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# Gelation of chemically cross-linked methylcellulose studied by DSC and AFM

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**Abstract**

Gelation of methylcellulose (MC) and chemically cross-linked MC via urethane linkage (MCPU) with various molecular weights was investigated in a concentration range from 0.1 to 4.0 wt %. On heating of aqueous solution of MC, three transitions, clear sol to turbid sol, sol to gel and phase separation due to water separation were observed. With increasing molecular weight the transition temperatures decrease. In contrast, no effect of molecular weight on the transition temperatures was observed for MCPU. Structural change of water restrained by MC and MCPU was investigated by DSC. Melting and crystallization of water in both series of sample showed no significant difference, however, a molecular weight dependency of the glass transition was observed for MC. The results obtained in this study indicate that hydrophobic aggregation is restricted by cross-linking. Images of atomic force microscopy (AFM) indicated that from 6 to 16 molecules piled in two layers form a bundle. By chemical cross-linking, molecular chains align in the mono layer, molecular bundles consisting of more than 10 molecules coaggregate and form a large flexible ring.


*Keywords:* Methylcellulose; Urethane; Water; DSC; AFM

## 1. Introduction

Various kinds of polysaccharides are known to form hydrogels when they are homogeneously dissolved in water and maintained for a certain period at around room temperature. Among a large variety of physical hydrogel forming polysaccharides, methylcellulose (MC) shows unique characteristics i.e. the gel state of MC can be obtained by the heating of aqueous solution (Desbrieres, Hirrien, & Rinaudo, 1998a, 1998b; Desbrieres, Hirrien, & Ross-Murphy, 2000; Haque & Morris, 1993; Haque, Richardson, Morris, Gidley, & Caswell, 1993; Hatakeyama & Hatakeyama, 2004; Hirrien, Hevillard Desbrières, Axelos, & Rinaudo, 1998; Kato, Yokoyama, & Takahashi, 1978; Kobayashi, Huang, & Lodge, 1999; Kuhn, Moser, & Majer, 1961; Li, 2002; Li et al., 2001; Nishinari, 1997; Nishinari, Hofmann, Moritaka, Kohyama, & Nishinari, 1997; Rinaudo & Desbrieres, 2000; Sarkar, 1979, 1995; Sarkea & Walker, 1995; Wang & Li, 2005). The gelation mechanism of MC is thought to be similar to that of the cloud point of nonionic surfactants. It is thought that the cloud point is attributed to molecular coaggregation via hydrophobic interaction at high temperature where surfactant molecules do not readily hold the surrounding water molecules. On this account, the cloud point increased with increasing hydrophilicity of the sample. By heating MC solution, water molecules attached to the hydroxyl group of MC separate from the molecular chains by thermal enhancement. MC chains coaggregate with each other via hydrophobic interaction and three dimensional networks are gradually established.

MC is a thermoreversible hydrogel that does not readily maintain a gel structure at room temperature. In practical terms, stable hydrogels derived from cellulose derivatives are thought to have a large variety of applications.

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Through our series of studies of gel formation of polysaccharides, chemical gelation is thought to be a possible choice in solving the above problem (Hatakeyama, Asano, Hatakeyama, & Kennedy, 2002; Park & Ruckenstein, 2001). At the same time, it is interesting to know the length of molecular chains which are connected with cross linking formation. On this account, MC was chemically cross-linked in aqueous solution via urethane linkage (MCPU).

In this study, gelation of MC and MCPU with various molecular weights was systematically investigated in a wide concentration range. The aim of this paper is to clarify the effect of chemical cross-linking on the gelation mechanism of MC in order to develop stable hydrogels in a wide temperature range. Nano-level conformation of both MC and MCPU is also investigated using atomic force microscopy.

## 2. Materials and methods

### 2.1. Materials

Four fractions of MC with different degrees of polymerization were purchased from Nakrai Tesk, Ltd. Osaka. The viscosity of 2% solution at 20 °C of each fraction was 100, 400, 1500 and 4000 mPa s, respectively. The degree of methoxy group substitution was 1.8. Each fraction was designated as MC100, MC400, MC1500 and MC4000, respectively.

Chemically cross-linked MC was prepared as follows, (1) MC powder was dissolved in water (concentration = 8.2%) and stirred until a homogeneous solution was obtained. (2) water soluble hexamtethylene diisocyanate derivative (HDI) was mixed with water and stirred until a homogeneous solution was obtained, (3) a small amount of dibutyltin dilaulate was added to HDI solution as a catalyst, (4) MC and HDI aqueous solutions were mixed, (5) mixing ratio was controlled in order to obtain a sample with NCO/OH ratio = 0.2 mol $mol^{-1}$, (6) after vigorous stirring, the solution was annealed at 70 °C for 0.5 h, (7) the obtained gel (MCPU) was maintained in a refrigerator. A schematic chemical structure is shown in . Fig. 1. MCPU prepared from MC with different viscosity is designated as MCPU100, MCPU400, MCPU1500 and MCPU4000, respectively.

### 2.2. Visual observation of sol–gel transition temperature

MC powder and MCPU were dissolved in deionized water at 25 °C. After the solutions were maintained for 2 days at 25 °C, they were stirred for 2 h at 25 °C. Concentrations of aqueous solutions of MC and MCPU used for measuring sol–gel transition temperature are shown in Table 1.

Five milliliters of aqueous solution was poured in a test tube with diameter of 1.6 cm. The height of the sample was 3.0 cm. A thermometer was inserted into the solution and

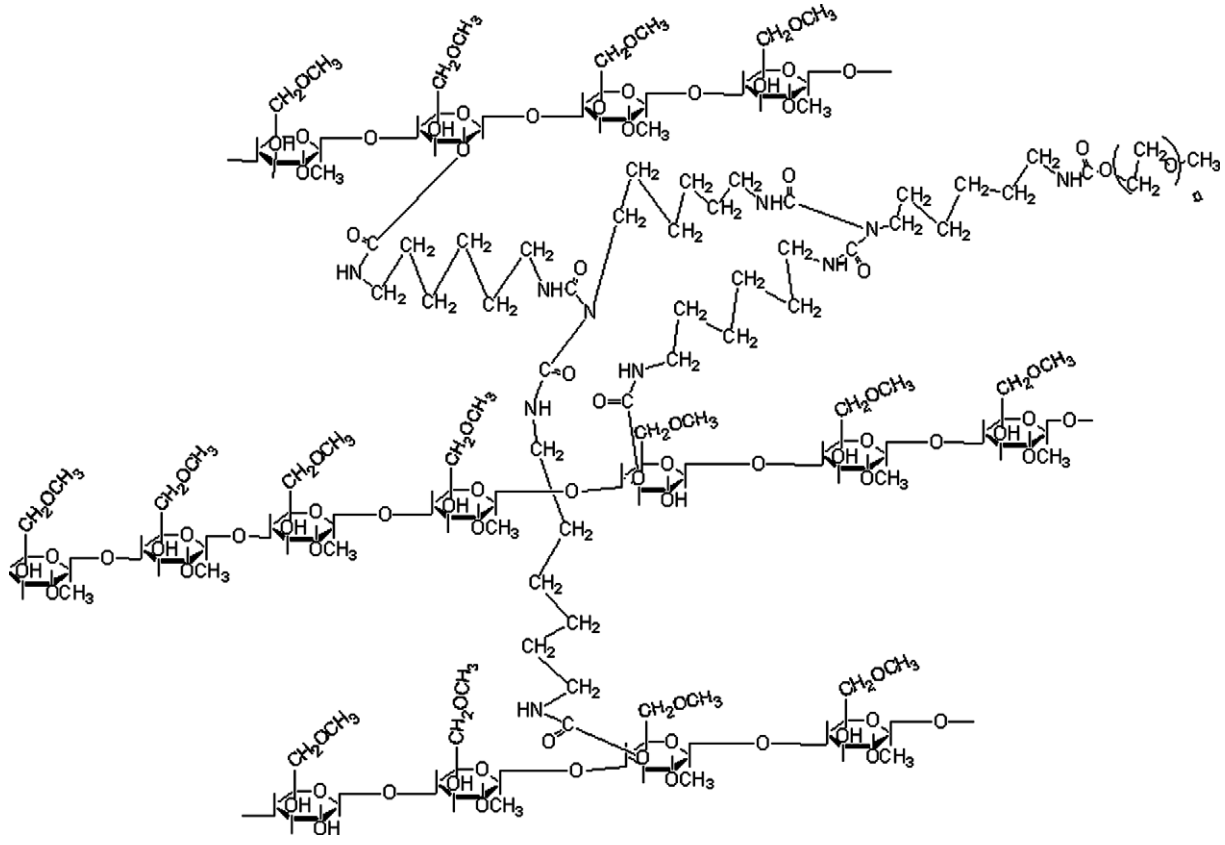

Fig. 1. Schematic chemical structure of MCPU.

Table 1
Concentrations used for sol–gel transition temperature measurements

| Sample | Concentration/wt % | | | | | | |
|---|---|---|---|---|---|---|---|
| MC100, MCPU100 | | | 0.4 | 0.5 | 1.0 | 2.0 | 4.0 |
| MC400, MCPU400 | | 0.2 | 0.4 | 0.5 | 1.0 | 2.0 | |
| MC1500, MCPU1500 | | 0.2 | 0.4 | 0.5 | 1.0 | 2.0 | |
| MC 4000, MCPU4000 | 0.1 | 0.2 | 0.4 | 0.5 | 1.0 | | |

the test tube was placed in a water bath, which was heated from 25 to 95 °C. Heating rate was 3–5 °C/min. The temperatures at which the transparent aqueous solution started to become turbid ($T_t$), the turbid solution became completely rigid ($T_{s-g}$) and phase separation occurred ($T_{ps}$) were noted. In order to confirm the repeatability of each experiment, the same sample was cooled and heated three times.

Thermal hysteresis of gelation was measured as follows. After the phase separation was observed, the sample was maintained for 5–6 min at that temperature. After that, the test tube was cooled to 25 °C. The temperature where the gel starts to be transparent was recorded ($T_{s(-g)}$). The temperature difference ($\Delta T = T_{sg}$-$T_{g\text{-}s}$) was calculated.

### 2.3. Differential scanning calorimetry

A Seiko differential scanning calorimeter 220 C was used to measure the phase transition of water in MC and MCPU. Sample weight was ca. 5 mg, heating rate was 10 °C $min^{-1}$ and an aluminium sealed type sample pan was used. Both MC and MCPU with various water contents were measured. Temperature was varied from −150 to 80 °C. The sample was cooled from 25 to −150 °C and heated from −150 to 80 °C at 10 °C $min^{-1}$ (first heating). After maintaining the sample at 80 °C for several minutes, the sample was cooled at 40 °C $min^{-1}$ to −150 °C. Again the sample was heated from −150 to 80 °C at 10 °C $min^{-1}$ (2nd heating). Data obtained from the 2nd heating was mainly used in this study. Water content [$W_c$ = (mass of water)/(mass of dry sample)] was varied from 0 to ca. 3.5 g $g^{-1}$. The exact water content of the sample was calculated as reported previously (Hatakeyama & Hatakeyama, 1998).

### 2.4. Atomic force microscopy

MC and MCPU were dissolved in purified water and the solution with 10 μg/ml was prepared. The above solution was diluted and the necessary concentrated solution obtained. The above solution was diluted according to measurement conditions. The solution, micro-filter, syringe and syringe needle were maintained at 40 °C for 30 min. Adhesive tape was attached to the mica surface and detached. Solution was dropped onto the newly cleaved surface thus obtained.

A Seiko Instruments scanning probe microscope, SPA400, was used. Frequency was 1 Hz and measurements were carried out by tapping mode. The value of measured width of the sample was calibrated taking into consideration the geometrical shape of the needle, i.e. the locus of cantilever tip is larger than real size of particle, since the size of the tip (radius = 10 nm) is larger than that of sample as illustrated in Fig. 2. In this study, the cross section of sample was assumed to sphere (radius = a) and real width (2a) was calibrated from apparent width ($W$) by $W = 4\sqrt{10a}$.

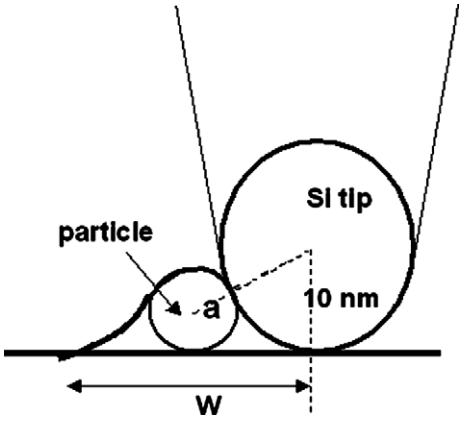


Fig. 2. Schematic illustration of locus of tip of cantilever.

## 3. Results and discussion

When aqueous solutions were heated from 25 °C, the solution starts to become turbid at around 40–60 °C ($T_t$). $T_t$ depended on molecular weight and concentration. With increasing temperature, the turbid solution became rigid and a homogeneous gel was formed when the sample was not stirred. In this study, the temperature where the turbid solution changed into a homogeneous gel was defined as sol–gel transition temperature ($T_{s\to g}$). The gel samples with high molecular weights were stable and gel shape was maintained even when they were inverted. However, the gel samples with low molecular weights were fractured. In the cases of concentrated and high molecular mass samples, the whole solution was completely converted into the gel at $T_{s\to g}$. In the case of MCPU, gel was formed in the same concentration range as MC, however $T_t$ could not be observed. When the gel was successively heated under slow stirring, the gel portion suddenly coaggregated accompanied with a large amount of water exclusion, and phase separation ($T_{ps}$) could be observed. The above abrupt syneresis was observed for both MC and MCPU samples with all molecular mass range. In general, the above coaggregation was observed at a temperature 5–10 °C higher than $T_{s-g}$ under mild stirring. If the gel was vigorously stirred, the gel was separated into a small fragment and did not coaggregate in one assembly.

Fig. 3a and b show the relationships between $T_t$, $T_{s\to g}$, $T_{ps}$ and concentration for the sample of MC400 (Fig. 3a)

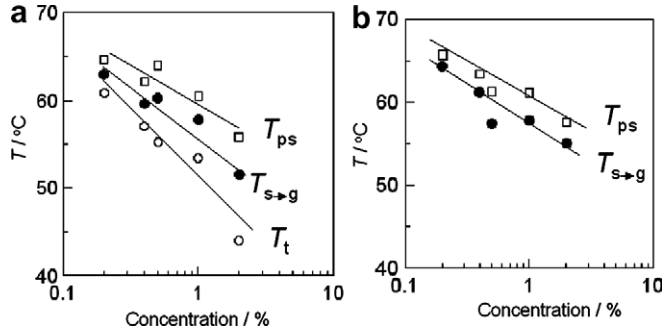


Fig. 3. Clear sol to turbid sol ($T_t$), sol–gel ($T_{s\to g}$) and phase separation ($T_{ps}$) temperatures of MC400 and MCPU400 with NCO/OH ratio = 0.2 as a function of concentration. (a); MC400, (b) MCPU400.

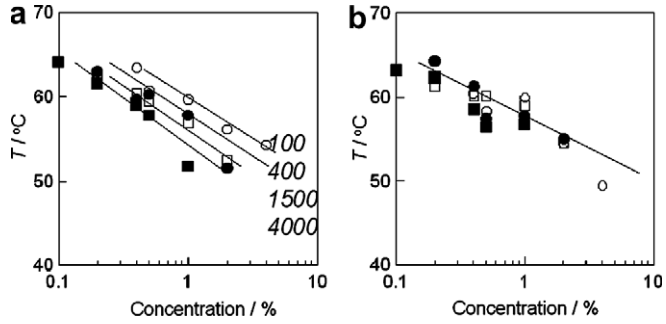


Fig. 4. Relationships between sol–gel transition temperature ($T_{s\to g}$) and concentration of MC and MCPU with various viscosities. (a); MC, (b) MCPU (○) 100 mPa s, (□) 400. (●) 1500, (■) 4000.

and MCPU400 (Fig. 3b), respectively. As clearly seen in Fig. 3a, the three temperatures, $T_t$, $T_{s\to g}$ and $T_{ps}$ decrease with increasing concentration. In MCPU, $T_t$ is not observed, however, $T_{s\to g}$ and $T_{ps}$ decrease with increasing concentration in a similar manner to MC samples. A similar tendency was obtained for the other MC and MCPU samples having different molecular mass, although the figures are not shown here.

Fig. 4a and b show relationships between sol–gel transition temperature and concentration of MC and MCPU with various viscosities. Clear sol to turbid sol ($T_t$), sol–gel ($T_{s\to g}$) and phase separation ($T_{ps}$) temperatures decreased with increasing concentration. This observation did not agree with the reported results of Wang & Li (2005). Gradients of the curves for all the MC samples are almost similar. Curves overlap with each other when the concentration axis shifts to a certain extent. This suggests that gelation occurs in a similar mechanism regardless of molecular weight. In contrast, $T_{s-}$ values of all MCPU samples are located on a line although data are scattered compared with those of MC. This suggests that all MCPU samples form gels in a similar manner. The fact that no effect of molecular mass was observed indicates that the chemical cross-linking homogeneously takes place and that the molecular distance between cross-linking points is almost even.

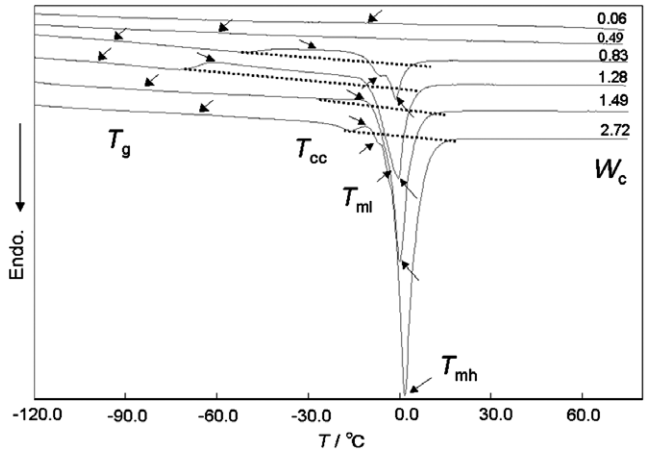


Fig. 5. Representative DSC heating curves of water restrained by MC (=1500 mPa s). Numerals in the figure show water content (g g$^{-1}$).

It is known that the sol–gel ($T_{s\to g}$) and gel–sol transitions ($T_{g\to s}$) show a large temperature hysteresis for other gel-forming polysaccharides. As described in the experimental section, temperature difference ($\Delta T$) of both transitions was visually observed. $\Delta T$ value of MC was ca. 25–30 °C and decreases with increasing molecular mass. $\Delta T$ value of MCPU showed no significant difference to those of MC.

In order to investigate the structural change of water in MC and MCPU, MC and MCPU with various water contents were measured by DSC. Fig. 5 shows representative stacked DSC heating curves of MC (=1500 mPa s) with water contents, ($W_c$) = g g$^{-1}$. As indicated by the arrow, glass transition ($T_g$), a small cold crystallization ($T_{cc}$) and melting peak ($T_{mh}$) with a shoulder in the low temperature side ($T_{ml}$) can be seen. Fig. 6 shows representative stacked heating DSC curves of MCPU (=1500 mPa s). From DSC heating curves of both samples, no significant difference was observed, except for the base line deviation due to glass

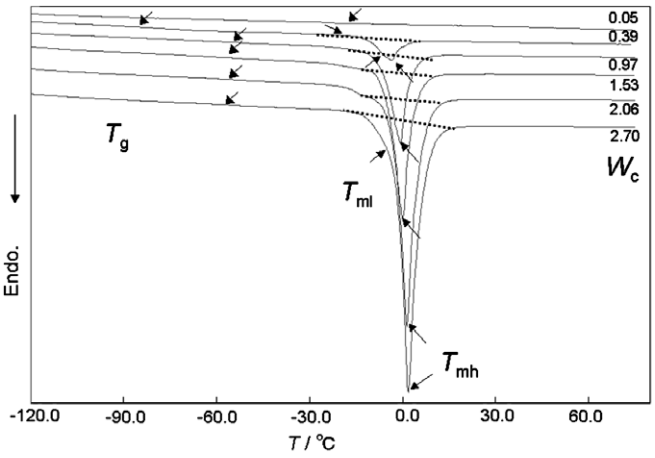


Fig. 6. Representative DSC heating curves of water restrained by MCPU (=1500 mPa s). Numerals in the figure show water content (g g$^{-1}$).

transition of MCPU samples which was slightly difficult to identify.

Each transition peak temperature is designated as $T_g$, $T_{cc}$, $T_{ml}$ and $T_{mh}$ from the order of low to high temperature. Water content of MC and MCPU samples with different molecular mass was varied from 0 to ca. 3.5 g $g^{-1}$. Each transition temperature was determined using 2nd heating curve and phase diagram for all samples was established. In Fig. 7, a schematic phase diagram is shown. $T_g$, decreases with increasing $W_c$ and reaches a minimum point. The $T_g$, value of the minimum point is designated as $T_{gmin}$ and $W_c$ where $T_{gmin}$ is observed is defined as $W_{c\ Tgmin}$. The first-order phase transition, $T_{cc}$, $T_{ml}$ and $T_{mh}$ are recognizable at a $W_c$ range larger than $W_{c\ Tgmin}$. The phase diagram indicates that water is solidified as non-freezing water and no ice was formed in the system in a $W_c$ smaller than $W_{c\ Tgmin}$.

Fig. 8a and b show magnified $T_g$ curves of both MC (Fig. 6a) and MCPU (Fig. 6b) with various viscosities. $W_{c\ Tgmin}$ of MC samples shifts to the high $W_c$ side and $T_{gmin}$ decreases with increasing viscosity. In contrast, $T_{gmin}$ of MCPU was maintained at −95 °C and $W_{c\ Tgmin}$ at 0.5 g $g^{-1}$ regardless of viscosity.

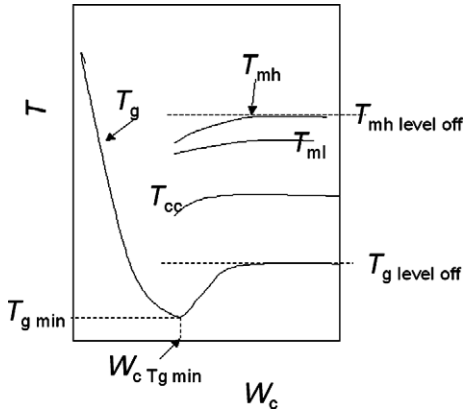


Fig. 7. Schematic phase diagram of MC and MCPU. $T_g$; glass transition, $T_{cc}$; cold crystallization, $T_{mh}$; melting peak in the high temperature side, $T_{ml}$; shoulder in the low temperature side.

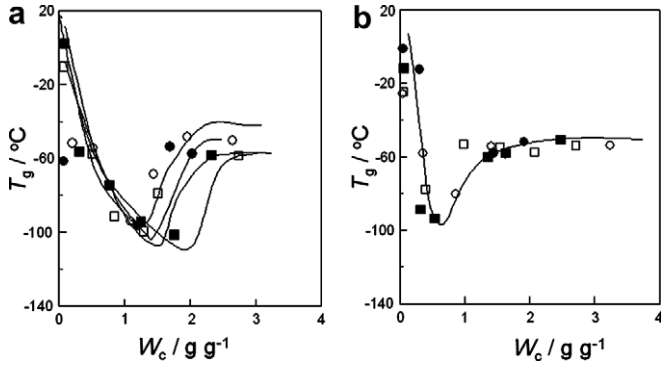


Fig. 8. Relationships between glass transition temperature ($T_g$) and water content. (a) MC, (b) MCPU (○) 100 mPa s, (□) 400. (●) 1500, (■) 4000.

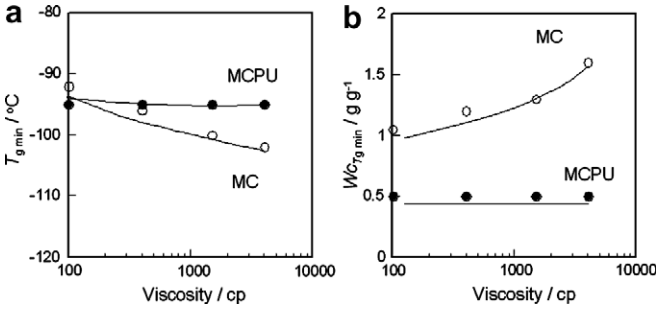


Fig. 9. (a), Relationships between $T_{gmin}$ and viscosity, (b) $W_{c\ Tgmin}$ and viscosity (○) MC, (●) MCPU.

Fig. 9a and b show relationships between $T_{gmin}$ (Fig. 9a), $W_{c\ Tgmin}$ (Fig. 9b) and viscosity. $T_{gmin}$ of MC linearly decreases with increasing viscosity. In contrast, values of MCPU maintain a constant value as a function of viscosity. $W_{c\ Tgmin}$ of MC increases with increasing viscosity, however that of MCPU maintains a constant. The above results indicate that the molecular motion of MCPU is restricted by chemical cross-linking.

The amount of non-freezing water ($W_{nf}$) restrained by MC and MCPU was calculated using melting enthalpy of ice (Hatakeyama & Hatakeyama, 1998). $W_{nf}$ increases with increasing $W_c$ and levels off at a characteristic amount ($W_{nf\ level\ off}$) which is varied by chemical and higher order structure of each sample. $W_{nf}$ values were calculated for all samples measured in this study. Representative $W_{nf}$ curves are shown in Fig. 10a. No significant difference was observed between two samples. The value of $W_{nf\ level\ off}$ was obtained for all samples and relationships between $W_{nf\ level\ off}$ and viscosity are shown in Fig. 10b. Values of $W_{nf\ level\ off}$ linearly increase with increasing viscosity and no difference is found between MC and MCPU.

Morphological observation was carried out by AFM. In order to find a suitable condition for sample preparation, MC samples (=25 mPa s) with various concentrations were at first observed by AFM, since the low molecular mass sample was easier to drop the solution onto mica surface. As shown in Fig. 11, molecular bundles are separated observed at the concentration 0.0001%. The height of each molecular bundle was ca. 1.4 nm and calibrated width was

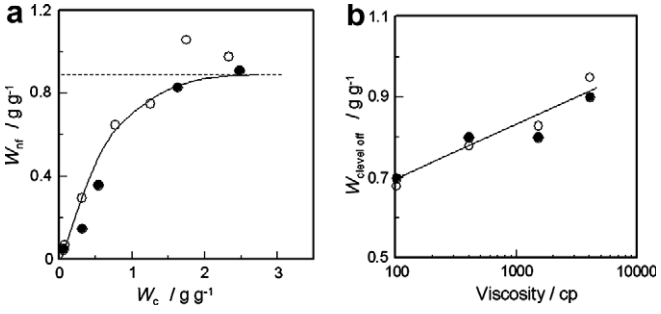


Fig. 10. (a) Relationships between $W_{nf}$ and $W_c$ of MC (=4000 mPa s) and MCPU (=4000 mPa s, NCO/OH ratio = 0.2), (b) $W_{nf\ level\ off}$ as a function of viscosity for MC and MCPU. (○) MC, (●) MCPU.

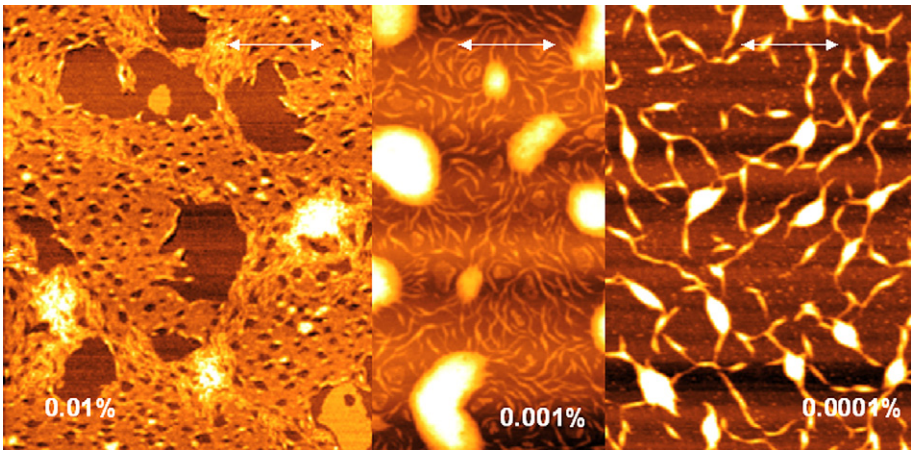


Fig. 11. AFM images of MC (=25 mPa s) with various concentrations. Numerals in the figure show concentration. Arrows indicate 0.5 μm.

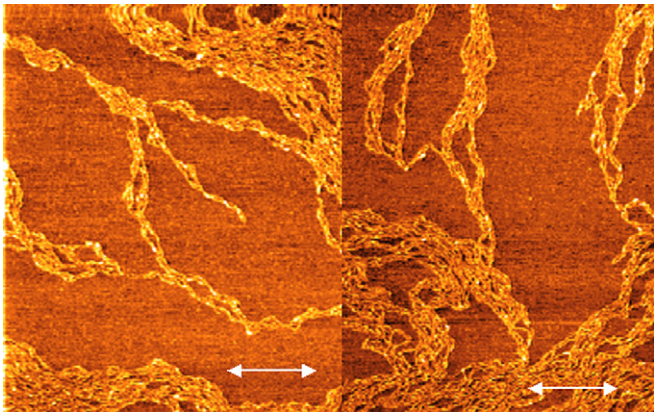

Fig. 12. AFM images of MCPU (=25 mPa s). Concentration 0.01 wt%. Arrows indicate 0.5 μm.

4.3 nm. By chemical cross-linking, it became difficult to prepare the dilute solution. As shown in Fig. 12, the ring-like structure can be seen in some parts while the other part is covered with flat, coaggregated molecular assemblies. By chemical cross-linking, the height of molecular assemblies changed to 0.7 nm, although the width was scattered in a wide range, from 1 to 60 nm. This suggests that a part of the molecule exists in a single form, and the other part is connected with an assembly whose size is ca. 60 nm.

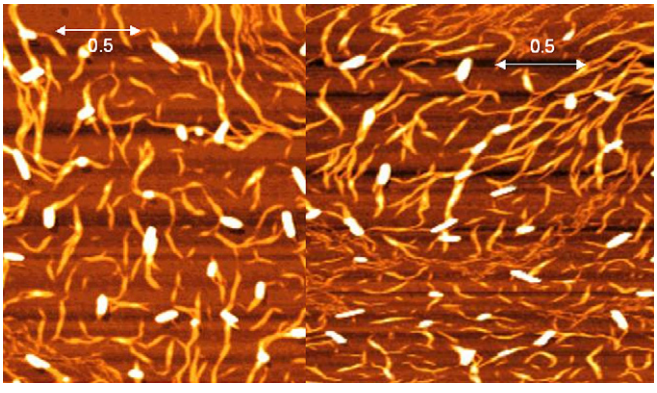


Fig. 13. AFM images of MC (=100 mPa s). Concentration = 0.0001 wt%. Arrows indicate 0.5 μm.

Fig. 13 shows AFM images of MC (=100 mPa s) with concentration 0.0001 wt%. The height of molecular bundles was ca. 1.4 nm and width was categorized into several groups, i.e. 2.1, 3.5, 4.2 and 6.3 nm. The standard deviation of each group was small. By chemical cross-linking, as shown in Fig. 14, the height became 0.7 nm and width was ca. 10 nm.

## 4. Conclusions

From the above results, it is considered that MC gelation proceeds in the following manner. When MC molecules are dissolved in aqueous media, each molecule is wrapped with water molecules. The DSC results indicate that each hydroxyl group of MC molecules restrains non-freezing water molecules. MC molecules that restrained the non-freezing water are surrounded by free water molecules. By heating, molecular motion is enhanced and water molecules surrounding MC molecules become easily separated, thus hydrophobic interaction between MC chains is established. By chemical cross-linking, free molecular movement is restricted. As shown in Fig. 2, $T_{s-g}$ shifted to the high temperature side by cross-linking. At the same time, molecular weight dependency on $T_{s-g}$ could not be observed for MCPU. It is thought that the molecular mobility becomes equal since the molecular weight between cross-linking points is the same when NCO/OH ratio is the same value. The effect of the chain end structure seems to be negligible. The molecular motion of whole chain molecules of MC is affected by molecular mass. In contrast, the glass transition temperature of MCPU was almost similar to the value of the lowest molecular mass sample. This indicates that free rotation of MC chains accompanied by a characteristic number of non-freezing water depends on the molecular mass between cross-linking points. AFM images show that MC molecules (=100 mPa s) form bundles of 5–16 molecules which are piled in two layers. By chemical

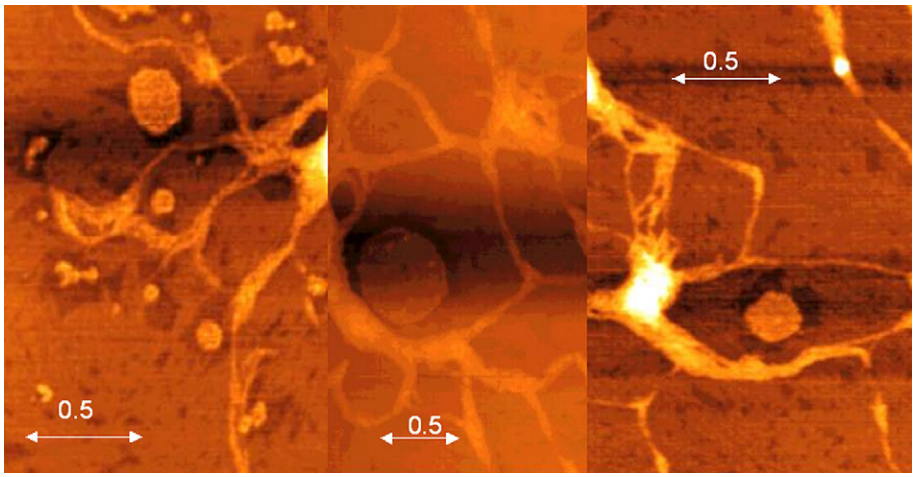


Fig. 14. AFM images of MCPU (=100 mPa s). Concentration 0.01 wt%. Arrows indicate 0.5 μm.

cross-linking, molecular bundles change to form one layer and more than 10 molecules align forming large rings.

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