

Phase transition of 2,3-*O*-methylcellulose

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Summary

In this work, a series of 2,3-*O*-methylcellulose (MC) with different DS value were prepared. Its phase transition behavior in aqueous solution was studied in terms of DS value, concentration and molecular weight. The the following conclusions were obtained. (1) All the 2,3-*O*-MC samples show no sol-gel transition in aqueous solution despite the molecular weight. (2) No phase separation was observed for the 2,3-*O*-MCs with a DS value lower than 1.0, even when the temperature was raised to 95°C. (3) The precipitation temperature is surprisingly different between 2,3-*O*-MCs. and other MCs possessing comparable total DS value. (4) The precipitation temperature of 2,3-*O*-MCs depends on the molecular weight rather than on the concentration.

Introduction

Recently, regioselectively substituted MC such as 2,3-*O*-MC has become an important member in the MC family. By using it, many works have dedicated to clarify the formation of intra- and inter-molecular hydrogen bonds and the relationship between hydrogen bonds and certain physical properties (1-3). We also reported some results of relationship between degree of substitution (DS) and water solubility of *O*-methylcellulose and 2,3-*O*-carboxymethylcellulose, and determined that the water solubility of cellulose derivatives strongly depends not only on the degree of substitution, but also on the distribution of substituents along the cellulose chain (4-6). Besides these researches, phase transition of MC sample in aq. solution has also obtained much attention. It's well known that commercial MC samples show a thermally reversible sol-gel transition in aqueous solution, but the MC samples prepared by homogeneous reaction shows no sol-gel transition though phase separation may occur at high temperature in aq. solution (4,7).

However, few reports have concerned on the phase transition behavior of 2,3-*O*-MC sample, only Itagaki *et al.* (8,9) reported the gelation of cellulose whose hydroxyl groups are specifically substituted by the fluorescent groups. We think the phase transition behavior of MC can be elucidated more clearly by using the regioselectively substituted MC directly. To this end, the phase transition behavior of 2,3-*O*-methylcellulose was studied. By comparing with other kinds of MC, it was demonstrated that-OH group at C-6 position of every anhydroglucose (AHG) unit

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plays an important role for the phase transition behavior of MC samples. We further learned that phase transition may occur when DS value higher than a critical value (DS=1.2), which confirmed that the “crosslinking loci” was a necessary step for the transition.

Experimental

Materials

Whatman CF-11 cellulose powder (DP=220, England) and cellulose pulp (DP=1,200, Asahi Co., Japan) were used as starting materials. They were dried at 100°C under vacuum before use. Dimethylsulfoxide (DMSO), N,N-dimethylacetamide (DMAc) and pyridine were dehydrated over type 3A molecular sieves. Powdered sodium hydroxide was pulverised by grinding NaOH pellets in a domestic coffee mill. Other chemical reagents were used without further purification.

Cellulose/LiCl-DMAc

2% cellulose powder or pulp in LiCl-DMAc solution was prepared according to the method of McCormick (10).

6-O-triphenylmethylcellulose(6-O-tritylcellulose)

It was prepared by the Takahashi's method (11) with minor modification. Into a three-necked flask containing 200 g of the above cellulose solution, 70 ml of pyridine was added dropwise under stirring, then 40 g of tritylchloride was added successively. The reaction was performed at 100°C for 6 h. The product was precipitated by pouring the solution into methanol, washed and dried at 60°C under vacuum for 10 h. The degree of substitution of trityl group was determined to be 1.09 by elemental analysis and ¹H-NMR, and the yield was 95%.

6-O-trityl-2, 3-O-methylcellulose

It was synthesized according to Kondo's procedure (1). Samples with different DS values were prepared by step reaction.

2,3-O-methylcellulose

6-O-trityl-2,3-O-methylcellulose (1.0 g) was treated with dry HCl gas in 30 ml of CH₂Cl₂ at 0°C for 4 min under strong stirring (12). The detritylated mixture was washed with acetone, filtered, and redissolved into water, purified by dialysis and subsequent lyophilization. The 2,3-O-MCs from Whatman CF-11 and pulp were coded as MC-W and MC-P, respectively. Its structure was showed in figure 1.

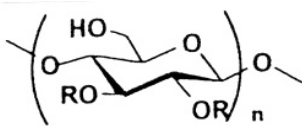


Figure 1 Chemical structure of 2,3-O-methylcellulose R=CH₃ or H

Methylcellulose prepared from homogeneous reaction was according to Turbak's (13) procedure by using whatman CF-11 as starting material, and was coded MC-H. Methylcellulose prepared by alkali process was according to Savage's method (14) by using the same material as MC-H, and was coded as MC-C.

Characterization

IR spectra were recorded on FTS6000 spectrometer. ^{13}C -NMR spectra were obtained with a JEOL GX400 spectrometer operating at 100.8 MHz. Deuterated dimethylsulfoxide (DMSO-d_6) was used as solvent at 80°C . The quantitative-mode ^{13}C -NMR measurement conditions followed closely those in the structural analysis of other cellulose derivatives (15). The relative DS value at an individual hydroxyl group was estimated from the ratio between peak areas. The peak areas were determined by the weight cut from photocopies.

Gelation temperature (T_g) and precipitation temperature (T_p) were measured on 1 wt% aqueous solutions of MC samples. A Shimadzu UV-2200 spectrophotometer was used for the evaluation of T_g and T_p . The transmittance at 600nm wavelength was measured as a function of temperature from the MC aqueous solutions, and the temperature to get 50 percent of the original transmittance value was considered as T_g or T_p (16).

Results and discussion

Preparation of 2,3-O-MCs It was reported that trityl protecting group shows high selectivity for the primary hydroxyl group on the 6-position of the AHG units in the cellulose chain (17,18). It can be deprotected easily with HCl gas. Therefore, it is useful to be used as starting material to prepare regloselectively methylcellulose. FT.i.r spectra of 6-O-trityl-2,3-O-MC and 2,3-O-MC samples showed that the characteristic absorbance at 3059 and 700 cm^{-1} for trityl group disappeared and a strong absorbance at 3400 cm^{-1} for hydroxyl group appeared in the spectrum of MC. Figure 2 shows the ^{13}C -NMR spectrum of 2,3-O-methylcellu-

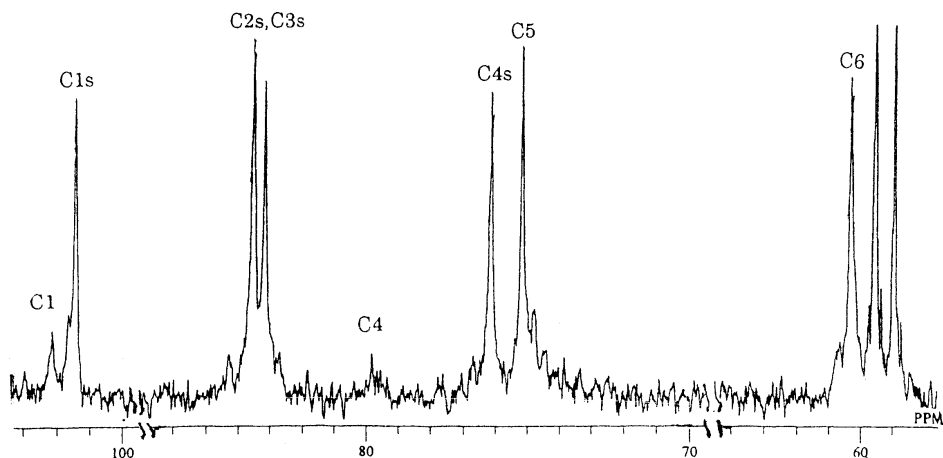


Figure 2 ^{13}C -NMR spectrum of 2,3-O-MC (DS=1.8) measured at 80°C in deuterated DMSO.

-lose sample from Whatman CF-11. The assignment of the peaks is according to ref. 4. No peak of C6s which appeared at 72 ppm is observed, which suggested that the -OH group at C-6 position was completely protected by trityl group. These results of FT i.r. and ^{13}C -NMR indicate that the trityl group was an effective protected group for preparation of 2,3-*O*-methylcellulose.

Relationship between sol-gel transition and DS value It is well known that the water-soluble commercial MC with a DS value range of 1.2-2.4 show thermally-reversible sol-gel transition in aqueous solution, and the gel temperature (T_g) of these MC is in a range of 30-60°C, and it decreases with the DS value increasing (4). Concerning the mechanism of sol-gel transition, both Kato (19) and Savage (14) contributed it to the presence of tri-and/or di- methylglucose sequence, which act as “crosslinking loci” on warming, and the less substituted hydrophilic units are stable in the water molecule environmental. In the case of MC samples prepared by this work, as shown in Table 1, all the 2,3-*O*-MC shows no sol-gel transition in aqueous solution. For example, when MC samples with a DS value lower than 1.10, no phase separation was observed even the temperature was raised to 95°C despite the molecular weight. From this view point, it may be concluded that the gelation or precipitation can't take place until the DS value reaches a critical volume, where the forces of the hydrophobic interaction between methylcellulose molecules are strong enough to form gel or precipitation. The critical DS value is approximately 1.2, since for MC-W-2 with a DS value of 1.2 the precipitation occurred at about 90°C in aqueous solution, which is much higher than the commercial MC with corresponding DS value. While comparing with the MC prepared from homogeneous reaction, the transition manner is also so different from each other. MC-H with DS value of 1.3 by methylation of cellulose in 10% LiCl-DMAc have a precipitation temperature at 35°C. On the other hand, the sample MC-P-2 with a DS value of 1.2 precipitated at 70°C. From the results mentioned above, the T_p or T_g is affected heavily by the distribution of substituents in the AHG unit, the absence of methoxyl group at C-6 hydroxyl position may increase the T_p .

Table 1 Phase transition of some representative MC in water

Sample Code	Total DS	Distribution of substitution			Gelation/precipitation Temperature
		C2	C3	C6	
MC-W-1	0.99	0.57	0.42	0	No gelation
MC-W-2	1.2	0.67	0.53	0	T_p at 90°C
MC-P-1	1.1	0.59	0.51	0	No gelation
MC-P-2	1.2	0.66	0.54	0	T_p at 70°C
MC-H	1.3	0.5	0.4	0.6	T_p at 35°C
MC-C	1.7	0.6	0.4	0.7	T_g at 50°C

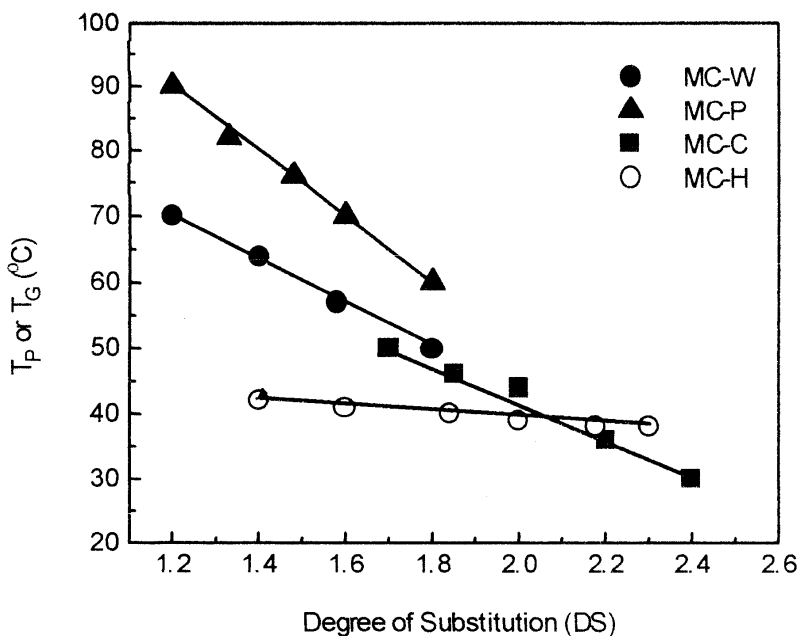


Figure 3 The relationship between T_p or T_g and DS value

Concerning the reasons, it may be caused by the uniform structure of 2,3-*O*-MC whose every AHG unit in its backbone was substituted by methyl group at C_2 , C_3 hydroxyl group positions. When heated in solution, every AHG unit can play the same role, i. e., “crosslinking loci”, to result in the occurrence of precipitation. Unlike commercial MC, only the tri-/or di- methylglucose sequence act as ‘crosslinking loci’, other sequences are stable in the water, to resulting the formation of gel.

Figure 3 shows the relationship between total DS value and T_g or T_p of MC samples in aqueous solution. For 2,3-*O*-MC samples such as MC-W and MC-P in the DS range of 1.2 - 2.0, the phase separation can be occurred when the temperature higher than 50°C. The upper side of curve MC-W or MC-P is two-phase area, i.e., solid-liquid coexist. The lower side is one phase area, i.e., liquid. While for commercial MC (MC-C) in the DS range of 1.7 - 2.4, gelation may take place when the temperature lower than 50°C, the upper side is gel state, and the lower side is liquid state. The curve of MC from homogeneous methylation is also shown in the figure. From the figure, a large difference of T_p between MC-W and MC-P was also observed, that is, the higher molecular weight the lower precipitation temperature. In general, the following equation supposed by Flory (20), later modified by Kato (19), can be applied to describe the relationship between T_p or T_g , and molecular weight,

$$1/T_p = A + B \ln x$$

where, x is the degree of polymerization, A and B are positive constant. Therefore, the result in our experiment is reasonable. it likes the classical polymer which decreases in T_p with increase in molecular weight.

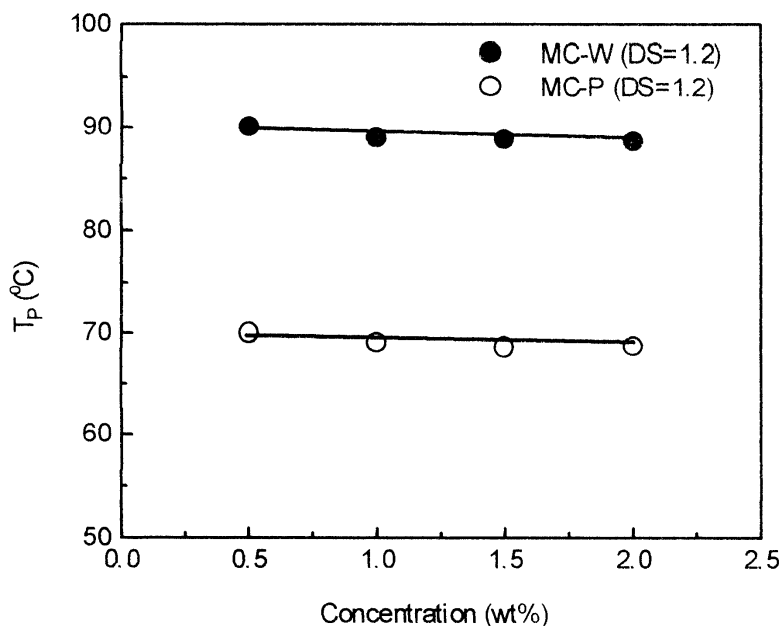


Figure 4 The relationship between T_p and concentration

It should be pointed out that another interesting fact. Figure 4 shows the relationship between concentration and T_p , of MC sample. The result showed the precipitation temperature has no noticeable difference under the concentration range of 0.5 -2.0 wt% for 2,3-*O*-MC. Whereas Nishinari (21) reported that T_g shifted to lower temperature with increasing concentration of commercial methylcellulose, Sarkar (22) and Isogai (23) also reported phase separation temperature of polymer solutions depends on the polymer concentration. For 2,3-*O*-MCs, it seems that the molecule-molecule interaction which results precipitation, is a function of temperature only, and has no relation with concentration.

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