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# Structure and physical properties of methylcellulose synthesized in NaOH/urea solution

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## Summary

A series of methylcellulose (MC) samples were successfully synthesized using dimethyl sulphate (DMS) as a methylation reagent in 7 wt % NaOH/12 wt % urea aqueous solution through controlling the reaction conditions. The MC samples were characterized with $^{1}H$ and $^{13}C$ NMR, gas chromatography (GC), ultraviolet spectroscopy, viscometry and solubility measurement. Analysis of GC showed that there were no unsubstituted anhydroglucose units (AGU) and few completely substituted AGU along the molecular chains of the MC samples, and there was a uniform distribution of methyl substitution along the MC molecular chains. The stability of 7 wt % NaOH/12 wt % urea solution for the methylation of cellulose was investigated for the first time. The results showed 2 wt % cellulose solution in the 7 wt % NaOH/12 wt % urea solvent was almost stable at room temperature, and little decomposition of the cellulose molecular chains occurred during the methylation reaction.

## Introduction

Methylcellulose (MC) is widely used in the fields of textile, paper, food, pharmaceutical, building, and painting industries. Commercial MC is prepared by heterogeneous etherification with methyl chloride in accordance with the principle of the Williamson ether synthesis, and has a heterogeneous distribution of substituents along the polymeric chains [1]. The distribution of the methyl substituents along the cellulose chains has a strong influence on its solubility and viscosity in water. It's well known that commercial MC samples show a thermally reversible sol-gel transition in aqueous solution, and these behaviors are attributed to aggregation caused by hydrophobic interactions [2], and are heavily dependent on their substitution patterns, molecular weights and concentration of solution [3-6].

In the past 3 decades, it has been reported that many cellulose solvents are suitable for the derivatization of cellulose, i.e., LiCl/*N,N*-dimethylacetamide (DMAc), *N*-methylmorpholine-*N*-oxide (NMMO), LiCl/1,3-dimethy-2-imidazolidinone (DMI), and $SO_2$/diethylamine (DEA)/dimethyl sulfoxide (DMSO) [7, 8]. In particular, cellulose ethers with a uniform degree of substitution, including MC, hydroxyethylcellulose (HEC), and hydroxypropylcellulose (HPC) have been successfully prepared in LiCl/DMAc. Compared with commercial MC, the aqueous

solutions of MC samples prepared by homogeneous reaction show a phase separation at high temperature [5]. However, the production of cellulose ethers in LiCl/DMAc does not appear to have advantages over conventional processes because significant degradation of derivatives occurs [9]. The NMMO system has been commercially used for the fabrication of fibers such as Tencel and Lyocell [7, 8], but the modification reaction of cellulose in NMMO has been reported only for carboxymethylation [10, 11]. At present, most of solvents suitable for cellulose modification are organic solvents, and there are a number of inherent problems, i.e., the toxic solvents, high reaction temperatures, and long reaction times, etc. However, few reports on the etherification of cellulose in the homogenous aqueous system have appeared [7].

In our laboratory, we have found two solvent systems for cellulose, including NaOH/urea and NaOH/thiourea aqueous solution [12-14]. It has been reported that NaOH/urea solution is a suitable solvent for preparing cellulose ethers [15,16], but the degradation extent of MC and the relative reactivity of each hydroxyl group during the methylation in 7 wt % NaOH/12 wt % urea aqueous solution are still not clear. In this study, a series of MC are synthesized through homogeneous reaction in 7 wt % NaOH/12 wt % urea aqueous solution. Our main objective is to study structure and physical properties of the MC samples, and estimate the stability of the 7 wt % NaOH/12 wt % urea solution for the methylation of cellulose.

## Experimental

### *Materials*

The cellulose (cotton linter pulp) was supplied by Hubei Chemical Fiber Group Ltd. (Hubei, China), and its viscosity-average molecular weight ($M_\eta$) in cadoxen [17] was determined using viscometry to be $10.00 \times 10^4$. Dimethyl sulphate (DMS) was chemical grade, and other chemical reagents were analytical grade. All chemical reagents were obtained from commercial sources in China, and were used without further purification.

### *Methylation of cellulose*

The cellulose solution in 7 wt % NaOH/12 wt% urea aqueous solution was prepared according to the method of our laboratory [13, 14]. Into a 500 mL beaker, adequate amounts of NaOH, urea and distilled water (7:12:81 by weight) were added, and the resulting mixture aqueous solution was stored in a refrigerator. When the solution was precooled to –12 °C (± 0.5 °C), cellulose was added immediately into it with stirring vigorously for 5 min at ambient temperature to obtain the transparent cellulose solution with 2 wt % concentration.

The cellulose solution was subjected to centrifugation at 10000 rpm for 20 min at 5–10 °C to exclude the slightly remaining undissolved part. 200 g of 2 wt % cellulose solution was put into a 250 mL three-neck flask to be ready for the derivative reaction. DMS (14–28 mL) was added dropwise into the cellulose solution with stirring. The reaction mixtures kept transparent during the reaction, and the reaction solutions were neutralized with acetic acid. A series of MC samples were prepared by controlling the reaction temperature and time, and coded as MC-1, MC-2, MC-3, MC-4, MC-5, MC-6, and MC-7, respectively. MC-3, MC-4 and MC-6 were attained by being washed with acetone over four times and then dried for 24 h in vacuum oven at 60 °C, and others

were dialyzed with water and then freeze-dried. The sample number and reaction conditions were listed in Table 1.

*Measurements*

The $M_\eta$ values of the native cellulose and the cellulose after degradation were determined in cadoxen by viscometry at 25 °C as [17]:

$$[\eta] = 3.85 \times 10^{-2} M^{0.76} \text{ (mL/g)} \quad (\mathbf{1})$$

To determine $M_\eta$ values, the MC samples were dissolved in water at 4 °C for 48 h to ensure complete dissolution. The $[\eta]$ values of the MC samples were measured in the water solution at 20 °C, and $M_\eta$ values were calculated by [18]:

$$[\eta] = 0.28 M^{0.63} \quad \text{(mL/g)} \quad (\mathbf{2})$$

$^1$H and $^{13}$C NMR spectra of the samples in $D_2O$ were recorded on a Mercury-VX 600 spectrometer (Varian, Inc. USA) at ambient temperature. The sample concentration was about 2 wt %.

Gas chromatography (GC) analysis of the substituent distribution of the MC samples was performed according to the method described by Tezuka [19]. Fifty milligrams of the MC sample was hydrolyzed with 3.5 mL of 1.0 wt % sulfuric acid at 140 °C for 2 h. After neutralization with calcium carbonate, the solvent was removed by heating at 80 °C for 6-7 h. The sample was redissolved in 5.0 mL of 80 wt % aqueous methanol and filtrated with a 0.45 μm filter. The sample solution was then condensed to 1.0 mL. Thereupon, 100 μL of sodium borohydride solution, prepared with 1.5 g of sodium borohydride in 10 mL of 0.2 N sodium hydroxide, was added and stirred for 1 h. 100 μL of acetic acid was then added, and the solution was dried up by heating followed by washing and evacuating twice with 3.0 mL of methanol. Finally, 1.0 mL of acetic anhydride and 1.0 mL of pyridine were added into it and the mixture was heated at 120 °C for 3 h. The acetylated hydrolyzates of MC were analyzed by the injection of 0.2 μL of a sample solution into an HP 6890 gas chromatograph (Hewlett Packard, USA) using a capillary split/splitless injector and a flame ionization detector on an HP-5MS capillary column (25 m × 0.32 mm × 0.25 μm). The oven temperature was set at 150 °C and was increased with ratio of 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.

The solubility of the 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 the MC sample. A UV-160A sepectrophotometer (Shimadzu, Japan) with a device (Yiye, China) controlling the heating rate about 0.1 °C/min is used for the measurement of $T_p$. The optical transmittance of the aqueous solution at a 700-nm wavelength was measured as function of temperature. $T_p$ in this study is expressed in terms of the temperature at which 50 % of the incident light is transmitted [4].

## Results and discussion

*Structural Analysis*

Figure 1 shows the $^1$H and $^{13}$C NMR spectra of the sample of MC-5 in $D_2O$. The proton signals of methyl groups at C-2, C-3, and C-6 positions are labeled as 2-, 3-, and 6-Me,

respectively. According to Kondo's report [20], the sharp signals at 3.2 and 3.5 ppm are respectively responsible for the protons of methyl groups at C-2, C-3 positions and methyl groups at C-6 positions in the $^{1}$H NMR spectrum. The possible assignments of the peaks are also shown in the $^{13}$C NMR spectrum [19].

A more accurate way to determine the substitution pattern of polysaccharides is by gas chromatography (GC) coupled with mass spectrometry (GC-MS) [21]. Figure 2 shows the GC trace for the MC-6 sample after total hydrolysis and acetylation, and the peak assignment was performed with mass spectroscopy analysis. Table 1 summarizes the results of GC analysis for the distribution of methyl group (Xn; $n$ = 2, 3, and 6) on the MC samples calculated according to Kondo's method [22]. The unsubstituted glucose units ($S_0$) were not detected in the GC trace of all MC samples, and there were also few 2,3,6-tri-O-methyl glucitol derivatives ($S_{236}$) detected. These results suggest that the MC samples don't consist of unsubstituted anhydroglucose units (AGU) and include few completely substituted AGU along the MC molecular chains, indicating that AGU along the molecular chains of cellulose are equally accessible for the methylation reagent in 7 wt % NaOH/12 wt % urea aqueous solution. This differs from the commercial MC prepared in accordance with the principle of the Williamson ether synthesis. Because the cellulose starting material need a procedure of pre-swelling or activation before reaction, some areas that are not properly swollen don't react to attain

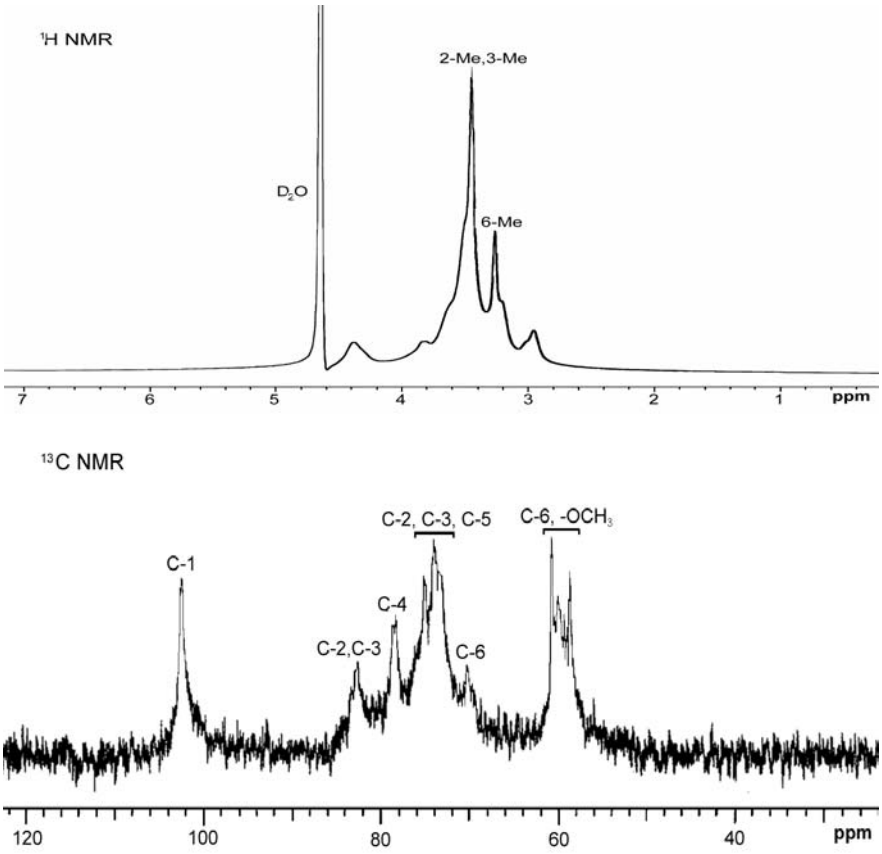


**Figure 1.** $^{1}$H and $^{13}$C NMR spectra of the MC-5 sample in $D_2O$.

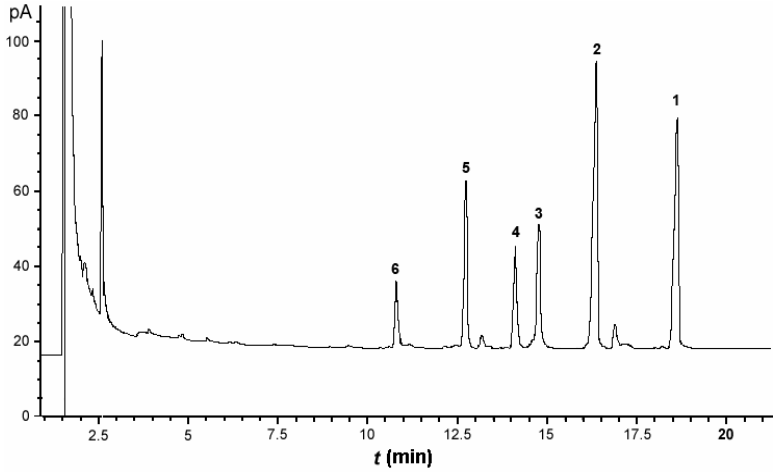


**Figure 2.** Gas chromatography trace of the MC-6 sample after total hydrolysis and acetylation. Signals1─6 represent 3-O, 2-O, 6-O, 2,3-di-O-, 2,6-di-O-, and 3,6-di-O-methyl glucitol derivatives, respectively.

**Table 1.** Reaction conditions and distribution of methyl groups in the MC samples.

| Reaction conditions and Substituent distribution | MC-1 | MC-2 | MC-3 | MC-4 | MC-5 | MC-6 | [a]MC-7 |
|---|---|---|---|---|---|---|---|
| Temperature (°C) | 25 | 25 | 25 | 25 | 30 | 35 | 25/35 |
| [b]Mole Ratio | 2 | 2 | 3 | 3 | 3 | 4 | 4 |
| Time (h) | 16 | 24 | 12 | 16 | 16 | 8 | 24 |
| $S_0$ | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| $S_2$ | 46.33 | 31.36 | 49.04 | 41.18 | 30.06 | 29.25 | 19.79 |
| $S_3$ | 23.17 | 35.95 | 14.87 | 20.03 | 25.68 | 23.52 | 3.99 |
| $S_6$ | 27.03 | 11.17 | 7.73 | 10.06 | 9.66 | 12.71 | 5.55 |
| $S_{23}$ | 1.54 | 6.97 | 7.69 | 4.60 | 13.27 | 10.50 | 14.07 |
| $S_{26}$ | 0.78 | 11.22 | 16.49 | 17.70 | 12.84 | 17.02 | 29.68 |
| $S_{36}$ | 1.16 | 2.60 | 4.17 | 5.67 | 7.69 | 6.99 | 24.87 |
| $S_{236}$ | 0 | 0.01 | 0 | 0.77 | 0.80 | 0 | 2.06 |
| $X_2$ | 0.49 | 0.50 | 0.73 | 0.64 | 0.57 | 0.57 | 0.66 |
| $X_3$ | 0.26 | 0.46 | 0.27 | 0.31 | 0.47 | 0.41 | 0.45 |
| $X_6$ | 0.29 | 0.25 | 0.28 | 0.34 | 0.31 | 0.37 | 0.62 |
| Total DS | 1.03 | 1.20 | 1.28 | 1.30 | 1.35 | 1.35 | 1.73 |

[a] Being firstly reacted in 25 °C for 12 h, and in 35 °C for 12 h with extra mounts of NaOH added.
[b] Mole ratio represents the mole amount of DMS divided by the mole amount of the OH groups of cellulose reacted.
$S_0$–$S_{236}$ are respectively glucitol and its mono-, di-, and tri-methyl derivatives determined by a gas chromatographic analysis.
*X*n is the mole fraction of glucitol derivatives substituted on the OH of C – $n$ ($n$ = 2, 3, and 6). For example, $X_2 = (S_2 + S_{23} + S_{26} + S_{236})/100$ [22]. Total DS equals $X_2 + X_3 + X_6$.

a heterogeneous substitution along the molecular chain of polymers [1, 9]. The GC results show clearly that the $X_2$ values are higher than $X_3$ and $X_6$ values in all MC samples, indicating the hydroxyl group at the C-2 position has the highest relative reactivity during the reaction. It is well known that the order of the relative reactivities is OH-2>OH-6>OH-3 for MC prepared from alkali-cellulose in aqueous solvent system [22]. Miyamoto et al [23] researched commercial MC using $^{13}C$ MNR to show that the ease of methylation is C-6≈C-2>C-3. Under ideal homogeneous reaction conditions, it is assumed that all AGU along the molecular chains of cellulose should be equally accessible for the reagent, and the hydroxyl groups at C-2, C-3, and C-6 positions in these AGU have the same relative reactivities. Thus the distribution of substituents in the monomers should be random. However, the vicinal substituent effects can't be neglected. Due to the adjacent acetyl function, the C-2 position has the highest acidity, and it is preferentially attacked in aqueous solution [1, 7]. Therefore, it is reasonable that the hydroxyl group at the C-2 position has the highest relative reactivity during the methylation reaction of cellulose in 7 wt % NaOH/12 wt % urea aqueous solution. The GC results also show that the $X_3$ values of the MC-2, MC-5, and MC-6 samples are higher than the $X_6$ values, but $X_6$ has higher values than $X_3$ in other samples, which differs from commercial MC. As mentioned previously, the relative reactivity of the hydroxyl group at the C-6 position is higher than that of the hydroxyl group at C-3 position for commercial MC. In this case, the relative reactivities of hydroxyl groups at C-3 and C-6 positions seem to be random and comparable, further indicating that AGU along the molecular chains of cellulose are equally accessible for the methylation reagent in the aqueous solution. Taking vicinal substituent effects into account, we can conclude that the MC samples synthesized in 7 wt % NaOH/12 wt % urea aqueous solution have a uniform distribution of substituents along the molecular chains.

As shown in Table 1, the reaction temperature, reaction time, and added amount of DMS affect the procedure of methylation in 7 wt % NaOH/12 wt % urea aqueous solution. Specially, the effect of the amount of DMS is obvious. With an increase of DMS amount, the DS values of the MC samples increased. Usually, it is well known that etherification of cellulose proceeds under the base conditions, because the hydroxyl functionality of cellulose is not a strong nucleophile even in the homogeneous solution to initiate reaction [1, 9]. Due to the existence of the sodium hydrate, the NaOH/urea aqueous solution is suitable for etherification of cellulose [15, 16]. In our study, DMS can react with water to form sulfuric acid neutralized with NaOH, which may result in the decrease of the reaction reactivity. It is difficult to attain MC with higher DS value using DMS as a methylation reagent in the 7 wt % NaOH/12 wt % urea system. In addition, cellulose is easy to precipitate when the reaction temperature is higher than 45 °C.

*Physical properties of MC samples*

The solubility of the MC samples in water and some other solvents is shown in Table 2. All MC samples have good solubility in organic solvents, i.e., dimethyl sulfoxide (DMSO) and pyridine. The MC-1 sample can't be dissolved in water at the room temperature; whereas other MC samples have good solubility in water and the 2 % (w/v) aqueous solutions of these samples show a reversible thermal behavior. Figure 3 shows the temperature dependence of the transparency of 2 % (w/v) aqueous solutions of the MC-2 and MC-7 samples; the values of $T_p$ were determined to be 50 °C and 59 °C, respectively. An obvious two-phase separation appeared in their aqueous solutions of the MC-2 and MC-7 samples when temperature was higher than 80 °C.

**Table 2.** Solubility, [$\eta$], $M_\eta$, and $M_\eta$ (th.) values of the MC samples.

| Sample | Solubility | | | | | [$\eta$] | $M_\eta$ | [a]$M_\eta$(th.) |
|---|---|---|---|---|---|---|---|---|
| | $D_2O$ | Methonal | THF | DMSO | Pyridine | (mL/g) | $\times 10^{-4}$ | $\times 10^{-4}$ |
| MC-1 | × | × | × | O | O | — | — | 10.89 |
| MC-2 | O | × | × | O | O | 382.2 | 9.47 | 11.04 |
| MC-3 | O | × | × | O | O | 407.8 | 10.50 | 11.11 |
| MC-4 | O | × | × | O | O | 404.1 | 10.35 | 11.12 |
| MC-5 | O | × | × | O | O | 409.4 | 10.56 | 11.17 |
| MC-6 | O | × | × | O | O | 428.6 | 11.36 | 11.17 |
| MC-7 | O | × | × | O | O | 335.1 | 7.69 | 11.50 |

O: Soluble, ×: Insoluble
[a] $M_\eta$ (th.) represents the theoretical molecular weight.

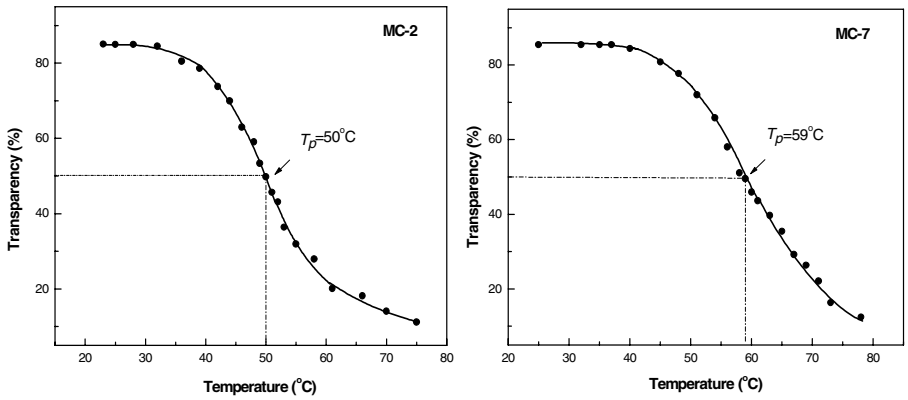


**Figure 3.** Precipitation behavior of the MC-2 and MC-7 samples indicated by the temperature-dependence of transparency for 2 % (w/v) aqueous solutions.

*Stability of NaOH/urea for methylation*

Table 2 lists the values of [$\eta$], $M_\eta$ and the theoretical molecular weights, $M_\eta$ (th.), of the MC samples. The $M_\eta$ (th.) values were calculated according to the molecular weight of starting cellulose ($M_\eta = 10.00 \times 10^4$) and the DS values. Compared with the $M_\eta$ (th.) values, the values of $M_\eta$ indicate that little degradation of the MC samples expect MC-7 occurred during the reaction in 7 wt % NaOH/12 wt % urea solution, which differs from cellulose ethers synthesized in LiCl/DMAc. The MC-7 sample exhibited obviously degradation; it might be due to extra amounts of NaOH added dropwise during the reaction. It has been reported that cellulose ethers synthesized in LiCl/DMAc have significant degradation during the procedure of the derivative reaction. Specially, the degradation extent of MC produced in LiCl/DMAc even exceeds 50 % [9]. To further clarify the stability of cellulose in 7 wt % NaOH/12 wt % urea solution, the $M_\eta$ change of cellulose in the solution with stored time increasing was measured. Figure 4 shows

the hydrolysis curve of 2 wt % cellulose solution in the 7 wt % NaOH/12 wt % urea solvent. The $M_\eta$ value of original cellulose material only decreased from $10.00 \times 10^4$ to $8.50 \times 10^4$ after the storage of 24 h at 25 °C, further suggesting that there was not significant decomposition of the cellulose molecules in the process of methylation.

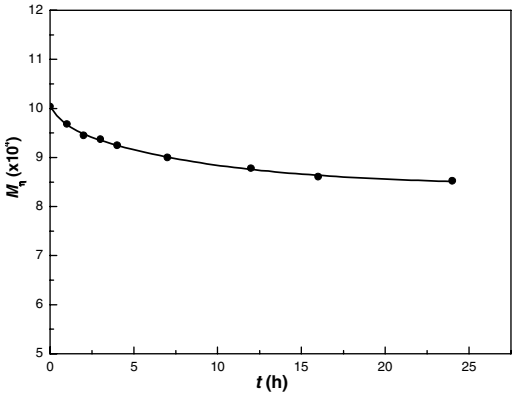


**Figure 4.** The hydrolysis curve of 2 wt % cellulose solution in the 7 wt % NaOH/12 wt % urea solvent.

## Conclusions

The methylation of cellulose in 7 wt % NaOH/12 wt % urea aqueous solution was a homogeneous reaction. The results from GC indicated there was a uniform distribution of methyl substitution along the MC molecular chains. Compared with the reaction temperature and time, the amount of dimethyl sulphate (DMS) as a methylation reagent had more obvious effect on the reaction. With an increase of DMS amounts, the DS values of the MC samples increased. All samples with DS values higher than 1.20 had a good solubility in water and some organic solvents, and showed a reversible thermal behavior in the 2 % (w/v) aqueous solutions. 2 wt % cellulose solution in the 7 wt % NaOH/12 wt % urea solvent was almost stable at the room temperature, and only little decomposition of the molecular chains occurred during the reaction. Therefore, the methylation of cellulose in 7 wt % NaOH/12 wt % urea solution appears to have advantages over convenient processes.

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## References

1. Dönges R (1990) Br Polym J 23: 315
2. Desbrières J, Hirrien M, Ross-Murphy SB (2000) Polymer 41: 2451
3. Liu H, Zhang L, Takaragi A, Miyamoto T (1998) Polym Bull 40: 741
4. Nishimura H, Donkai N, Miyamoto T (1997) Macromol Symp 120: 303
5. Takahashi S, Fujimoto T, Miyamoto T, and Inagaki H (1987) J Polym Sci Part A Polym Chem 25: 987
6. Takahashi M, Shimazaki M, Yamato J (2001) J Polym Sci Part B Polym Phys 39: 91

7. Heinze T, Liebert T (2001) Prog Polym Sci 26: 1689
8. Fink HP, Weigel P, Purz HJ, Ganster J (2001) Prog Polym Sci 26: 1473
9. McCormick CL, Callais PA (1987) Polymer 28: 2317
10. Chaudhari SNK, Gouden KC, Srinivasan G, Ekkundi VS (1987) J Polym Sci Part A Polym Chem 25: 337
11. Heinze T, Liebert T, Klüfers P, Meister F (1999) Cellulose 6: 153
12. Zhou J, Zhang L (2000) Polym J 2: 86
13. Cai J, Zhang L, Zhou J, Li H, Chen H, Jin H (2004) Macromol Rapid Commun 25: 1558
14. Zhang L, Cai J, Zhou J (2005) CN ZL 03128386.1
15. Zhou J, Zhang L, Deng Q, Wu X (2004) J Polym Sci Part A Polym Chem 42: 5911
16. Zhou Q, Zhang L, Li M, Wu X, Cheng G (2005) Polym Bull 53: 243
17. Brown W, Wiskstön R (1965) Eur Polym J 1: 1
18. Uda K, Meyerhoff G (1961) Macromol Chem 47: 168
19. Tezuka Y, Imai K, Oshima M, Chiba T (1987) Macromolecules 20: 2413
20. Sekiguchi Y, Sawatari C, Kondo T (2002) Polym Bull 47: 547
21. Arisz PW, Kauw JJ, Boon JJ (1995) Carbohydr Res 271: 1
22. Kondo T (1997) J Polym Sci Part B Polym Phys 40: 717
23. Takahashi S, Fujimoto T, Barua BM, Miyamoto T, Inagaki H (1986) J Polym Sci Part A Polym Chem 24: 2981