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Microstructure and aggregation behavior of methylcelluloses prepared in NaOH/urea aqueous solutions

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Three water-soluble methylcelluloses (MCs) were prepared through homogeneous reaction in NaOH/urea aqueous solution, using dimethyl sulfate as a methylation reagent. The microstructure of the MC samples was characterized by IR, GC/MS, NMR, while dilute solution properties were measured by SEC–LLS, DLS and viscometer. The total degrees of substitution (DS) of the MC samples were 1.09, 1.42 and 1.56, respectively. However, we found that the relative DS value varies with the position of the hydroxyl group, i.e., C-2 > C-3 ≈ C-6, indicating the difference of reaction activity of different hydroxyl groups. In aqueous solution, MC has a trendency to form aggregates and hard to form actual solution, even at low concentration and low temperature, which was confirmed by the SEC–LLS and DLS result that isolated MC chains and large aggregates coexisted in the dilute aqueous solution. MC aqueous solutions showed two-stage temperature dependence of hydrodynamic radius. In the first stage, i.e., the temperature ranges from 20 to 65 °C, the hydrodynamic radius of MC displayed bimodal distribution, corresponding to the single chains and large aggregates. While in the second stage, i.e., the temperature higher than 70 °C, only large aggregates appeared. The results also proved that the microstructure of MC had a great influence on its physical properties.

1. Introduction

Methylcellulose (MC) is the simplest derivative of cellulose and is prepared by replacing the cellulose hydroxyl groups by methoxyl groups (Dönges, 1990). Commercial MC has been widely used as a thickener for foods and cosmetics, a coating material for medicines and a binder for ceramic and cement since it was first produced in 1938 (Dönges, 1990; Sekiguchi, Sawatari, & Kondo, 2003; Viera, Filho, de Assuncão, Meireles, Vierira, & de Oliveira, 2007; Yin, Nishinari, Zhang, & Funami, 2006). Usually, commercial MC is synthesized in a heterogeneous procedure with the cellulose slurry under alkaline condition, because of the insolubility of cellulose in water and in most organic solvents on account of its strong hydrogen bonding and high crystallinity. Therefore, commercial MC is a heterogeneous polymer consisting of highly substituted zones called "hydrophobic zones" and less substituted ones called "hydrophilic zones" (Arisz, Kauw, & Boon, 1995). It is well known that commercial MC is water-soluble over a degree of substitution (DS) range from 1.2 to 2.4, and it exhibits an interesting thermally reversible sol–gel transition in aqueous solutions (Haque & Morris, 1993; Heymann, 1935; Kato, Yokoyama, & Takahashi, 1978; Sarkar, 1979). The extensive studies have been conducted to examine the thermal gelation properties, the mechanism of gelation, as well as the gel network structure of MC (Desbrières, Hirrien, & Rinaudo, 1998; Desbrières, Hirrien, & Ross-Murphy, 2000; Hirrien, Chevillard, Desbrières, Axelos, & Rinaudo, 1998; Kobayashi, Huang, & Lodge, 1999; Li, 2002; Li, Liu, & Lim, 2007; Li, Shan, Yue, Lam, Tam, & Hu, 2002; Li, Thangamathesvaran, Yue, Tam, Hu, & Lam, 2001; Onoda-Yamamuro, Ramamuro, Inamura, & Nomura, 2007; Takahashi, Shimazaki, & Yamamoto, 2001a,b; Vigouret, Rinaudo, & Desbrières, 1996; Wang & Li, 2005; Wang, Li, Chen, & Yang, 2007; Wang, Li, Liu, Xu, & Liu, 2006; Xu & Li, 2005). The peculiar solution properties of MC are considered to be consequence of associative behavior due to hydrophobic interactions among methyl substituents and strong hydrogen bonding among hydroxyl groups (Desbrières et al., 1998; Desbrières et al., 2000; Hirrien, Chevillard, Desbrières, Axelos, & Rinaudo, 1998; Sekiguchi et al., 2003; Vigouret et al., 1996).

Physicochemical properties of MC strongly depend not only on its total DS, but also on the distribution of methyl group within an anhydroglucose unit (AGU) and the substituent along the molecular chain. Abe et al. reported that all the MC samples prepared from cotton linters with dimethyl sulfate and alkali in toluene were insoluble in water, despite their DS values ranging from 0.5 to 2.0 (Abe, Matsuzaki, Hatano, & Sobue, 1955). MC samples prepared by homogeneous reactions are considered to have a more uniform distribution of substituent than those of the commercial MC, which are soluble in water at the lower limit of DS values than those obtained in heterogeneous conditions (Bock, 1937; Liu, Zhang, Takaragi, & Miyamoto, 1997;

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Takahashi, Fujimoto, Miyamoto, & Inagaki, 1987). However, regioselectively substituted 2,3-di-*O*-MC with a DS of 2.0 and 6-*O*-MC with a DS of 1.0, which were prepared by homogeneous reactions, are insoluble in water (Kondo, 1997; Liu et al., 1997). The lower limit DS values of water-soluble MCs homogeneously synthesized in LiCl/DMAc (Nishimura, Donkai, & Miyamoto, 1997) and NaOH/urea aqueous solutions (Ke, Zhou, & Zhang, 2006) are similar to those of the commercial products. It has also been reported that MC samples prepared by homogeneous reactions showed a normal phase separation rather than a sol–gel transition in an aqueous solution (Ke et al., 2006; Liu, Zhang, Takaragi, & Miyamoto, 1998; Liu et al., 1997; Nishimura et al., 1997; Takahashi et al., 1987; Takaragi, Minoda, Miyamoto, Liu, & Zhang, 1999; Zhou, Zhang, Deng, & Wu, 2004). Moreover, Kondo et al. found that the gelation behavior and enzymatic degradation of regioselectively substituted 2,3-di-*O*-MCs differed from those of randomly substituted MC samples (Nojiri & Kondo, 1996; Sekiguchi et al., 2003). Such differences are obviously due to the difference in the distribution of substituents in the AGU units as well as along the cellulose chain.

In this work, three water-soluble MC samples were homogeneously synthesized in NaOH/urea aqueous solution, and their microstructure and aggregation behavior in dilute solution were investigated by using gas chromatography (GC) coupled with mass spectrometry (MS), NMR, size exclusion chromatography (SEC) combined with laser light scattering (LLS), dynamic laser light scattering (DLS) and viscometer.

2. Experimental

2.1. Materials

Cellulose (cotton linter pulp) was supplied by Hubei Chemical Fiber Group Ltd. (Hubei, China), and its viscosity–average molecular weight (M_η) in cadoxen (Brown & Wiskstön, 1965) at 25 °C was determined using viscometry to be 10.3×10^4. Dimethyl sulfate (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.

2.2. Homogeneous synthesis of methylcelluloses

Cellulose solution was prepared according to the previous method (Zhang, Cai, & Zhou, 2005). Into a 500 mL beaker, an adequate amount of NaOH, urea and distilled water (7:12:81 by weight) was added, and the resulting mixture aqueous solution was stored in a refrigerator. After the solution was precooled to −12.3 °C, cellulose was added immediately into it with stirring vigorously for 5 min at ambient temperature to obtain the transparent cellulose dope containing 3 wt% cellulose.

A certain amount of DMS was added drop wise to the 500 g cellulose solution mentioned previously, and the mixture was stirred at room temperature for 20 h. Under the conditions for methylation, the solution kept transparent and remained completely homogeneous as the reaction proceeded. The reaction solution was neutralized with acetic acid, dialyzed with distilled water for 7 days, then precipitated into a large excess of acetone, and dried in vacuum finally. By changing the mole ratio of anhydroglucose unit (AGU) to methyl group of DMS as 1:7.5, 1:9 and 1:12, three water-soluble methylcelluloses were prepared and coded as MC-1, MC-2 and MC-3, respectively.

2.3. Measurements

^{13}C and ^{1}H NMR measurements were carried on a Varian INOVA-600 spectrometer in the proton noise-decoupling mode with a standard 5-mm probe. Acetylation of MC samples was carried out before NMR analysis according to the improved characterization of the substitution distribution in MC (Tezuka, Imai, Oshima, & Chiba, 1987). Acetylated MC samples were dissolved in deuterated dimethyl sulfoxide (DMSO-d_6), and the NMR spectra were recorded at 70 °C. The chemical shift values were referenced to the signals of DMSO-d_6 and tetramethylsilane (TMS). IR spectra of MC samples and their acetylated derivatives were performed with a Nicolet 170SX Fourier transform infrared spectrometer. The test specimens were prepared by the KBr-disk method.

GC analysis of the substituent distribution of MCs were performed according to the method described by Tezuka et al. (1987). The acetylated hydrolyzates of MCs was 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 × 0.32 mm × 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.

MC samples were dissolved in water at 4 °C for 48 h to ensure complete dissolution. The initial concentration of MC in water for viscosity measurement was about 2.0×10^{-3} g/mL. The viscosity of MC in water was measured at 20 ± 0.1 °C with a Ubbelohde viscometer, and the M_η values were calculated from intrinsic viscosity ($[\eta]$) by the following equation (Uda & Meyerhoff, 1961):

$$[\eta] = 0.28\ \mathrm{M}^{0.63}(\mathrm{mL/g}).$$

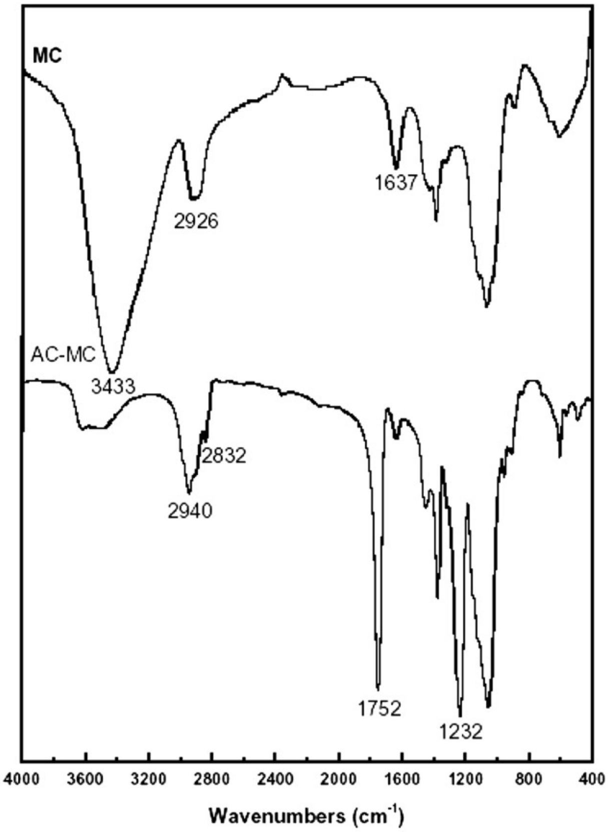

Fig. 1. IR spectra of MC-2 and its acetylated derivative (AC-MC).

SEC–LLS measurement was performed on a multi-angle laser light scattering instrument (DAWN DSP, Wyatt Technology Co., United States) equipped with a He–Ne laser ($\lambda = 632.8$ nm), and combined with a p100 pump (Thermo Separation Co. USA) equipped with TSK GEL G6000 and G4000 PWXL column (7.8 mm × 300 mm) and an Optilab refractometer (Wyatt Technology) at 25 °C. The fluent was 0.15 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 increment of MC in 0.15 mol/L NaCl aqueous solution was 0.140 mL/g and was taken with an Optilab refractometer (Wyatt Technology) at 632.8 nm and 25 °C.

Dynamic laser light scattering (DLS) was performed on PD Expert 24 angle static/dynamic light scattering detector (Precision Detector, USA) and observed in the temperature range from 20 °C to 80 °C at 5 °C intervals. The MC solutions were kept 10 min at the required temperature before each measurement. The concentration of MCs for SEC–LLS and DLS measurements was 5.0×10^{-4} g/mL.

3. Results and discussion

3.1. Microstructure of methylcellulose

NMR technical data for acetylated derivatives of cellulose ethers have been proved to be a convenient and reliable method of elucidating their microstructure over a wide DS (the average number of substituted hydroxyl groups in the monomer unit) and MS (the average number of moles of the substituent groups per monomer unit) range (Richardson, Andersson, Brinkmalm, & Wittgren, 2003; Tezuka et al., 1987). In this work, the acetylation pretreatment of the hydroxyl groups at the unsubstituted position on the anhydroglucose unit of the MC samples was performed by refluxing with acetic anhydride/pyridine mixture. IR spectra of a MC sample and its acetylated derivative (AC-MC) are shown in Fig. 1. The strong absorption at 3433 cm^{-1} for MC disappeared along with the formation of the strong carbonyl absorption at 1752 cm^{-1} for AC-MC, which confirmed the complete acetylation of the hydroxyl groups in MC.

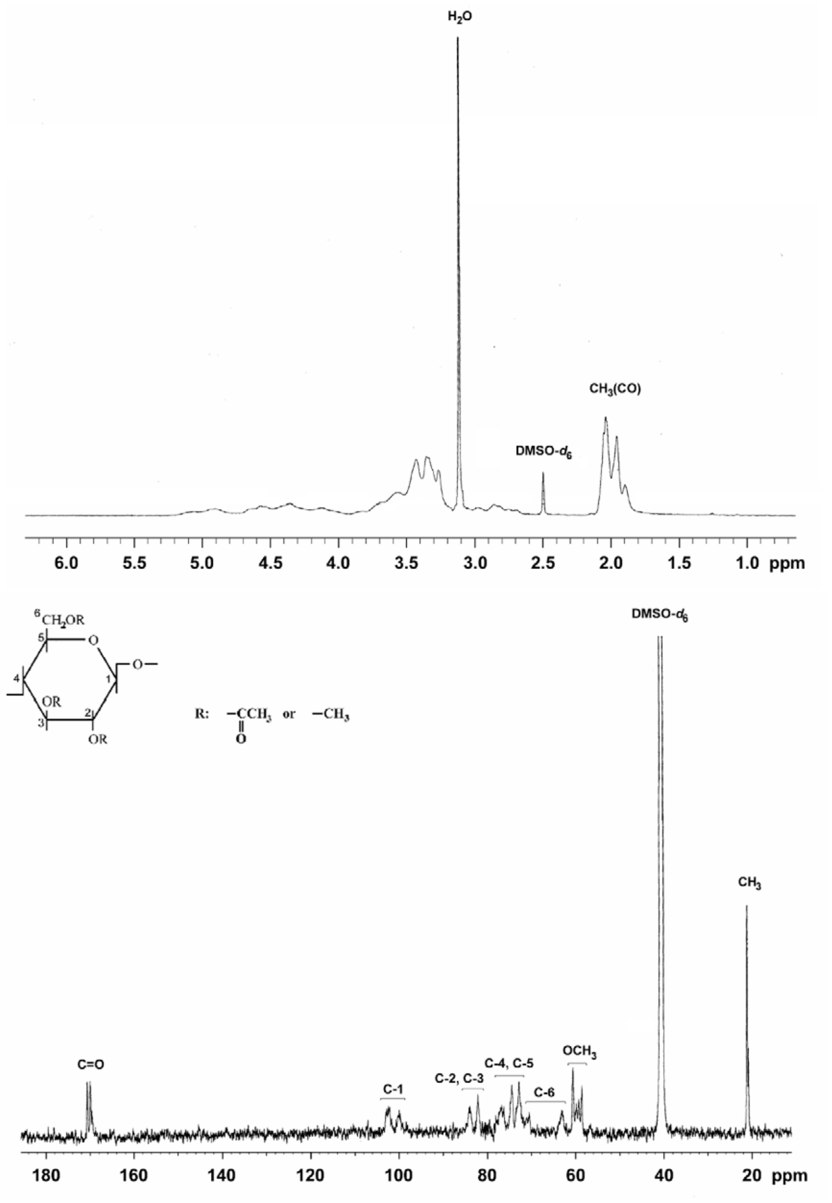

Fig. 2. ^{1}H and ^{13}C NMR spectra of the acetylated MC-2 sample in DMSO-d_6 at 70 °C.

The ^1H and ^{13}C NMR spectra of the acetylated MC in DMSO-d_6 at 70 °C are shown in Fig. 2. In ^1H NMR spectrum, signals at 1.8–2.1 ppm are assigned to protons of acetyl methyl groups (CH_3CO). Chemical shifts at the range of 3.2–3.5 ppm are ascribed to protons of methoxy methyl groups ($—OCH_3$), which are overlapped with the chemical shifts of AGU protons (2.5–5.5 ppm). In ^{13}C NMR spectrum, the possible assignments of the peaks are shown according to Tezuka et al. (1987). The acetyl methyl carbon signal was observed as a doublet at 20.7 ppm and 21.1 ppm, respectively. The C-6 methylene carbon signal was found to be sensitive to the type of substituent, i.e., methyl at around 70.8 ppm and by acetyl at 63.2 ppm. The C-1 carbon resonance also split into two well-resolved peaks after acetylation, which referenced the neighbouring methyl substituent at the C-2 position, i.e., methyl at 102.7 ppm while acetyl at 99.9 ppm. A quadruplet at 58.5–60.5 ppm can be assigned to the methoxy methyl carbon signals. The carbonyl carbon signal was observed to split into a triplet at 169.6, 170.0 and 170.6 ppm, representing the substitution position of C-2, C-3 and C-6, respectively. Therefore, through the integration of the well-resolved acetyl methyl and carbonyl carbon signals, the total DS and relative DS values at C-2, C-3 and C-6 positions of the MC samples can be calculated and are summarized in Table 1. The total DS of MC-1, MC-2 and MC-3 is 1.09, 1.42 and 1.56, respectively. The relative DS value at C-2 position is slightly higher than those at C-3 and C-6 positions, and the hydroxyl groups at C-3 and C-6 positions indicate a close reaction activity. They obviously differed from those synthesized in heterogeneous reactions and homogeneous reaction in other systems. Usually, the relative reactivity of hydroxyl groups of cellulose is in the order C-6 ⩾ C-2 > C-3 in a nonaqueous solvent system (Heinze & Liebert, 2001).

Table 1
Distribution of methyl groups on the anhydroglucose unit of MC samples by ^{13}C NMR and GC

Sample	DS at positions[a]			Total[a]	DS at positions[b]			Total[b]
	C-2	C-3	C-6		C-2	C-3	C-6	
MC-1	0.55	0.27	0.27	1.09	0.52	0.26	0.30	1.08
MC-2	0.57	0.40	0.45	1.42	0.66	0.38	0.39	1.43
MC-3	0.67	0.46	0.43	1.56	0.69	0.41	0.41	1.51

[a] Determined by ^{13}C NMR spectra of the acetylated MC samples.
[b] Determined by the GC trace of MC after total hydrolysis and acetylation.

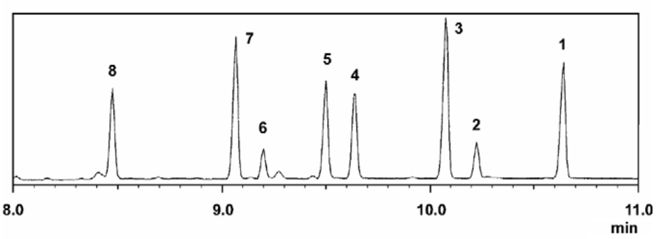

Fig. 3. GC trace of the MC-2 sample after total hydrolysis and acetylated. Signals 1–8 represent none substituted glucitol, 3-*O*-, 2-*O*-, 6-*O*-, 2,6-di-*O*-, 3,6-di-*O*-, 2,3-di-*O*- and 2,3,6-tri-*O*-methyl-glucitol derivatives, respectively.

Table 2
Fractionation of methyl groups on the anhydroglucose unit of methylcellulose samples by GC/MS[a]

Sample	2,3,6	2,3	3,6	2,6	6	2	3	none
MC-1	7.40	10.47	2.51	7.99	11.63	26.21	5.54	27.95
MC-2	10.96	19.63	3.56	12.16	10.93	23.05	4.01	15.70
MC-3	13.64	19.68	3.63	12.33	11.56	23.18	4.10	11.88

[a] Fractions in percent.

Gas chromatography (GC) coupled with mass spectrometry (MS) is a more accurate way to determine the substitution pattern of polysaccharides; it could measure the distribution of the methyl group within an AGU unit and the substituent along the molecular chain. Fig. 3 shows the GC trace for an MC sample after total hydrolysis and acetylation, and the peak assignment is performed with mass spectroscopy analysis. Signals 1–8 represents none substituted glucitol, 3-*O*-, 2-*O*-, 6-*O*-, 2,6-di-*O*-, 3,6-di-*O*-, 2,3-di-*O*- and 2,3,6-tri-*O*-methyl-glucitol derivatives, respectively. Table 2 summarizes the fractionation of methyl groups (in percent) on the AGU unit of MC samples. With an increase of the total DS, the unsubstituted glucose units decreased from 27.95% to 11.88%, while the full substituted glucose units increased from 7.40% to 13.64%. The total DS and DS at C-2, C-3 and C-6 positions were calculated according to Kondo's method (Kondo, 1997) and are listed in Table 1. The total DS of MC-1, MC-2 and MC-3 is 1.08, 1.42 and 1.51, respectively, and the relative DS value at C-2 position is higher than those at C-3 and C-6 positions, which are well agreed with those as obtained by the ^{13}C NMR technical with acetylated MC. The results further proved that the MC samples synthesized in NaOH/urea aqueous solution have uniform distribution of substituent within an AGU unit.

3.2. Aggregation behavior

MC samples as prepared have good solubility in cold water and organic solvents such as dimethyl sulfoxide (DMSO) and pyridine. Table 3 lists the values of $[\eta]$ for MC in water at 20 °C, and the M_η values calculated from $[\eta]$. The $[\eta]$ and M_η of MC samples slightly decreased with the increase of total DS, which might be due to the degradation of cellulose for the large amount of DMS added during the reaction.

SEC–LLS chromatograms for MC in 0.15 mol/L aqueous NaCl ($c = 5.0 \times 10^{-4}$ g/mL) at 25 °C are shown in Fig. 4. The chromatograms obtained both by LLS and the refractive-index detectors contain two distinct peaks, indicating the occurrence of aggregation by the biomodal distribution, though it has been reported that an actual MC solution without any aggregate could be obtained at low temperature and low polymer concentration (Kobayashi et al.,

Table 3
Intrinsic viscosity and molecular weight of MC samples

Sample	$[\eta]$[a] (mL/g)	$M_\eta \times 10^{-4}$ [b] (g/mol)	Peak I[c]			Peak II[c]		
			$M_{w,ag} \times 10^{-6}$ (g/mol)	$M_{n,ag} \times 10^{-6}$ (g/mol)	d	$M_{w,s} \times 10^{-4}$ (g/mol)	$M_{n,s} \times 10^{-4}$ g/mol)	d
MC-1	425.5	11.23	26.72	25.51	1.05	18.60	12.08	1.54
MC-2	420.0	11.00	17.94	16.26	1.10	16.65	10.90	1.53
MC-3	378.2	9.31	18.85	17.45	1.11	15.76	10.10	1.56

[a] Determined in H_2O at 20 °C.
[b] Calculated from $[\eta]$ of the MC samples in H_2O at 20 °C according to $[\eta] = 0.28\ M_w^{0.63}$ (mL/g).
[c] Determined by SEC–LLS chromatograms as shown in Fig. 4.

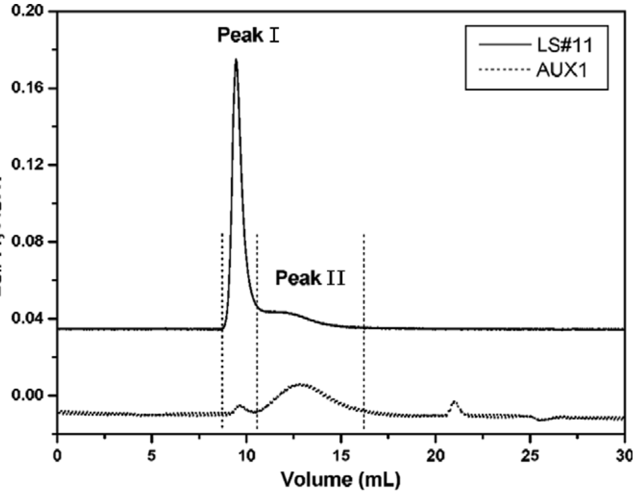

Fig. 4. SEC chromatogram of MC-3 ($c = 5.0 \times 10^{-4}$ g/mL) in 0.15 mol/L NaCl aqueous solution at 25 °C, as detected by LLS and differential refractometry. LS#11 and AUX1 represent signals from LLS at 90 °C and the refractive-index detection.

1999; Vigouret et al., 1996). The peak (I) at the low elution volume corresponds to the aggregates with a large molecular weight, and the peak at large elution volume (II) corresponds to the single chains with low molecular weight. Table 3 lists the molecular weight of the aggregates ($M_{w,ag}$, $M_{n,ag}$) and single chain ($M_{w,s}$, $M_{n,s}$) for MC samples, respectively, from the individual GPC peak. The number average molecular weight ($M_{n,s}$) of the single chains of MC samples was close to the molecular weight determined by viscosity, and slightly decreased with increasing DS values. The apparent aggregation number (N_{ap}) was 144, 108 and 120 for MC-1, MC-2 and MC-3, respectively, which was estimated by the formula $N_{ap} = M_{w,ag}/M_{w,s}$. The weight ratio of the aggregates about 10% for the MC samples in 0.15 mol/L aqueous NaCl at 25 °C, because the signals obtained from the refractive-index detector represent the concentration of each fraction.

Fig. 5 shows the hydrodynamic radius of MC-3 in distilled water ($c = 5.0 \times 10^{-4}$ g/mL) in the temperature range of 20 °C–80 °C determined by DLS. According to the temperature dependence of hydrodynamic radius, MC displays two different behaviors in its dilute aqueous solution. In the temperature range of 20–65 °C, the hydrodynamic radius of MC displays biomodal distribution, which is similar to the results determined by SEC–LLS, suggesting that a small amount of large aggregates and large amount of single chains coexist in the dilute solution. At 20 °C, the content of single chains was about 90%, and the hydrodynamic radius of MC was about 11.2 nm. When the temperature increased to 35 °C, the content of single chains decreased to 85%, and the hydrodynamic radius of MC slightly increased due to the expand of chain with increasing temperature. As the temperature further increased to 65 °C, hydrodynamic radius of MC decreased due to the compaction of single chains, however, the content of single chains just slightly decreased from 85% at 35 °C to 79% at 65 °C. At the temperature of 70 °C, the isolated MC chains disappeared and just gave a hydrodynamic radius of 99.1 nm for the large aggregates. The hydrodynamic radius of the aggregates decreased with further increasing of temperature, indicating a denser structure on account of the hydrophobic associations and hydrogen bonding among the MC molecules. Hirrien et al. reported that water-soluble MC displayed different behavior as a function of temperature according to the DS value, when DS > 1.5, intermolecular interactions occurred for $T > 35$ °C, but when DS > 1.5, there was no clear evidence for aggregation (Hirrien, Desbrières, & Rinaudo, 1996). Funami et al. also studied the thermal aggregation of MC with different molecular weights; they found that MC (DS = 1.87) with relatively large M_w (e.g., >30.0 × 10^4 g/mol) aggregates at higher temperatures (e.g., >60 °C) to form compact or tightly packed aggregation (Funami, Kataoka, Hiroe, Asai, Takahashi, & Nishinari, 2007). The aggregation behavior of MC homogeneously synthesized in NaOH/urea aqueous solution further proved that the microstructure of MC had a great influence on its solution properties, even at low temperature and low polymeric concentration.

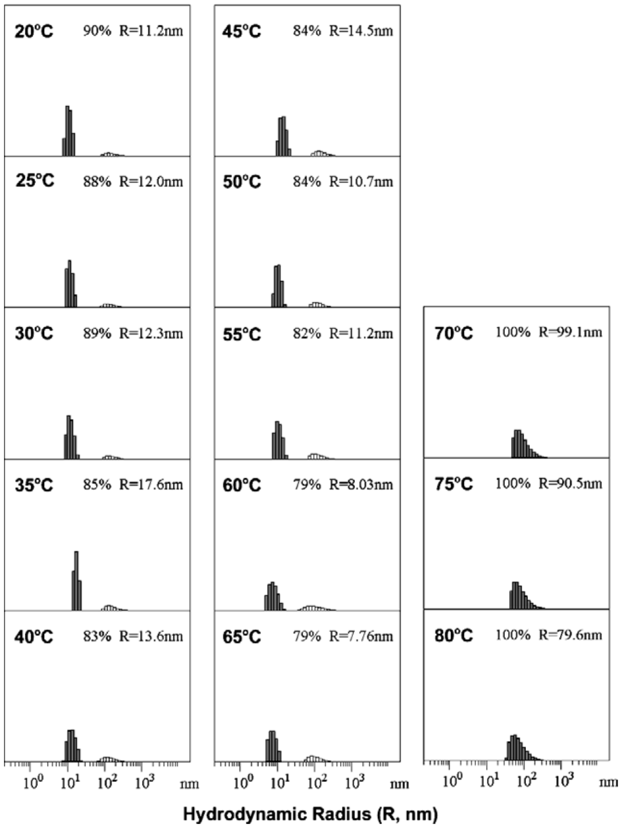

Fig. 5. Hydrodynamic radius of MC-3 ($c = 5.0 \times 10^{-4}$ g/mL) in H_2O at different temperature.

4. Conclusions

Three water-soluble methylcelluloses (MCs) have been homogeneously synthesized in NaOH/urea aqueous solution by using dimethyl sulfate as a methylation reagent. NaOH/urea aqueous solution is a stable and more homogeneous reaction medium for preparing MC with a more uniform microstructure than heterogeneous reactions and the other homogeneous reactions. The total degrees of substitution (DS) of the MC samples were 1.09, 1.42 and 1.56, respectively, and the relative DS value at C-2 position was slightly higher than those at C-3 and C-6 positions. An actual MC solution without any aggregate could not be obtained even at low temperature and low polymer concentration. Isolated MC chains and small amount of large aggregates with aggregation number over than 100 coexisted in the dilute aqueous solution in the temperature range of 20–65 °C. Aqueous of MC changed markedly at over 70 °C, and only large aggregates appeared in the solution for the strong intermolecular interactions.

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