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Thermal Gelation of Methylcellulose in Water: Scaling and Thermoreversibility

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ABSTRACT: Thermally induced gelation was studied for aqueous solutions of methylcellulose with a substitution degree of 1.8 and molecular weight of 310 000. The dynamic viscoelastic and microcalorimetric properties were measured as functions of temperature and polymer concentration. An attempt was made to elucidate the validity of scaling laws and the mechanism involved in the thermoreversible gelation of methylcellulose. For a given high concentration of methlycellulose, the gel elasticity evolved with temperature, but it did not obey a single scaling law. At the gelation temperature of 70 °C, the gel elasticity increased with polymer concentration, and it could be expressed with a two-step scaling, from which the weak gels and the strong gels could be defined. For the weak gels ($c \le 1$ wt %), the elasticity G_e at 70 °C scaled with polymer concentration c as $G_e \sim c^{1.34}$, while G_e scaled with c as $G_e \sim c^{3.03}$ for the strong gels ($c > 1$ wt %). The thermoreversibility was examined through a cycle of heating to cooling, and the rheological thermoreversibility is found to correlate excellently with the microcalorimetric thermoreversibility. It is also proved that the gelation of methylcellulose is an entropy-driven process.

Introduction

A hydrogel is defined as the system formed in water through either chemical or physical cross-linking of water-soluble natural or synthetic polymers.[1,2] A physical hydrogel may be formed through ionic bonding, hydrogen bonding, or hydrophobic association.[1,2] The physical gelation is usually a complex process due to the transient nature of physical network junctions. A physical hydrogel may exhibit reversibility that the gel can change its physical state from a liquid (solution) to a solid (gel), and vice versa, corresponding accordingly to the external stimuli such as temperature, pH, electric field, magnetic field, salt, surfactant, solvent composition, and light. The response is determined by the chemical structure and composition of the gelling system. Thermoreversibility refers to the reversibility responding to temperature.[1] Typical examples of polymers for thermoreversible hydrogels are hydrophobically modified cellulose[1,3−12] and poly(ethylene oxide) (PEO)−poly(propylene oxide) (PPO) triblock copolymers (PEO−PPO−PEO, PPO−PEO−PPO, or their modified forms),[2,13,14] which form gels in water through the hydrophobic association that is a function of temperature. This means that the strength of hydrophobic association is controlled by the different degrees of hydrophobic to hydrophilic phase separation at different temperatures. Overall, a gel system formed via the hydrophobic association can be affected by many factors such as the number of aggregates per unit volume of the system, the average size of hydrophobic aggregates (aggregation number), the structure of junctions (aggregates), and the association strength.

The sol−gel transition and physical properties in the vicinity of the sol−gel transition can be characterized by means of many techniques such as cloud-point, light scattering, X-ray diffraction, small-angle neutron scattering, and rheology. The rheological method is the most direct and reliable way for determination of the sol−gel transition and characterization of rheological properties for gels. The rheological characteristics in the vicinity of the sol−gel transition can be described using the power laws or scaling laws.[15−17] Three scaling laws, which have been extensively applied to many types of polymeric gels (both chemical and physical gels), are established for (i) the zero-shear viscosity η_0, (ii) the dynamic moduli G' and G'', and (iii) the equilibrium modulus G_e before, at, and beyond the sol−gel transition, respectively:[18−25]

$$\eta_0 \propto \epsilon^{-\gamma} \qquad \text{for } p < p_g \tag{1}$$

$$G'(\omega) \sim G''(\omega) \propto \omega^{n} \qquad \text{at } p_g \tag{2}$$

$$G_e \propto \epsilon^{z} \qquad \text{for } p > p_g \tag{3}$$

where $\epsilon = |p - p_g|/p_g$ is the relative distance of a gelling variable p from the sol−gel transition point p_g, and γ, n, and z are the three indexes for the scaling laws, which are always positive. The typical experimental values of γ are between about 1.3 and 1.7. n must be within 0−1, and the z values are typically reported to be 2.0−3.0.[18−26] ω is the angular frequency. Although a number of publications can be found for the validity of the above scaling laws,[18−26] there have been almost no reports directly investigating the invalidity of the scaling laws.

In the family of thermoreversible gelling polymers for hydrogels, hydrophobically modified cellulose such as methylcellulose is one of the largest members.[1,3−12] In aqueous solutions, the gelation from a hydrophobically modified cellulose is considered to be due to the intermolecular association of the hydrophobic groups on the polymer chains, which is a function of temperature. At low temperatures (room temperature and below), water molecules are presumed to form enclosed structures to surround the hydrophobic groups, causing the cellulose derivatives to be water-soluble. Upon heating, these structures are distorted due to the increased phase

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separation between the hydrophobic and hydrophilic groups to result in the formation of hydrophobic aggregates and subsequently in the formation of a gel. One of the important derivatives of cellulose is methylcellulose made from the hydrophobic substitution by methyl groups. Methylcellulose is water-soluble and extensively used as a binder or thickener in pharmaceutical, cosmetic, and food applications. When heated, methylcellulose gels in water, and it is of a thermoreversible nature. Although there have been many studies conducted on the thermal gelation of the methylcellulose solutions,[1,3−12] the thermoreversible gelation bahvior and the gelation mechanism have not been well understood. In addition, the validity of the scaling laws (eqs 1−3) to the methylcellulose system has not been fully examined.[6−16]

In this work, a methylcellulose with a substitution degree of 1.8 and molecular weight of 310 000 was used to prepare aqueous solutions with various concentrations, and their rheological and calorimetric properties were measured. The investigation focused on the validity of the scaling laws, the thermoreversibility, and the gel structure.

Experimental Section

Materials and Sample Preparation. A cellulose derivative, methylcellulose (MC), with the trade name of SM4000, made by etherification of pulp cellulose, was kindly provided by Shinetsu Chemical Co. Ltd., Japan. The original MC was in a form of white fine powder. According to the manufacturer, the methylcellulose has an average degree of substitution (DS) of 1.8 and a weight-average molecular weight of 310 000 determined using light scattering. The polydispersity of molecular weight for this methylcellulose was unknown due to the technical difficulty in determining it using GPC. The viscosity range was reported by the manufacturer to be 4.54 Pa•s at 20 °C for a 2 wt % aqueous solution. Although SM4000 is a commercial product, this material is considered to be highly pure because of two reasons. First, Kobayashi et al.'s studies of SM4000 using small-angle neutron scattering and light scattering did not find any effects of low molecular impurities.[6] Second, our micro-DSC did not also detect any signals from low molecular impurities. Therefore, the material was used as received without further purification. Prior to use, they were vacuum-dried at 55 °C for 24 h and kept in a desiccator at room temperature. The aqueous solutions of MC with various concentrations ranging from 0.30 to about 2.50 wt % were prepared with deionized water from the Millipore water purifier. The weight percentage is used to represent all the polymer concentrations in this work because of the convenience and accuracy. Although it is simple to convert wt % to g/L, the interaction between MC and water may cause an error in computing the solution volume by simply summing the component volumes calculated from the component densities and weights. Each solution was prepared by dispersing the weighed MC powder in hot water (about 70 °C) and shaking it well. Since the MC could not be completely dissolved for a short period of time at room temperature, the dispersion was transferred to a refrigerator with a temperature below 10 °C and kept for a minimum period of 48 h prior to measurements. All the solutions obtained were clear and transparent at room temperature (25 °C) or below.

Rheological Measurements. The solution was transferred from a glass bottle to the rheometer (ARES 100FRTN1, Rheometric Scientific). The rheometer was equipped with two sensitive force transducers for torque measurements ranging from 0.004 to 100 g cm. Parallel plates of 25 and 50 mm diameter were used for relatively high-viscosity and low-viscosity solutions, respectively. The dynamic viscoelastic functions such as the shear storage modulus G' and loss modulus G'' were measured as a function of time, temperature, or angular frequency. To prevent dehydration during 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 (i.e., temperature sweep) were carried out at an angular frequency of 1 rad/s and low shear strains to ensure the linearity of viscoelasticity.

Micro-Thermal Analysis. A micro-differential scanning calorimeter (VP-DSC Microcalorimeter, Microcal Inc.) was used to determine the thermal properties of a cellulose solution during a heating or cooling process. The microcalorimeter is designed for liquid samples, where the sample is injected by a specific syringe into a 0.516 mL sample cell and the reference cell is filled with pure water or the same solvent used for the sample solution. In this work, we employed the deionized water as the reference. A slow heating or cooling rate of 1 °C/min was employed for all samples to explore details of the thermal gelation behavior of the cellulose polymer in water. The reason for use of such a low heating or cooling rate was because the hydrophobic association from the relatively stiff cellulose chains was expected to be slow. The effect of heating (or cooling rate) has been studied in our other report[29] where it was found that a faster heating rate could cause a shift of the endothermic peak to the higher temperature, which is a similar phenomenon with the effect of heating rate on the glass transition temperature T_g. However, for an accurate and reliable measurement of micro-DSC, a slow heating (or cooling rate) is always recommended because it allows an efficient heat transfer between the sample and the heater. For the micro-thermal analysis, the sample underwent heating from room temperature of 25 °C or below to about 85 °C, and subsequently it was immediately submitted to cooling from 85 to about 10 °C. After each cycle was completed for the sample, the sample cell was cleaned by a continuous flow of deionized water through a thin plastic tube for more than 1 h. No contamination of the sample cell by the last sample was confirmed by running deionized water before the next sample was injected into the sample cell. If an endothermic or exothermic peak was detected from the sample cell filled with water, the sample cell had to be cleaned again until a no-contamination condition was reached. One of the major limitations of this micro-DCS calorimeter is that a high viscous liquid cannot be injected into the sample cell. Therefore, the concentrations were restricted to be below 2.5 wt % of SM4000. All the micro-DSC runs were performed at 1 °C/min.

Results and Discussion

Dynamic Viscoelastic Properties at Different Temperatures and Scaling. The temperature effect on gelation of the methylcellulose solutions was studied using the dynamic viscoelastic method. As all the aqueous solutions of methylcellulose did not gel at the storage temperature (∼10 °C), the gelation of a given solution was promoted at a desired temperature by measuring the dynamic moduli G' and G'' as a function of time. As soon as the solution reached a plateau in G', the dynamic frequency sweep was conducted to determine G' and G''.

Figures 1 and 2 show the shear storage modulus G' at various temperatures as a function of angular frequency ω for 2.98 and 3.93 wt % solutions of methylcellulose, respectively. For comparison, the G' and G'' data below 25 °C (down to 10 °C) are also included. The typical characteristics of these modulus curves can be figured out directly. For example, from Figure 1, it can be found that there are approximately two distinct groups separated by the temperature: (1) below 50 °C and (2) above 50 °C. In the first range (i.e, below 50 °C), when the temperature is below 15 °C (but excluding 15 °C), the solutions exhibit the liquidlike behavior that G' scales approximately with ω by $G' \sim \omega$ in the range

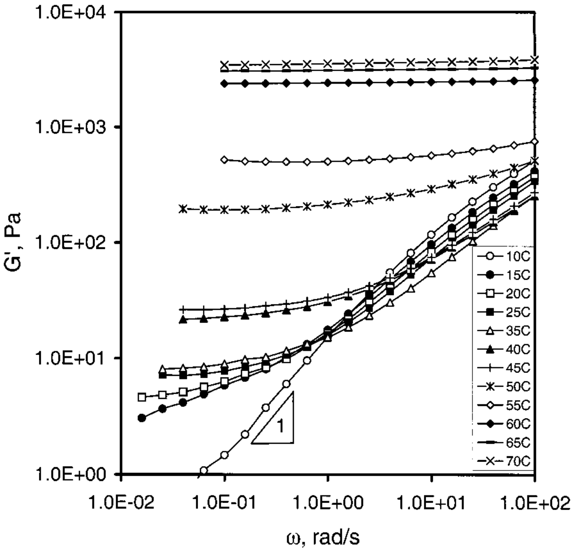

Figure 1. Storage modulus G' of a 2.98 wt % methylcellulose solution as a function of angular frequency ω at various temperatures indicated by the numerals in the box where C is in °C.

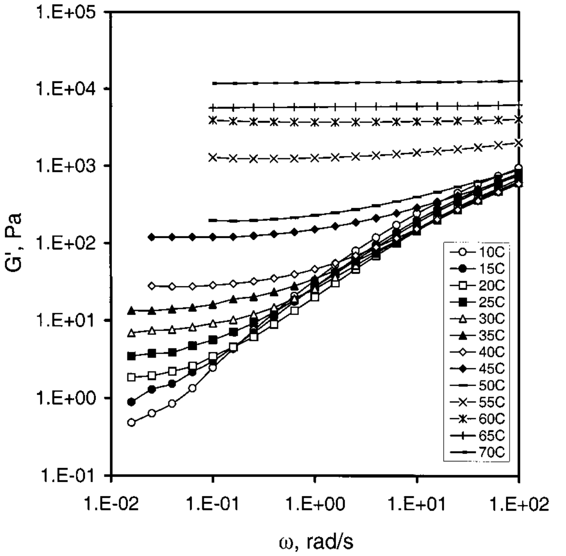

Figure 2. Storage modulus G' of a 3.93 wt % methylcellulose solution as a function of angular frequency ω at various temperatures indicated by the numerals in the box where temperatures have units of °C.

of low frequency, but the terminal behavior, $G' \sim \omega^2$, for a Newtonian fluid,[27] is not observed. The more significant deviation from the terminal behavior is shown at higher temperatures (15−45 °C). In the low-frequency range, the G' curves exhibit a plateaulike behavior, and the height of the plateau increases with temperature. The deviation of the methylcellulose solution from the terminal behavior at low temperatures was explained by Kobayashi et al.[6] to be due to a supermolecular structure maintained by some weak reversible association. However, the mechanism for this weak reversible association has not been identified by the authors.[6] As we have confirmed from our microcalorimetric study shown later in Figure 8, in the temperature range from 10 to 45 °C, it is impossible for the methylcellulose solution to gel through the hydrophobic association. Therefore, we would like to propose the supermolecular structure that is formed through the hydrogen bonding among unmodified hydroxyl groups of the cellulose chains. To avoid any confusion, it should be noted that the discussion here is limited to the temperature range below the onset temperature (about 51 °C) of the endothermic peak determined by micro-DSC as shown later in Figure 8. Since the onset temperature can be defined as the lower critical solution temperature (LCST), the physical state in the temperature range below 51 °C is a solution (sol). The transparent solution state has also been confirmed by our turbidity measurement.[29] At temperatures below 50.9 °C, there are hydrogen bonds between methylcellulose chains and between methylcellulose and water, which can be reversible in water. The hydrophobic association from the methyl groups of methylcellulose is considered not to form in this temperature range because of the fact that neither endothermic nor exothermic heats are detected below 50 °C (see Figure 8). In this temperature range, when temperature is enhanced, the hydrogen bonding between methylcellulose and water will be weakened, but more hydrogen bonds between cellulose chains would be formed to result in a stronger network at a higher temperature. This mechanism would be true because of the inherent poor water solubility of cellulose, which is due to the strong intermolecular hydrogen bonding. Another characteristic in this temperature range (below 51 °C) is that G' at high frequencies decreases with increasing temperature. If there are not any temperature-induced effects, it is common for a polymer solution to show decrease in G' with temperature. The inconsistent behavior of G' between low and high frequencies is considered to be due to the balance between the macromolecular network structure and the temperature-induced decrease in G'. At low frequencies, the formation of a weak network structure through hydrogen bonding is promoted by increasing temperature, but the formed network would not be affected by low frequencies. In contrast, high frequencies would have an effect on destruction of the weak network, and this effect becomes relatively stronger when temperature is higher. This mechanism can be further understood through the temperature-dependent viscosity of water where a high frequency would be able to destroy some weak network structures in a lower viscosity matrix (water) at a higher temperature.

Above 50 °C, all the G' curves show a clear plateau at low frequencies, indicating the existence of gel network structures. The reason for us to consider the establishment of a gel network is simply because of the G' plateau. As is well-known, a strongly entangled polymer solution may also give rise to this G' plateau behavior. However, methylcellulose aqueous solutions are different. If methylcellulose can form entanglements in water, it should have more entanglements at low temperatures compared to high temperatures because methylcellulose chains are more extensive in water at low temperatures. At high temperatures (≥50 °C), the G' plateaus are considered to be due to the formation of a gel network with junctions formed mainly through the hydrophobic association of methylcellulose. Some molecular entanglements may be possible between neighboring hydrophobic junctions so that it would be difficult to distinguish between the hydrophobic junctions and the entanglements. As shown in Figure 1, the plateau height increases with temperature, and the width of each plateau also expands pronouncedly as temperature increases. As a result, we can simply find a frequency-independent plateau at each temperature.

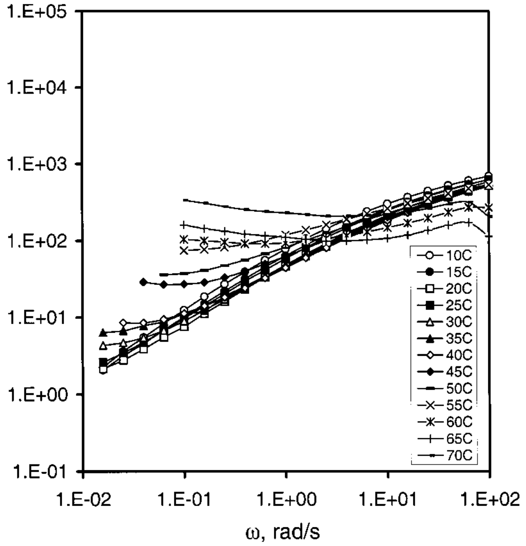

Figure 3. Loss modulus G'' of a 3.93 wt % methylcellulose solution as a function of angular frequency ω at various temperatures indicated by the numerals in the box where temperatures have units of °C.

The viscoelastic behavior of the 3.93 wt % solution is quite similar to the 2.98 wt % solution, but the deviation from the terminal flow behavior occurs more earlier than the latter. This may be considered to be due to a higher packing density of the supermolecular structure, or a higher density of cross-linking due to the hydrogen bonding, or a higher density of molecular entanglements for the higher polymer concentration.

The shear loss modulus G'' at various temperatures as a function of angular frequency ω is illustrated in Figure 3 for the 3.93 wt % solution of methylcellulose. Below 40 °C, G'' shows the weak dependence on temperature. And G'' begins to exhibit the temperature dependence when the temperature is higher than 40 °C, and a plateaulike behavior appears at low frequencies, which increases and widens with temperature. To examine whether a frequency-independent loss tangent tan δ exists to indicate the sol−gel transition, G' and G'' values in Figures 2 and 3 were used to compute tan δ values at various frequencies. The results are shown in Figure 4 where each curve represents tan δ at a given frequency. Although it is believed that the gelation has occurred from the solution state within the temperature range from 10 to 70 °C, tan δ does not show an independence of frequency over the whole temperature range. Therefore, we could not use the scaling law of eq 2 to define the sol−gel transition temperature for the given polymer concentration. As the invalidity of the frequency-independence of tan δ to the methylcellulose aqueous solutions has not been found from the literature, we would like to propose some possible reasons in this report, which may be helpful for understanding of this particular gelling system. First, to allow a gelling system to show a frequncy independence of tan δ, tan δ in the vicinity of the gel point has to be a monotonic function of the gelling variable but with different slopes depending on frequency. For the case of Figure 4, however, in the initial gelation temperature range from 50 to 60 °C, tan δ at each frequency is a monotonically decreasing function of temperature, but all curves seem to be in parallel with each other and no a common convergent point can be found. This phenomenon may be due to the nature of the low critical solution temperature (LCST). This nature provides the polymer with the critical temperature (LCST) above which a phase separation (that causes gelation) can take place immediately. This case would be different from other physical gelation processes like PVC gels studied previuously,[26d] where PVC forms a gel by undergoing a continuous change from the solution state at high temperatures to the gel state at low temperatures. The second important point we have to consider is the thermoreversible gelation of methylcellulose in water. In the temperature range, degelation is always competitive with gelation so that the relaxation time of hydrophobic associative junctions for this gel would not be infinite.

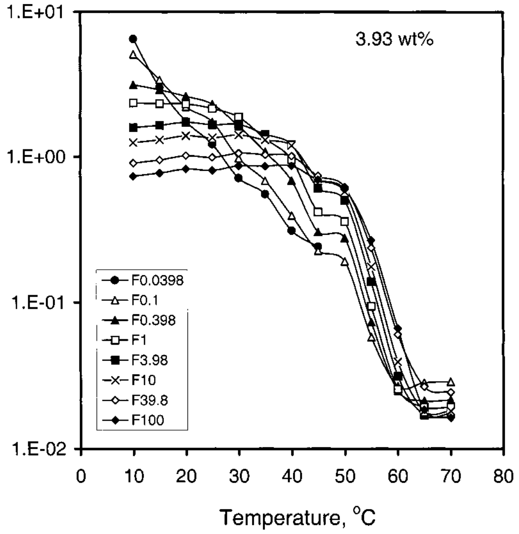

Figure 4. Loss tangent tan δ as a function of temperature for a 3.93 wt % methylcellulose solution at various angular frequencies F (= 0.0398, 0.1, 0.398, 1, 3.98, 10, 39.8, and 100 rad/s) as indicated in the box.

We took all the G' values at the lowest frequency of each curve in Figures 1 and 2 and approximately defined them as G_e, the quasi-equilibrium modulus.[27] These G_e values are plotted linearly in Figure 5a against temperature. Interestingly, in the linear scale (Figure 5a), the effect of temperature on G_e is observed only when temperature is higher than 50 °C. For 2.98 wt %, G_e increases with temperature from 50 °C and tends to level off at 70 °C. But for 3.93 wt %, G_e sharply increases with temperature. The different patterns of the G_e curves for different concentrations may reflect the difference in formation of the gel network from different concentrations of methylcellulose. As the critical temperature of 50 °C is consistent with the onset temperature of the endothermic peak on heating, which was determined using the microcalorimetric analysis, one may consider to use 50 °C as the critical temperature T_c to examine the scaling law of eq 3. As shown in Figure 5b, when 50 °C is used as T_c and the relative gelation temperature of $(T - T_c)/T_c$ is defined, in the semilogarithmic scale G_e can approximately scale with $(T - T_c)/T_c$ through the following relation:

$$\log G_e \propto 4.37\ (T - T_c)/T_c \tag{4a}$$

or

$$G_e \propto \exp[10.1(T - T_c)/T_c] \tag{4b}$$

over the whole range of temperature for 3.93 wt %. The

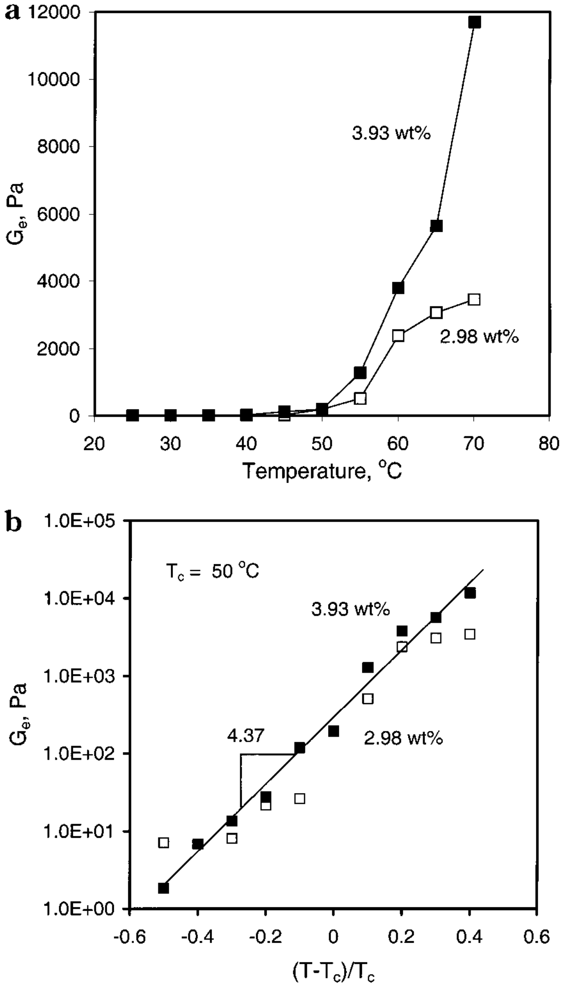

Figure 5. Quasi-equilibrium modulus G_e as a function of temperature for 2.98 and 3.93 wt % solutions and gels of methylcellulose: (a) in a linear scale; (b) in a semilogarithmic scale. G_e is defined by the storage modulus G' at the lowest angular frequency in Figures 1 and 2. The critical temperature T_c of 50 °C was used to define the relative gelation temperature $(T - T_c)/T_c$.

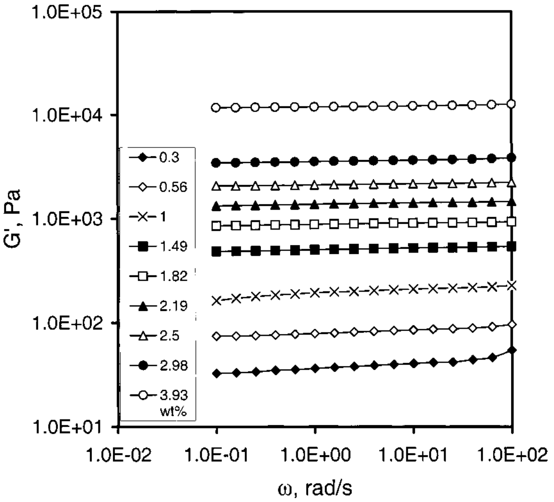

Figure 6. Storage modulus G' as a function of angular frequency ω for various concentrations of methylcellulose at 70 °C. The concentrations are indicated by the numerals in wt % in the box.

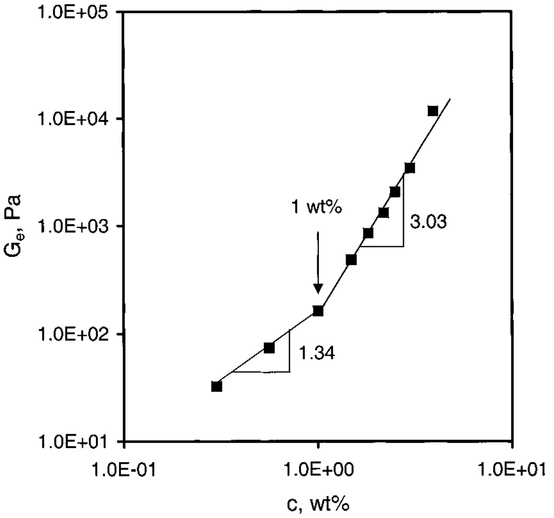

Figure 7. Quasi-equilibrium modulus G_e evolved at 70 °C as a function of methylcellulose concentration c. G_e was defined by G' at the lowest frequency of 0.1 rad/s in Figure 6. Two solid straight lines with the slopes 1.4 and 3.03 are obtained from the linear fittings to the data.

2.98 wt % system also shows the similar scaling relation, but the fitting to the straight line is not as good as the 3.93 wt % one. We note that the scaling relation represented by eqs 4a or 4b is a different expression from eq 3. This result proves the invalidity of eq 3 for the system studied when 50 °C is used as the critical gelation temperature. This also reflects the technical difficulty in defining the critical gelation temperature T_c for examination of the scaling law of eq 3. The failure of the scaling law to the G_e data might be due to the different fractal structures of junctions developed at different temperatures.

Elasticity Evolution at 70 °C and Scaling. From our previous study on thermally induced association of methylcellulose in water using microcalorimetry, we have known that the methycellulose gels in the temperature range between about 50 and 72 °C, which is slightly dependent on polymer concentration.[29] Now in this temperature range of gelation, we choose a temperature of 70 °C, which is close to the highest side of the range in order to quickly observe the stabilization of gelation, to investigate the viscoelastic behavior and the validity of scaling laws at this gelation temperature. The more important reason for us to measure the gelation behavior of methylcellulose at the fixed temperature is because of the hypothesis that the similar (or fractally similar) gel network structure would be formed at the same temperature, even for different concentrations.

Figure 6 shows the dynamic storage modulus G' as a function of angular frequency ω for various concentrations of methylcellulose at 70 °C. For all the concentrations of methylcellulose studied, G' exhibits a weak dependence on ω, and the ω dependence decreases with increasing polymer concentration. When the concentration is higher than 1 wt % (excluding 1 wt %), G' is almost independent of ω to result in a nice plateau. For consistency, however, we took the G' values at the lowest frequency of 0.1 rad/s for all the concentrations and plotted them against concentration c in Figure 7. To examine the scaling law again, the log−log scale is used in Figure 7.

As shown in Figure 7, one could not use a single straight line to fit all the data points. Instead of a single straight line, the two straight lines can fit the data nicely. From the slopes of the straight lines, we obtain the following two scaling relations immediately.

$$G_e \sim c^{1.34} \quad \text{for } c \leq 1 \text{ wt \%} \tag{5a}$$

$$G_e \sim c^{3.03} \quad \text{for } c > 1 \text{ wt \%} \tag{5b}$$

From these two scaling laws, we can classify the gels. That is, when 1 wt % is defined as a critical concentration, the gels can be classified into two groups: weak gels (for $c \leq 1$ wt %) and strong gels (for $c > 1$ wt %). The definition of the weak and strong gels here is made only based on the scaling relations found from eqs 5a and 5b, and no further correlation with the gelation structure has been proposed in this report. It should be also noted that the scaling relations represented by eqs 5a and 5b are still different from eq 3 because the relative distance ϵ was not used. To define ϵ, one needs to find the critical gelation concentration c_g at 70 °C. However, it is technically difficult to determine c_g using the method[20-22] of the frequency independence of loss tangent for these MC solutions. The failure in measuring the sol–gel transition using the frequency independence of tan δ has been illustrated in Figure 4. Although eq 5 is not the same as eq 3, the characteristic of the two-step scaling will not change with using the relative distance of gelation c_g.

The invalidity of single scaling laws for the gelation of methylcellulose in water is considered to be due to a heterogeneous formation of the gel network. To form a physical gel in water from the hydrophobic association of methylcellulose, the polymer chains have to be close enough to allow the hydrophobic association as the cellulose glucose units (the ring structure) are modified just by methyl groups but not by a long hydrophobic side chain like cetylhydroxyethylcellulose.[8-10] This chemical structure in methylcellulose would cause the difficulty for the stiff cellulose chains to equally move to junction domains, resulting in a nonuniformity (polydispersity) or a nonfractal structure in the gel network. However, this point needs to be proved by a future work.

Calorimeric and Rheological Thermoreversibilities. Thermoreversibility of methylcellulose is of both fundamental and applied interests. For example, it is interesting to know how a gel network is formed upon heating and how the gel formed returns to a liquid state upon cooling. In this work, we have employed two techniques, micro-DSC and rheology, to characterize the thermoreversible gelation behavior of methylcellulose. First, the calorimetric behavior was measured using micro-DSC for a 2.49 wt % solution of methylcellulose, and the results are given in Figure 8.

The relative thermal capacity C_p is used in this report because of the nature of DSC where a relative heat between the sample and the reference is always measured. In the heating process, the sharp endothermic peak with the peak temperature of 61.3 °C is observed from the onset temperature 50.9 °C to the offset temperature 71.9 °C, while the broad exothermic peak appears at 31.3 °C in the subsequent cooling process. The heating and cooling rates were 1 °C/min. The whole thermal cycle from the beginning of heating to the end of cooling represents a thermally reversible process. This has been evidenced from the exactly same calorimetric curves reproduced when the second thermal cycle is subsequently run after the first cycle as confirmed by our other experiments.[29]

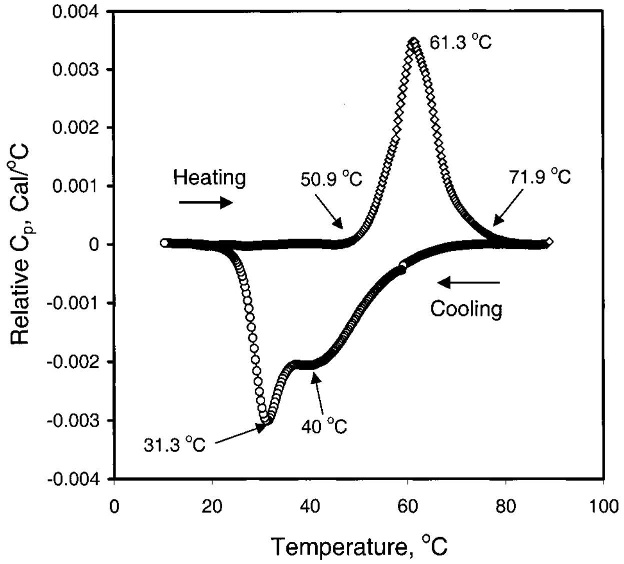

Figure 8. Calorimetric thermograms of a 2.49 wt % aqueous solution of methylcellulose during a thermal cycle from heating to cooling. The heating and cooling rates were 1 °C/min. The numerals in the figure indicate the transition or characteristic temperatures.

The methylcellulose solution in the cooling process behaves completely differently from those in the heating process where a relatively narrow endothermic peak appears at about 61.3 °C. A shoulder is observed at about 40 °C, which is above the peak temperature of 31.3 °C. We define the main peak of 31.3 °C as the primary peak and the shoulder at 40 °C as the secondary peak. In the cooling process, the dissociation of the associated structures of methylcellulose in water, which were formed in the heating process, appears to have to overcome two energy barriers: a primary barrier at about 31.3 °C and a secondary one in the broad temperature range from about 70 to 35 °C. The most remarkable feature of this thermoreversible gelation is that the difference in the peak temperature between the heating and the cooling processes is as large as 30 °C.

From Figure 8, we have known that the endothermic heat is observed on heating while the exothermic heat does on cooling. Here an interesting question raised is why the heat change on heating is endothermic while the heat change on cooling is exothermic. The hydrophobic association of cellulose molecules in water is considered to be a thermodynamic process that is determined by the difference in the free energy (ΔG) between the free state and the associative state. The association in the solution will occur only when ΔG is negative at a given constant temperature T:

$$\Delta G = \Delta H - T\Delta S < 0 \tag{6}$$

where ΔH and ΔS are the differences in enthalpy and entropy, respectively. On heating, methylcellulose chains associate to form aggregates or clusters through the hydrophobic attraction between polymer chains. For this kind of hydrophobic association, one would consider that when aggregates of methylcellulose chains are formed in water, the change in entropy (ΔS) should be negative due to the restriction of molecular chains within the aggregates. If ΔS is negative, ΔH has to be negative. To examine this hypothesis, let us do some simple thermodynamic calculations.

For simplicity, we define the peak area as the total heat of endotherm or exotherm [in joules (J)], normalized by the sample volume of 0.516 mL. As we know the thermal capacity $C_p(T)$, the entropy change ΔS can be directly calculated using

$$\Delta S = \int_{T_1}^{T_2} (C_p/T)\,\mathrm{d}T \tag{7}$$

where T is temperature, and T_1 and T_2 are the onset and offset temperatures of an calorimetric (endothermic or exothermic) peak. The entropy change ΔS on heating obtained using eq 7 is 0.814 J K^{-1} L^{-1} for 2.49 wt %, which is a positive value. Now, the new question is why ΔS has to be positive.

When an endothermic heat is detected, the entropy change must be positive in order to meet the requirement of $\Delta G < 0$ as indicated in eq 6. This condition has been verified from the calculation using eq 7. However, the process that methylcellulose chains associate on heating to form aggregates or eventually a gel is normally considered as an entropy-decreasing process so that the entropy change should be negative. The discrepancy between the experimental result and this consideration could be due to the role of water, which could be vital in governing the thermodynamic properties of a methylcellulose solution. The fact that methylcellulose is soluble in water is because of the hydrogen bonding between methylcellulose molecules and water molecules. The polar water molecules pull methylcellulose chains to associate with water through the formation of hydrogen bonding. In this state, individual methylcellulose chains can be considered to be surrounded by water molecules, and the water molecules that form the hydrogen bonds with the methylcellulose chains are not free. These water molecules may have some degree of order in the solution. When a methylcellulose solution is heated, the energy added will be consumed to destroy the hydrogen bonds between water and methylcellulose to enable the subsequent hydrophobic association. The hydrophobic association of methylcellulose should reach the maximum level when all the surrounding hydrogen bonds have been removed by heat. The water molecules released from the hydrogen bonds will become free again. Therefore, the water molecules in this dehydration process undergo a change from the relatively ordered state to the random state so that the entropy change for these water molecules should be positive. This mechanism provides an explanation why the heat in the heating process is endothermic and why the entropy change should be positive. Conversely, the cooling process should be an opposite process that makes both the heat change and the entropy change negative.

A positive change of enthalpy or an endothermic peak has also been found by Hauque et al.[3] and Hirrien et al.[5] when heating an aqueous solution of methylcellulose. Again, when ΔH is positive, ΔS must be positive to yield a negative ΔG. In this case, the hydrophobic association will be driven by entropy rather than by enthalpy. With at least a phenomenological similarity, it is interesting to know that many ionic surfactants show positive changes in entropy when they micellize in water.[30] For example, the micellization of sodium dodecanesulfonate in water at 25 °C gives that $\Delta H = +2.06$ kJ mol^{-1} and $\Delta S = 0.077$ kJ mol^{-1} K^{-1}. ΔH and ΔS are $+2.56$ kJ mol^{-1} and 0.061 kJ mol^{-1} K^{-1}, respectively, for the micellization of sodium decanesulfonate in water at 25 °C.[31] Our recent studies[32] on interactions of sodium dodecyl sulfate (SDS) and PEO−PPO triblock copolymers in aqueous solutions have also proved that the physical bonding of SDS onto the water-soluble polymer to form the polymer/SDS aggregation complex is an entropy-driven process, associated with a positive ΔH. In all the cases, it is believed that water plays a vital role in determining their thermodynamic properties.

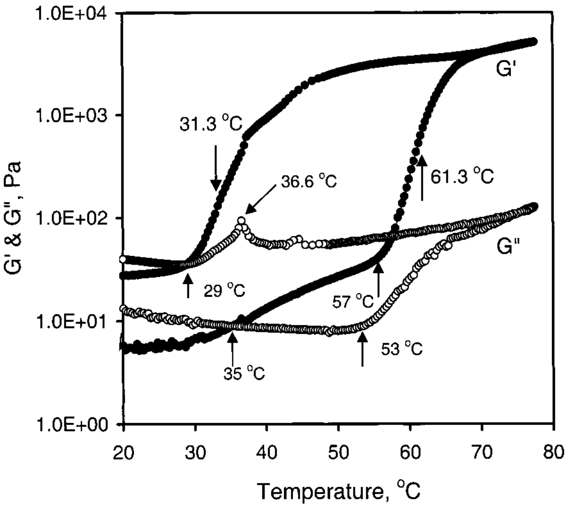

Figure 9. Storage modulus G' (filled circles) and loss modulus G'' (empty circles) as a function of temperature in a heating and a cooling processes for a 2.49 wt % methylcellulose solution. A shear strain amplitude of 5% and an angular frequency of 1 rad/s were applied. The heating and cooling rates were about 1 °C/min.

In contrast to to the heating process, when cooling from a high temperature (e.g., 80 °C, Figure 8), the dissociation of the hydrophobic aggregates formed in the heating process takes place where ΔG must be negative, which requires a negative ΔH and/or a positive ΔS. It should be noted here that this kind of hydrophobic association or dissociation is different from crystallization or melting at least because of the difference in ΔH. ΔH is always negative on crystallization, while ΔH is always positive on melting because the system must absorb heat to disrupt the bonding within crystallites.

For comparison with the calorimetric thermoreversibility shown in Figure 8, the dynamic viscoelastic measurements were carried out. The results are presented in Figure 9 for the same 2.49 wt % solution where the heating and cooling rates of about 1 °C/min and an angular frequency of 1 rad/s were used for the measurement.

As shown in Figure 9, in the heating process from 20 to about 78 °C, there are at least three distinct regions. The first region is by the crossover of storage modulus G' and loss modulus G'', where G' is below G'', showing the common viscoelastic behavior of a liquid. G' crosses over G'' at 35 °C. Beyond 35 °C, G' gradually increases until about 57 °C. In this second region, G' gradually increases with temperature while G'' decreases slightly until about 53 °C. Since G' is always higher than G'' in this region, one can consider that a weak but elastic structure of methylcellulose is being formed in water with temperature. On the basis of the micro-thermal analysis results shown in Figure 8, if one considers that the hydrophobic association is the only driving force for the formation of a gel or a microgel, the second region would not be responsible for the gelation because there are no endothermic peaks in this range. G' speedily increases from 57 °C, passes a transition at about 61.3

°C, and eventually reaches the plateau at about 70 °C.

Traditionally, the crossover of G' and G'' is used as an indication of the sol−gel transition point.[27] This method is simple and convenient, but the gel point defined by this method is usually dependent on frequency used in the measurement. Winter's group[20−22] defined the sol−gel transition as the point at which both G' and G'' scale with ω^n so that the ratio of G'' to G' (i.e., tan δ) is independent of frequency ω. In other words, at the sol−gel transition with the frequency independence, G' must be parallel to G''. For the methylcellulose aqueous solutions, however, we have confirmed that there is not such a condition that can be found to satisfy the requirement in applying the Winnter's scaling law at the sol−gel transition.[28] However, it is also unreasonable to employ the traditional definition (i.e., the crossover of G' and G'') to define the sol−gel transition for the case of Figure 9, for the following two reasons: (1) in the temperature range from 35 to 57 °C G' values were below a few tens of pascals, and the solution did not behave like a gel; (2) the crossover temperature of 35 °C is far below the onset temperature (50.9 °C) of the endothermic peak as shown in Figure 8. The most significant finding here is that there is an abrupt increase of G' in the vicinity of 61.3 °C, which correlates excellently with the endothermic peak observed by the micro-DSC (Figure 8). Therefore, it would be more appropriate to use 61.3 °C to define the sol−gel transition rather than the crossover point of G' and G''. We intend to develop this concept further toward a new definition of the sol−gel transition for thermoreversible gels such as gels formed from hydrophobically modified cellulose.

In Figure 9, the heating process was continued until 78 °C, but the sample still showed a slight increase in modulus and did not show any drop even through the temperatures have been beyond the offset peak temperature of about 72 °C as found by micro-DSC. This would be because the phase separation beyond 72 °C is a time-dependent process, and it does not occur during the short period of measurement.

Starting from the plateau, the cooling process was conducted at a similar cooling rate of 1 °C/min. In contrast to the sharp increase of G' in the heating process in the temperature range from 57 to 70 °C, the gradual decrease in G' with temperature in the cooling process shows an outstanding deviation from the heating curve. This clearly indicates that the thermally induced hydrophobic dissociation is not an exact reversal of the hydrophobic association occurring in the heating process. Interestingly, the crossover of G' and G'' is observed at 29 °C, which is below the crossover point of 35 °C found in the heating process. Before this crossover point, G' rapidly decreases from the plateau by passing the transition temperature near 31.3 °C.

By comparing Figure 9 with Figure 8, it is significant to know that the rheological thermoreversibility excellently correlates with the calorimetric thermoreversibility for the whole process from gelation to degelation of methylcellulose in water.

Conclusions

The thermal gelation of methylcellulose (weight-average molecular weight was 310 000) in water was investigated as a function of methylcellulose concentration and temperature by means of rheology and micro-DSC. The validity of the scaling laws for these methylcellulose solutions and gels was examined. It was found that the gel elasticity G_e evolved with temperature did not obey a single scaling law with the relative gelation distance defined by $(T - T_c)/T_c$, but the gel elasticity could be expressed by $G_e \propto \exp[10.1(T - T_c)/T_c]$ over a wide range of temperature, where $T_c = 50$ °C. At 70 °C, the gel elasticity increased with polymer concentration, and it could be described by a two-step scaling law. For the weak gels ($c \leq 1$ wt %), the elasticity G_e at 70 °C scaled with polymer concentration c as $G_e \sim c^{1.34}$, while G_e scaled with c as $G_e \sim c^{3.03}$ for the strong gels ($c > 1$ wt %). The thermoreversibility of methylcellulose's gelation in water was examined by both rheology and micro-DSC, and the cellulose polymer showed the excellent thermoreversibility in gelation. As a significant result, the rheological thermoreversibility was able to excellently correlate with the micro-calorimetric thermoreversibility. From the thermodynamic analysis, we also proved that the gelation of methylcellulose is an entropy-driven process.

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