Characterization of Anisotropic Mesophase of Cellulose Acetate in Inorganic Solvent Mixture

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ABSTRACT: An attempt was made to determine phase diagram of cellulose acetates (CA) with total degree of substitution ⟨⟨F⟩⟩ ranging from 0.52 to 2.86, in a mixture of sulfuric acid (SA), poly(phosphoric acid) (PPA), and water (W). In the mixture with very specific composition of SA/PPA/W (=0.1/0.8/0.1, wt/wt/wt), in which cellulose has been reported to form liquid crystal by Kamide et al. [Polym. J., 25, 453 (1993)], all of the cellulose acetates showed anisotropic behavior. Circular dichroism (CD) spectra of the cellulose acetate mesophase indicated that the texture is left handed cholesteric irrespective of ⟨⟨F⟩⟩. The helicoidal cholesteric pitch (P) determined by the CD method remarkably depends on ⟨⟨F⟩⟩, polymer concentration (C_p) and temperature (T). The pitch monotonically increases with an increase of ⟨⟨F⟩⟩ at constant temperature and polymer concentration. The reciprocal pitch of all samples is proportional to T and $C_p{}^3$. The coefficients of these relations indicated that the pitch of the sample with larger ⟨⟨F⟩⟩ tends to show less dependency on temperature and polymer concentration.
KEY WORDS Anisotropic Mesophase / Celluloseacetate / Inorganic Solvents Mixture / Degree of Substitution / Cholesteric Pitch / Circular Dichroism /

Since Werbowyi–Gray, Maeno, and Pannar-Willcox independently reported[1−3] liquid crystal of cellulose derivatives, such as hydroxylpropylcellulose and cellulose esters and ethers in 1976, various kinds of cellulose derivatives including cellulose have been found to form thermotropic and lyotropic liquid crystals.[4,5] Concurrently a great deal of attention has been focused on the structure and properties of the cellulose derivatives mesophase from a desire to prepare high performance cellulosic materials as well as purely scientific interest. At present, several specific features of cellulose derivative liquid crystals have been disclosed to exhibit: Almost all the mesophases show that cholesteric nature and the structural parameters such as the helicoidal cholesteric pitch and sense are variations of temperature, polymer concentration, chirality of the polymer and the solvent nature.[6] The total degree of substitution (⟨⟨F⟩⟩) dependence of these structural parameters is also suggested. Guo and Gray[6] reported that the cholesteric pitch (P) of mesophase of acetylethyl cellulose (AEC)–chloroform system, where AEC is prepared by acetylation of ethylcellulose with ⟨⟨F⟩⟩_ethyl = 2.5, monotonically changes with the acetyl content and the helicoidal sense reverses at ⟨⟨F⟩⟩_acetyl ∼ 0.2, accordingly ⟨⟨F⟩⟩_ethylacetyl = 2.7. They suggested that the minor change of the acetyl content influences the chain conformation which may play a important role in the cholesteric properties. Gilbert[7] pointed out that cellulose in trifluoroacetic acid (TFA) and dichloroethane (DCE) mixture (TFA : DCE = 7 : 3) forms mesophase with right handed cholesteric texture, while Ritchey et al. reported[8] that cellulose triacetate in a similar solvent (TFA) shows left handed helicoidal sense. However, their studies should be criticized from several experimental points of view such as very limited ⟨⟨F⟩⟩ range of the samples, and no information on gradual change of polymer concentrations and degradation of polymers during preparation and optical measurements due to high volatility and high acidity of the solvent used.

Very recently, Kamide et al.[9] found that cellulose in the mixture of sulfuric acid (SA), poly(phosphoric acid) (PPA), and water (W) (SA/PPA/W = 1/8/1, w/w/w) generates lyotropic liquid crystal above some cellulose concentration, depending on the degree of polymerization (DP). This type of solvent mixture is advantageous with respect to low volatility, easiness to handle, and low degree of decomposition of polymer in relatively low temperature range. Successively, cellulose acetates (CA) with ⟨⟨F⟩⟩ ranging from 0.5 to 2.9 were found to be dissolved into the solvent mixture up to 30 wt% around which lyotropic mesophase with cholesteric texture forms. In this study an attempt was made to disclose effects of ⟨⟨F⟩⟩ and temperature on the cholesteric structure of the CA and cellulose mesophases. For this purpose, we prepared the mesophases of cellulose and CA with various ⟨⟨F⟩⟩ (0.5—2.9) in the mixture of SA/PPA/W (=1/8/1) and determined the cholesteric pitch of the mesophases using circular dichroism method.

EXPERIMENTAL

Sample

An Alaska pulp with α cellulose content of 90.1 wt% supplied from Alaska Pulp Co. (U.S.A.) was used for the cellulose sample (sample code CA-0). The viscosity-average molecular weight M_v of the cellulose sample was determined to be 5.36×10^4 by viscosity method. Here, viscosity equation used for determination is as follows[10]:

$$[\eta] = 3.85 \times 10^{-2} M_w{}^{0.76} \quad (\mathrm{cm^3\,g^{-1}}) \qquad (1)$$

where, $[\eta]$ and M_w are the limiting-viscosity number in cadoxen (cadmium oxide/ethylenediamine/NaOH/ $H_2O = 5/28/1.4/166$, w/w/w/w) and the weight-average molecular weight, respectively.

Five kinds of CA samples with ⟨⟨F⟩⟩ = 0.66—2.46 (sample code CA-1—CA-6) were obtained from cellulose

triacetate with $\langle\langle F \rangle\rangle = 2.89$ by acid–hydrolysis method using acetic acid as homogeneous reaction.[11] M_v of the CA samples thus prepared was conveniently determined through a series of viscosity equations established for CA with $\langle\langle F \rangle\rangle = 0.5$, 1.75, 2.46, and 2.92 in N,N'-dimethyl acetamide (DMAc).[11]

For estimation of total degree of substitution, ^{13}C NMR measurement on CA in dimethyl sulfoxide (DMSO) was carried out using GSX-400 FT NMR spectrometer (JEOL, Japan) with 100.2 MHz for [13]C. From the intensity ratio of methyl carbon of acetyl groups to skeletal C1 carbon of cellulose in the NMR spectrum of the sample, $\langle\langle F \rangle\rangle$ was determined within an accuracy of 10%. The measuring conditions were summarized as follows: Spectral width, 25000 Hz; Data point, 32678; pulse mode, ^{1}H noise-decoupled mode without NOE (SGNNE); accumulation,15000—20000; flip angle, 45°; repetition time, 5s; internal standard, tetramethylsilane (TMS).

The M_v and $\langle\langle F \rangle\rangle$ of the CA samples including cellulose are listed in Table I. According to Kamide and Saito[11] the degree of substitution at C2, C3, and C6 positions ($\langle\langle f_2 \rangle\rangle$, $\langle\langle f_3 \rangle\rangle$, $\langle\langle f_6 \rangle\rangle$, respectively) is almost equal for each CA prepared by above mentioned method.

Solvent

Sulfuric acid of 97 wt% concn and polyphosphoric acid ($H_3P_4O_{13}$) of 88 wt% concn and more were used as received from Wako Chemical Co. (Japan). Deionized water with electroconductivity less than $0.3 \mu S \, cm^{-1}$ was prepared using ion exchanger resin. The three solvents were mixed at $-5°C$ and stored.

Solution

The cellulose and CA samples were mixed with the solvent mixture of SA/PPA/W at the polymer concentration (C_p) up to 30 wt%. In order to avoid the decomposition of the polymer, the mixture of polymer and solvent was immediately transferred to refrigerator controlled at $-5°C$ and then stirred sometimes by hand. The maximum time required for making clear solution was *ca.* 40 hours. The solution thus prepared served for polarizing microscope observation and circular dichroism (CD) measurement at 48 hours and 100 hours after mixing, respectively.

Polarizing Microscope Observation

The sample for the observation was prepared by sandwiching the solution between a microscope slide and cover glasses. The microscope observation was made with a Polarizing Microscope type 63227 (Nippon Kogaku, Japan) under crossed nicols. From the image of the sample under the shear the solution was classified into three categories; optically isotropic solution which gives dark image even under the shear, flow orientation solution which shows bright image only in a few second, and optically anisotropic mesophase which retains colored image during the observation.

Circular Dichroism Measurements

The mesophase samples for CD measurement were set between two quartz plates to be $5 \mu m$ thick. CD spectra were reordered with a JASCO J-720 type spectropolarimeter equipped with thermocontroller. Stabilization of the cholesteric structure was reached about 2 hours later from the set of the mesophase samples. The cholesteric pitch (P) was calculated using an equation[12] relating P to the wavelength λ_0 of the reflection peak maximum in CD spectra, as follows:

$$P = \lambda_0/\bar{n} \qquad (2)$$

where $\bar{n}$ is the average refractive index of the mesophase, measured with an Abbe refractometer.

RESULTS AND DISCUSSION

An image of the polarizing microscope of the CA with $\langle\langle F \rangle\rangle = 2.89$ in a mixture of SA/PPA/W $(= 1/8/1, w/w/w)$ is representatively shown in Figure 1. This solution gives typical colored image peculiar to mesophase. Figure 2 shows phase diagrams determined by polarizing microscopic observation for the CA–SA/PPA/W system at constant polymer concentration (25 wt%). This figure also includes the result of the cellulose–SA/PPA/W system (polymer concentration is 18 wt%) for comparison. Here, 16 mixtures with different composition of SA/PPA/W, which did not give arise any decomposition of the polymer for 10 hours at least, were chosen as solvent of the samples. With the decrease of $\langle\langle F \rangle\rangle$, the region of optically anisotropic mesophase becomes narrower indicating that CA with higher $\langle\langle F \rangle\rangle$ readily tends to form liquid crystal in SA/PPA/W system. The solvent mixture with SA/PPA/W $(= 1/8/1, w/w/w)$ is a common solvent to form liquid crystal for cellulose and
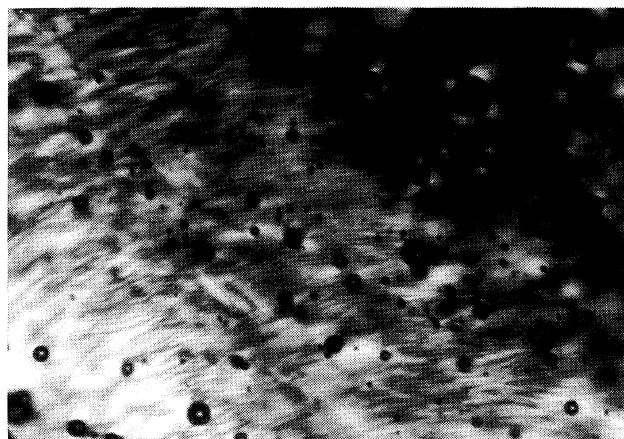
Table I. Total degree of substitution $\langle\langle F \rangle\rangle$ and the viscosity-average of molecular weight M_v of the samples

Sample No.	$\langle\langle F \rangle\rangle$	$M_v \times 10^{-4}$ (DP[a])
CA-0	0.00	5.4 (330)
CA-1	0.66	5.1 (300)
CA-2	0.90	4.8 (240)
CA-3	1.70	6.5 (350)
CA-4	1.75	4.5 (190)
CA-5	2.46	9.6 (360)
CA-6	2.89	23.0 (810)

[a] Degree of polymerization.

Figure 1. Polarized photomicrograph of mesophase of CA–SA/PPA/W system. $\langle\langle F \rangle\rangle = 2.89$, $C_p = 30\%$.

$\langle\langle F\rangle\rangle = 0$

$\langle\langle F\rangle\rangle = 0.9$

$\langle\langle F\rangle\rangle = 1.75$

$\langle\langle F\rangle\rangle = 2.46$
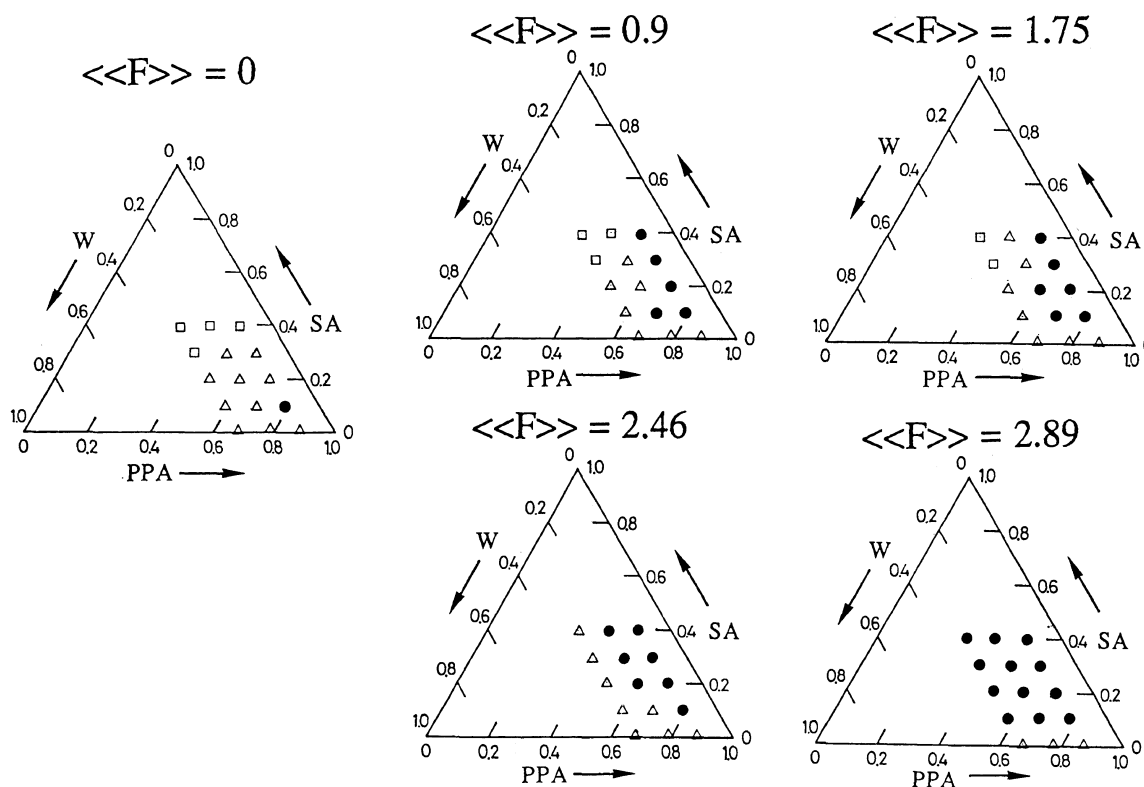
$\langle\langle F\rangle\rangle = 2.89$

Figure 2. Phase diagrams of CA–SA/PPA/W system. ●, optically anisotropic solution; △, flow orientation solution; □, optically isotropic solution.
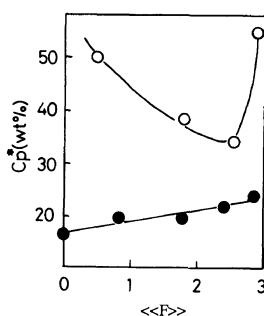
Figure 3. Lower critical concentration of mesophase solution of CA–SA/PPA/W system. ●, CA–SA/PPA/W system; ○, CA–aq nitric acid system.

CA with $\langle\langle F\rangle\rangle$ ranging from 0.9 to 2.9.

The lower critical concentration of the CA in the common solvent to form liquid crystal, $C_p{}^*$, is plotted against $\langle\langle F\rangle\rangle$ in Figure 3. In the figure the results of CA–aq nitric acid soln system[13] are also depicted for comparison. $C_p{}^*$ of the CA–SA/PPA/W system, which shows slight increase with $\langle\langle F\rangle\rangle$, is for lower than that of the CA–aq nitric acid system. The effect of the molecular weights of the CA samples must not be so serious because Patel and Gilbert have already reported[14] that the molecular weight of CTA does not affect the critical volume fraction for the A and B points in case of CTA/TFA liquid crystal system.

Based on the lattice model, Flory proposed[15] a theoretical relationship between the lower critical volume (v_2) of the polymer to generate anisotropic phase and an aspect ratio (x) of Kuhn statistical segment of the polymer;

$$v_2 = 8/x(1 - 2/x) \qquad (3)$$

Here, x is able to be calculated from a persistence length q and diameter d of the polymer chain. Kamide et al. reported[16] that the q of CA in DMAc, determined by light scattering method becomes maximum at $\langle\langle F\rangle\rangle = 2.5$ due to specific polymer–solvent interaction (solvation). From this fact, total degree of substitution dependence of $C_p{}^*$ of CA–aq nitric system was reasonably explained in terms of chain rigidity of CA. The quite different dependence of $C_p{}^*$ in SA/PPA/W system against $\langle\langle F\rangle\rangle$ and lower values of C_p of this system suggest that CA molecular chains are far rigid in the mixture than aq nitric acid soln due to strong interaction between CA chains and SA/PPA/W molecules. The chain rigidity in the mixture may monotonically decrease with an increase of $\langle\langle F\rangle\rangle$.

Figure 4 shows CD spectra of CA ($\langle\langle F\rangle\rangle = 0.9$)–SA/ PPA/W ($= 1/8/1$, w/w/w) with $C_p = 30\,\mathrm{wt}\%$ at 15°C. The t_{CD} for each spectrum means the time from set of the mesophase into the cell of CD apparatus to start of the CD measurement. The passage of the time brings about an increase of CD peak intensity and the shift of λ_0 to higher side, indicating that the cholesteric texture which is broken at the set of the sample is gradually rebuilt in the CD cell. Peak intensity and λ_0 does not change above $t_{CD} = 120\,\mathrm{min}$, suggesting that cholesteric structure attains to the equilibrium state.

Figure 5 depicts CD spectra of the CA ($\langle\langle F\rangle\rangle = 0.66$— 2.46) mesophase with $C_p = 30\,\mathrm{wt}\%$ at 0°C in the steady state. All of the mesophase show positive dichroism in the wavelength range observed, indicating that the CA with $\langle\langle F\rangle\rangle = 0.66$—2.46 forms left handed cholesteric liquid crystal. λ_0 of the CA with $\langle\langle F\rangle\rangle = 0.9$—1.75 increases monotonically with $\langle\langle F\rangle\rangle$. The CD peak of the CA with $\langle\langle F\rangle\rangle = 0$, 0.66, and 2.46, 2.89 was out of detec-
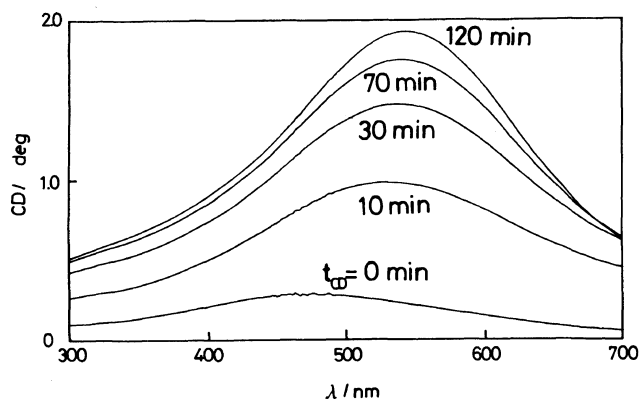
Figure 4. CD spectra of mesophase of CA–SA/PPA/W system. $\langle\!\langle F\rangle\!\rangle = 0.9$, $C_p = 30\,\text{wt}\%$; measurement temperature, 15°C.
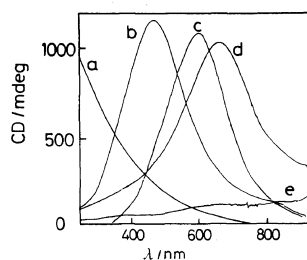
Figure 5. CD spectra of mesophase of CA–SA/PPA/W with various $\langle\!\langle F\rangle\!\rangle$ $C_p = 30\,\text{wt}\%$, measurement temperature, 0°C. a, $\langle\!\langle F\rangle\!\rangle = 0.66$; b, $\langle\!\langle F\rangle\!\rangle = 0.9$; c, $\langle\!\langle F\rangle\!\rangle$ 1.70; d, $\langle\!\langle F\rangle\!\rangle = 1.75$; e, $\langle\!\langle F\rangle\!\rangle = 2.46$.

Table II. Refractive index $\bar{n}$, peak wave length λ_0 in CD spectra and calculated pitch P for different CA samples in SA/PPA/W at 0°C

Sample No.	$\langle\!\langle F\rangle\!\rangle$	$\bar{n}$	λ_0/nm	P/nm
CA-0	0.00	—	—	67[a]
CA-1	0.66	—	—	158[a]
CA-2	0.90	1.438	455	316
CA-3	1.70	1.440	547	380
CA-4	1.75	1.444	650	450
CA-5	2.46	—	>800	>570
CA-6	2.89	—	>800	>570

[a] Estimated by the extrapolation method using the polymer concentration dependence of λ_0.

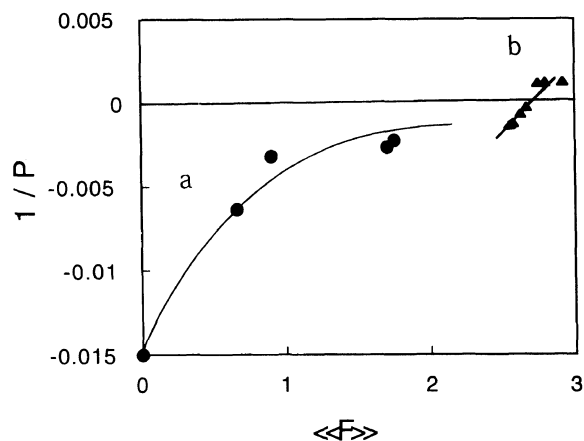**Figure 6.** Reciprocal plot of cholesteric pitch of mesophase on various system. a, SA/PPA/W system; b, AEC–chloroform system.

tion in the range of 250 nm $< \lambda_0 <$ 800 nm. In general the cholesteric liquid crystal with the pitch larger than a few micrometer shows finger print pattern in a visual field of polarizing microscope. Unfortunately, that kind of pattern was not clearly observed for these CA mesophases. As shown later (Figure 9), λ_0 of the CA mesophase increases with decreasing of the polymer concentration. Using the polymer concentration dependence of λ_0, the cholesteric pitch of CA with $\langle\!\langle F\rangle\!\rangle = 0$ and 0.66 at $C_p = 30\,\text{wt}\%$ was estimated by the extrapolation method.

Table II summarizes refractive index $\bar{n}$, λ_0, and the cholesteric pitch (P) calculated using eq 2 for each sample. $\bar{n}$ shows slight increase with $\langle\!\langle F\rangle\!\rangle$. P of the CA with $\langle\!\langle F\rangle\!\rangle$ more than 2.46 is expected larger than 570 nm because of λ_0 of these polymer higher than 800 nm. Evidently, P of cellulose and CA mesophases concomitantly increases with $\langle\!\langle F\rangle\!\rangle$, coinciding with the results of AEC–chloroform systems reported by Guo and Gray.[6]

Reciprocal P of CA–SA/PPA/W system is plotted against $\langle\!\langle F\rangle\!\rangle$ in Figure 6, where the pitch of left handed cholesteric texture is taken as negative for convenience. The line a) represents the relationship between $1/P$ and $\langle\!\langle F\rangle\!\rangle$ for the CA–SA/PPA/W system. In the figure line b) is the results of the AEC/chloroform system reported by Guo and Gray.[6] Here we took the sum of total degree of substitution of O-acetyl and O-ethyl groups as $\langle\!\langle F\rangle\!\rangle$ of AEC. $\langle\!\langle F\rangle\!\rangle$ dependence of reciprocal P of the two systems is in sharp contrast each other. The inversion of the helicoidal sense from left handed to right handed is observed in AEC–chloroform system at around $\langle\!\langle F\rangle\!\rangle = 2.7$. On the other hand, the solid line which shows the data of CA–SA/PPA/W system does

not seem to cross the transversal axis even if the line is extended to $\langle\!\langle F\rangle\!\rangle \fallingdotseq 2.9$. Guo and Gray suggested[6] that significant dependence of cholesteric pitch of AEC–chloroform system on minor changes in $\langle\!\langle F\rangle\!\rangle$ are originated to the properties of helical chain conformation of cellulose molecule in the solution, which controls the torsional power between neiboring cholesteric layers. We suggest that no observation of helicoidal sense inversion in CA–SA/PPA/W system may relate to the slight dependence of polymer–solvent interaction on $\langle\!\langle F\rangle\!\rangle$ as mentioned before, which affects the properties of helical conformation of cellulose molecule.

In Figure 7 CD spectra of CA–SA/PPA/W liquid crystal system at various temperatures are depicted. The peak wave length shifts to longer side with increasing temperature and this dependence of λ_0 is thermally reversible. Because $\bar{n}$ of the system was almost constant, this λ_0 dependence means that P increases with temperature. The temperature dependence of P is empirically described as a function of temperature T as follows[17]

$$1/P = a(1 - T/T_N) \tag{4}$$

Here, coefficient a is independent of temperature and T_N is temperature at which the pitch of the system becomes infinite, i.e., nematic liquid crystal. The plot of $1/P$ vs. T is shown in Figure 8. Almost all the data for each system obey the above relation. The slope, coefficient a and T_N obtained from the figure were summarized in Table III. T_N shows almost no $\langle\!\langle F\rangle\!\rangle$ dependence to be in the range of 342—380 K. On the other hand, the value of slope of each line is apparently smaller for larger $\langle\!\langle F\rangle\!\rangle$
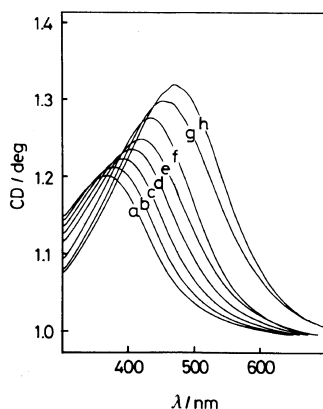
Figure 7. CD spectra of mesophase of CA–SA/PPA/W system measured at various temperature. $\langle\!\langle F \rangle\!\rangle = 0$; $C_p = 20\,\text{wt}\%$; a, 0°C; b, 4°C; c, 7°C; d, 10°C; e, 13°C; f, 15°C; g, 17°C; h, 20°C.
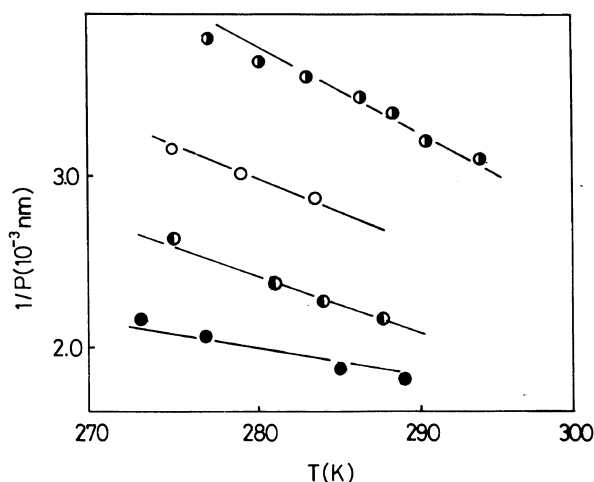

Figure 8. Reciprocal plot of cholesteric pitch of mesophase against temperature. ●, SA/PPA/W system ($\langle\!\langle F \rangle\!\rangle = 1.75$); ◐, SA/PPA/W system ($\langle\!\langle F \rangle\!\rangle = 0.90$); ○, SA/PPA/W system ($\langle\!\langle F \rangle\!\rangle = 0.66$); ◑, SA/PPA/W system ($\langle\!\langle F \rangle\!\rangle = 0.00$).

Table III. Slope and T_N in eq 4 for cellulose and celluloseacetate mesophase

Sample No.	$\langle\!\langle F \rangle\!\rangle$	Slope/$10^{-5}\,\text{nm}^{-1}\text{K}^{-1}$	T_N/K	$a/10^{-2}\,\text{nm}^{-1}$
CA-0	0.00	4.55	361	1.64
CA-1	0.66	4.44	342	1.70
CA-2	0.90	3.88	382	1.33
CA-3	1.75	2.04	376	0.77

indicating that temperature dependence of the pitch becomes smaller with $\langle\!\langle F \rangle\!\rangle$. Guo and Gray have already reported that temperature dependence of the cholesteric pitch is originated to the change of the twist angle between the cholesteric layers.[6] We suggest that the high steric hindrance of O-acetyl groups with high $\langle\!\langle F \rangle\!\rangle$ sample cause the insensitiveness of the twisting power between layers to temperature.

The pitch for the CA–SA/PPA/W system also depends on the polymer concentration C_p. For many lyotropic liquid crystal systems, it is well-known that C_p dependence of P at constant temperature can be represented as follows[18]

$$1/P = a'C_p{}^x + b \tag{5}$$
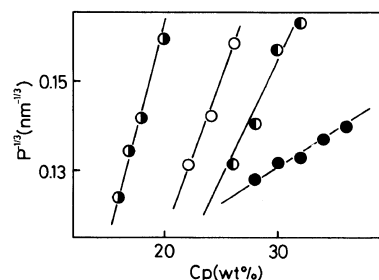
Here, coefficient a', exponent x, and constant b are

Figure 9. $(1/P)^{-1/3}$ plot of mesophase of CA–SA/PPA/W system against C_p. ●, $\langle\!\langle F \rangle\!\rangle = 1.75$; ◐, $\langle\!\langle F \rangle\!\rangle = 0.90$; ○, $\langle\!\langle F \rangle\!\rangle = 0.66$; ◑, $\langle\!\langle F \rangle\!\rangle = 0.00$; measurement temperature, 0°C.

independent of C_p. As shown in Figure 9, the exponent x of these systems is about 3, in good accord with the result for cellulose/liq NH_3/NH_4SCN.[18] The coefficient a' becomes smaller with larger $\langle\!\langle F \rangle\!\rangle$ for possibly same reason as the case of temperature dependence of P.

CONCLUSION

Cellulose and cellulose acetates (CA) with various $\langle\!\langle F \rangle\!\rangle$ (0.52—2.89) can form lyotropic liquid crystal in the mixture of sulfuric acid (SA), polyphosphoric acid (PPA), and water (W) with specific composition (SA/PPA/W = 1/8/1, w/w/w). Circular dichroism (CD) spectra of the cellulose acetate mesophase indicated that the texture is left handed cholesteric irrespective of $\langle\!\langle F \rangle\!\rangle$. The cholesteric pitch determined by the CD method remarkably depends on polymer concentration and temperature, and monotonically increases with an increase of $\langle\!\langle F \rangle\!\rangle$ at constant temperature and polymer concentration. $1/P$ almost depends linearly on temperature and the cube of the polymer concentration.

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