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Effects of molecular weight on thermoreversible gelation and gel elasticity of methylcellulose in aqueous solution

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Abstract

Aqueous solutions of two methylcellulose (MC) polymers with different molecular weights ($M_w = 100{,}000$ and 400,000) have been studied. The thermoreversible gelation ‘properties and the gel elasticity were measured as a function of polymer concentration by means of micro differential scanning calorimetry and rheology, respectively. The experimental results prove that the aqueous solutions of MC are completely thermoreversible and the thermoreversibility of MC is independent of either polymer concentration or molecular weight. The total enthalpy required for the sol–gel transition is a linear function of polymer concentration, which is again independent of molecular weight. The quasi-equilibrium modulus G_e could be scaled with concentration c as $G_e \sim c^{2.19}$ ($c > 1.0$ wt%) and $G_e \sim c^{3.12}$ ($c < 1.0$ wt%) for the high molecular weight MC, while $G_e \sim c^{3.12}$ and ($c < 1.0$ wt%)for the low molecular weight MC. At the same concentration of MC, with increasing molecular weight, G_e increases while the heat absorbed during the sol–gel transition remains constant.

Keywords: Gelation; Thermoreversibility; Methylcellulose; Scaling; Hydrogel

1. Introduction

Many natural polymers and their derivatives often form physical gels that are of thermoreversible nature. (Guenet, 1992; Nijenhuis, 1997). Methylcellulose (MC), a modified product of natural cellulose is one of them.

MC is well known to gel in water upon heating and is able to turn back to the original liquid state without any changes upon cooling. In the past decades, many studies have been carried out to examine the thermal gelation properties, the mechanism of gelation, and the gel network structure of MC using various experimental techniques, which can be found in many publications (Chevillard & Axelos, 1997; Desbrieres, Hirrien, & Rinaudo, 1998; Desbrieres, Hirrien, & RossMurphy, 2000; Haque & Morris, 1993; Hirrien, Chevillard, Desbreieres, Axelos, & Rinaudo, 1998; Kobayashi, Huang, & Lodge, 1999; Kundu & Kundu, 2001; Kundu et al., 2003; Li, 2002; Li et al., 2002; Matsuoka et al., 2002; Nishinari et al., 1997; Sakar, 1979; Sarkar, 1995; Sarkar & Walker, 1995; Takahashi, Shimazaki, & Yamamoto, 2001).

Thermodynamically, an aqueous solution of MC exhibits the lower critical solution temperature (LCST) below which the MC aqueous solution is a single-phase solution and above which a turbid gel is formed as reported by Chevillard & Axelos (1997); Desbrieres, Hirrien and RossMurphy (2000); Hirrien et al. (1998). Precipitation of MC may take place when temperature is further increased to be higher than 80 °C (Takahashi et al., 2001). Although the sol–gel transition of MC on heating is well confirmed physically or rheologically, as reported by Desbrieres, Hirrien, and RossMurphy (2000); Haque and Morris (1993); Hirrien et al. (1998); Kobayashi et al. (1999); Sakar (1979); Sarkar (1995); Takahashi et al. (2001), it is demonstrated by Semenov and Rubinstein that a continuous reversible gelation is not an exactly thermodynamic transition because all thermodynamic quantities are continuous at the gel point (Rubinstein & Semenov, 1998; Semenov & Rubinstein, 1998).

Rheological, calorimetric or optical methods have been often employed to study the thermoreversible gelation of MC in water. Haque and Morris (1993) reported that in the cooling process there was a bimodal exothermic peak

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over a broad temperature range from 55 to 25 °C. The endothermic peak was able to correlate with dynamic storage modulus G' well while the bimodal exothermic peak was linked with the two waves of reduction in G'. However, the mechanism involved in the bimodal exothermic peak was not presented by the authors. Other techniques such as NMR (Haque & Morris, 1993), static and dynamic light scattering (Kobayashi et al., 1999) and small angle neutron scattering have also been used to investigate the aggregation structures of MC in water. The formation of clusters or other molecular structures in semi-dilute solution of MC at low temperatures is considered to be important in affecting gelation mechanisms and network structures formed by a subsequent gelation process upon heating. However, no reports have been found on the direct observation of MC gel structures. The lack of direct observation of MC gel network structures would be due to the technical difficulty in preparing appropriate samples of MC gels for SEM, TEM or AFM because MC does not gel at room temperature.

The rheological characteristics in the vicinity of the sol–gel transition can be often described using power laws or scaling laws. One of the most important characteristics of a gel is its elasticity evolution, which is depicted as a function of the relative distance $\varepsilon=|p-p_g|/p_g$ by the scaling law as reported by De Gennes (1979); Flory (1941, 1953); Martin and Adolf (1991); Martin, Adolf, and Wilcoxon (1998); Stockmayer (1943) and which is expressed by:

$$G_e \propto \varepsilon^z \quad \text{for } p>p_g \tag{1}$$

where G_e is the quasi-equilibrium modulus, p is the gelling variable, p_g is the value of p at the sol–gel transition point, and z is the index for this scaling law, which is always positive. The theoretical and experimental values of z are typically reported to be 2.0–3.0 (De Gennes, 1979; Koike, Nemoto, Watanabe, & Osaki, 1996; Li & Aoki, 1997, 1998; Li, Uchida, Aoki, Yao, 1997; Martin, Adolf, & Wilcoxon 1998; Winter & Mours, 1997).

Although many studies have been conducted on the thermal gelation of MC, no other reports have been found on the validity of the scaling law (Eq. (1)). In our previous work, (Li, 2002), we initially examined the validity of the scaling law for a commercial methylcellulose with a substitution degree of 1.8 and molecular weight of 310,000. It was observed that at 70 °C the gel's elasticity G_e increased with polymer concentration and G_e could be expressed with a scaling law of $G_e \sim c^{3.03}$ ($c>1$ wt%). We also proposed a new mechanism of degelation for explanation of the bimodal exothermic peak. (Li, 2002)

In this report, as a continuous work on the thermoreversible gelation of MC, two MCs with different weight-average molecular weights (100,000 and 400,000) and the same degree of substitution (DS = 1.8) are used to prepare aqueous solutions with various concentrations, and their rheological and calorimetric properties are measured as a function of temperature, polymer concentration, or dynamic frequency. This work aims at the thermoreversible gelation behavior, and the validity of the scaling law. In particular, the effects of molecular weight on the gelation and scaling are investigated and discussed.

2. Experimental

2.1. Materials

Cellulose derivatives, methylcellulose (MC), with the trade name of SM100 and SM8000, made by etherification of pulp cellulose, were kindly provided by Shinetsu Chemical Co. Ltd, Japan. According to the product specification, the weight-average molecular weights of SM100 and SM8000 are 100,000 and 400,000, respectively, as determined by light scattering. The degree of substitution (DS) is 1.8. The molecular polydispersity of these two products is unknown, but it is expected to be relatively broad. The materials were directly used without further purification. Despite the fact that the SM series of MC are commercial products, they are very pure as proved by Kobayashi et al. (1999) studies and our micro DSC experiments (Li, 2002). Prior to use, these materials were vacuum dried at 50 °C for 24 h and stored in a desiccator at room temperature. A wide range of polymer concentrations from 0.5–4 wt% were prepared with deionized water from the Millipore water purifier. The partially dissolved samples were put into a refrigerator and kept for 24 h before use.

2.2. Micro-thermal analysis

A micro-differential scanning calorimeter (VP-DSC Microcalorimeter, Microcal Inc.) was used to determine the thermal properties of the MC solutions during a thermal cycle of heating–cooling. The reference cell is filled with deionized water. A slow heating and cooling rate of 1 °C/min was employed to fully explore the details of the thermogelation behavior of MC in water. After each cycle was completed for the sample, the sample cell was cleaned by a continuous flow of deionized water for more that 1 h. No contamination of the sample cell by the last sample was confirmed by running a water–water DSC test. Since, the major disadvantage of the micro DSC is that high viscosity samples cannot be injected to the sample cell, the highest concentration applicable in this study were below about 3 wt%.

2.3. Rheological measurements

The rheometer (ARES 100FRTN1, Rheometric Scientific) with a geometry of parallel plates was used. The parallel plates of 25 and 50 mm in diameter were used for the relatively high and low viscosity solutions, respectively. The dynamic viscoelastic functions such as shear storage modulus G' and loss modulus G'' were measured as a function of angular frequency. To prevent dehydration during the rheological measurements, a thin layer of low viscosity silicone oil was placed on the periphery surface of the solution held between the plates. All the dynamic viscoelastic measurements (e.g. temperature sweep) were carried out at an angular frequency of 1 rad/s and low shear strains to ensure the linearity of viscoelasticity. In the experiments for obtaining G' and G'' as a function of angular frequency at a given gelling temperature, the sample in the liquid state was first loaded to the bottom plate of the rheometer at room temperature and then the temperature was raised to the required temperature. Then, the sol–gel transition occurred at the desired temperature. To make sure that the gel was fully developed, each sample was allowed to stay at the temperature for 30 min before testing.

Some of MC solution samples were tested through a temperature sweep mode, in which G' and G'' were measured during a thermal cycle of heating from about 20 to 75 °C and subsequently cooling from 75 to 20 °C. The heating and cooling rates were adjusted to be about 1 °C/min.

3. Results and discussion

3.1. Thermal behavior of MC solutions on heating and cooling

A typical example of calorimetric thermogram determined using micro DSC is shown in Fig. 1 for a 0.5 wt% solution of SM8000. The relative thermal capacity C_p is employed throughout this report, with regard to the nature of the DSC, which measures the relative heat between the sample and the reference. In the heating process, a sharp endothermic peak is observed at around 61 °C, while a broad exothermic peak appears at about 32 °C in the subsequent cooling process. The broad exothermic peak is also featured with a shoulder or a secondary peak at the higher-temperature side. Compared with our previous work (Li, 2002; Li et al., 2002) which studied the aqueous solutions of another MC (SM4000) with a lower molecular weight of 310,000, the thermogram obtained for SM8000 is very similar to that of SM4000 although the molecular weights are different. This result indicates that SM8000 has a similar mechanism of gelation and thermoreversibility as described for SM4000 previously.

Fig. 2(a) and (b) show the effects of polymer concentration on the heating and cooling thermograms, respectively, for SM8000. All the thermogram curves have been normalized by choosing an appropriate baseline in the original graph (e.g. Fig. 1). For the ease of visualization, the thermogram curves for all the concentrations were vertically lifted by a stepwise amount to prevent the curves from overlapping. In Fig. 2(a), the endothermic peak increases in height with increasing MC concentration but the peak temperature remains almost the same at around 61 °C. In addition, the endothermic peak, although it still remains relatively narrow, becomes broader with increasing MC concentration. However, the MC solutions in the cooling process (Fig. 2(b)) behaves completely differently from

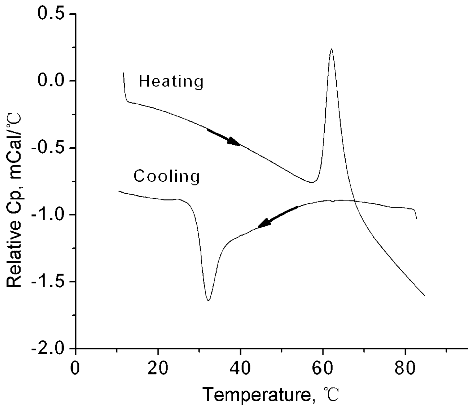

Fig. 1. Calorimetric thermograms for a 0.5 wt% aqueous solution of SM8000 during a thermal cycle. The heating and cooling rates were 1 °C/min.

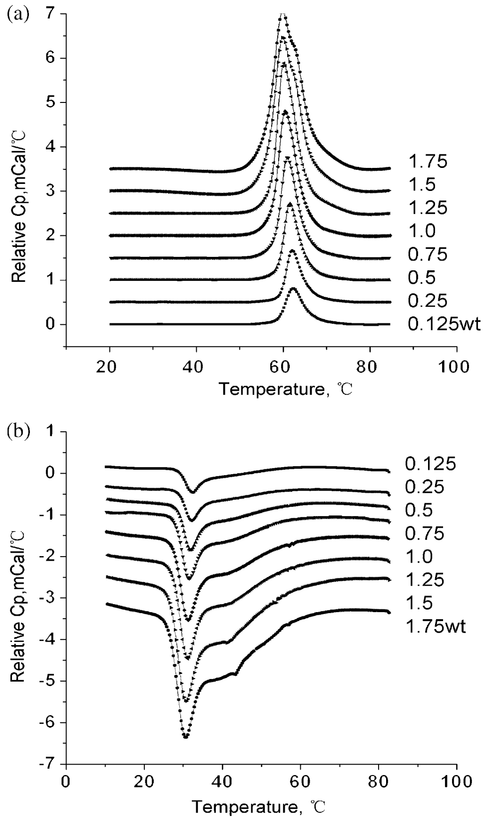

Fig. 2. Calorimetric thermograms of aqueous solutions of SM8000 with various concentrations: (a) on heating and; (b) on cooling, at 1 °C/min. The numerals (0.125–1.75) indicate the SM8000 concentrations in wt%.

those in the heating process. A shoulder was observed above the peak temperature of around 32 °C, and the shoulder became more prominent with increasing concentration to eventually appear as a secondary peak at about 40 °C. In the cooling process, the dissociation of the associated structures of MC in water, which was formed in the heating process, appears to have to overcome two energy barriers: a primary barrier at about 32 °C and a secondary one in the broad range of temperature from 70 to 35 °C. This thermoreversible behavior is similar to SM4000, as we elucidated previously. It has also been proved that SM100 has a similar thermal behavior with SM4000 and SM8000, indicating an independence of gelation thermodynamics from molecular weight.

The enthalpies of gelation can be calculated directly by integrating the endothermic peaks in Fig. 2(a) over temperature. Fig. 3 gives a comparison of endothermic enthalpies for SM100, SM4000 and SM8000. It is found that the total enthalpy absorbed by a MC solution with the same concentration for SM100, SM4000 and SM8000, is approximately the same. As a result, all the data in Fig. 3 can be fitted to one single straight line. The values of enthalpy were normalized for 1 L of MC solution. Fig. 3 indicates that the endothermic heat is a linear function of MC concentration. And as it is concluded that SM8000, SM100 or SM4000, which have different molecular weights, exhibit straight lines with approximately the same slope. This indicates that for the same amount (mass) of MC in solution, a MC solution needs to absorb the same amount of heat to undergo the thermal hydrophobic association, which is independent of molecular weight. It should be noted that the degree of substitution (DS) of the three MCs here is the same, which enables the comparison itself since the number (or mass) of the hydrophobic group, –OCH$_3$, greatly affects the chemical properties of the polymer. It was reported that MCs with DS$<$1 or DS$=$2 were not soluble in water (Liu, Zhang, Takaragi, & Miyamoto, 1997), thus MC solutions with different DS will not follow the above thermal properties. From the similarity in the thermal properties of MC with different molecular weights, it is reasonably considered that the main mechanism of hydrophobic association, which results in the sol–gel transition of MC, is similar or independent of molecular weight. In the hydrophobic association mechanism of MC, the heat is absorbed to destroy the cagelike structures formed from the water molecules surrounding the methyl groups of MC and the hydrophobic association then takes place (Li et al., 2002). Thus, despite the difference in molecular weight among SM100, SM4000 and SM8000, this mechanism of hydrophobic association is valid. However, the strength of a final gel formed from different molecular weights of MC at the same concentration may be different as discussed in the following session.

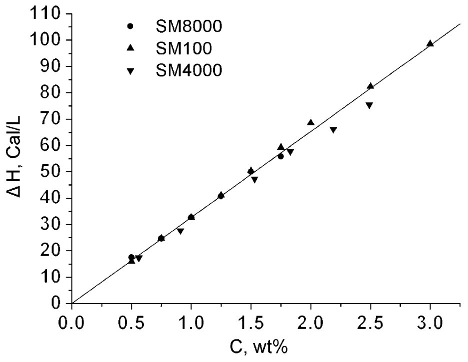

Fig. 3. Heat absorbed per liter of solution on heating as a function of polymer concentration for SM100 ($M_w=100{,}000$), SM4000 ($M_w=310{,}000$) and SM8000 ($M_w=400{,}000$). The heating rate was 1 °C/min.

3.2. Viscoelastic behavior on heating and cooling

Fig. 4(a) shows the dynamic viscoelastic properties of a MC (SM8000) solution of 2 wt%, at the heating and cooling rates of 1 °C/min and an angular frequency of 1 rad/s. Fig. 4(b) shows the dynamic viscoelastic properties of a MC (SM100) solution of 2.8 wt%, at the same heating and cooling rate. As shown in Fig. 4(a) in the heating process, there are at least four distinct regions. The first region is before the crossover of G' and G'', where G' is below G'',

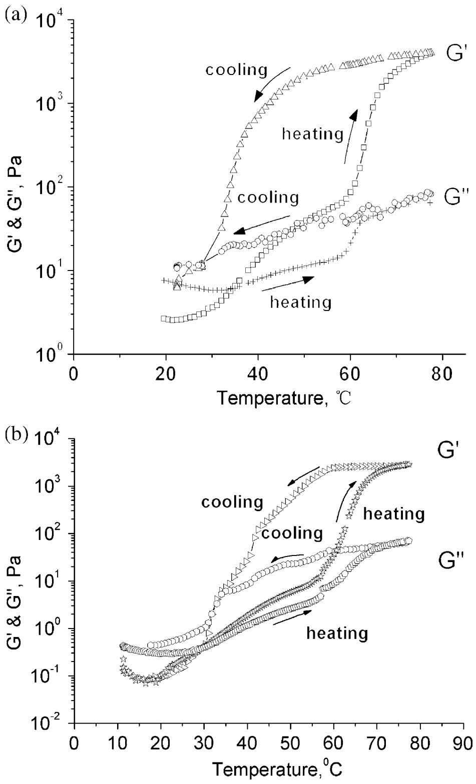

Fig. 4. Storage modulus G' and loss modulus G'' as a function of temperature in a heating to cooling thermal cycle: (a) for a 2.0 wt% solution of SM8000; and (b) for a 2.8 wt% solution of SM100. The heating and cooling rates were about 1 °C/min.

indicating a common viscoelastic behavior of a liquid. G' crosses over G'' at about 35 °C. In this region, G' increases with temperature, while G'' decreases with temperature slowly. Beyond the crossover point, G' becomes superior to G'' and G'' increases with temperature gradually until about 57 °C. After 57 °C, both G' and G'' curves increase sharply until about 65 °C. After that, both curves again increase slowly with temperature and tend to reach their, respective, plateaus. For SM100, as shown in Fig. 4(b), a similar trend is shown.

Traditionally, two methods are used to determine the sol–gel transition point. Firstly, the crossover of G' and G'' is used as the indication of the sol–gel transition point (Ferry, 1980). Secondly, Winter et al. defined the sol–gel transition as the point where the ratio of G'/G'' is independent of frequency (Chambon & Winter, 1985, 1987; Winter & Chambon, 1986). As described in our previous work (Li et al., 2002), neither method was suitable for determination of the sol–gel transition of a MC aqueous solution. It is quite obvious that the sharply increasing part of the G' curve should indicate the sol–gel transition regime, which correlates excellently with the endothermic peak observed by micro DSC (Fig. 2).

In the subsequent cooling process, in contrast to the sharp increase within the temperature range from 57 to 65 °C in the heating process, the decreasing rate of G' with decreasing temperature is very slow. This suggests that the thermally induced hydrophobic dissociation in the cooling process is not an exact reversal of the hydrophobic association occurring in the heating process. However, there is a sharp decrease region for the G' found in a lower temperature range near 31 °C, which is consistent with the primary exothermic peak in Fig. 2(b). In the cooling process, it is noted that the crossover point of G' and G'' also shifts to a lower temperature of about 29 °C.

At low temperatures, MC is soluble in water. The concept of cagelike structures, which is just a hypothesis, is often used to explain the solubility and thermodynamic behavior of a solute in solution (Guenet, 1992; Sakar, 1979). When water molecules form hydrogen bonds with the hydroxyl groups along MC chains and/or the cagelike structures surround the methyl groups of MC chains, these water molecules will not be free and random, and they will have a certain degree of order. Heating of such a MC solution will cause the destruction of (a) the hydrogen bonds and/or the cage structures and (b) the exposure of the hydrophobic regions of MC, leading to the formation of hydrophobic aggregates of MC. This is the so-called hydrophobic association. Compared to the energy needed in the destruction of the cage structures, the energy for the formation of hydrophobic aggregates is much lower. As a result, the total detectable endothermic heat in the heating process is mainly attributed to the destruction of the cage structures formed from water molecules. As temperature increases, the number and the size of hydrophobic aggregates increase and a gel will be eventually formed when a percolation of the polymer chains connecting the hydrophobic aggregates is achieved across the solution volume.

The characteristic temperatures at which the endothermic or exothermic peaks occur indicate the most outstanding difference between the heating and cooling processes for the MC aqueous system. The peak temperature on heating is about 61 °C, whereas the primary peak temperature on cooling is about 32 °C. There is also a secondary peak, observed only in the cooling process. This secondary peak becomes more notable for the higher concentrations of MC. We consider that the different peak temperatures are due to the kinetic association and dissociation of MC in water. A delay seems to be involved in the dissociation of the gel network formed in the heating process.

The primary exothermic peak at 32 °C corresponds to the sharp drop in G' (Fig. 4(a)); this step can be considered as the massive destruction of the whole gel network. Below 32 °C, all the hydrophobic junctions are disintegrated so that MC chains become free again. Simultaneously, the arrangement of water molecules for the re-formation of the cage structures takes place so that the large exothermic heat is required. As a result, the system returns to the original liquid state when the cooling temperature is below the offset temperature of the endothermic peak for each MC concentration.

3.3. *Effects of molecular weight on dynamic viscoelastic properties and scaling*

The dynamic viscoelastic properties of MC solutions with different concentrations were measured at a gelling temperature of 70 °C for SM100 and SM8000, respectively. As the endothermic peak temperature is about 61 °C, the temperature 70 °C was chosen to be higher than the critical gelation temperature to ensure a fully developed gel. Fig. 5(a) and (b) show G' as a function of angular frequency ω for various concentrations of MC SM8000 and SM100, respectively. For all the concentrations concerned, G' exhibits a weak dependence on ω, and the ω dependence of G' decreases with increasing concentration. When the concentration is higher than 1.0 wt% (inclusive), G' is almost independent of ω, resulting in a nice plateau. These ω-independent plateaus of G' indicate the formation of well-developed elastic solid-like gels. The second important feature is that G' increases with MC concentration, meaning that a denser or stronger gel can be formed from a more concentrated MC solution.

Now we use the results obtained in Fig. 5(a) and (b) to examine the scaling law for the elastic evolution as a function of polymer concentration. For consistency, we took the G' values at the frequency of 0.1 rad/s for all the

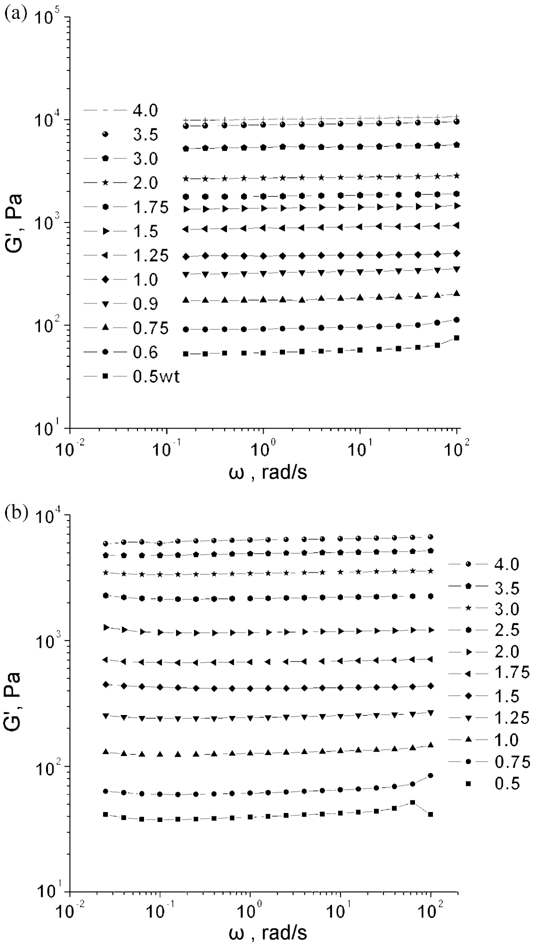

Fig. 5. Storage modulus G' as a function of angular frequency ω for various concentrations of MC at 70 °C: (a) SM8000; and (b) SM100.

concentrations of MC and defined them as G_e, the quasi-equilibrium modulus. In order to evaluate the dependence of G_e on polymer concentration and to examine the effect of molecular weight on scaling, the values of G_e for SM100 and SM8000 at 70 °C were plotted against MC concentration c as shown in Fig. 6.

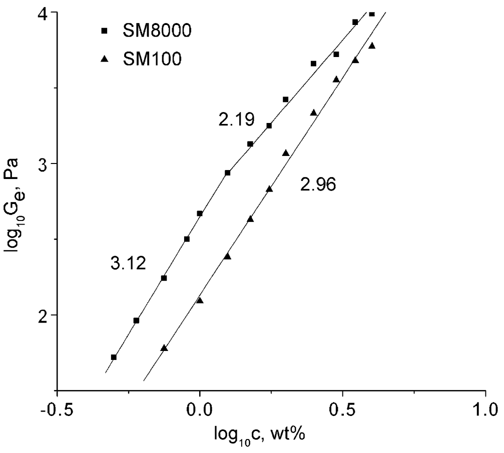

Fig. 6. Quasi-equilibrium modulus G_e as a function of concentration in a log–log scale for SM8000 and SM100 at 70 °C.

The best fittings to the straight lines are given with the slopes as indicated in Fig. 6. Although they are different in slope, the important feature of this figure is that G_e of SM8000 is always greater than that of SM100 in the concentration range studied. The result in Fig. 6 is considered to be reasonable and it is consistent well with those found from PVC physical gels, which are: (1) at the same concentration, G_e is increased by increasing PVC molecular weight and (2) the effect of molecular weight on G_e becomes weaker with increasing concentration and the G_e values of different molecular weights tend to converge with increasing polymer concentration (Li & Aoki, 1998).

This result can be also simply explained by the percolation model that deals with the three-dimensional connection for formation of a network. For a percolation, a long chain can be considered to be equivalent to a connection of several small chains, which produce the same total length as the long chain. Longer chains not only make the sol–gel transition occur more probably, but also act as some inherent junctions. The inherent junctions are stronger than the junctions formed by the hydrophobic association. But at high concentrations, as the number of the junctions formed by the hydrophobic association has been significantly increased to contribute to a significant increase in G_e, the inherent junctions become less important. As a result, the dependence of G_e on molecular weight tends to be weaker with increasing polymer concentration.

4. Conclusions

Thermoreversible gelation and scaling of methylcellulose (MC) in aqueous solutions have been investigated using micro DSC and rheology with a specific interest in finding the effects of molecular weight. All the MC aqueous solutions exhibited the excellent thermoreversible gelation behavior. It is found that all the typical thermal transitions (gelation and degelation) of MC in water are independent of either polymer concentration or molecular weight. The total energy used in the sol–gel transition is a linear function of polymer concentration, but changing of molecular weight does not change the total energy at a given polymer concentration.

The effect of molecular weight on the evolution of gel elasticity was also examined. By comparing three molecular weights (from 100,000 to 400,000) of MC, the quasi-equilibrium modulus G_e was observed to increase with increasing molecular weight and the different scaling relations are found. The mechanisms for the results have been explained in detail.

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