Phase Transition of Cellulose Solutions in
N-Methyl Morpholine N-Oxide Hydrates

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ABSTRACT: Melting dissolution conditions of cellulose in N-methyl morpholine N-oxide(NMMO) hydrate had a profound effect on the phase behavior of cellulose/NMMO/H_2O systems. Introducing an antioxidant, n-propyl gallate (PG; 0.5 wt% for cellulose), during melting dissolution proved effective in obtaining reproducibility of results. Cellulose with higher molecular weight gave anisotropic to isotropic transition at lower temperature. Rheological analysis of cellulose solution systems in NMMO hydrate with hydration number $(n) = 0.65$ revealed that cellulose with weight-average degree of polymerization (DP_w) of 600, 694, and 940 exhibited the transition over the temperature range of 112—127.5, 105—125, and 105—120 in the concentration range of 15—20, 15—21, and 15—21 wt%, respectively. This result was ascertained by optical microscopy as well. The transition temperature previously observed in the temperature range 85—92°C seemed to originate from experimental errors associated with existence of unmelted NMMO hydrate crystals. The unmelted NMMO hydrate crystals were confirmed by thermal characterization.
    KEY WORDS   Cellulose / N-Methyl Morpholine N-Oxide Hydrate Solution / Phase Transition / Rheology / Mesophase /

It is long recognized that the solutions of some derivatives of cellulose such as hydroxy propyl cellulose produce mesophase.[1−3] However, it is very difficult to find out a solvent which can readily dissolve a pure cellulose because of the chain rigidity of cellulose molecules and strong inter- and intra-molecular hydrogen bonding. Only a few solvents are reported to be able to dissolve cellulose up to the concentration high enough to form mesophase. Example of the solvents includes N-methyl morpholine N-oxide (NMMO), and lots of studies have been carried out for the phase change of cellulose solutions in the solvent.[4−10]

The N—O group of NMMO can form strong physical bonds with the H—O groups of cellulose through hydrogen bonding, so it can dissolve cellulose.[11,12] Anhydrous NMMO proved best solvent for cellulose. However, its T_m is as high as 172°C, which easily causes the thermal decomposition of cellulose during melting dissolution. Hence NMMO hydrates with lower T_m are generally used for the solvent of cellulose in the commercial production of cellulose films and lyocell fibers. The NMMO hydrates have various crystal structures according to the hydration number; from NMMO(1.0)H_2O(monohydrate) to NMMO(2.5)H_2O. Corresponding to the degree of hydration, the T_m varies from 72 to 39°C.[6] If the hydration number is greater than 1.5, however, the NMMO hydrate cannot dissolve cellulose but only swells it. The NMMO hydrates with the hydration number greater than 2 become a nonsolvent for cellulose.[13]

Chanzy et al.[9,14] reported that the phase of the cellulose solutions in NMMO hydrate was determined by complicated factors such as temperature, polymer concentration, the hydration number of NMMO, and the

molecular weight of cellulose. Navard[15] reported that the cellulose solutions in NMMO hydrate with hydration number less than 1 gives an isotropic/anisotropic phase transition at 85—92°C. The required concentration was dependent on DP_w; 30 wt% for DP_w 600 and 25 wt% for DP_w 900. Further they reported that only isotropic phase is obtained if the hydration number ranges from 1 to 1.5 irrespective of concentration.[6,16] However, these results should be re-examined because they did not exactly refer to the extent of solubility of cellulose to the solvent. According to the patent[8] NMMO with hydration number greater than 0.65 cannot completely dissolve cellulose when the concentration exceeds 20 wt%. Further, they did not make allowances for the decomposition of cellulose during melting dissolution in the absence of an antioxidant. In addition, it is unavoidable to obtain homogeneous solution to heat the solution above the T_m of the NMMO hydrate when the solution was prepared from the mixture of anhydrous NMMO and NMMO monohydrate. This probably leads to a serious thermal decomposition of cellulose. In this study we examined the phase behavior of the homogeneous cellulose solutions in NMMO hydrate properly stabilized by an antioxidant.

EXPERIMENTAL

Materials and Dissolution of Cellulose in NMMO Hydrates

The cellulose sample, Rayonex-P, was supplied by ITT Rayonier Co. (USA), whose DP_w was 940, 694, and 600. Cellulose was dried at 80°C for 24 h prior to use. The solvent, NMMO/H_2O (50 wt%/50 wt%), and the antioxidant, n-propyl gallate (PG), was purchased from Aldrich Co.

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(USA). NMMO/H_2O (50 wt%/50 wt%) was condensed in a rotary evaporator at 60—100°C for 3 h at reduced pressure to lower the water content less than 10 wt%. The dried cellulose was dissolved in the NMMO hydrate by heating the solution above the T_m of the NMMO hydrate. The concentration of cellulose examined was 6, 10, 12, 15, 18, 20, and 21 wt%. As an antioxidant n-propyl gallate (PG) was used, whose content was 0.5 wt% for cellulose, to minimize the decomposition of cellulose during melting dissolution. The homogeneous cellulose solutions were prepared by dissolving with fully melting and defoaming the granules at 140°C for 40 min to make sure of complete melting of NMMO hydrates.

Measurement of Molecular Weight of Cellulose

To begin with, the 1 mol cupriethylene diamine (CUENE) solution was prepared according to ASTM-D 539-51 T. The ratio of ethylene diamine to copper ranged from 1.95 to 2.0.

The cellulose solution in NMMO hydrate was immersed in distilled water to eliminate NMMO from the solution, and dried for 4 h at 105°C. The 100, 200, 300, and 400±0.3 mg of cellulose specimens were wetted in 50 mL of distilled water in a bottle with stirring. Into this bottle 50 mL of the 1 mol CUENE solution was added, and stirred to give a homogeneous solution in nitrogen atmosphere. The solution was filtered through a glass filter in nitrogen atmosphere and the flow time was measured with an Ubbelhode type viscometer (No.1 C 503, No.1 H 58; Fischer Co.) at 25±0.1°C (ASTM-D 1795-62).

Measurements of Physical Properties

The water content in NMMO hydrates was determined by the method suggested by Fischer[17] and ascertained that the water content in NMMO was 8.7 wt% (the hydration number=0.65).

The thermal properties of NMMO hydrates and cellulose solutions were measured by Perkin—Elmer DSC 7 at nitrogen atmosphere. In DSC measurement stainless steel capsule (Perkin—Elmer part 319-0218) equipped with an o-ring to withstand high pressure generated by steaming of water. The scan rate was 2, 5, and 10°C min^{-1}.

The transition temperature of solutions of cellulose in NMMO hydrates was measured by Nikon polarizing microscope (Type 104) equipped with a hot-stage (Toledo Co.). Temperature was measured by placing the sample between parallel silde glasses whose gap was 0.16 mm with or without shear. Shearing was given to the specimen in one-direction by rotating the upper slide glass with varing rotational speed. Temperature of hot-stage ranged from room temperature to 150°C.

The rheological properties of cellulose/NMMO/H_2O solution were measured by Instron capillary rheometer (model 3211). The diameter and L/D ratio of the capillary die in rheological measurement were 1.275 mm and 30 or 40, respectively. To obtain fully melted cellulose solutions, the pregellated specimen was placed in the rheometer barrel heated to 100°C for 10 min, and adjusted to the desired temperature for rheological measurement.
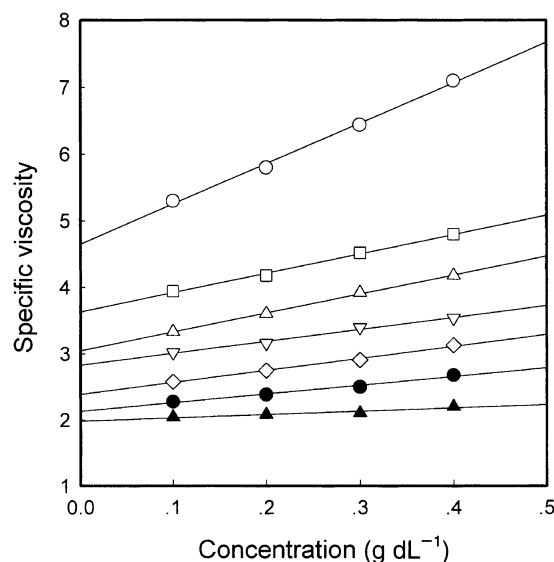
Figure 1. Variation of specific viscosity of cellulose solution in cupriethylene diamine with time. The cellulose samples were taken during melting dissolution in NMMO hydrate at 110°C in the absence of PG; ○ : 0 min, □ : 10 min, △ : 20 min, ▽ : 30 min, ◇ : 60 min, ● : 90 min, and ▲ : 120 min.
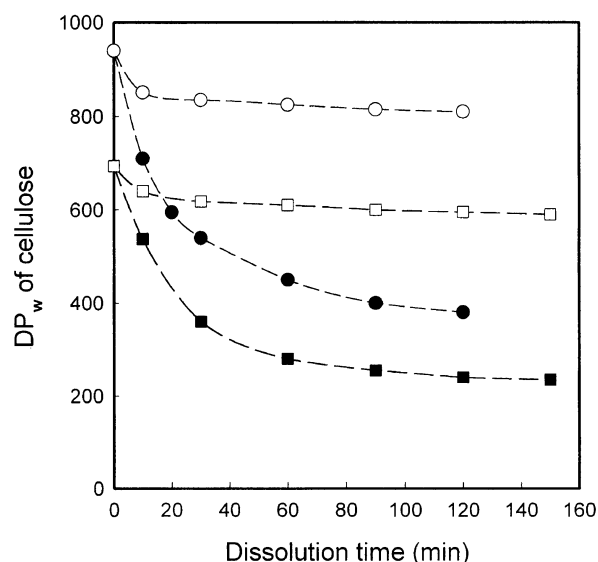

Figure 2. Variation of molecular weight of cellulose during melting dissolution in NMMO hydrate at 110°C ; Open symbol: in the presence of PG (0.5 wt% for cellulose) and closed symbol: in the absence of PG.

RESULTS AND DISCUSSION

Decomposition of Cellulose During Melting Dissolution in the Absence of Antioxidant

The NMMO hydrate with $n < 1.5$ can dissolve cellulose at the temperatures higher than its T_m (in the case of NMMO monohydrate, 78°C). However, it takes long time to dissolve cellulose at this elevated temperature, which inevitably brings about thermal decomposition of cellulose in the absence of an antioxidant such as PG. This can be ascertained by reduction of DP_w of cellulose with melting dissolution time.
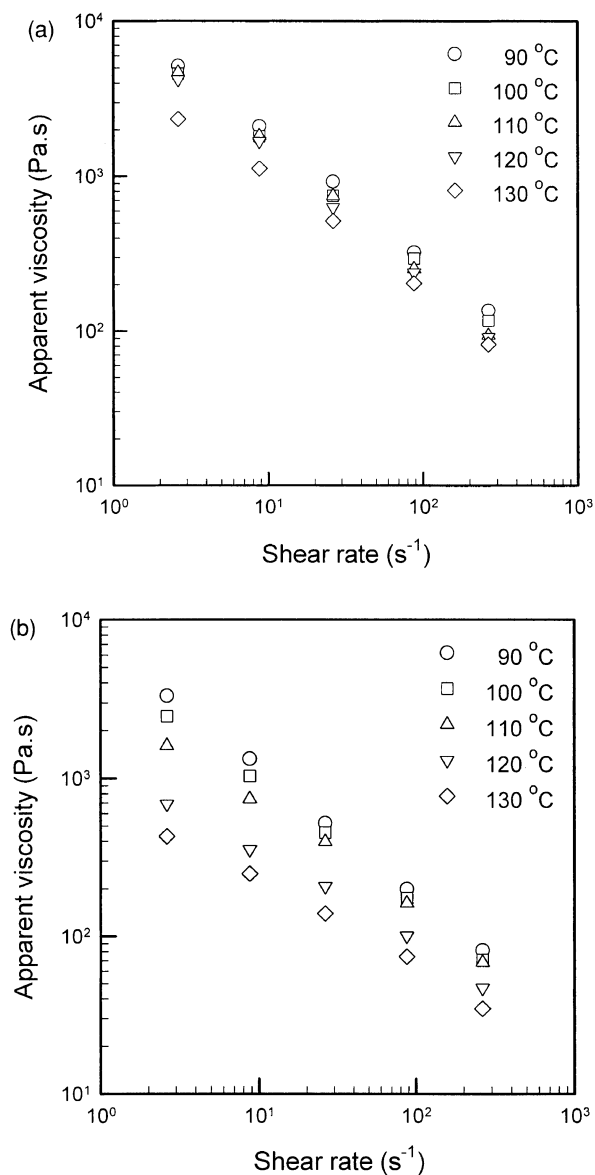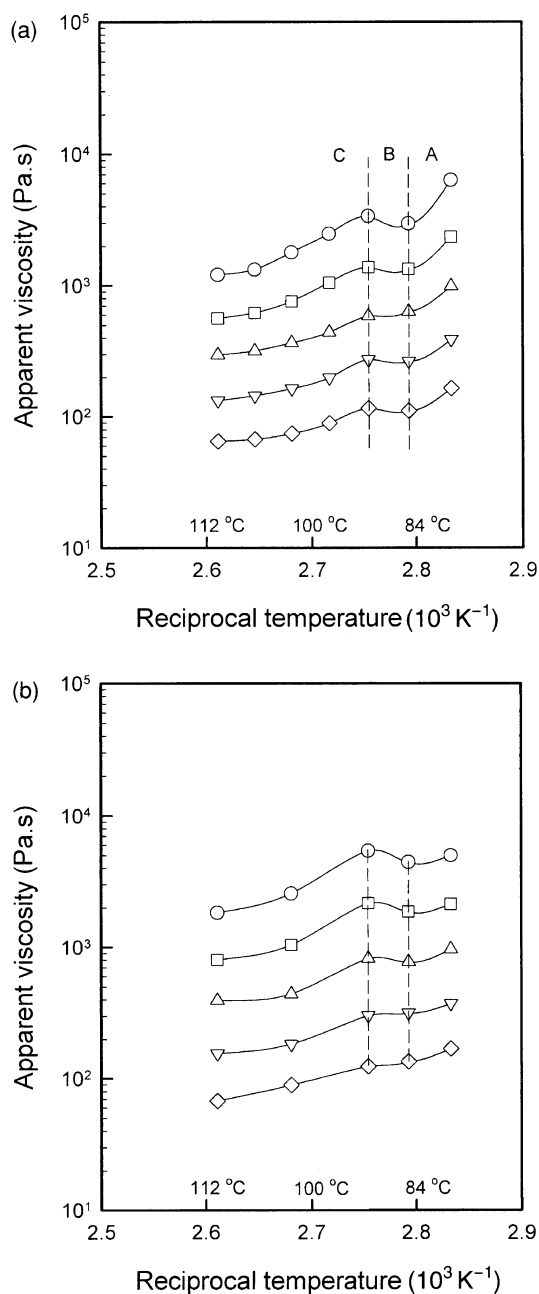
Figure 3. Viscosity curve of 15 wt% cellulose (DP$_w$ 940) solution in NMMO(0.65)H$_2$O at various temperatures; (a) in the presence of PG (0.5 wt% for cellulose) and (b) in the absence of PG.

Figure 4. Temperature dependence of apparent viscosity (η_a) of 12 wt% cellulose solution in NMMO(0.65)H$_2$O containing PG (0.5 wt% for cellulose) at various shear rates; $\bigcirc$: 2.63, $\square$: 8.77, $\triangle$: 26.3, $\triangledown$: 87.7, and $\diamondsuit$: 263 s^{-1} ; (a) DP$_w$ 694 and (b) DP$_w$ 940.

The cellulose specimens were taken from the melting dissolution systems at the desired time periods and its specific viscosity in CUENE was measured by Ubbelhode viscometer at 25℃. Figure 1 shows variation of specific viscosity of cellulose at several concentration with melting dissolution time in the absence of PG. On the plot, the intercept of specific viscosity is the intrinsic viscosity, [η] in dL g^{-1}. The molecular weight of cellulose given in Figure 2 is determined by the following equation.[16]

$$[\eta] = 0.98 \times 10^{-2} \, DP_w^{0.9}$$

In the absence of the antioxidant, a notable reduction of molecular weight of cellulose is observed. This can be further ascertained by the rheological properties of the 15 wt% cellulose solution in Figure 3. Comparing Figure 3a and 3b, one can also observe a notable reduction in shear viscosity in the absence of PG, particularly above
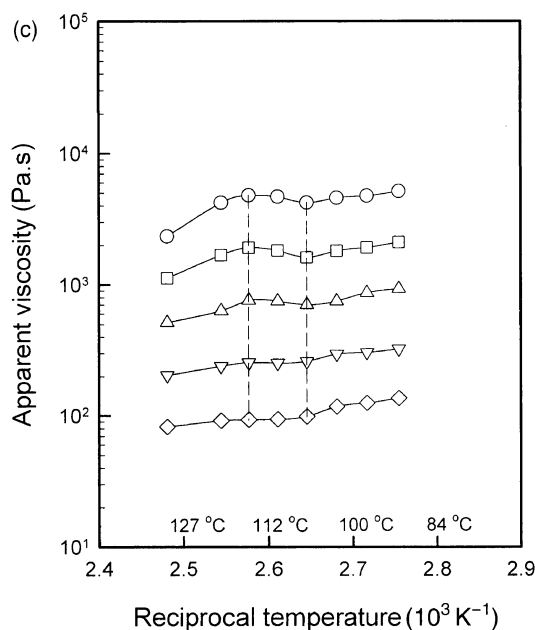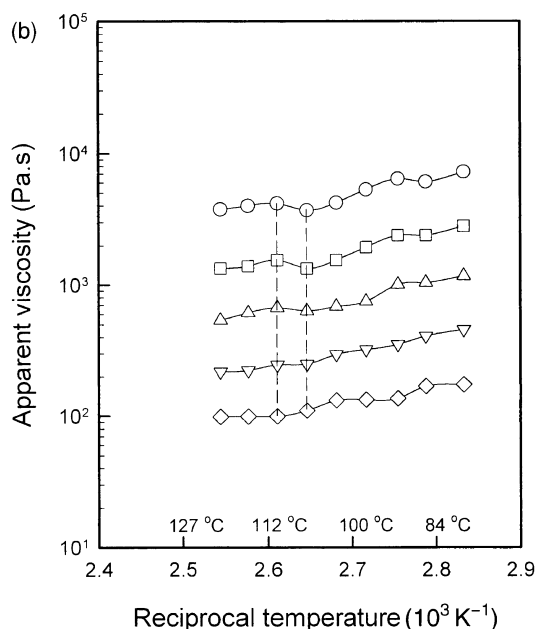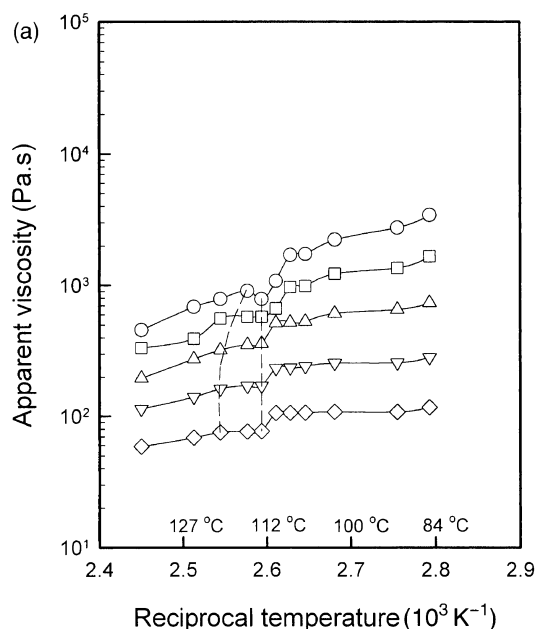
120℃. Thus, incorporation of an antioxidant is essential to acquire reproducible rheological data of cellulose/NMMO/H$_2$O solution systems. Up to now, however, most of previously rheological studies have been carried out for the cellulose solutions without any antioxidant.

Rheological and Optical Considerations on the Phase Transition Behavior

It is often convenient to introduce activation energy (E_a) to trace the phase transition of polymer solutions with temperature. The value of E_a is evaluated from the slope on the plot of lnη_a *vs.* 1/T according to the following expression.

(a)

(b)

(c)

Figure 5. Temperature dependence of apparent viscosity (η_a) of 15 wt% cellulose solution in NMMO(0.65)H_2O containing PG (0.5 wt% for cellulose) at various shear rates; $\bigcirc$: 2.63, $\square$: 8.77, $\triangle$: 26.3, $\triangledown$: 87.7, and $\diamondsuit$: 263 s^{-1} ; (a) DP$_w$ 600, (b) DP$_w$ 694, and (c) DP$_w$ 940.

$$\eta_a = A \exp(E_a/RT)$$

where, η_a is apparent viscosity, A is constant, R is gas constant, and T is temperature in K. In general, an abrupt change of E_a over a temperature range suggests that a phase transition takes place. In the case of liquid crystalline polymer systems, an abrupt change of the slope from positive to negative is indicative of the anisotropic-isotropic transition. The cellulose solutions in NMMO(0.54)H_2O are reported to exhibit the transition in the temperature range 87—92℃ when the DP$_w$ of cellulose is 600 and the concentration is 24—30 wt%; and at 85℃ for DP$_w$ 900 at 25 wt%.[15]
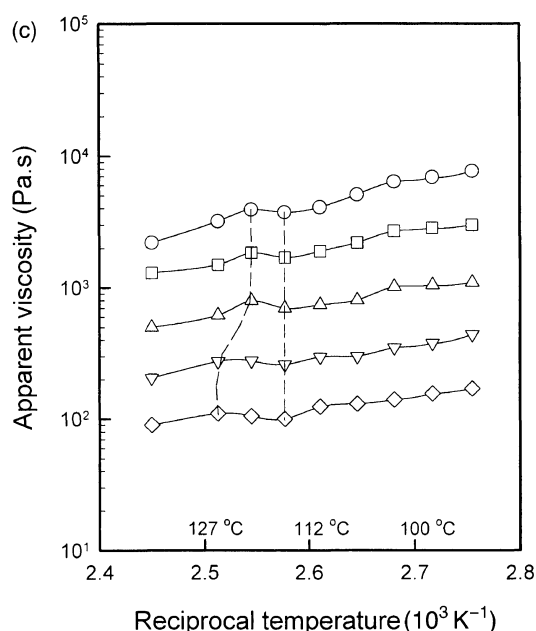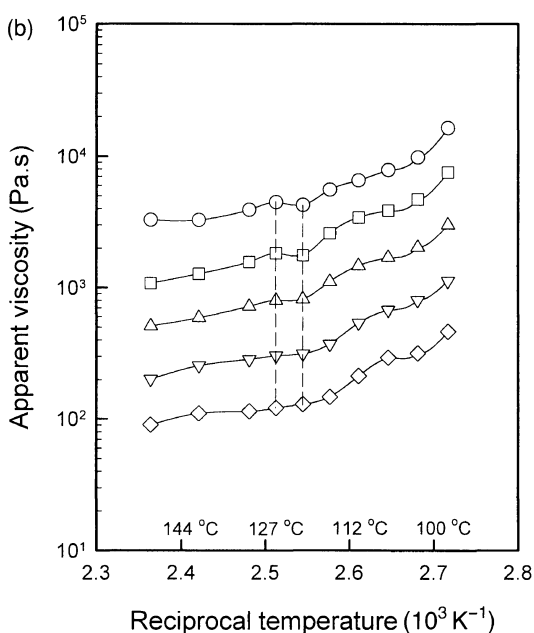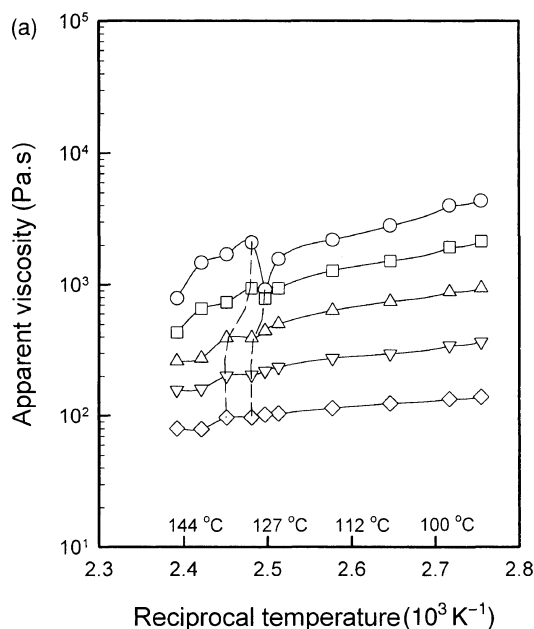
Arrhenius plots for 12 wt% cellulose solutions in NMMO(0.65)H_2O at various shear rates are shown in Figure 4a for cellulose with DP$_w$ 694 and in Figure 4b for cellulose with DP$_w$ 940. They show three distinct regions; anisotropic+solid phase (region A), biphase (region B), and isotropic phase (region C). It should be noted that at this low temperature the cellulose solution does not produce liquid crystalline phase. Thus, the anisotropic+solid phase does not result from existence of originally undissolved cellulose fibrils in the NMMO hydrate but originate from existence of the unmelted portion of NMMO hydrate during rheological measurement with cooling the cellulose solution in NMMO hydrate, which had been completely melt-dissolved at 140℃.

As the concentration of cellulose is increased viscosity increases up to the critical concentration to produce the liquid crystalline phase. Hence, viscosity decreases with increasing concentration as a result of mesophase formation, giving rise to the biphase. It is recognized that most lyotropic liquid crystalline polymers show thermotropic liquid crystalline transition with temperature as well. For example, phase transition from anisotropic to isotropic with raising temperature can be observed if the polymer concentration is higher than the critical concentration.[18,19] Figure 5, 6, and 7 present the Arrhenius plots of 15, 18, and 20/21 wt% cellulose solutions in NMMO(0.65)H_2O at various shear rates, respectively.

Two distinct transition temperatures are observed in the plots, which indicates mesophase formation.

To verify the mesophase formation more clearly we took optical photographs of the 18 wt% cellulose (DP$_w$ 600) solution in NMMO hydrate with $n = 0.65$ at the mesophase under no shear. The experimental procedure was as follows. The 18 wt% cellulose (DP$_w$ 600) solution in NMMO hydrate with $n = 0.65$ was heated to 150℃ on the hot-stage. The optical photographs in Figures 8a and 8b were respectively taken at 130 and 127.5℃ under no shear during cooling the melt on the hot stage at the scan rate of 2℃ min^{-1}. In the photograph one can see orientation of molecules begins at 130℃, which tempera-

(a)

(b)

(c)

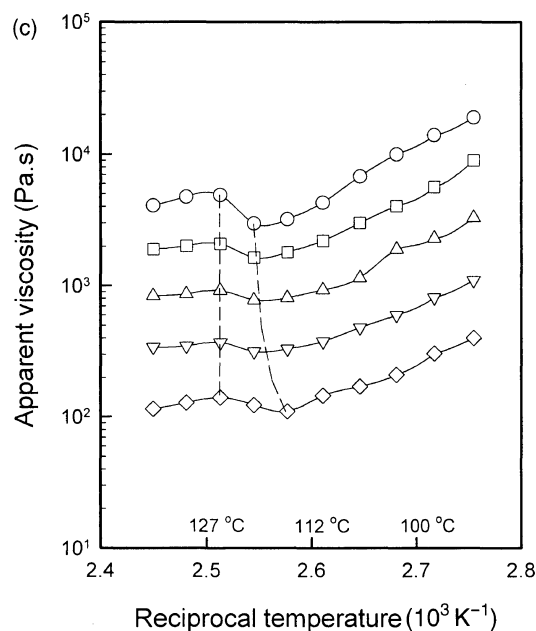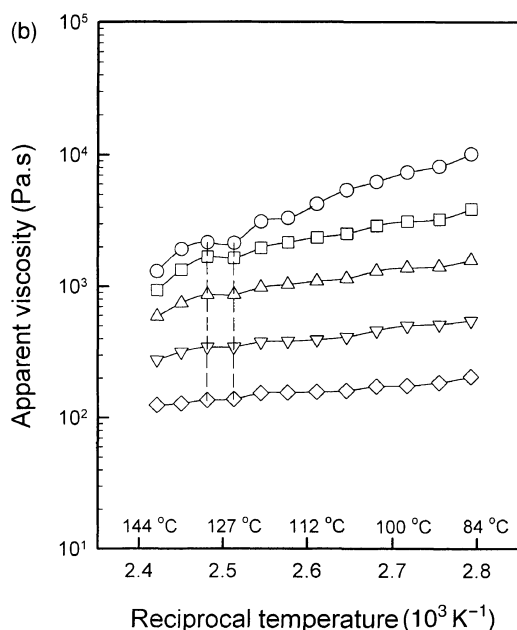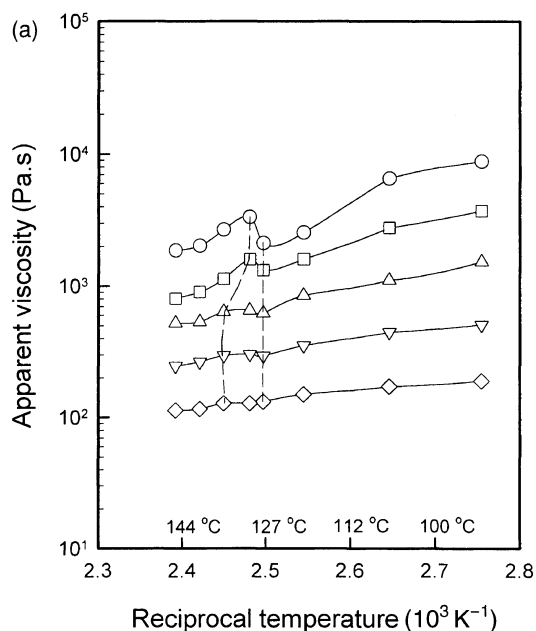**Figure 6.** Temperature dependence of apparent viscosity (η_a) of 18 wt% cellulose solution in NMMO(0.65)H$_2$O containing PG (0.5 wt% for cellulose) at various shear rates; ○ : 2.63, □ : 8.77, △ : 26.3, ▽ : 87.7, and ◇ : 263 s^{-1}; (a) DP$_w$ 600, (b) DP$_w$ 694, and (c) DP$_w$ 940.

(DP$_w$ 940) solution was cast on the hot stage and heated to 150℃ and cooled to 120℃ under no shear, at which optical anisotropy was observed. Cooling the cast solution to 115℃ also exhibits the optical anisotropy but partially. However, shearing this cast solution at 5 s^{-1} more clearly develops molecular orientation to the shear direction. This sheared solution was quenched to room temperature and NMMO hydrate was extracted with water and methanol. The regenerated cellulose film was dried and the optical photograph was taken. The result is shown in Figure 9b. It clearly exhibits orientation of cellulose molecules in microfibrils resulting from mesophase. Thus, these optical measurements with or without shear further verify mesophase formation at the suggested temperature.

The phase transition temperatures (T_a: from anisotropic phase to biphasic and T_i: from biphasic to isotropic phase) of the cellulose solutions are determined from the slopes in Figures 5, 6, and 7. The transition temperatures are plotted against concentration and molecular weight in Figure 10. On the whole, the transition temperature (T_a) increases with increasing concentration but decreases with increasing molecular weight of cellulose. It is very interesting to see that cellulose with higher molecular weight exhibits transition from anisotropic to isotropic phase at lower temperature. This odd phenomenon may be reasoned as follows. The phase transition observed under shear is not obtained in the steady state (thermodynamically) but in the transient state (kinetically) because the cooling rate on the hotstage, 2℃ min^{-1}, is too fast to reach the equilibrium state for the semi-rigid chain cellulose molecules with long relaxation times. Consequently the cellulose molecules of lower molecular weight forms mesophase more rapidly during cooling on account of higher mobility of

ture is considered as T_i. Figure 8b shows an oriented morphology which means T_a to be 127.5℃. Figure 8c shows polarized optical photographs for the cellulose solution at 127.5℃. One can see orientation of molecules more clearly. The various color textures seem to result from NMMO hydrate. These transition temperatures, T_i and T_a, measured by optical microscope respectively correspond to those previously determined by rheological data, 130 and 127.5℃.

The 18 wt% cellulose (DP$_w$ 600) solution was cast on the hot stage and heated to 150℃ and cooled to 127.5℃ under no shear. The cast film was quenched to room temperature and NMMO hydrate was extracted with water and methanol. The regenerated cellulose film was dried and the optical photograph was taken. The result is shown in Figure 9a. We can see that the oriented structure of cellulose molecules in microfibrils resulting from mesophase still remains. The 18 wt% cellulose

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(a) Apparent viscosity (Pa.s) vs Reciprocal temperature (10^3 K^{-1}); temperature markers 144 °C, 127 °C, 112 °C, 100 °C

(b) Apparent viscosity (Pa.s) vs Reciprocal temperature (10^3 K^{-1}); temperature markers 144 °C, 127 °C, 112 °C, 100 °C, 84 °C

(c) Apparent viscosity (Pa.s) vs Reciprocal temperature (10^3 K^{-1}); temperature markers 127 °C, 112 °C, 100 °C

Figure 7. Temperature dependence of apparent shear viscosity (η_a) of 20/21 wt% cellulose solution in NMMO(0.65)H$_2$O containing PG (0.5 wt% for cellulose) at various shear rates; ○ : 2.63, □ : 8.77, △ : 26.3, ▽ : 87.7, and ◇ : 263 s^{-1} ; (a) DP$_w$ 600 (20 wt%), (b) DP$_w$ 694 (20 wt%), and (c) DP$_w$ 940 (21 wt%).

molecules. This assessment is feasible because both celluloses, DP$_w$ 600 and 940, have chain length much greater than the Kuhn segment length, DP$_w$ $ca.$ 50.

It should be also noticed in Figure 10 that for cellulose with DP$_w$ 694, the 12 wt% solution shows single T_a and T_i temperatures at 85 and 90℃, respectively. However, at concentrations higher than 12 wt%, the cellulose solutions give double T_a and T_i temperatures. In addition, the transition temperature reported by Navard et al.[15] is also observed, which are marked in Figure 8 as well. The lower transition temperatures in the range 85—92℃ are believed to result from the existence of crystals of NMMO hydrates with $n < 1$, resulting from incomplete melting of the starting cellulose solution. Only the higher transition temperatures result from phase transition of the solution.

Figure 11 shows concentration dependence of viscosity of cellulose solution in NMMO(0.65)H$_2$O with concentra-

tion at 110℃ at the shear rate 2.63 s^{-1}. As previously mentioned, viscosity is notably decreased in the absence of PG after rheological measurement. It seems like a critical concentration curve of lyotropic liquid crystalline polymer systems, particularly when the molecular weight is high. In fact, the critical concentration for mesophase formation seems to lie in concentrations between 18 and 20 wt% when the DP$_w$ of cellulose is greater than 550. This result is somewhat different from the result of Navard and Haudin[15] reporting that the critical concentration for the phase transition of the cellulose solution in NMMO(0.54)H$_2$O is 24 wt%. This discrepancy obviously results from thermal decomposition of cellulose. One can picture in Figure 11 that the critical concentration would be 24 to 25 wt% in the absence of antioxidant.

### Thermal Characterization of Cellulose / NMMO Hydrate Solution

We carried out DSC measurement to support the rheological and optical results. The rheological analysis suggested that the critical concentration for the anisotropic-isotropic phase transition of cellulose solutions in NMMO(0.65)H$_2$O ranged from 18 to 20 wt%, which is inconsistent with the critical concentration 25 wt% previously reported by others for the cellulose (DP$_w$ 900) solution in NMMO(0.54)H$_2$O.[15] Although we take difference in hydration level of NMMO hydrates into consideration, the critical concentration is much lower than the previously reported values.[15,20] The difference comes from two factors. Firstly, thermal decomposition of cellulose during melting dissolution and rheological measurement. Secondly, existence of some unmelted NMMO crystals in the cellulose solution in the temperature range in which rheological measurement was carried out. The latter suggests that the phase transition at 85—92℃ previ-
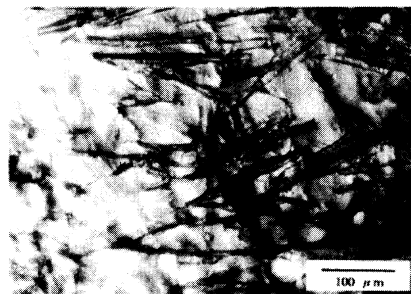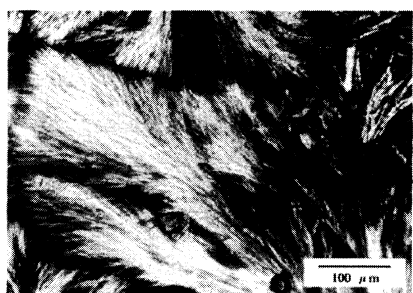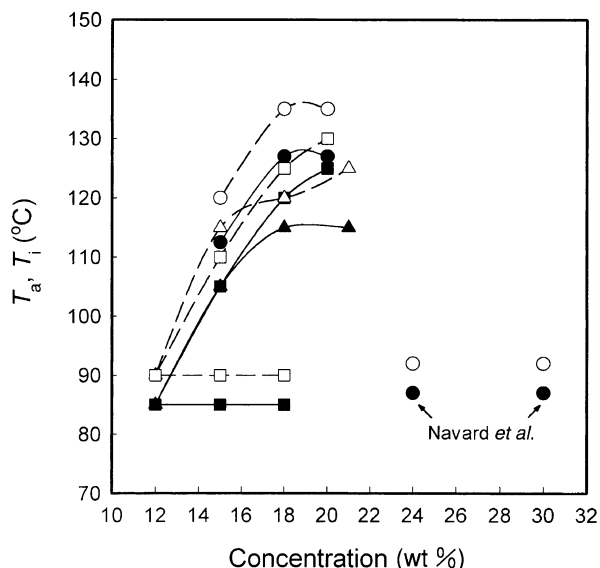
(a)
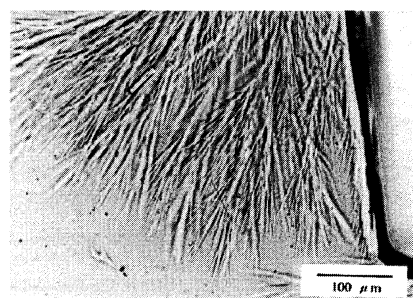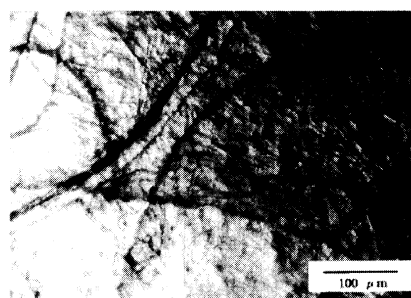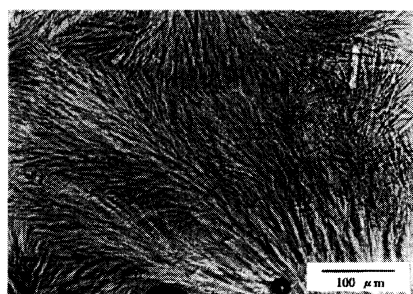
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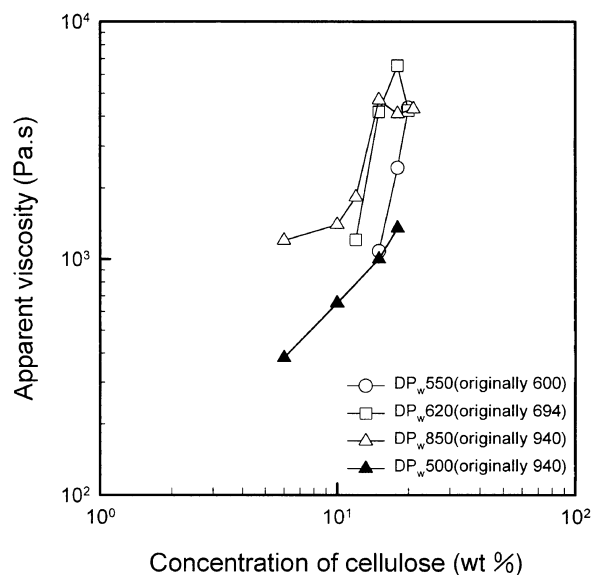

(c)

Figure 8. Optical micrograph of 18 wt% cellulose (DP$_w$ 600) solution in NMMO(0.65)H$_2$O at; (a) 130℃ (not polarized), (b) 127.5℃ (not polarized), and (c) 127.5℃ (polarized).

(a)

(b)

Figure 9. Optical micrograph of regenerated cellulose film from 18 wt% cellulose solution in NMMO(0.65)H$_2$O; (a) 127.5℃, DP$_w$ 600, and (b) 115℃ after having sheared at 5 s^{-1}, DP$_w$ 940.

Concentration of cellulose (wt %)

Figure 11. Concentration dependence of apparent viscosity (η_a) of solutions of celluloses with various molecular weights in NMMO hydrate at 110℃ at 2.63 s^{-1} ; ○ : DP$_w$ 550, □ : DP$_w$ 620, △ : DP$_w$ 850, ▲ : DP$_w$ 500; Open symbol: with PG and closed symbol: without PG.

Concentration (wt %)

Figure 10. Behavior of transition temperature (T_a and T_i) of solutions of cellulose with various molecular weights in NMMO hydrate with $n = 0.65$) ; ○ : DP$_w$ 600, □ : DP$_w$ 694, △ : DP$_w$ 940, and ◇ : DP$_w$ 900 ; Open symbol: T_i, and closed symbol: T_a.
*The result of Navard et al. cited from reference 15 used NMMO hydrate with $n = 0.54$.

ously reported by others results from the heterogeniety of the system by existence of unmelted NMMO crystals as already discussed.

To explain it more clearly we checked the crystallization behavior of NMMO hydrate itself by DSC. As reported NMMO monohydrate exhibits a single T_m at 78℃. However, NMMO(0.65)H$_2$O gives various melting peaks at 78, 90, 98, and 130℃ at the heating rate of 5℃ min^{-1} as shown in Figure 12a, indicating coexis-

(a)

(b)
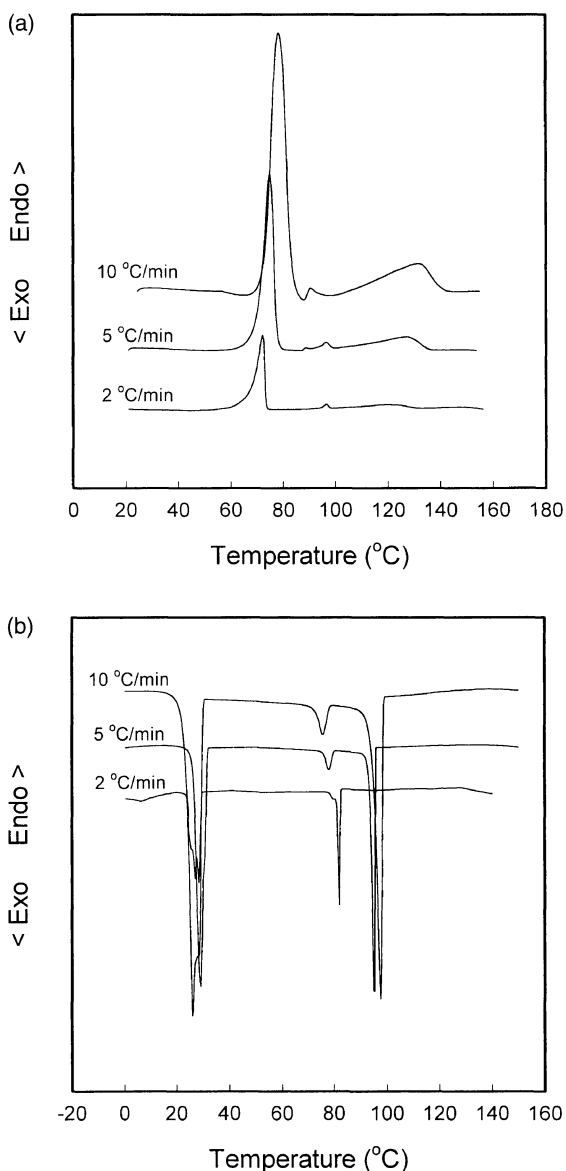
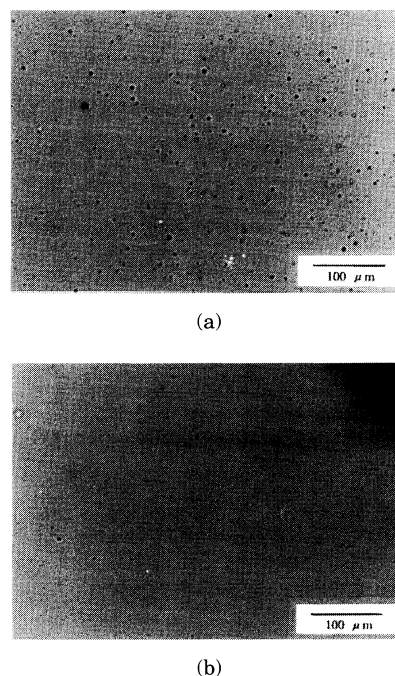**Figure 12.** DSC thermogram of NMMO(0.65)H₂O, showing the effect of heating rate; (a) heating scan and (b) cooling scan.

(a)

(b)

Figure 13. Optical micrograph of 18 wt% cellulose (DP_w 600) solution in NMMO(0.65)H₂O; (a) 90℃ and (b) 130℃.

Figure 14. DSC thermogram of cellulose (DP_w 600) solution in NMMO(0.65)H₂O at the heating rate of 5℃ min⁻¹, showing the effect of cellulose concentration; (a) 20, (b) 18, (c) 15, and (d) 12 wt%.
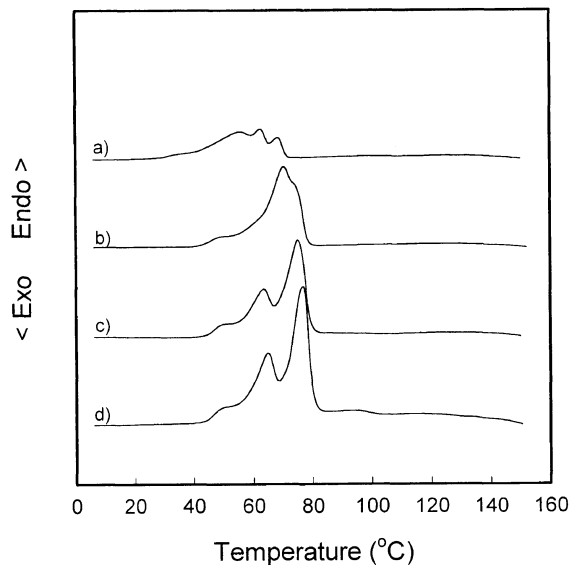
tence of various crystal structures in the hydrate. This can be more clearly ascertained by cooling experiment shown in Figure 12b.

The 18 wt% cellulose (DP_w 600) solution in NMMO was heated from room temperature at the scan rate of 2℃ min⁻¹ without shearing. During heating the optical microscope photographs were taken at 90 and 130℃, and shown in Figures 13a and 13b, respectively. Figure 13a exhibits that some tiny unmelted particles present in the solution. This seems to be particles of NMMO hydrates with $n < 1$.[21] Figure 13b indicates that the tiny particles are completely melted at 130℃, which coincides with DSC thermograms in Figure 12a.

In the case of the cellulose solution in NMMO(0.65)-H₂O the T_m of the NMMO hydrate is naturally decreased. Figure 14 proves that the melting point goes down to below 78℃. At 12 wt% the melting peak exhibits peak separation below 78℃. In addition, a weak shoulder peak is observed in the vicinity of 50℃, which is obliged to an internal ordering of cellulose molecules. At

the concentrations higher than 12 wt%, the T_m is decreased and the peak separation gets less clear as the concentration is increased. This is ascribed to the strong interactions between cellulose and NMMO hydrate at higher concentrations.

DSC study suggests that the cellulose solution in NMMO monohydrate crystallizes over the range 20 to 40 ℃ according to scan rate if the concentration is lower than 6 wt%.[22] In addition, 10 wt% cellulose solution in anhydrous NMMO is reported to crystallizes at 100℃.[23] However, the crystallization behavior is not observed at high cellulose concentrations due to interactions be-

tween cellulose and NMMO.[6,20] DSC study reveals that the cellulose solution in NMMO hydrate with $n = 0.65$ does not exhibit crystallization if the concentration exceeds 15 wt%.[21] In fact, this solution produces crystals only after having been placed still for 24 h.

CONCLUSION

Incorporation of PG as an antioxidant proved essential in the rheological measurement of cellulose solutions in NMMO hydrates. In the absence of PG a notable reduction in molecular weight of cellulose was produced during melting dissolution and rheological measurement, which had a significant effect on the phase transition behavior as well. In addition, if one choose improper melting dissolution conditions in the sample preparation, some unmelted NMMO hydrate crystals still exist in the cellulose solution under rheological or optical measurements. This also might lead to incorrect conclusion on the phase behavior.

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