SHORT COMMUNICATIONS

Formation of Lyotropic Liquid Crystals of Cellulose Derivatives Dissolved in Inorganic Acids

Kenji KAMIDE, Kunihiko OKAJIMA, Toshihiko MATSUI,
and Shuji KAJITA

*Fundamental Research Laboratory of Fibers and Fiber-Forming Polymers,
Asahi Chemical Industry Co., Ltd., 11 7 Hacchonawate,
Takatsuki, Osaka 569, Japan*

Recently, the formation of liquid crystalline systems from solutions in water and organic solvents of cellulose and its derivatives, including hydroxypropylcellulose (HPC), ethylcellulose (EC), cellulose di- and tri-acetates (CA) has been extensively reported by many investigators.[1-19]

In this communication, we demonstrate that some cellulose derivatives form lyotropic liquid crystals in inorganic solvents.

EXPERIMENTAL

Cellulose Derivatives

Five commercial grade methylcellulose (MC) samples with a total degree of substitution $\langle\!\langle F\rangle\!\rangle = 1.80$ and viscosity-average degree of polymerization P_v ranging 95—750 and two commercially available EC samples ($\langle\!\langle F\rangle\!\rangle = 2.63$) having the solution viscosity of 43 and 87 centipoise in chloroform (1 wt% at 25°C) were supplied by Kishida Chemicals Co., Japan and used as received. Four CA whole polymers with $\langle\!\langle F\rangle\!\rangle$ of 2.92, 2.46, 1.78, and 0.49 were synthesized in this laboratory by the methods described in the previous papers.[20-24] Each CA whole polymer was fractionated using successive solution fractionation methods, al-

ready established by Kamide *et al.*[20-24] into 7 fractions and the fractions having the viscosity-average degree of polymerization P_v of 250 were employed for further study. A cyanoethyl cellulose (CyEC) with $\langle\!\langle F\rangle\!\rangle = 2.87$ was synthesized by reaction of alkalicellulose with acrylonitrile and four carboxyethyl/carbamoylethyl cellulose (CE/CmEC) samples with $\langle\!\langle F\rangle\!\rangle$ of 0.5—1.4 were prepared by hydrolysis of CyEC with 40 wt% aq sodium hydroxide at 60°C for given periods. $\langle\!\langle F\rangle\!\rangle$'s of carboxyl and carbamoylethyl group of CE/CmEC were determined by applying back-titration method with 0.1 N hydrochloric acid and 0.1 N sodium hydroxide to the solution and by elemental analysis on Nitrogen. A HPC sample with the weight-average molecular weight M_w of 1.0×10^5 and the molecular substitution (MS) of 3, and a cellulose tripropionate (CP) sample were supplied by Scientific Product Inc., USA. Here, MS was defined as the average molar number of propylene oxide reacting with a glucose unit. Four sodium cellulose sulfate (NaCS) samples with $\langle\!\langle F\rangle\!\rangle = 1.67$—2.46, prepared by the method of Schweiger[25] as employed in the previous paper,[26] were used.

Solvent

Hydrochloric, nitric, phosphoric, pyrophosphoric and perchloric acids were used. All solvents were of guaranteed grade (Kishida Chem. Co., Japan) and were used by diluting with distilled and deionized water.

Preparation of Solutions

To 0.5 gram of cellulose derivative in a glass vessel a given amount of acid, cooled at 0°C, was added and the mixture was quickly mixed with a microspatula, stocked at 5°C for 24 h.

Lower Critical Concentration

A 0.03 ml of the solution thus prepared was inserted between a slide glass of 7.6 cm × 2.6 cm (length × width) and a cover glass of 1.8 cm × 1.8 cm (length × width). Shearing stresses were applied to the solution at 25°C, and the lower critical concentration for the appearance of lyotropic liquid crystals C_L was determined 10 minutes after application of the shearing stresses as the minimum concentration at which the optical birefringence was observed under crossed polarizers. A typical liquid crystal system (CA/nitric acid) was photographed with a polarizing microscope (Nicon Semi-Automatic Microflex EFM).

Electroconductivity and pH of the Solvents

The electroconductivity and pH of the acids were measured at 25°C using a conductometer model CM-2A and a pH meter model HM-18E (both, manufactured by Toa Denpa Co., Japan), respectively.

RESULTS AND DISCUSSION

Figure 1 shows a typical photograph of the lyotropic liquid crystal of CA ($\langle\!\langle F \rangle\!\rangle = 2.46$, $P_v = 250$)/65 wt% nitric acid (polymer concentration, 45 wt%) taken at 25°C.

Figure 2 illustrates an example of the viscosity of the solution η plotted as a function of concentration C for the case of CA ($\langle\!\langle F \rangle\!\rangle = 2.46$, $P_v = 250$)/65 wt% nitric acid at 25°C. In
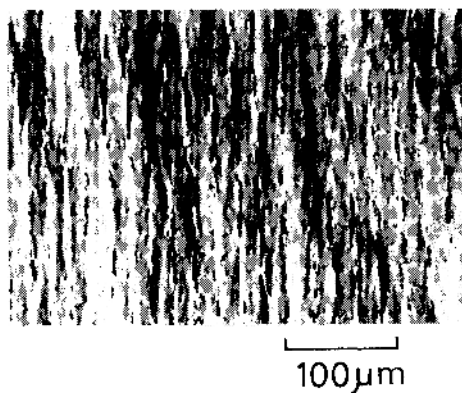

Figure 1. A photograph of a typical lyotropic liquid crystal for cellulose acetate ($\langle\!\langle F \rangle\!\rangle = 2.46$, $P_v = 250$)/65 wt% nitric acid system at 25°C. Polymer concentration, 45 wt% (×230).
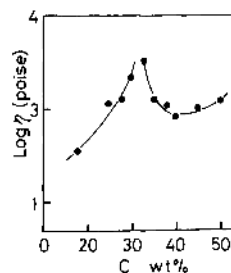

Figure 2. Plots of log η vs. polymer concentration C (wt%) for CA ($\langle\!\langle F \rangle\!\rangle = 2.46$, $P_v = 250$)/65 wt% nitric acid system at the shear rate of 20 s^{-1} and at 5°C.
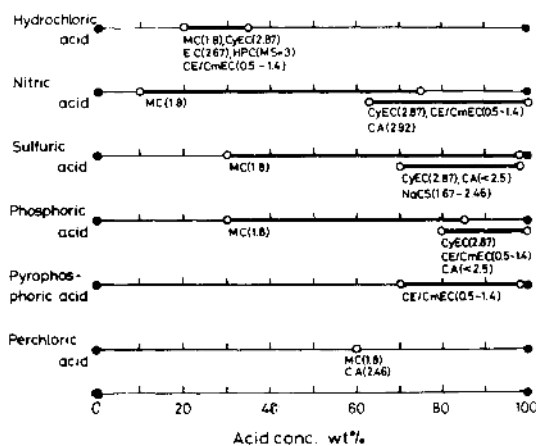

Figure 3. Schematic expression of the liquid crystal formation of cellulose derivative/inorganic acid systems. The numbers on the axis denote the concentrations of inorganic acid in water (wt%) as solvent.

this system C_L (31 wt%), as determined microscopically, was found to coincide with the concentration at which viscosity of the solution began to decrease (31 wt%).

Figure 3 summarizes the suitable combination of some cellulose derivatives and inorganic acids, giving lyotropic liquid crystals. The concentration range, in which lyotropic liquid crystal is formed, is shown as the bold line ending with unfilled circles or as an unfilled circle. Obviously, ⟪F⟫ > 1, as claimed by Panar et al.[5] in their laid-open patent, but not registered, is not the necessary condition for cellulose derivatives to form liquid crystals. All HPC (MS = 3.0), MC (⟪F⟫ = 1.8) and CyEC (⟪F⟫ = 2.87) samples were found to form liquid crystals in almost all inorganic acids utilized here, but EC (⟪F⟫ = 2.67) was found to become liquid crystals only in hydrochloric acid. A possible thermodynamic interaction between O-methyl group in MC and the acids is considered not to be so different from that between O-ethyl group in EC and acids. Therefore, a significant difference in the ability to form liquid crystals between MC and EC samples may be accounted for by the differences in the number of residual hydroxyl groups per given glucopyranose ring (i.e., 3 − ⟪F⟫). The difference between EC (⟪F⟫ = 2.67) and CyEC (⟪F⟫ = 2.87) cannot be interpreted by the degree of unsubstitution (3 − ⟪F⟫), but by the difference in the polarity between cyanoethyl group in CyEC and ethyl group in EC: The former is much more polar than the latter and an interaction of cyanoethyl group with the inorganic acid is strong enough to lead finally to liquid crystals.

CA with ⟪F⟫ = 2.92 was dissolved in nitric acid and phosphoric acid, to yield liquid crystals and showed flow birefringence, respectively. All CA samples having ⟪F⟫ less than 2.5 form liquid crystals in nitric, sulfric, perchloric and phosphoric acids.

Figure 4 shows the effects of the average molecular weight as denoted by P_v on C_L for MC with ⟪F⟫ = 1.8 in 35 wt% hydrochloric,
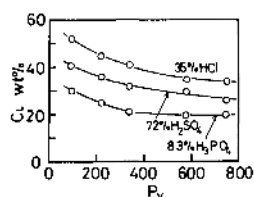

Figure 4. Dependence of the lower critical concentration C_L on degree of polymerization P_v for methylcellulose/inorganic acid systems.
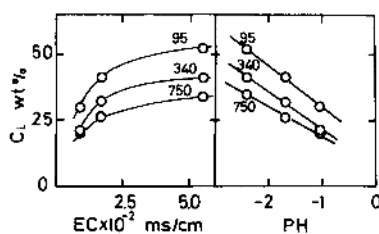

Figure 5. Dependence of the lower critical concentration C_L on electroconductivity (EC) and pH of the solvent for methylcellulose/inorganic acid systems. The numbers on the curves denote p_v of methylcellulose.
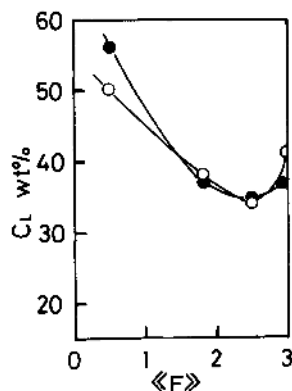

Figure 6. Dependence of the lower critical concentration C_L on total degree of substitution ⟪F⟫ for cellulose acetate/65 wt% nitric acid (○) and cellulose acetate/DMAc (●) systems.

72 wt% sulfric and 83 wt% phosphoric acids. C_L decreases monotonically with an increase in P_v, approaching an asymptotic value. C_L of MC with the same P_v increases with an increase in electroconductivity or with a decrease in pH of the solvent. In other words, a less acidic and less electroconductive solvent is preferable to form the liquid crystalline solu-

tion. These features are clearly pictured in Figure 5.

Figure 6 shows the effects of $\langle\!\langle F\rangle\!\rangle$ on C_L for CA with $P_v = 250$ in 65 wt% nitric acid. The figure also contains the results (as filled mark) for CA in dimethylacetamide (DMAc) solution.[27] C_L decreases with increasing $\langle\!\langle F\rangle\!\rangle$ in both nitric acid and DMAc, if $\langle\!\langle F\rangle\!\rangle < 2.46$. C_L for both nitric and DMAc reveals minimum at $\langle\!\langle F\rangle\!\rangle \cong 2.46$. Kamide and Saito demonstrated that the time-averaged flexibility of CA chain attains maximum at $\langle\!\langle F\rangle\!\rangle = 2.46$ in DMAc.[28] Then, it can be said that the rigidity of the CA chains is closely correlated with C_L as was theoretically predicted by Flory.[29]

More detailed account of the fine structure of the liquid crystals formed from acidic solution of cellulose derivatives will be given elsewhere.

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