MORPHOLOGICAL AND RHEOLOGICAL ANALYSES OF THE GEL PHASE IN THE CELLULOSE/NH_3/NH_4SCN SYSTEM

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Abstract

Recent morphological and rheological studies of the gel phase in the cellulose/NH_3/NH_4SCN system have provided valuable information regarding the structure of the gel network, as well as the kinetics of gel formation. Such information is critical to the establishment of an accurate experimental phase diagram for this complex system. A potential window of fiber spinnability, in which a liquid crystalline phase forms separately from the gel phase, is identified at temperatures as low as 1°C above the gel melting temperature.

Introduction

Since cellulose is the most abundant polymer on earth, it constitutes a primary material of choice for applications that can exploit its inherent molecular rigidity. One such application of tremendous commercial interest is high-modulus fiber production. Processing of cellulose is, however, hindered due to the ability of cellulose to hydrogen-bond and crystallize into a very stable lattice. Flory (1983) recognized that, based on the semi-rigid cellulose backbone, cellulose solutions, if formed, could exhibit liquid crystallinity. Unlike crystals, which exhibit three-dimensional order, and simple liquids, which possess only short-range (nearest-neighbor) order, liquid crystalline systems are capable of exhibiting either orientational or orientational/positional order. Such thermodynamically-driven order is usually accompanied by a reduction in solution or melt viscosity, which greatly facilitates processing (especially fiber spinning). It is well-established that many cellulose derivatives (e.g., hydroxypropylcellulose) form chiral nematic liquid crystals (in a *mesophase*) in a variety of common solvents, including water (Werbowyj and Gray, 1980; Conio *et al.*, 1983; Fried and Sixou, 1985). It is therefore not surprising that the parent cellulose molecules should also be able to form a mesophase under the proper conditions.

Hudson and Cuculo (1980) first established that ammonia/ammonium thiocyanate (NH_3/NH_4SCN) could be used as an effective solvent for cellulose. As efforts began to spin cellulose fibers and simultaneously construct a phase diagram for the cellulose/NH_3/NH_4SCN system (Hudson and Cuculo, 1982; Chen and Cuculo, 1986; LaMarre *et al.*, 1991), it was soon confirmed that cellulose formed a mesophase in this solvent. A variety of analytical methods have been used to construct the current experimental phase diagram for the cellulose/NH_3/NH_4SCN system, which is presented in Figure 1. In addition to a liquid crystalline phase, a unique gel phase is also evident in this phase diagram. Gels may be generally classified as either *chemical*, in which stabilization occurs via permanent covalent crosslinking, or *physical*, in which temporary, non-covalent crosslinks are thermally reversible. The cellulose gel phase behaves as a physical gel, and is presumably stabilized by liquid crystalline or hydrogen-bonded regions, rather than by covalent or crystalline crosslinks. In this work, we employ electron microscopy and dynamic rheology to examine the morphological characteristics and formation kinetics of this unique gel phase with the intent of discerning whether a mesophase forms independently of the gel phase. If this occurs, a window of spinnability may exist and can be exploited to facilitate cellulose fiber spinning.

Experimental

Solution Preparation

Whatman celluloses varying in degree of polymerization (DP) were dried by solvent exchange in methanol, acetone and hexane under dry nitrogen. To differentiate their DP, the cellulose grades examined here will hereafter be referred to as DPn, where n denotes the DP value. The specimens were dried overnight in a vacuum oven held at 70°C. Sigma ACS reagent-grade NH_4SCN was also dried overnight in a vacuum oven, while anhydrous NH_3 (Air Products & Chemicals Inc.) was used as-received. The solvent was prepared by condensing NH_3 over NH_4SCN to a predetermined concentration (24.5/75.5 w/w NH_3/NH_4SCN in this study). Cellulose/NH_3/NH_4SCN solutions were prepared by adding the NH_3/NH_4SCN mixture to a given mass of cellulose contained in a centrifuge tube. The tube was first shaken by hand, subsequently mixed for 1 min in a vortex mixer and then immediately placed in dry ice. To guarantee complete cellulose dissolution and solution homogeneity, each solution was cycled 6 times at 1 hr intervals between dry ice and a water bath held at 40°C. All samples were stored in dry ice prior to analysis.

Dynamic Rheology

Dynamic rheology is a very sensitive probe to gel formation in polymer systems, and can be used to obtain a precise measurement of the gel point during the gelation process. In this technique, samples are subjected to small-amplitude

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oscillatory deformation. The resulting shear stress (tyx) is related to the strain amplitude (γo) through

$$\tau_{yx} = G' \gamma_o \cos\omega t + G'' \gamma_o \sin\omega t \qquad (1)$$

where ω and t denote oscillatory frequency and time, respectively, G' is the elastic (storage) shear modulus, and G" is the viscous (loss) shear modulus (Bird *et al.*, 1987). The frequency behavior of G' and G" is sensitive to the existence of microstructure and the extent of crosslinking (Winter and Chambon, 1986; Chambon and Winter, 1987; Khan and Zoeller, 1993).

Concentration- and temperature-variable rheological measurements were conducted on DP210 cellulose solutions using a Rheometrics Stress Rheometer (DSR II) with a parallel-plate geometry, 25 mm plates and a 1 mm gap. Samples were first warmed to 25°C prior to loading and then heated to 40°C and sheared for 5 min after loading to remove any trace of the gel structure. Each sample was then cooled to a desired temperature between 15 and 30°C while being continuously subjected to a large-amplitude oscillatory strain outside the linear viscoelastic (LVE) regime to prevent premature sample gelation. Upon reaching the desired experimental temperature, frequency sweeps were performed in the LVE regime at a constant stress of 100 dyn/cm^2 to follow changes in the dynamic elastic (G') and viscous (G") moduli with time.

Polarized Light and Scanning Electron Microscopies

Several solutions containing 11-13% w/v cellulose were stored at temperatures just above the gel melting point and examined under crossed polars with a Nikon Optiphot light microscope. Additional specimens were maintained at 25°C (within the gel phase) for one month to expedite development of the gel network, which is believed to occur by spinodal decomposition (Domszy *et al.*, 1986; Frey *et al.*, 1995). Specimens for electron microscopy were prepared by two different methods to identify preparation-related artifacts. In the first method, samples were exchanged with ethanol, which caused no gross change in sample appearance, and subjected to supercritical CO_2 extraction in a Tousimis Sandri PVT-3B dryer at 31°C and 7.58 MPa. This technique is not very intrusive to delicate microstructure, since it has been used successfully to image *ca*. 10 nm fibrils in a chemically dissimilar gel system (Ilzhoefer and Spontak, 1995). In the second method, virgin cellulose/NH_3/NH_4SCN samples were quenched in liquid ethane at its melting point (cooled by liquid nitrogen) and subjected to freeze drying at -100°C for 24 hrs in a JEOL JFD-9000C freeze-fracture/etching unit maintained at -170°C and *ca*. 10^{-7} torr. This method has likewise been shown to preserve ultrafine microstructural elements in complex liquids (Zasadzinski and Bailey, 1989; Mazur *et al.*, 1993). Specimens obtained from both preparation methods were sputter-coated with about 30 nm of Au/Pd and examined with a JEOL JFE-6400F field-emission scanning electron microscope (FESEM) operated at 5 kV.

Results and Discussion

Dynamic Rheology

Shown in Figure 2 is the time evolution of the dynamic moduli G' and G" as functions of oscillatory frequency (ω) in a 12% w/v DP210 cellulose solution at 25°C. Up to 800 s (Figures 2a and 2b), G" clearly exceeds G' by over two orders of magnitude in ω, indicating that the sample exhibits liquid-like (i.e., viscous) characteristics. At 1900 s (Figure 2c), G' and G" are seen to cross at a frequency of about 5 rad/s. If gelation is permitted to continue to 4200 s (Figure 2d), G' becomes not only greater than G" over the ω range examined here, but also less dependent on the magnitude of ω. The variation of G' (evaluated at 1 rad/s) with time (t) at four different temperatures for the 12% w/v DP210 cellulose solution is seen in Figure 3. From this figure, it is clear that, as the temperature is increased, G'(t) increases less in magnitude and less quickly with time. Note that G' is nearly independent of t at 30°C, revealing that gelation does not occur in this system at this temperature. A similar trend is observed in Figure 4, in which G'(t) is shown for two solution concentrations (12% and 16% w/v cellulose) at two different temperatures (20°and 25°C). At either concentration, an increase in temperature is accompanied by reductions in the magnitude of G' and the rate by which G' increases with time. At constant temperature, however, an increase in DP210 cellulose concentration results in increases in both the magnitude of G' and the rate by which G' increases with time. This is consistent with the expectation that gelation should occur more rapidly, and produce stiffer (more elastic) gels, as the concentration of cellulose is increased. The shape of the G'(t) curves in Figures 3 and 4 suggests that the gelation mechanism can be described in terms of a three-step process starting with an induction period in which G' does not vary much with time. In the second step, G' increases exponentially with time. This is followed by a third step wherein G' increases relatively slowly with time. It is of interest to note that three-step gelation mechanism is similar to that observed in crystal-containing gels (Lin *et al.*, 1991).

While the variation of G' with time demonstrates that the cellulose/ NH_3/NH_4SCN solutions investigated here are in the process of gelation, this dependence is not capable of providing a quantitative assessment of the gelation point. According to the criterion proposed by Winter and co-workers (Winter and Chambon, 1986; Chambon and Winter, 1987), stress relaxation at the gel point obeys the following expression:

$$G(t) = St^{-n} \qquad (2)$$

Here, S is the strength of the gel and depends on molecular rigidity and crosslink density, whereas n, the relaxation

exponent, assumes values between zero and unity and is related to the cluster geometry at the gel point. It immediately follows that

$$G'(\omega) = \Gamma(1-n)\cos(\pi n/2)\, S\omega^n \quad (3a)$$
$$G''(\omega) = \Gamma(1-n)\sin(\pi n/2)\, S\omega^n \quad (3b)$$

where Γ denotes the gamma function. Since $G'(\omega) \sim \omega^n$ and $G''(\omega) \sim \omega^n$ from Equations 3a and 3b, respectively, the loss tangent ($\tan \delta$) is found to be independent of w at the gel point:

$$\tan \delta = G''/G' = \tan(\pi n/2) \quad (4)$$

Shown in Figure 5 is $\tan \delta$ as a function of time for the 12% w/v DP210 cellulose solution at three different frequencies. At the experimental temperature corresponding to these measurements (15°C), $\tan \delta$ is seen to become independent of ω at about 375 s, which corresponds to the gel point. It is comforting that the Winter criterion, which is often applied to covalent and crystalline crosslinked systems, appears to be equally applicable to the present systems, which are stabilized through liquid crystalline and hydrogen-bonded regions. Such regions, or junction zones, are known to stabilize biopolymers (Draget *et al.*, 1994). Gelation times deduced according to the Winter criterion at other DP210 cellulose concentrations and temperatures are listed in Table 1. As observed in Figures 3 and 4 and described in detail elsewhere (Frey *et al.*, 1996b), the gelation time is found to increase with increasing temperature at constant cellulose concentration, but decrease with increasing cellulose concentration at constant temperature. Note that no samples gelled at temperatures above 30°C, and that the 8% w/v DP210 cellulose system did gel at 25°C. These data help to establish the boundaries of the cellulose/NH_3/NH_4SCN gel phase.

Polarized Light and Scanning Electron Microscopies

Figure 6 is a polarized light micrograph of a 13.7% w/v DP210 cellulose solution held at 31°C for 1 week. According to the rheological measurements described above, this solution should not exist in the gel phase. The birefringence (light regions) evident in this micrograph demonstrate that the solution exhibits liquid crystallinity. This observation suggests that, at temperatures just above the melting point of the gel phase, there exists a regime which may serve as a window of cellulose spinnability.

A FESEM micrograph of the gel network formed in a 12% w/v DP374 cellulose system and isolated through a combination of solvent exchange and supercritical fluid extraction is provided in Figure 7. The network is seen to consist of fibrils measuring on the order of 20-70 nm in diameter. Upon close examination of micrographs such as the one presented in Figure 7, it is evident that the fibrils are not smooth, but instead exhibit nodules and radial bands. The nodules are believed to be remnants of ultrafine structure that did not survive sample preparation and consequently collapsed (Frey *et al.*, 1996a). Confirmation of the cellulose network morphology is obtained from FESEM micrographs of cellulose/ NH_3/NH_4SCN samples subjected to freeze-drying. An example of such a micrograph is displayed for a 12% w/v DP760 cellulose system in Figure 8, which again reveals a fibrillar network composed of fibrils measuring on the order of 20-70 nm in diameter. While the fibrils in micrographs such as the one shown in Figure 8 also exhibit nodules, there exists a significant difference between specimens prepared by the two different sample preparation methods employed here. Seen in Figure 8 are ultrathin films that appear to connect the fibrils. These fibrils are not observed in any of the systems examined after solvent exchange/supercritical fluid extraction, suggesting that the films collapsed during either the exchange or extraction steps. These films, observed in solutions containing cellulose grades differing in DP, are consistent with the possibility that, while the loosely connected, molecularly anisotropic fibrils in the network are liquid crystalline and serve to stabilize the network, a fraction of the cellulose molecules must also exist in an isotropic state. Phase separation during the course of gelation therefore yields coexisting cellulose-rich and solvent-rich phases.

Summary

Cellulose/NH_3/NH_4SCN solutions exhibit liquid crystallinity at relatively low cellulose concentrations. At temperatures below approximately 30°C (depending on cellulose molecular weight and concentration), such solutions phase-separate via spinodal decomposition to form a gel phase, which is predicted by thermodynamic theories developed to elucidate polymer/solvent phase behavior. The nature of the gel is unique, unlike that of common polymer gels, in that it is stabilized through liquid crystalline regions (junction zones), rather than covalent linkages or crystals. Dynamic rheology has demonstrated that gel stiffness and rate of gelation are strongly dependent on both temperature and cellulose molecular weight. Moreover, data collected during the gelation process can be accurately described by the Winter criterion, which has proven highly valuable in interpreting conventional polymer gelation. Phase separation results in a cellulose-rich fibrillar network that stabilizes the gel. From electron microscopy, the fibrils are found to measure between 20 and 70 nm, depending on cellulose concentration and molecular weight. In addition, thin cellulose films that connect nodule-covered fibrils in the solvent-rich phase have been observed in specimens prepared via freeze-drying. These films are extremely fragile and apparently collapse during solvent exchange. Above the gelation temperature, cellulose/NH_3/NH_4SCN solutions are incapable of gelling and exhibit a mesophase, which may be ideally suited for spinning high-modulus cellulose fibers.

Acknowledgments

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References

Bird, R. B., R. C. Armstrong and O. Hassager. 1987. *Dynamics of Polymeric Liquids*, 2nd ed., Vol. 1: Fluid Mechanics, Wiley, New York.

Chambon, F. and H. H. Winter. 1987. Linear viscoelasticity at the gel point of a crosslinking PDMS with imbalanced stoichiometry. J. Rheol. **31**, 683-697.

Chen, Y. S. and J. A. Cuculo. 1986. Lyotropic mesophase of cellulose in ammonia/ammonium thiocyanate solution. J. Polym. Sci., Polym. Chem. Ed. **24**, 2075-2084.

Conio, G., E. Bianchi, A. Ciferri, A. Tealdi and M. A. Aden. 1983. Mesophase formation and chain rigidity in cellulose and derivatives. 1. (hydroxypropyl)cellulose in dimethylacetamide. Macromolecules **16**, 1264-1270.

Domszy, R. C., R. Alamo, C. O. Edwards and L. Mandelkern. 1986. Thermoreversible gelation and crystallization of homopolymers and copolymers. Macromolecules **19**, 310-325.

Draget, K. I., G. S. Braek and O. Smidsrod. 1993. Gel strength of Ca-limited alginate gels made in-situ. Hydrobiologia **261**, 563-569.

Flory, P. J. 1983. Molecular theory of liquid crystals. Adv. Polym. Sci. **59**, 1-36.

Frey, M. W., J. A. Cuculo, A. Ciferri and M. H. Theil. 1995. A review of lattice theory for lyotropic liquid-crystalline polymers, spinodal decomposition, and gel formation. J. Macromol. Sci. Đ Rev. Macromol. Chem. Phys. **35**, 287-325.

Frey, M. W., J. A. Cuculo and R. J. Spontak. 1996a. Morphological characterization of the lyotropic and gel phases in the cellulose/NH_3/ NH_4SCN system. J. Polym. Sci. B: Polym. Phys. **34**, 2049-2058.

Frey, M. W., S. A. Khan and J. A. Cuculo. 1996b. Rheology and gelation of cellulose/ammonia/ammonium thiocyanate solutions. J. Polym. Sci. B: Polym. Phys. **34**, 2375-2381

Fried, F. and P. Sixou. 1984. Lyotropic mesophases in hydroxypropyl-cellulose in pure acetic acid, in water, and in mixed solvents. J. Polym. Sci., Polym. Phys. Ed. **22**, 239-247.

Hudson, S. M. and J. A. Cuculo. 1980. The solubility of cellulose in liquid ammonia/salt solutions. J. Polym. Sci., Polym. Chem. Ed. **18**, 3469-3481.

Hudson, S. M. and J. A. Cuculo. 1982. The solubility of cellulose in liquid ammonia/salt solutions: thermoreversible gelation and a preliminary report on fiber formation. J. Polym. Sci., Polym. Chem. Ed. **20**, 499-511.

Ilzhoefer, J. R. and R. J. Spontak. 1995. Effect of polymer composition on the morphology of self-assembled dibenzylidene sorbitol. Langmuir **11**, 3288-3291.

Khan, S. A. and N. J. Zoeller. 1993. Dynamic rheological behavior of flocculated fumed silica suspensions. J. Rheol. **37**, 1225-1235.

LaMarre, C. R., J. A. Cuculo, S. M. Hudson and A. Ciferri. 1991. Gelation and mesophase formation of cellulose in NH_3/NH_4SCN. Mol. Cryst. Liq. Cryst. Lett. **7**, 193-199.

Lin, Y. G., D. T. Mallin, J. C. W. Chien and H. H. Winter. 1991. Dynamic mechanical measurement of crystallization-induced gelation in thermoplastic elastomeric poly(propylene). Macromolecules **24**, 850-854.

Mazur, A. W., J. L. Burns, G. D. Hiler II and R. J. Spontak. 1993. Electron microscopy of reaction-controlling association structures in the enzymatic hydrolysis of triglycerides. J. Phys. Chem. **97**, 11344-11349.

Werbowyj, R. S. and D. G. Gray. 1980. Ordered phase formation in concentrated hydroxypropylcellulose solutions. Macromolecules **13**, 69-73.

Winter, H. H. and F. Chambon. 1986. Analysis of linear viscoelasticity of a crosslinking polymer at the gel point. J. Rheol. **30**, 367-382.

Zasadzinski, J. A. N. and S. M. Bailey. 1989. Applications of freeze-fracture replication to problems in materials and colloid science. J. Electr. Microsc. Tech. **13**, 309-334.

Table 1. Gelation time (in sec) as a function of temperature for several DP210 cellulose concentrations in 24.5/75.5 w/w NH_3/NH_4SCN.

Temperature (°C)	8%	10%	12%	14%	16%
15	1260	300	375	100	*
20	7875	3800	575	440	500
25	**	4680	1010	1500	830

* Rapid gelation precluded accurate measurement.
** Solution did not gel under these conditions.

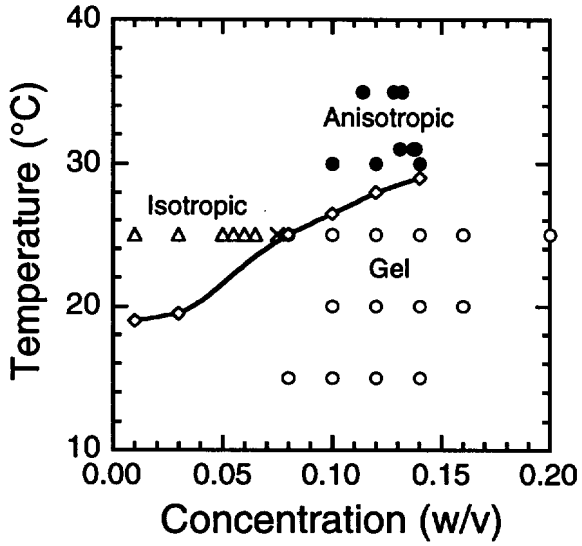

Figure 1. Experimental phase diagram for DP210 cellulose in 24.5/75.5 w/w NH_3/NH_4SCN.

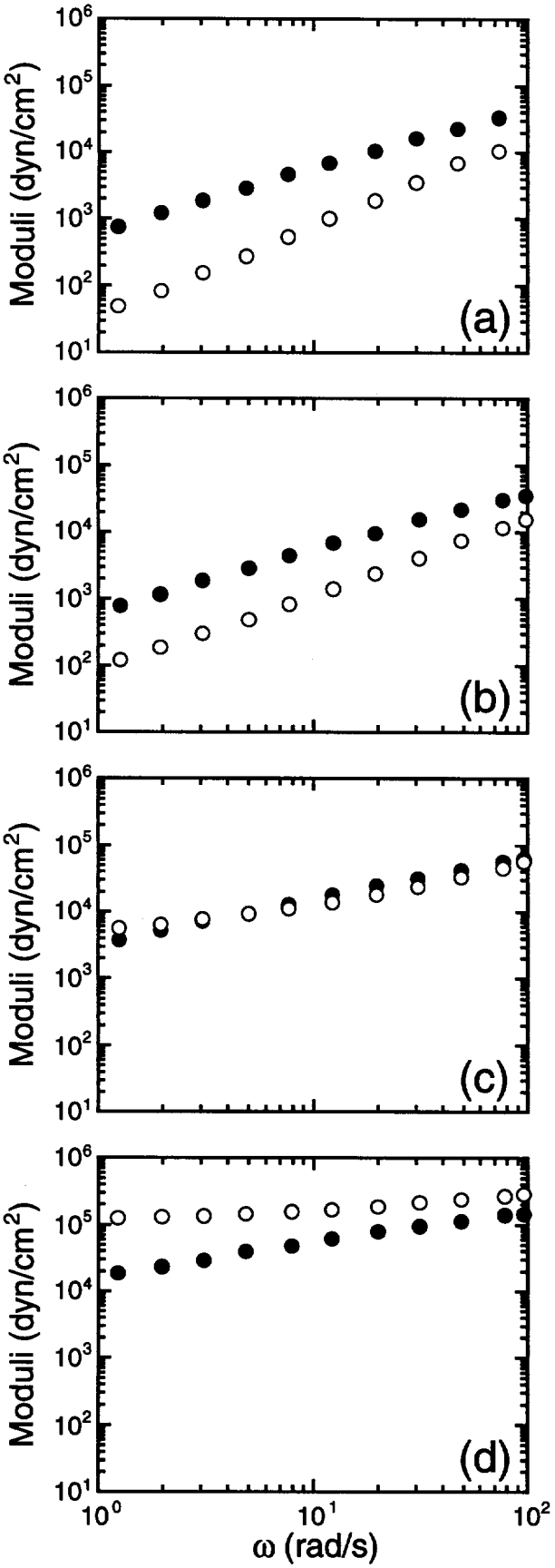

Figure 2. Double-logarithmic representation of the dynamic elastic (G', ○) and viscous (G",●) moduli as functions of frequency (ω) at four times during gelation (in sec): (a) 0, (b) 800, (c) 1900 and (d) 4200.

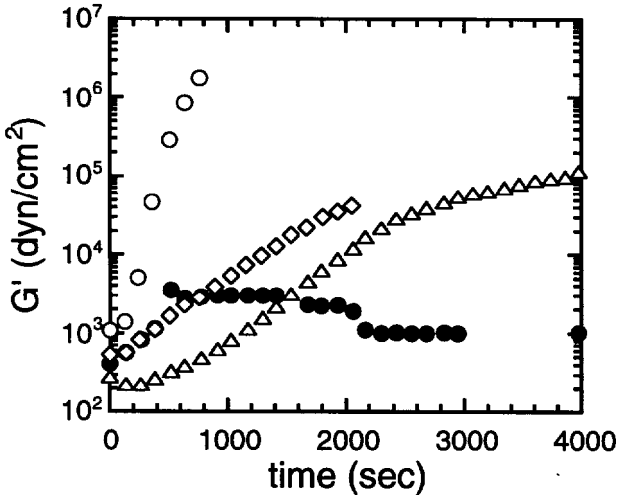

Figure 3. Time evolution of G' during the gelation of 12% w/v DP210 cellulose/NH_3/NH_4SCN solutions at four different temperatures (in °C): 15 (○), 20 (◇), 25 (△) and 30 (●). Gelation does not occur at 30°C.

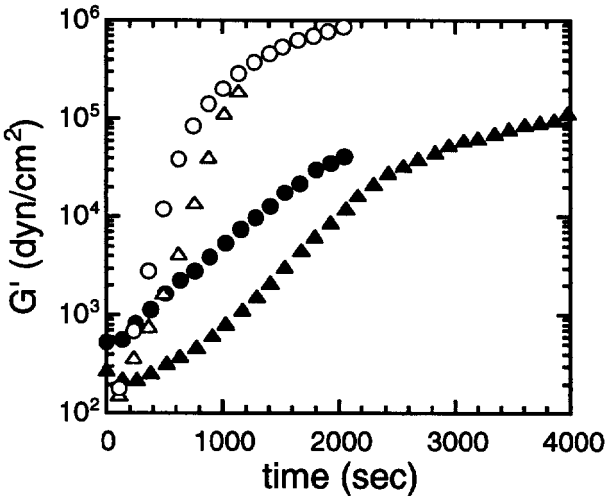

Figure 4. Dependence of G' on time for DP210 cellulose solutions at concentrations of 12% w/v (filled) and 16% w/v (open) measured at 20°C (circles) and 25°C (triangles). The frequency is constant at 1 rad/s.

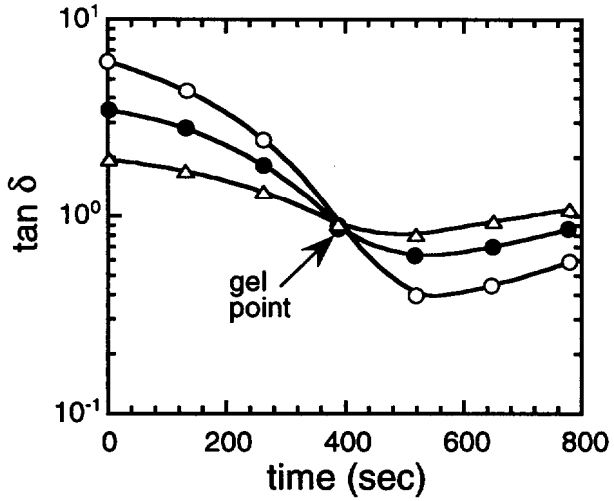

Figure 5. tan δ (=G"/G') shown as a function of time for three different oscillatory frequencies (in rad/s): 3.15 (○), 20.0 (●) and 79.2 (△). The frequency-independent gel point occurs at the intersection of the curves.

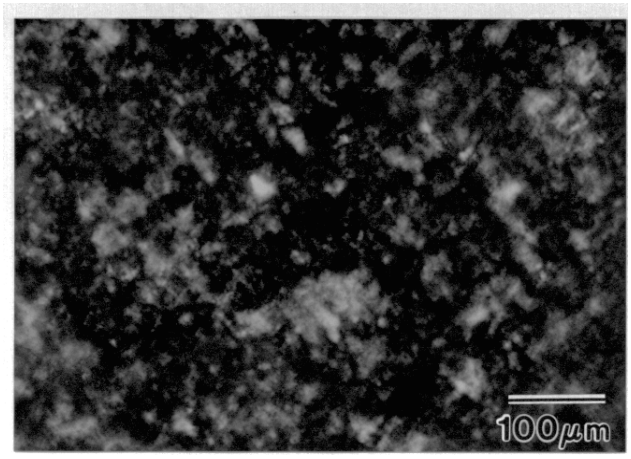

Figure 6. Polarized light micrograph of a 13.7% w/v DP210 cellulose solution after it was held at 31°C (above the gel melting temperature) for a period of one week. The bright regions correspond to birefringence arising from cellulose liquid crystals.

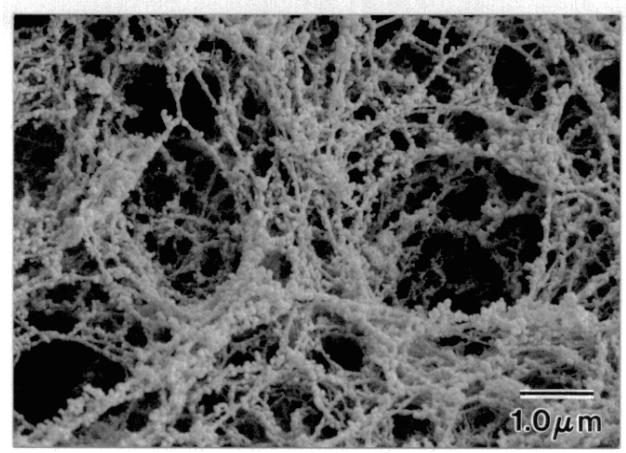

Figure 7. Field-emission scanning electron micrograph of a 12% w/v DP374 cellulose solution subjected to solvent exchange and supercritical fluid extraction to remove the non-cellulose constituents. Note that the cellulose fibrils, measuring 20-70 nm across, possess nodules.

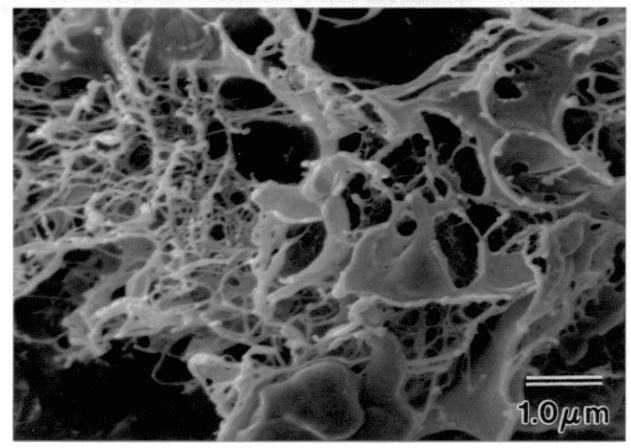

Figure 8. FESEM micrograph of a 12% w/v DP760 cellulose solution prepared via freeze-drying. Unlike the image in Figure 7, this micrograph reveals the existence of ultrathin cellulose films. These presumably isotropic films collapse during solvent exchange.