Unique Gelation Behavior of Cellulose in NaOH/Urea Aqueous Solution

Jie Cai[†] and Lina Zhang*[,†,‡]

Department of Chemistry, and Center of Nanoscience and Nanotechnology, Wuhan University,
Wuhan 430072, China

Received August 5, 2005; Revised Manuscript Received October 8, 2005

A transparent cellulose solution was prepared by mixing 7 wt % NaOH with 12 wt % urea aqueous solution which was precooled to below −10 °C and which was able to rapidly dissolve cellulose at ambient temperature. The rheological properties and behavior of the gel-formed cellulose solution were investigated by using dynamic viscoelastic measurement. The effects of temperature, time, cellulose molecular weight, and concentrations on both the shear storage modulus (G') and the loss modulus (G'') were analyzed. The cellulose solution having a viscosity-average molecular weight (M_η) of 11.4×10^4 had its sol−gel transition temperature decreased from 60.3 to 30.5 °C with an increase of its concentration from 3 to 5 wt %. The gelation temperature of a 4 wt % cellulose solution dropped from 59.4 to 30.5 °C as the M_η value was increased from 4.5×10^4 to 11.4×10^4. Interestingly, at either higher temperature (above 30 °C), or lower temperature (below −3 °C), or for longer gelation time, gels could form in the cellulose solutions. However, the cellulose solution remains a liquid state for a long time at the temperature range from 0 to 5 °C. For the first time, we revealed an irreversible gelation in the cellulose solution system. The gel having been formed did not dissolve even when cooled to the temperature of −10 °C, at which it was dissolved previously. Therefore, this indicates that either heating or cooling treatment could not break such stable gels. A high apparent activation energy (E_a) of the cellulose solution below 0 °C was obtained and was used to explain the gel formation under the cooling process.

Introduction

There are no covalent bonds forming or breaking in the formation of physical gels, and polymers form a cross-linked network through ionic bonding, hydrogen bonding, or chain entanglements of polymer-to-polymer interactions. A physical gelation is more complex than a chemical one. Some hydrocolloids can be changed reversibly between a solution state and a gel state by lowering or raising the temperature. The change depends on the nature of the secondary structure or noncovalent molecular forces such as hydrogen bonds, hydrophobic interaction, and Coulombic interaction.[1,2] Recently, polysaccharides and proteins from renewable resources have attracted more attention due to their wide applications as texture modifiers for controlling rheological properties, gelling agents, thickeners, emulsifiers, stabilizers, and coating and packaging films in various fields including foods, pharmaceuticals, cosmetics, textiles, and biomedical sectors.[1] Cellulose is considered as a nearly inexhaustible raw polymeric material with fascinating structures and properties for the remarkable demand for environmentally friendly and biocompatible products.[3,4] Therefore, the hydrogel developed from cellulose is getting more interest due to its characteristics of hydrophilicity, solute permeability, and nontoxicity. However, as is well-known, cellulose is very difficult to dissolve in common solvents; thus, chemical modification has to provide a dominant route toward cellulose utilization in polymer-based materials.[5] It has been reported that cellulose derivatives, such as methylcellulose (MC),[6−10] cellulose diacetates (CDA),[11] and benzylcellulose[12] can form a thermoreversible gel in their solution upon heating. The thermal gelation from MC with an appropriate degree of substitution can take place because of the hydrophobic association that becomes pronounced at elevated temperatures[8,13−15] and the cooperation of the hydrophobic interaction among substituent groups with the intermolecular hydrogen bonds among hydroxyl groups at the C(6) position.[9,11] So far, the rheological properties of various cellulose solutions without derivatizing have not been studied extensively yet because of their insolubility in water and in many other solvents. Frey et al.[16] have reported that the cellulose/ammonia/ammonium thiocyanate solution can form thermoreversible gels at temperatures below 30 °C. Thermal gelation also occurs in cellulose/cuprammonium solution as a result of the partial destruction of the complex that leads to the formation of intermolecular hydrogen bonds of cellulose at above 40 °C.[17] A phase behavior of 5 to 25 wt % cellulose in an *N*-methylmorpholine-*N*-oxide (NMMO)/H_2O solution system has been investigated by rheological methods,[18−20] with the findings of an anisotropic phase for the solution occurring over 20 wt % concentration and the isotropic phase transition around 100 °C.

In recent years, we have developed a new solvent which is made of 7 wt % NaOH mixed with 12 wt % urea aqueous solution,[21] in which cellulose was dissolved within 5 min without derivatization.[22] Moreover, novel regenerated cellulose fibers have been successfully spun from the cellulose solution in such NaOH/urea aqueous solutions.[23] It is well-known that the rheological properties of the cellulose solution exert a great influence on the spinning process, structure formation, and fiber properties. Furthermore, the sol−gel transition of the cellulose solution is an important physical phenomenon with both considerable scientific and industrial importance. However, the rheological properties of cellulose in the NaOH/urea aqueous

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[*] To whom correspondence should be addressed. Phone: +86-27-87219274. Fax: +86-27-68754067. E-mail: lnzhang@public.wh.hb.cn.
[†] Department of Chemistry.
[‡] Center of Nanoscience and Nanotechnology.

10.1021/bm0505585 CCC: $33.50

solution have not been investigated much. In this article, we studied the rheological behavior and gel formation of cellulose in the 7 wt % NaOH and 12 wt % urea aqueous solution with regard to the impact of different temperatures and times, as well as cellulose concentration and molecular weight. Our objective was to gain a better understanding of the factors that govern the rheological behaviors and gelation of the cellulose solution system.

Experimental Details

Materials. Five kinds of cotton linter pulps supplied by Hubei Chemical Fiber Co. Ltd. (Xiangfan, China) were selected as cellulose samples. Their viscosity-average molecular weights (M_η) were determined in cadoxen at 25 °C by viscometry and calculated by[24]

$$[\eta] = 3.85 \times 10^{-2}\, M_w^{0.76}\ (\text{mL g}^{-1}) \qquad (1)$$

The obtained M_η values were 4.5×10^4, 6.2×10^4, 8.3×10^4, 9.4×10^4, and 11.4×10^4, and they were coded as M4, M6, M8, M9, and M11, respectively. The cellulose samples were vacuum-dried at 55 °C for 24 h to remove any moisture before use. NaOH and urea of analytical grade (Shanghai Chemical Reagent Co. Ltd., China) were used without further purification.

Dissolution of Cellulose. The aqueous solution containing NaOH/urea/H_2O at the ratio of 7:12:81 by weight was used as a solvent for cellulose. The solvent was precooled to below −10 °C. Then the cellulose sample in the desired amount was added immediately into it at an ambient temperature of below 25 °C. The cellulose was completely dissolved within 5 min with stirring at 3000 rpm. The resultant solutions came out transparent and then were centrifuged to degas them at 4000 rpm for 10 min at 5 °C. M11 was used as the main cellulose sample for all experiments, and its concentration was kept constant at 4 wt % unless as particularly described.

Characterization. The dynamic rheology experiment was carried out on an ARES-RFS III rheometer (TA Instruments, U.S.A.). A double-concentric cylinder geometry with a gap of 2 mm was used to measure dynamic viscoelastic parameters such as the shear storage modulus (G') and loss modulus (G'') as functions of angular frequency (ω), time (t), or temperature (T). The rheometer was equipped with two force transducers allowing the torque measurement in the range from 0.004 to 1000 g·cm. The values of the strain amplitude were checked to ensure that all measurements were set as 10%, which is within a linear viscoelastic regime. For each measurement, a fresh cellulose solution was prepared, and then degassed cellulose solution was poured into the couette geometry instrument, which had been kept at each measurement temperature without preshearing or oscillating. Temperature control was established by connection with a julabo FS18 cooling/heating bath kept within ±0.2 °C over an extended time. To prevent dehydration during rheological measurements, a thin layer of low-viscosity paraffin oil was spread on the exposed surface of the measured solution. For the frequency and time sweep measurements, time $t = 0$ min was defined when the temperature reached the desired value. The sweep of the frequency was from 0.01 to 100 rad/s. The gelation kinetics were studied at constant temperature as a function of time at a constant frequency of 1 rad/s. The dynamic temperature sweep measurements were conducted from −8 to 70 °C at an angular frequency of 1 rad/s and with heating or cooling rates of 0.5 °C/min.

Results and Discussion

Dynamic Viscoelastic Properties of the Cellulose Solution. The temperature effect on gelation of the cellulose solutions was measured by using the dynamic viscoelastic method. Figure 1 shows the shear storage modulus (G') at various temperatures as a function of angular frequency (ω) for a 4 wt % cellulose solution. The typical characteristics of the G' curves can be divided into three segments: a G' strain line with the slope of 1 at 0 °C; a plateau of the G' curves that became obvious as the temperature is raised from 15 to ∼65 °C; a slight flat site with G' curves increasing as the temperature dropped in the range of −8 to −5 °C. It is interesting to see that below 0 °C, the G' values increase with a decrease of temperature over the entire accessible frequency. This suggests more aggregates and entanglements of the cellulose chains in the solution at lower temperature, because the cellulose chains become stiffer and have stronger interaction as confirmed later. At the range of 0 to 15 °C, the solutions exhibit liquidlike behavior with G' scaling approximately with ω by $G' \sim \omega$ in the range of low frequency, but the terminal behavior ($G' \sim \omega^2$) for a Newtonian fluid[25] was not observed. However, above 20 °C at low frequencies, the G' curves present a plateaulike behavior, and its height increases and the width expands with the raised temperature. Interestingly, the G' values increase rapidly and show significantly frequency-independent plateaus above 55 °C at 3×10^{-2} to 10 rad/s, which indicates the existence of the stable structure of the gel network. Within this temperature range, the G' plateau is shown as a result of the formation of a gel network with the junctions formed by self-associated cellulose chains. This can be attributed to phase separation by heating above 55 °C accompanied by gelation.[15] It suggests that the elastic behavior of the cellulose solution has occurred at elevated temperature, because of the molecular entanglements and interchain interaction caused by self-association junctions on the cellulose backbone.[26] There are several possible forms of hydrogen bonds between cellulose and solvent and those between cellulose molecules as follows: intra- and intermolecular hydrogen bonding between hydroxyl groups of cellulose; hydrogen bonding between the hydroxyl groups of cellulose and solvent molecules (NaOH hydrates, urea hydrates, and free water); hydrogen bonding and electrostatic interaction between the solvent molecules.[22] As the strength of hydrogen bonding is dependent on temperature, the formation of the gel will also be dependent upon temperature. Thus, the formation and destruction of the hydrogen bonds are relevant to temperature and other environmental conditions. In our work, when the temperature was raised, the hydrogen bond strength between cellulose and solvent became weakened, whereas the intra- and intermolecular

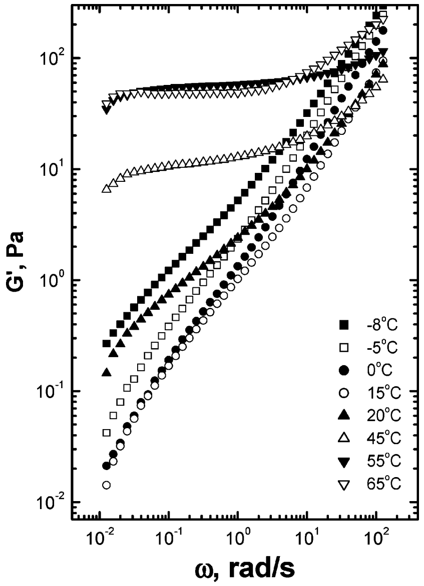

Figure 1. Storage modulus G' as a function of angular frequency ω at various temperatures for 4 wt % cellulose solution.

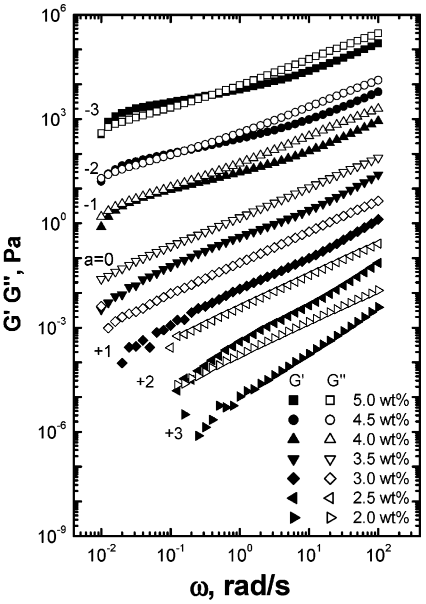

Figure 2. Storage modulus G' and loss modulus G'' as a function of angular frequency ω for cellulose solutions with different concentrations at 25 °C. The data are shifted along the vertical axis by 10^a to avoid overlapping.

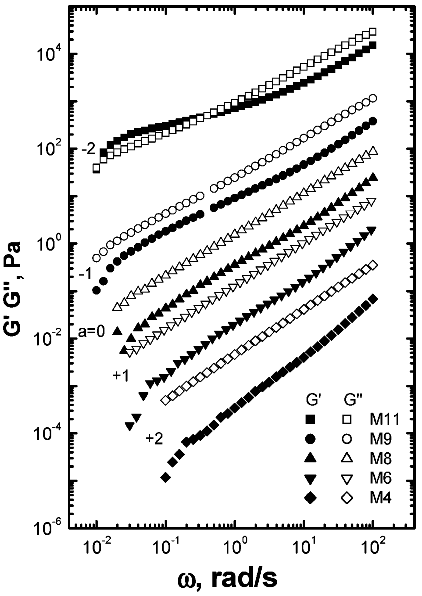

Figure 3. Storage modulus G' and loss modulus G'' as a function of angular frequency ω for 5 wt % cellulose solutions having different molecular weights at 25 °C. The data are shifted along the vertical axis by 10^a to avoid overlapping.

hydrogen bonds of cellulose tended to increase as a result of its strong self-association tendency. Such strong bonding is believed to cause aggregation and chain entanglements.

Figures 2 and 3 show the G' and G'' curves as a function of angular frequency for the cellulose solution with different concentrations and molecular weights, respectively. At the concentration below 3.5 wt %, the cellulose has a G' far smaller than G'' at all frequencies, and both G' and G'' are strongly dependent on the frequency in Figure 2. It is noted that at very low frequencies the relations $G' \sim \omega^2$ and $G'' \sim \omega$ can be observed for the cellulose solutions with the concentration of 2.0 to 2.5 wt %; this presents a nonentangled polymer solution behavior.[27] In such a case, deformation of the cellulose solution takes place so slowly that the majority of the energy is dissipated by viscous flow, leading to the liquid state. As the cellulose concentration increases from 3.5 to 5.0 wt %, the difference between the G' and G'' values becomes small. That is a sign of chain aggregation and entanglement taking place. The G' values for the cellulose solutions at 4.0 to 5.0 wt % are larger than G'' at lower frequencies, suggesting an elastic behavior. However, both G' and G'' increase with increased frequency and show a crossover, and then G' becomes smaller than G'' at higher frequencies. It shows that the ability of the temporary networks was enhanced with the increase of polymer concentrations and behaves more like an elastic solid. This can be explained by the observation that molecular chains of cellulose are more close to each other at higher concentration. The probability of the formation of a junction zone is higher than that at lower concentration. Similarly, the G' and G'' curves in Figure 3 for the cellulose solution having M_η below 9.4 × 10^4 exhibit dominant viscous behavior at 0.01 to 100 rad/s, whereas the one with M_η of 11.4 × 10^4 displays an elastic behavior at low frequency. As the length of the cellulose chain increases, its relaxation capacity decreases, resulting in easy entanglement. In view of the above results, either decreased molecular weight or lower cellulose concentration leads to the relatively stable liquid state of the cellulose solution.

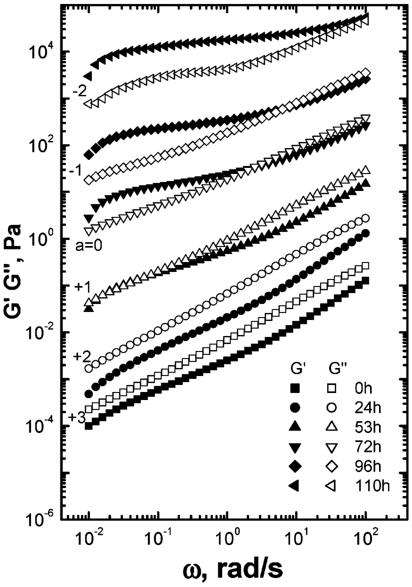

Figure 4. Storage modulus G' and loss modulus G'' as a function of angular frequency ω for 4 wt % cellulose solutions at different times at 8 °C. The data are shifted along the vertical axis by 10^a to avoid overlapping.

The G' and G'' curves of 4 wt % cellulose solution over a period of 0 to 110 h at 8 °C are illustrated in Figure 4. During 0 to 53 h, the G'' values are greater than G' for the entire frequency range measured, which indicates that a liquidlike behavior is occurring. However, after 53 h, the rheological behavior of the cellulose solution considerably differs from that of the earlier traces. The frequency dependence of the G' and G'' moduli decreases significantly with the longer duration of time. An examination of the frequency from 53 to 110 h indicated a progressive increase in the elastic moduli and G' over G''; this feature is characteristic of gel formation. Moreover, with the increase of time the crossover point shifts to a much higher frequency and shows a transition from frequency-dependent behavior with G'' values larger than those of G'. The result indicates that the relaxation of the cellulose chains in the solution becomes slower. Therefore, the sol–gel transition at 8 °C is a slow process transforming from a solution state, into a

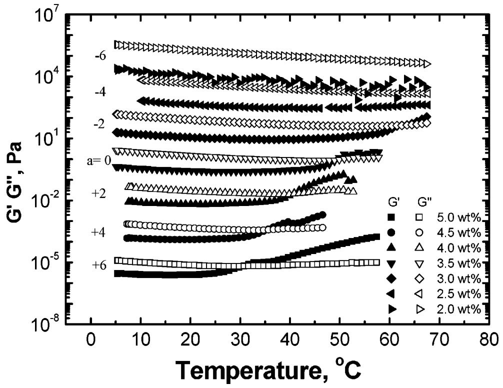

Figure 5. Temperature dependence of the storage modulus *G′* and loss modulus *G″* for cellulose solutions with different concentrations. The data are shifted along the vertical axis by 10^a to avoid overlapping.

weakly aggregated cellulose system, and finally to a gel network which remained for a long time.

Effects of Molecular Weight and Concentration on the Sol−Gel Transition. The study of the sol−gel transition has been attracting more attention because it is an important physical phenomenon with both considerable academic and industrial importance.[28] Winter and Chambon have proposed a criterion of the sol−gel transition as the point where both *G′* and *G″* are scaled with ω^n. Thus, the ratio of *G″* to *G′* (i.e., tan δ) is frequency-independent.[29−31] This criterion has been applied to describe gelation well especially for chemical gelation[29,32] and thermoreversible gelation.[33] To examine whether a frequency-independent tan δ exists in our cellulose/NaOH/urea aqueous system, the *G′* in Figure 1 and the corresponding *G″* values have been used to compute tan δ values at various frequency levels (not shown). Although it is a fact that the gelation has occurred from the solution state with the temperature range from 10 to 65 °C, tan δ does not show its frequency independence over the examined temperature range. This implies that our cellulose solution is a very complex system with various types of interactions going on among cellulose, NaOH hydrates, urea hydrates, and free water. So in our opinion the Winter−Chambon criterion is not powerful enough in determining the critical gelation point in the complex cellulose/NaOH/urea aqueous solution. Besides, it has not been theoretically proven that any gelling system should follow such a rule as well. In the methylcellulose solution[34] and poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO−PPO−PEO) triblock copolymer aqueous solution[35] the behavior of $G' \sim G'' \sim \omega^n$ was not found in the vicinity of the sol−gel transition. In addition, the application of this gelation criterion had been proposed originally for chemically cross-linked gels. It is important to access low-frequency data at a confident level to ensure the interactions are permanent instead of physical interactions at some infinite time scale.[36] Such a single scaling law may fail to explain inhomogeneous fractal gel structure or multifractals[37] over the entire temperature range. Therefore, the traditional method of using the crossover of *G′* and *G″* curves was chosen to determine the gel point of the cellulose/NaOH/urea aqueous solution. We discovered that the gel point determined by this is frequency-dependent as shown in Figure 1. To be consistent on gel point determination, the frequency of 1 rad/s was selected for all the samples and the values at crossover of the *G′* and *G″* curves was taken as as G_{gel}.

The effects of the cellulose concentrations on *G′* and *G″* values are illustrated in Figure 5, and the gelation temperature and G_{gel} as a function of concentration are plotted in Figure 6.

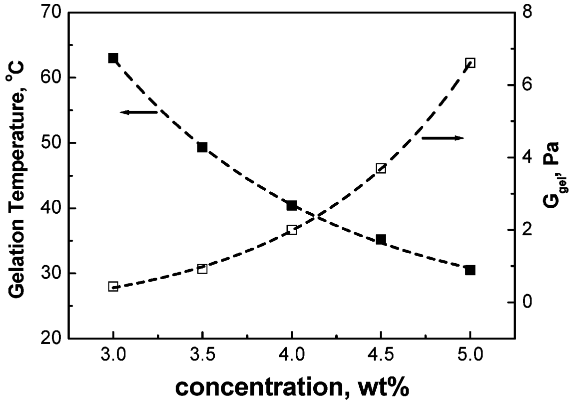

Figure 6. Gelation temperature and G_{gel} as a function of the cellulose concentration.

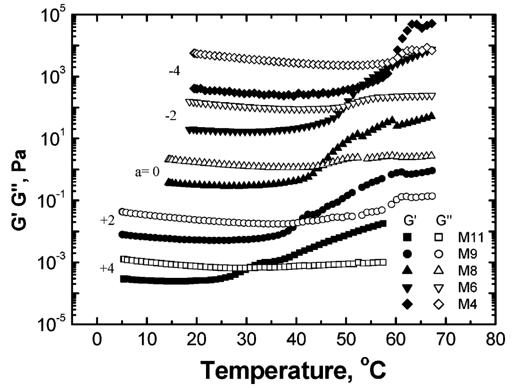

Figure 7. Temperature dependence of the storage modulus *G′* and loss modulus *G″* for 5 wt % cellulose solutions with different molecular weights. The data are shifted along the vertical axis by 10^a to avoid overlapping.

Apparently, the gelation temperature of the cellulose solution with M_η of 11.4×10^4 drops from 60.3 to 30.5 °C with the increase of cellulose concentration from 3.0 to 5.0 wt %. With the cellulose concentration below 3 wt %, no temperature-induced gelation behavior was observed. This suggests that aggregation and entanglement among the cellulose chains did not occur in a relatively dilute cellulose solution. The increase of G_{gel} with the cellulose concentration above 3 wt % was due to the progressively increased number of junction zones between the cellulose chains.

Figure 7 shows the temperature dependence of *G′* and *G″* analyzed in 5 wt % cellulose solution within different ranges of molecular weights. The gelation temperature decreases from 59.4 to 30.5 °C with the increase of M_η from 4.5×10^4 to 11.4×10^4. This can be explained by the observation that relatively large semiflexible cellulose could create a chance of self-association of the cellulose chains, further leading to the network structure. Hence the elastic modulus of gels at the gel point increases with increased molecular weight.

Effects of Temperature on Gelation. Figure 8 shows the effect of temperature on the gelation process in the 4 wt % cellulose solution at ω value of 1 rad/s. Interestingly, the gelation of the cellulose solutions took place much more easily at lower temperature (below −3 °C) or higher temperature (above 30 °C) compared to those at the temperature of 0 to 15 °C. At −8 °C, a rheological phenomenon with high *G′* and *G″* values and significant initial peak appears in the *G′* curve. The appearance of initial peaks of the *G′* curves has been reported in the gelation process of KGM.[38,39] It is suggested that the wall slip between samples and measuring geometry owing to a rapid gelation

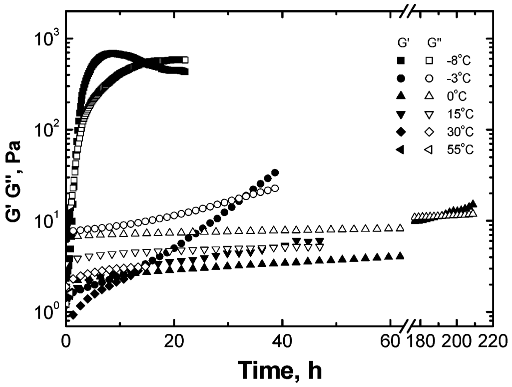

Figure 8. Time dependence of the storage modulus *G′* and loss modulus *G″* for 4 wt % cellulose solution with different temperature.

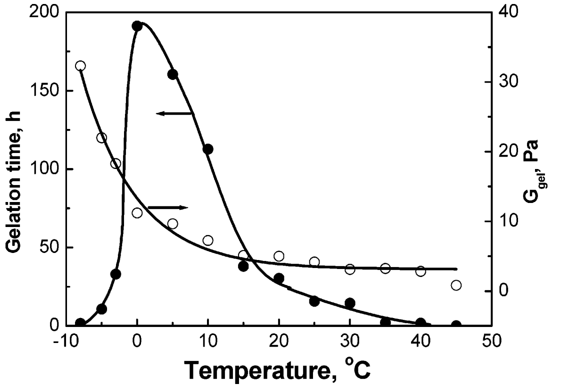

Figure 9. Gelation time and G_{gel} as a function of temperature for 4 wt % cellulose solution.

process might be the causes. And it was also related to other factors including temperature, applied strain, gap size, and the molecular weight and concentrations. It is noted that the values of *G′* and *G″* for 4 wt % cellulose solution at low temperature (−8 °C) are significantly larger than those at temperatures above 0 °C. This indicates more entanglement development of the cellulose chains and leads to the formation of elastic gels. Also more stronger intermolecular association and chain stiffness of cellulose had occurred in the solution below 0 °C than above that.

Figure 9 shows the dependence of the gelation time and G_{gel} on temperature. It appears that gelation time dramatically increases from 1.6 h at −8 °C to the maximum of 191.3 h at 0 °C, and then reduces greatly to 38 h at 15 °C. With further raised temperature, the decrease of gelation time slowly slows down. It is interesting to see that, above 45 °C, the cellulose solutions had been gelled prior to the measurement. The unique dependence of the gelation time on temperature in the cellulose solution was observed. For the first time, we experienced that either a heating or a cooling treatment can induce the gelation processing. However, the cellulose solution can be stored at 0 to 5 °C for a long time and still remains in its stable liquid state. In addition, the fact that the G_{gel} values decrease with increased temperature indicates a relatively high modulus formed at low temperature. This suggests that the energy of the hydrogen bonds is higher at low temperature causing the strong tendency of aggregation of the cellulose molecules, which is a necessary prerequisite for the interchain cross-linking. We have proved that the examined cellulose can be dissolved completely to form a transparent solution rather than suspensions of swollen cellulose by using polarized light microscopy, X-ray diffraction (XRD), and ^{13}C NMR in this case.[22] Therefore, cellulose gels were formed rather than becoming precipitated and/or suspended at low or high temperature, which was illustrated by the *G′* and *G″* curves continuing to grow across the whole range of temperature tested (see Figure 11).

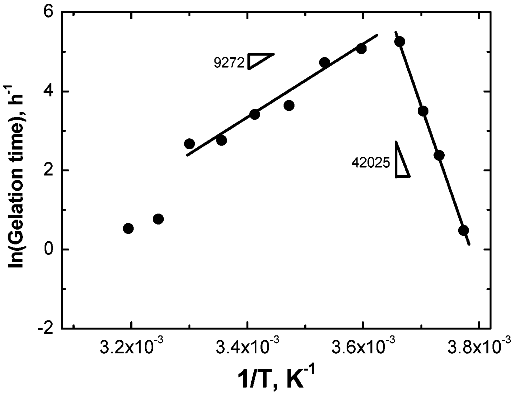

Figure 10. Arrhenius plots for the dependence of the gelation time of 4 wt % cellulose solution on temperature. The number represents the slope of the line.

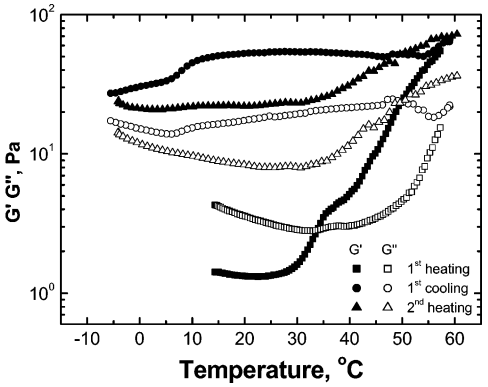

Figure 11. Storage modulus *G′* and loss modulus *G″* as a function of temperature in a heating and cooling process for 4.5 wt % cellulose solution.

Figure 10 shows the dependence of gelation time, t_{gel}, with temperature in the form of an Arrhenius plot for the cellulose solution. The apparent activation energy (E_a) was obtained from the slope of the straight lines. The calculated E_a value is 77.1 kJ/mol in the range from 0 to 30 °C and 349.4 kJ/mol from −8 to 0 °C, respectively. The activation energy usually is related to the interaction between macromolecules and chain conformation and can reflect the formation and rupture of linkages in "junction zones" during the gelation processes. There are several kinds of intermolecular interactions involved in such processes.[40] The effects of temperature and molecular conformation on the gelation process may be reflected in the Arrhenius plot of ln(t_g) vs $1/T$.[41] It is well-known that polymers with stiff chains have relatively high E_a values and their viscous behavior is more sensitive to temperature fluctuation than those with flexible macromolecules. The obtained E_a results show that the cellulose molecules in aqueous solution exist as a relatively stiff chain having strong intermolecular interaction below 0 °C, leading to enhanced aggregation and interchain cross-linking of cellulose, whereas above 0 °C they transformed to a semiflexible chain conformation.[42]

Irreversible Sol−Gel Transition by Heating and Cooling. To clarify the sol−gel behavior of the cellulose solutions, dynamic viscoelastic measurement was carried out in the similar range of temperature by using the same rate of thermal scanning cycles. Figure 11 shows the *G′* and *G″* curves for 4.5 wt % cellulose solution under the heating−cooling−heating process at rates of about 0.5 °C/min with an angular frequency of 1

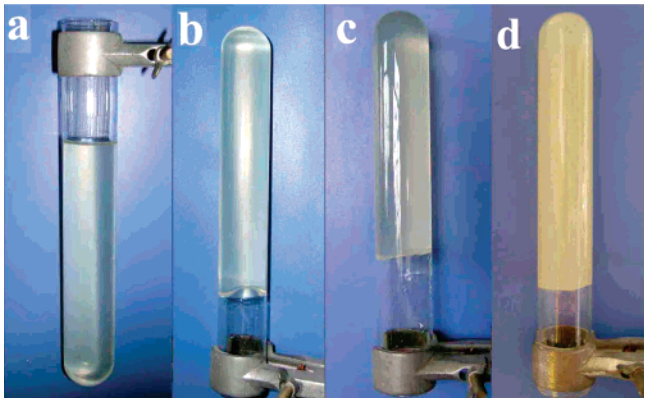

Figure 12. Photos of cellulose solution at ambient temperature (a), the cellulose gels formed at 8 °C for 4 days (b), at −20 °C for 1 h (c), and at 50 °C for 1 h (d).

rad/s. In the first heating process from 15 to about 60 °C, the crossover of G' and G'' lies at 34.5 °C, and the curves are divided into three parts as follows. Below 28 °C, G' values are lower than those of G'' and gradually decrease as the temperature increases, showing the common viscoelastic behavior of a liquid state. Then G' gradually increases as the temperature is raised, and G'' decreases slightly until about 34.5 °C. In this region, G'' values are always higher than those of G', suggesting that a weak gelation of cellulose has formed as a result of the partial formation of cellulose aggregates through self-association interactions. At the range of 30 to 40 °C, G' values exhibit a much faster increase rate than those of G'', and then both G' and G'' values increase sharply. This suggests there are two relaxation modes in the gelation of the cellulose solution: one is a pregel cluster and the other is a phase separation accompanied by gelation. To verify the thermoirreversible sol−gel transition, the cooling process starting from 60 °C was conducted at a similar cooling rate as that of heating. In contrast to the G' curves obtained by heating, the G' and G'' curves gradually decrease with reduced temperature, showing a large deviation from their original heating curves. The G' curve is always higher than G'' over the temperature range, showing a characteristic of the elastic behavior, and this indicates the gels formed from the cellulose solutions are thermoirreversible. After cooling to any temperature, including −10 °C at which it was dissolved previously, they were unable to dissolve into a transparent solution. Moreover, the examination of the second heating process was performed under the similar condition. With the temperature increased from −5 to 35 °C, the G' curve hardly changes, whereas G'' decreases slowly. This suggests the gel state remains. Subsequently, both G' and G'' increase with raised temperature suggesting the increase in the elasticity of the system.

To give straight evidence, the sol−gel transition was examined by visual observation. Figure 12 shows photos of the cellulose solution and gels formed at −20, 8, and 50 °C, respectively. The 4 wt % cellulose solution (a) shows a transparent liquid at ambient temperature, whereas it became a gel at 8 °C after 4 days (b), at −20 °C for 1 h (c), and at 50 °C for 1 h (d). Therefore, the sol−gel transition of the cellulose in 7 wt % NaOH/12 wt % urea aqueous solution is a thermoirreversible process by heating or cooling treatment. As indicated in our work,[22] at low temperature, active NaOH hydrates were bound to cellulose to bring it into the solvent, whereas urea hydrates serve as the hydrogen-bonding donor and receptor to prevent the approach toward each other of the cellulose molecules, leading to a good dispersion of cellulose in the solution. At elevated temperature the NaOH and urea hydrates bound on the cellulose chains were perturbed, so the junction between cellulose molecules occurred as a result of the self-association force of cellulose, resulting in the formation of network structure. Types of junction zones, such as hydrogen-bonded type junctions[43] and association by forming stereocomplex egg box junction zones[44,45] in which Na^+ ions were captured, have been reported. Additionally the cellulose solution became yellow gels (Figure 12d) by raising the temperature (at 50 °C), in which the reaction of NaOH with urea has occurred at high temperature.[46] It is worth noting that at ambient temperature cellulose can be dissolved in 7 wt % NaOH/12 wt % urea aqueous solution precooled to −10 °C, but the resultant cellulose solution could form gels by the temperature dropping to below 0 °C. This can be explained by using the concepts of competitive interaction between cellulose and solvent molecules as follows. Below 0 °C, the intermolecular interaction of cellulose was much stronger than those among cellulose and NaOH hydrates, urea hydrates, as well as free water, resulting in higher E_a values than that above 0 °C, with cellulose self-association. Therefore, cellulose can be dissolved in NaOH/urea aqueous solution precooled to −10 °C, whereas the formed cellulose solution cannot remain in its liquid state below 0 °C for certain time; this indicates an irreversible sol−gel transition.

Conclusion

Dynamic viscoelastic measurements showed a unique gelation behavior of cellulose in 7 wt % NaOH/12 wt % urea aqueous solution. The cellulose solution was proved to be a complex system, so it could not be well described by the Winter−Chambon criterion. The gelation point of the cellulose solution was determined successfully by the oversection of the G' and G'' curves and was impacted by temperature, stored time, cellulose molecular weight, and concentration. The gelation temperature of the cellulose ($M_\eta = 11.4 \times 10^4$) solution decreased from 60.3 to 30.5°C with the concentration from 3.0 to 5.0 wt %, and that of 5 wt % cellulose solution decreased from 59.4 to 30.5°C with the increase of molecular weight from 4.5×10^4 to 11.4×10^4. The gelation time of the 4 wt % cellulose ($M_\eta = 11.4 \times 10^4$) solution was relatively short below −3 °C or above 30 °C, but the cellulose solution was stable for a long time at about 0 to 5 °C. By heating or cooling, the cellulose solution changed into gels, and the sol−gel transition of the cellulose in a 7 wt % NaOH/12 wt % urea aqueous solution was an irreversible process. The results revealed a unique gelation of the cellulose solution, which was very sensitive to temperature change and cellulose molecular weight and concentrations, and the cellulose gels could not be broken by heating or cooling cycles.

Acknowledgment. This work was supported by the High-Technology Research and Development Program of China (2003AA333040), the Major Grant of the National Natural Science Foundation of China (59933070), and the CAS Key Laboratory of Cellulose and Lignocellulosic Chemistry, China.

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BM0505585