signals. The MS, total DS, and relative DS values at the C-2, C-3, and C-6 carbon positions of the four HPC samples are summarized in Table 1. The MS and DS values of the HPC samples increased with an increase in the reaction time and

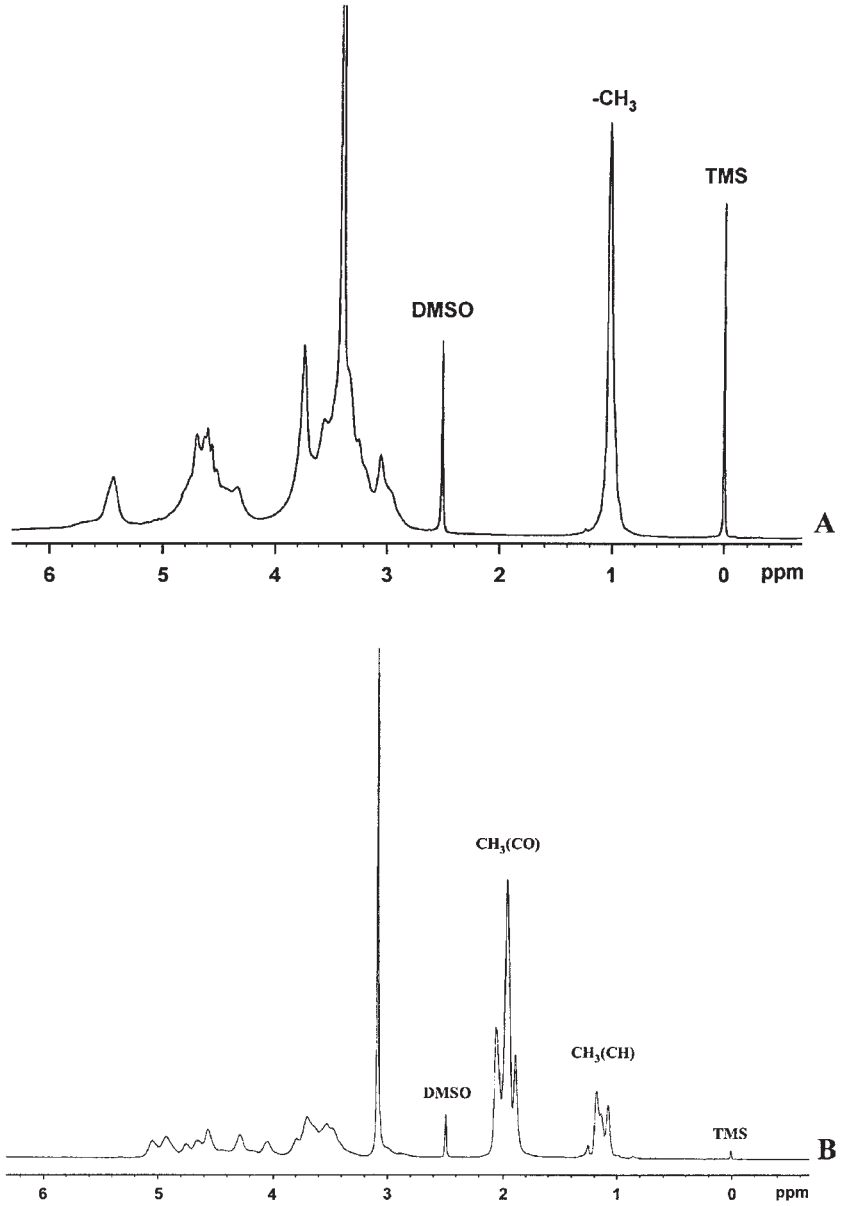

Figure 1. ^{1}H NMR spectra of (A) a typical HPC sample in DMSO-d_6 at 30 °C and (B) acetylated HPC-4 in DMSO-d_6 at 75 °C.

the dope of propylene oxide, and the highest MS value (1.7) was obtained with an AGU/propylene oxide molar ratio of 1:6 at 25 °C for 72 h.

Figure 3 shows the ^{13}C NMR spectrum of an MC sample in DMSO-d_6 at 30 °C, and the possible assignments of the peaks are also shown. According to Takahashi and coworkers,[22,23] the relative DS values at the C-2, C-3, and C-6 positions were calculated from the relative intensities of peaks C_1, C_{1s}, C_4, C_{4s}, and C_{6s} to be 0.63, 0.45, and 0.40, respectively.

NMR technical data for acetylated derivatives of cellulose ethers have been proved to be a convenient and reliable method of elucidating the microstructures of HPC and MC over a wide DS range.[17,18,24] Figure 1(B) presents the ^{1}H NMR spectrum of acetylated HPC-4 in DMSO-d_6 at 75 °C. The MS value (1.58) was calculated from the peak areas of the well-resolved proton signals from the methyl group of the introduced acetyl group and the methyl group of the hydroxypropoxy group. The ^{13}C NMR spectra of the

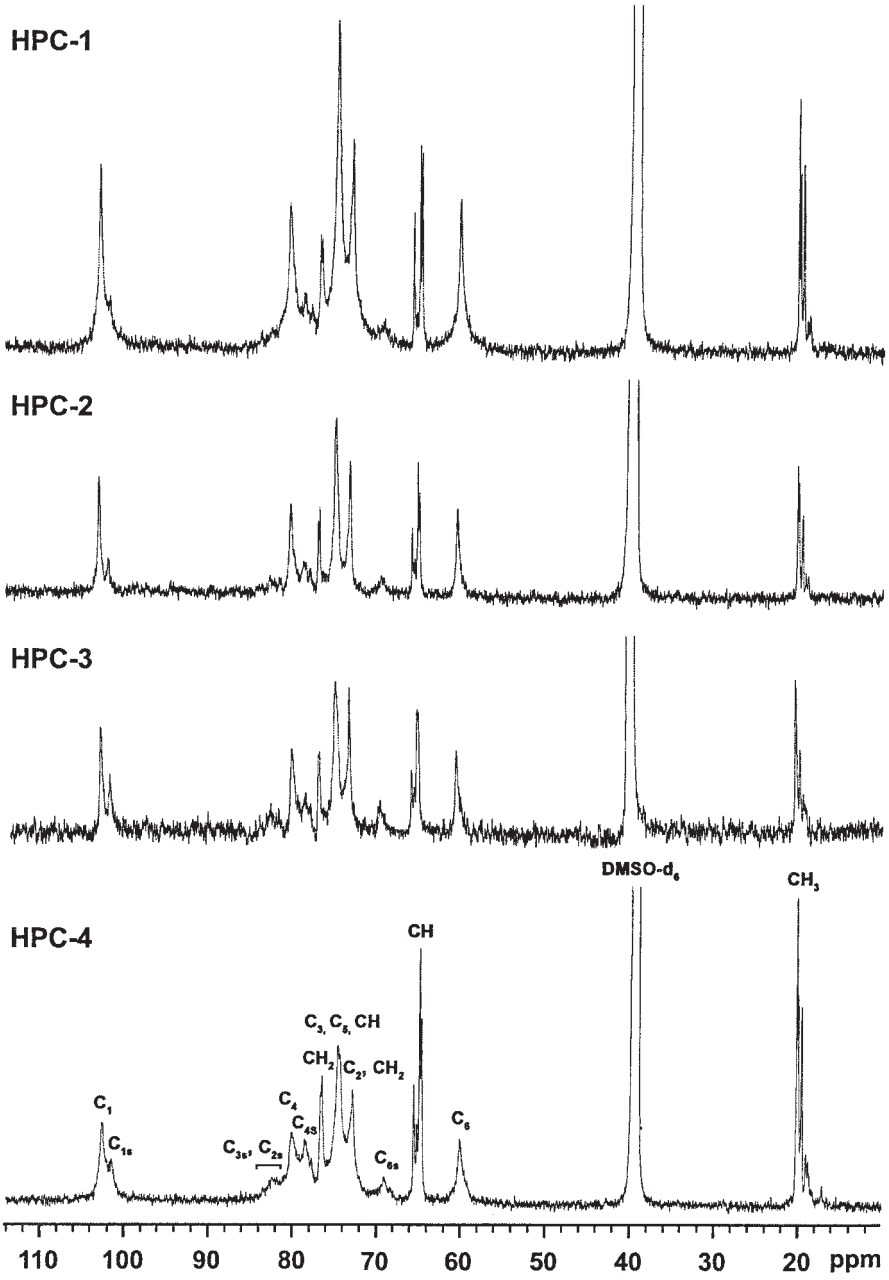

Figure 2. ^{13}C NMR spectra of HPC samples in DMSO-d_6 at 30 °C.

acetylated HPC-4 and MC samples in DMSO-d_6 at 75 °C are shown in Figure 4, and the peaks are assigned according to the references and are shown in the spectra. Through the integration of the well-resolved acetyl methyl and carbonyl carbon signals,[17,18] the total DS and DS values of individual anhydroglucose positions 2, 3, and 6 for HPC-4 and MC, respectively, were obtained and are listed in Table 1. There are some differences between the DS values, especially for the relative DS value at the C-6 position, obtained from acetylated and untreated samples.

Figure 5 shows the GC trace for an MC sample after total hydrolysis and acetylation, and the peak assignment was performed with mass spectroscopy analysis. According to the method reported by Kondo,[25] the relative DS values at the C-2, C-3, and C-6 positions were calculated to be 0.65, 0.42, and 0.56, respectively. The DS values obtained by GC showed good agreement with

Table 1. Distribution of Substitution in HPC and MC Samples

Sample	MS	Total DS	DS		
			C-2	C-3	C-6
HPC-1[a]	0.85	0.83	0.28	0.26	0.29
HPC-2[a]	1.03	0.85	0.25	0.30	0.30
HPC-3[a]	1.18	0.93	0.33	0.30	0.30
HPC-4[a]	1.73	1.18	0.41	0.38	0.39
HPC-4[b]	1.58	1.13	0.48	0.33	0.26
MC[a]	—	1.48	0.63	0.45	0.40
MC[b]	—	1.69	0.66	0.44	0.59
MC[c]	—	1.63	0.65	0.42	0.56

[a] From the ^{13}C NMR spectra of untreated HPC and MC samples.

[b] From the NMR spectra of acetylated HPC-4 and MC samples. For HPC-4, the MS value was calculated from ^{1}H NMR; the total DS and DS values at positions C-2, C-3, and C-6 were calculated from acetyl methyl region analysis and carbonyl region analysis of ^{13}C NMR, respectively.[17] The DS values of MC were calculated from C-1 region and carbonyl region analysis of ^{13}C NMR.[18]

[c] From the GC analysis.

those obtained by the ^{13}C NMR technique with acetylated MC. The unsubstituted glucose units were undetected in the GC trace, which reflected a homogeneous substituent along the molecular chain for the MC sample prepared in our solvent system.

Although there are some difference between the methods used for the determination of the DS values, we can still conclude that the DS value at C-2 hydroxyl groups is slightly higher than those at C-3 and C-6 hydroxyl groups for samples of HPC and MC prepared in NaOH/urea aqueous solutions, which are similar to carboxymethylcellulose (CMC) prepared in $Ni(tren)(OH)_2$ aqueous solutions (a fully homogeneous process)[2] and the commercial production of CMC prepared in a highly swollen states[26]; however, they obviously differed from the heterogeneous reactions and homogeneous reaction in other systems. Usually, the relative reactivity of hydroxyl groups of cellulose is in the order C-6 $\geqslant$ C-2 $>$ C-3 in a nonaqueous solvent system. The difference in the relative DS values among the three hydroxyl groups of the AGU residue reflects the reactivity of the cellulose derivatizations. A homogeneous procedure ensures a more uniform distribution of the substituents because of greater accessibility of —OH.[27] As mentioned previously, the etherification reactions in nonaqueous systems, such as LiCl/DMAc, LiCl/DMI and SO_2/DEA/DMSO, are not completely homogeneous because cellulose precipitates from the reaction solution through the addition of powdered NaOH. In comparison with traditional systems, an aqueous solution of NaOH and urea is a more homogeneous reaction medium for the etherification of cellulose, and the solution remains transparent during the reaction. Moreover, commercial HPC is prepared by a reaction of an alkali cellulose slurry with propylene oxide in two stages, and it needs a large amount of organic diluents during the reaction process.[28–31] Therefore, this work has provided a simple, ambient, and pollution-free method for preparing cellulose derivatives.

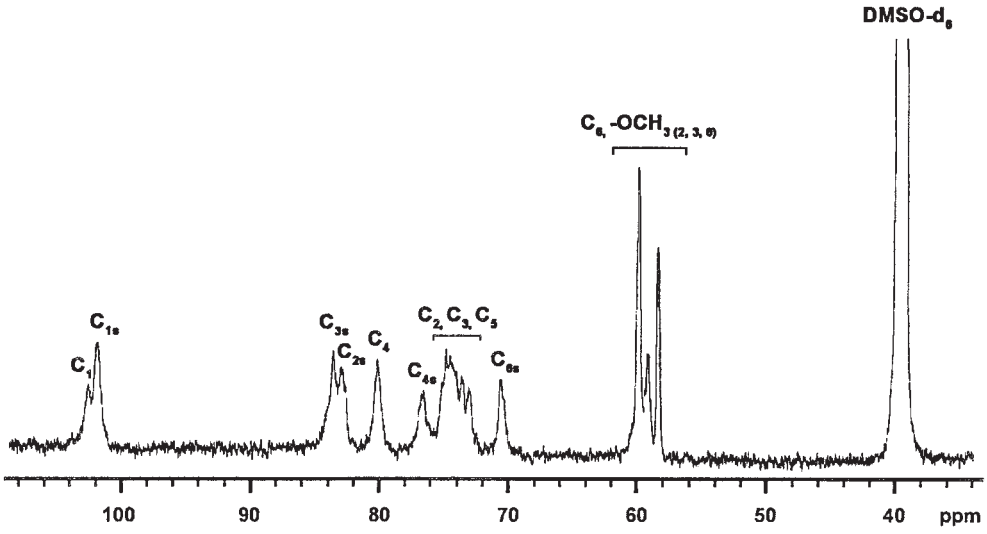

Figure 3. ^{13}C NMR spectrum of an MC sample in DMSO-d_6 at 30 °C.

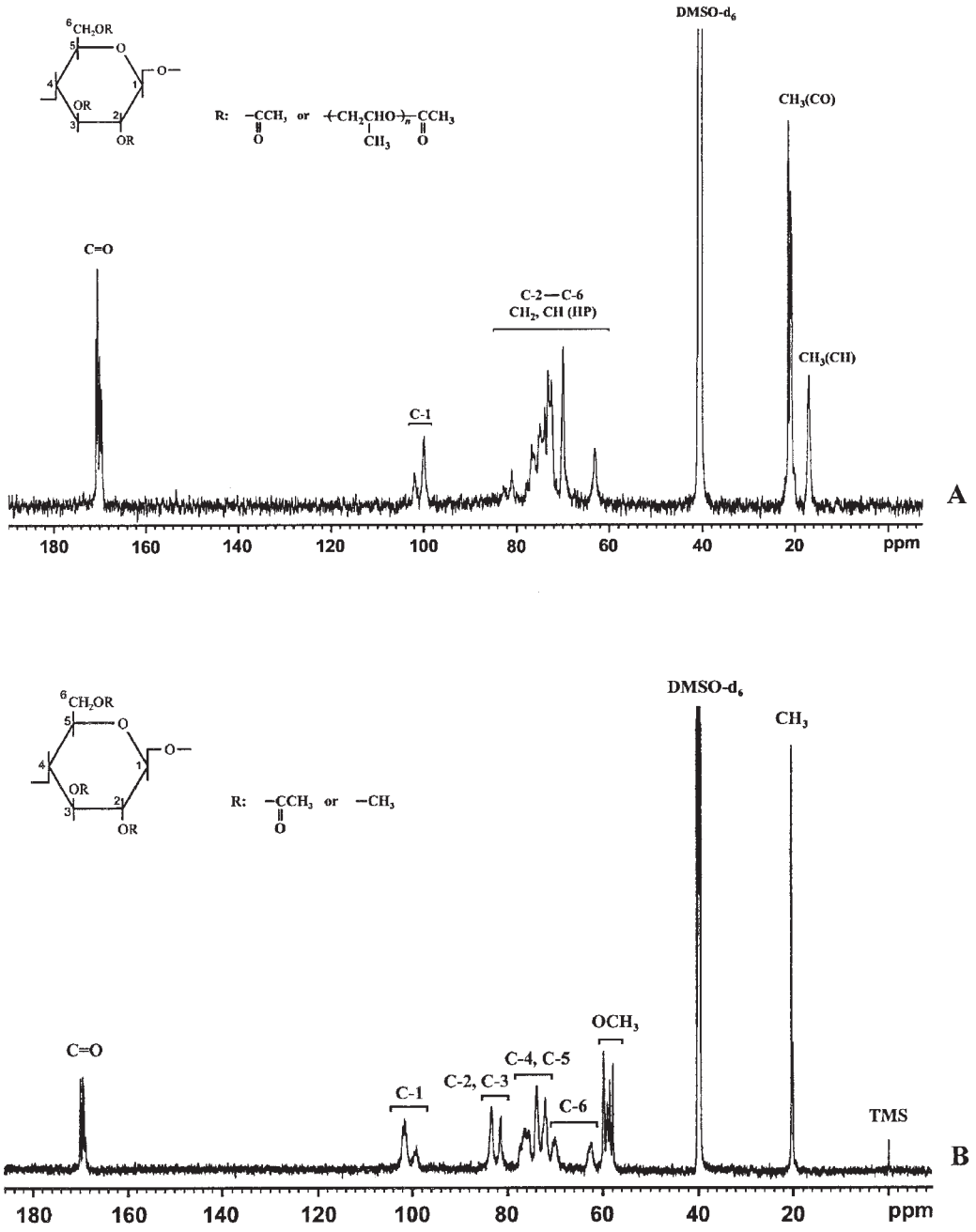

Figure 4. ^{13}C NMR spectra of (A) acetylated HPC-4 and (B) acetylated MC in DMSO-d_6 at 75 °C.

Solubility and Molecular Weights

The solubility of HPC samples in water, DMSO, tetrahydrofuran (THF), and pyridine is listed in Table 2. All four HPC samples had good solubility in pyridine. HPC-1 (MS = 0.85) could not dissolve in water; with the MS up to 1.03, samples HPC-2, HPC-3, and HPC-4 were completely soluble in water. The lower limit values for the MS and DS values of water-soluble HPC were 1.03 and 0.85, respectively. The MC sample had good solubility in both water and organic solvents such as THF and pyridine. SEC–LLS chromatograms for HPC-2 and MC in 0.2 mol/L NaCl aqueous solutions at 25 °C are shown in Figure 6. From the signals detected by LLS and differential refractometry, M_w, the number-average molecular

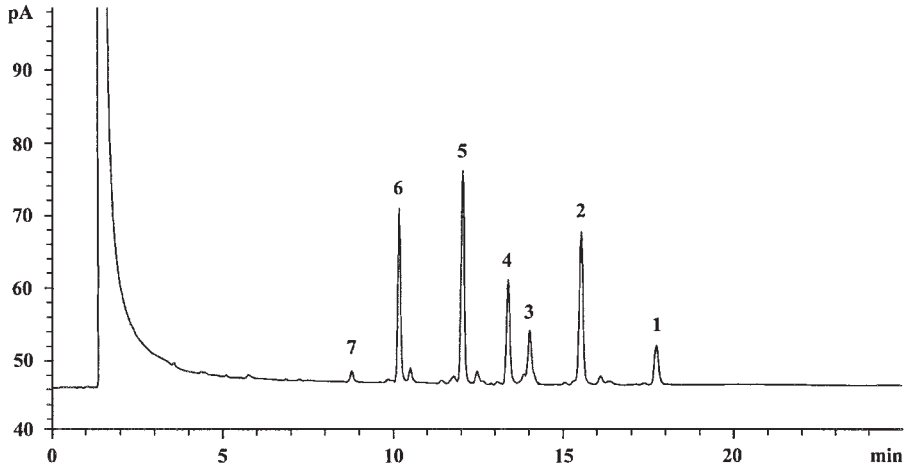

Figure 5. GC trace of an MC sample after total hydrolysis and acetylation. Signals 1–7 represent 3-*O*-, 2-*O*-, 6-*O*-, 2,3-di-*O*-, 2,6-di-*O*-, 3,6-di-*O*-, and 2,3,6-tri-*O*-methyl glucitol derivatives, respectively.

weight (M_n), and the polydispersity index ($d = M_w/M_n$) of derivatives HPC-2, HPC-3, and HPC-4 and MC were determined, and they are summarized in Table 2. The M_w values of HPC-2, HPC-3, and MC are in good agreement with the molecular weight calculated from M_w of the original cellulose. The M_w and M_n values of HPC-4 slightly decreased with the reaction time because of the degradation of cellulose in the solvent for a long time. In light of the molecular weights and yield of the HPC and MC samples, a 6 wt % NaOH/4 wt % urea aqueous solution is a stable system for cellulose derivatization.

It is well known that commercial MC prepared by the alkali cellulose process is water-soluble over a DS range of 1.2–2.4, and it exhibits a thermally reversible sol–gel transition in aqueous solutions.[32] The thermogelation of MC solutions has been studied extensively, and the distribution of the methyl group within an AGU unit and the substituent along the molecular chain are considered to be the most important factors determining the physicochemical properties of MC.[27,33–35] The MC sample prepared in this work showed a normal phase separation rather than a sol–gel transition in an aqueous solution, just like MC samples prepared by a homogeneous reaction in a nonaqueous system.[22] Figure 7 demonstrates the temperature dependence of the transparency of a 2% (w/v) aqueous solution of MC; T_p was 67 °C. The MC sample synthesized here exhibited a higher T_p than those of the MC-H series with similar and highly relative DS values[22]; this indicated a more uniform distribution of substituents along the chain than that found in the MC-H series. Interestingly, the 2% (w/v) aqueous solu-

Table 2. Solubility, M_w, M_n, and d Values of the HPC and MC Samples

Sample	$M_w \times 10^{-4}$ (g/mol)	$M_n \times 10^{-4}$ (g/mol)	d	Solubility[a]			
				H_2O	DMSO	THF	Pyridine
CF-11[b]	3.46	—	—	−	−	−	−
HPC-1	—	—	—	−	+	○	+
HPC-2	5.41	3.61	1.5	+	+	+	+
HPC-3	5.54	4.01	1.4	+	+	+	+
HPC-4	4.28	3.62	1.2	+	+	+	+
MC	5.30	3.94	1.3	+	+	○	+

[a] − insoluble; + soluble; ○ swelling for a 1% (w/v) solution at 25 °C.
[b] Determined by static laser light scattering.[16]

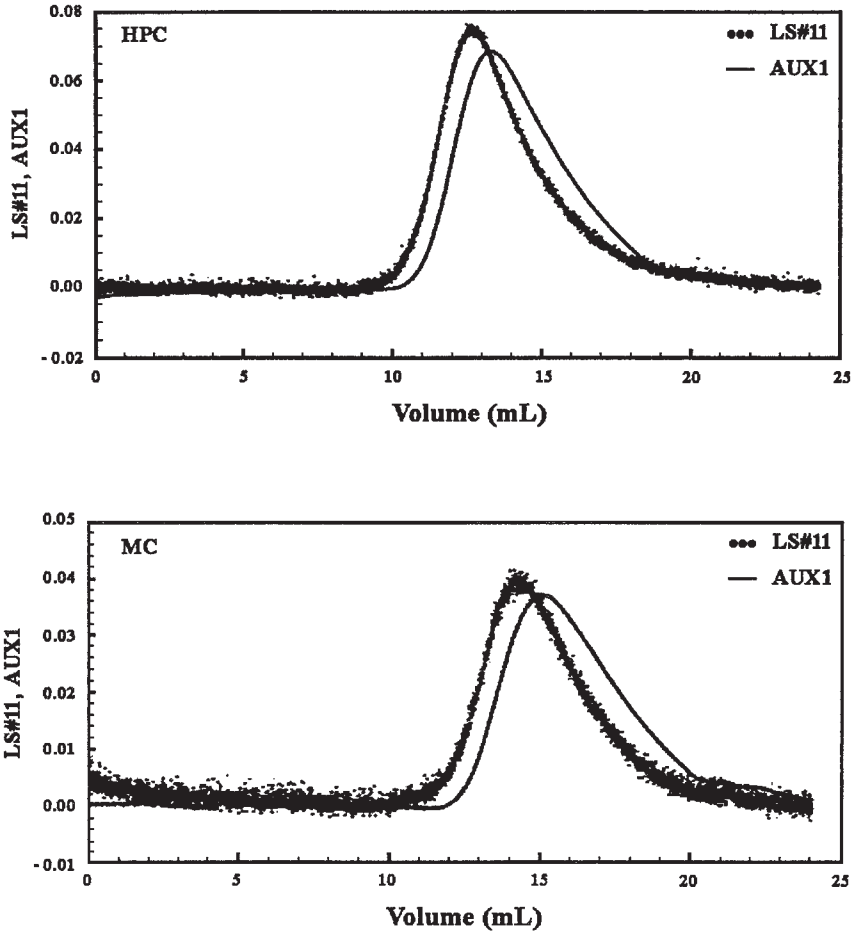

Figure 6. SEC chromatograms of HPC-2 and MC in 0.2 mol/L NaCl aqueous solutions at 25 °C, as detected by LLS and differential refractometry. LS#11 and AUX1 represent signals from LLS at 90° and from refractive-index detection.

tions of HPC-2, HPC-3, and HPC-4 remained transparent as the temperature increased from 25 to 95 °C, and this indicated a stable polymer solution.

CONCLUSIONS

Water-soluble HPC and MC were successfully synthesized from cellulose in 6 wt % NaOH/4 wt % urea aqueous solutions at room temperature. The relative reactivity of hydroxyl groups at the C-2 position of cellulose was slightly higher than that at the C-3 and C-6 positions. Moreover, NaOH/urea aqueous solutions were concluded to be a stable and more homogeneous reaction medium for preparing cellulose ether with a more uniform structure than other traditional heterogeneous and homogeneous reactive media. The

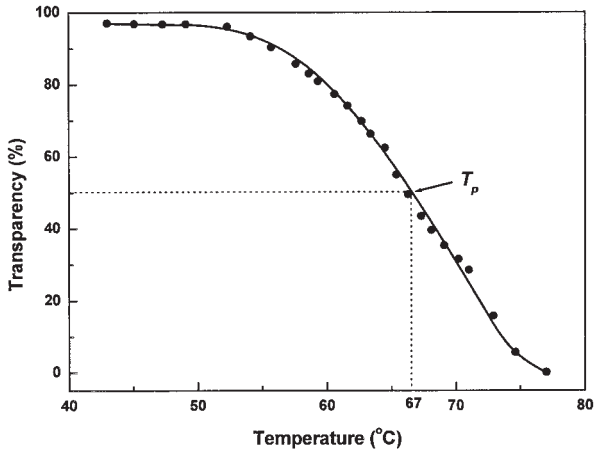

Figure 7. Precipitation behavior of MC (DS = 1.48) indicated by the temperature-dependent transparency of a 2% (w/v) aqueous solution.

low limits for the MS and DS values of water-soluble HPC were 1.03 and 0.85, respectively. The MC sample prepared in this work showed normal phase separation rather than a sol–gel transition in an aqueous solution because of the uniform distribution of substituents along the chain, and its T_p was determined to be 67 °C.

The authors are grateful for the financial support of the National Natural Science Foundation of China (20204011 and 59933070) and the High-Technology Research and Development Program of China (2004AA649250).

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