Determination of the Order Parameter in Cholesteric Liquid Crystalline Phase Cellulose Derivatives Solutions by Refractometry

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Synopsis

The macroscopic order parameter S in the cholesteric liquid crystalline phase of hydroxypropyl cellulose (HPC) and ethyl cellulose (EC) solutions was calculated using refractive index data. Haller's extrapolation approach was used. The S calculated was compared with the S predicted from Doi's theory. The calculated values of S for HPC and EC solutions were in the range of 0.4–0.8 within our experimental range, and agreed with the predicted values of S obtained with Doi's theory. This result suggests that Haller's approach is valid for determining S for liquid crystalline solutions of HPC and EC, despite the scattering of the data at higher temperatures.

INTRODUCTION

Polymeric liquid crystals are of considerable theoretical and practical interest,[1-4] because they are characterized by a high degree of molecular order. The degree of the order for nematic liquid crystals can be most simply described by the Maier-Saupe order parameter S[5]:

$$S = \tfrac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$$

where θ is the angle between an intrinsic molecular axis and a reference laboratory optic axis, and the brackets represent the ensemble average. Many researchers have investigated the S of nematic liquid crystals by means of NMR spectroscopy,[6] polarized IR spectroscopy,[7,8] X-ray measurements,[7] and refractometry.[9] However, there have been only a few studies on the order of cellulosic liquid crystals.

The extensive scientific and patent literature[10] indicates that many cellulose derivatives form lyotropic and thermotropic liquid crystals of the cholesteric type under suitable conditions, and that they exhibit anomalous optical and rheological properties. To understand those anomalies well, we are required to analyze the order of the molecules in the liquid crystalline phase.

Haller et al.[11] have proposed a technique to determine the macroscopic order parameter S for nematic liquid crystals from refractometry, and their approach has been successful in determining S for side-chain liquid crystalline polymers of the cholesteric type.[9,12]

Previously we tried to determine S of lyotropic cellulosic liquid crystals using both Haller's approach and another one and concluded that Haller's

TABLE I
Cellulose Derivative–Solvent Pairs and Concentration Range Investigated

Polymer	Solvent	Concentration range (wt %)
HPC	Acetic acid	30.0–60.0
	Water	35.0–60.0
	DMF	42.0–52.8
	DMSO	45.0–60.0
	DMAc	35.0–57.0
EC	m-Cresol	9.5–50.1
	Chloroform	27.2–40.0
	Acetic acid	20.4–61.1
	Benzyl alcohol	35.0–55.0
	Dioxane	35.0–55.0
	n-Butyl acetate	35.0–55.0

approach seemed to be preferable.[13] In this paper, the order parameter S in cholesteric phase of hydroxypropyl cellulose (HPC) and ethyl cellulose (EC) solutions were determined from refractometry, using Haller's approach. Our main object is to discuss the applicability of Haller's approach to the cellulosic liquid crystals: main-chain, semirigid liquid crystals. The experimental values of S are compared with predictions of Doi's theory.

EXPERIMENTAL

Samples

Commercial reagent grade hydroxypropyl cellulose (HPC) and ethyl cellulose (EC) were used as supplied from Tokyo Kasei Kogyo Co., Ltd. The weight-average molecular weight of the HPC was 9.3×10^4 and the number-average molecular weight of the EC was 1.8×10^4. The molar substitution of the HPC was 4.2 by the method of Ho et al.[14] Before use, HPC and EC powders were dried in vacuo at 60°C for about 24 h.

Reagent grade m-cresol, chloroform, benzyl alcohol, dioxane, acetic acid, dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), dimethylformamide (DMF), and distilled deionized water (hereafter water) were used. All solvents were obtained from Wako Pure Chemical Ind., Ltd., except for water which was prepared in our laboratory. The polymer–solvent pairs studied are summarized in Table I.

Concentrated solutions of the HPC and EC were prepared by mixing with a magnetic stirrer for about a week and were then stored in the dark for about 2 or 3 months at room temperature. HPC/water and EC/chloroform systems were prepared in a refrigerator. The concentration ranges for each system are also shown in Table I.

The critical concentration C_a at which the liquid crystalline phase first forms has been determined for many HPC and EC systems at given temperatures from both refractometry[13] and viscometry (shear rate of 1 s^{-1}).[15] There was a minor difference between the C_a's from refractometry and viscometry. Here we adopted the C_a from viscometry shown in Table II. No liquid

TABLE II
Critical Concentration C_a, Birefringence Δn, and Order Parameter S
for Each System

System	C_a^{a} (wt %)	$\Delta n^{b} \times 10^{3}$	S^{c}
HPC/acetic acid	32.5	−3.4	0.76
HPC/water	43.3	−4.5	0.56
HPC/DMF	46.5	−2.0	0.72
HPC/DMSO	47.2	−2.5	0.82
HPC/DMAc	47.5	−2.9	0.56
EC/m-cresol	32.0	−3.8	0.75
EC/chloroform	33.0	−7.5	0.52
EC/acetic acid	45.5	−4.1	0.69
EC/benzyl alcohol	46.5	−2.9	0.71
EC/dioxane	$50 < C_a < 55$	−1.5	0.77

[a] Determined from viscometry at 25°C.
[b] Value at $T^* = 0.9$.
[c] Value at $T^* = 0.85$.

crystalline phase formed for EC/n-butylacetate system in our experimental conditions.

Refractometry

An Abbe refractometer (Shimazu Seisakusho Ltd.) with a rotatable polarizer mounted on the eyepiece was used for measuring the two principal refractive indices. Before measurements, the prism surfaces were carefully rubbed in the longitudinal direction of the prism with cotton soaked in acetone. With this rubbing, macroscopic alignment of the sample molecules was achieved; therefore, the clear birefringence was found. The birefringence Δn was defined as the difference between extraordinary refractive index n_e and ordinary refractive index n_o,

$$\Delta n = n_e - n_o$$

The refractive indices needed about 5–10 min to come to equilibrium for lower concentrations (isotropic phase) but about 30–60 min for higher concentrations (anisotropic phase). Attention should be called to the following fact: In this study the sample solution was renewed at each temperature to minimize the effect of thermal history on the refractive indices, but when the same sample solution was used throughout measurement at each temperature, the refractive data were greatly different from those in this study.

A more detailed description of the refractometry is given elsewhere.[16]

Determination of S

S was determined by using Haller's extrapolation method.[11] This method has been successfully applied to nematic liquid crystals of low molecular weight.[17,18] Finkelmann et al.[19] showed that the method was applicable to the cholesteric phase of side-chain type polymers. Here, we describe only the main points of the method.

Haller et al.[11] related S to the refractive indices and showed the following relation:

$$\frac{S \Delta \alpha}{\bar{\alpha}} = \frac{n_{e,n}^2 - n_{o,n}^2}{\bar{n}^2 - 1} \tag{1}$$

where $\Delta \alpha = \alpha_{\parallel} - \alpha_{\perp}$, $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the molecular polarizabilities parallel and perpendicular to the long molecular axis, $\bar{\alpha} = \frac{1}{3}(\alpha_{e,n} + 2\alpha_{o,n})$; $\alpha_{e,n}$ and $\alpha_{o,n}$ are the polarizabilities of nematic phase parallel and perpendicular to the director, and $\bar{n}^2 = \frac{1}{3}(n_{e,n}^2 + 2n_{o,n}^2)$; $n_{e,n}$ and $n_{o,n}$ are the extraordinary and ordinary refractive indices of the nematic liquid crystal.

S was related to temperature in the relatively lower temperature regions;

$$S = (1 - T^*)^B \tag{2}$$

where $T^* = T/T_c$ and T and T_c are the measuring and critical temperature. At T_c the transformation from an anisotropic to an isotropic phase occurs. B is a constant.

From eqs. (1) and (2), one obtains the following expression:

$$\log \frac{n_{e,n}^2 - n_{o,n}^2}{\bar{n}^2 - 1} = \log \frac{\Delta \alpha}{\bar{\alpha}} + B \log(1 - T^*) \tag{3}$$

Hence, a straight line results when the left side of eq. (3) is plotted vs. $\log(1 - T^*)$, and, by extrapolation to zero, K, $\log(\Delta \alpha / \bar{\alpha})$ is obtained from the intercept. Then S can be determined by eq. (1). However, the method described above was for nematic liquid crystals. For cholesteric liquid crystals, we need the following conversion step. The measured cholesteric refractive indices n (index ch = cholesteric) are correlated to the nematic ones by Muller and Stegemeyer[20]:

$$n_{o,n} = n_{e,\text{ch}} \tag{4}$$

$$n_{e,n} = \left(2n_{o,\text{ch}}^2 - n_{e,\text{ch}}^2\right)^{1/2} \tag{5}$$

By means of eqs. (4) and (5), the measured cholesteric refractive indices are converted to the corresponding nematic refractive indices.

RESULTS AND DISCUSSION

Birefringence Δn_{ch}

Our systems formed cholesteric liquid crystals, except for the EC/n-buty-lacetate system. That was confirmed by the fact that the liquid crystalline solutions had irridescence in white light. For determination of S, first we need the birefringence data: ordinary and extraordinary refractive indices at given temperatures for the liquid crystalline phase. All systems in this study had
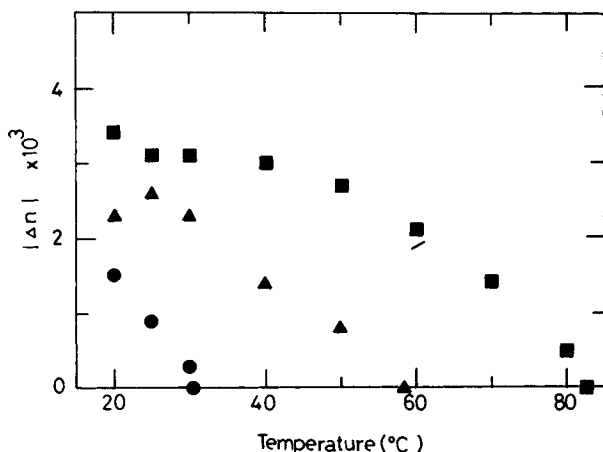
Fig. 1(A).   Temperature dependence of birefringence for HPC/DMSO system; concentration (wt %): (●) 50; (▲) 55; (■) 60 wt %.
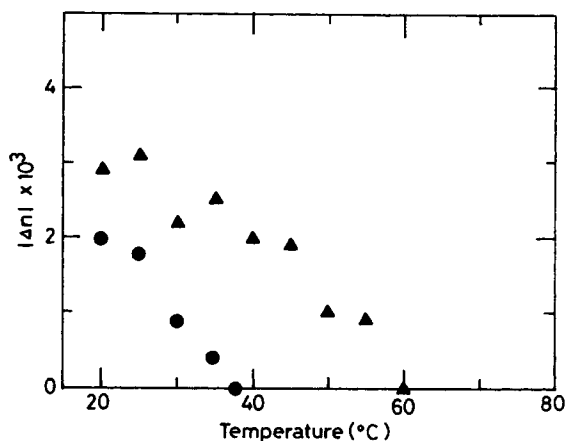

Fig. 1(B).   Temperature dependence of birefringence for EC/benzyl alcohol system; concentration: (●) 50; (▲) 55 wt %.

negative birefringence; the ordinary refractive index n_o was larger than the extraordinary one n_e.

The absolute values of the Δn_{ch} for HPC solutions in DMSO and for EC solutions in benzyl alcohol are shown as a function of temperature in Figures 1. The absolute values of the Δn_{ch} (hereafter we omit the absolute value and refer simply to Δn_{ch}) decreased with increasing temperature and finally became zero at a critical temperature T_c, which was dependent on the polymer concentration and increased with increasing concentration. The Δn_{ch} of the higher concentration was larger than that of the lower concentration at a given temperature. The behavior of the Δn_{ch} was shown for the other systems in this study and was similar to that for the other liquid crystals.[21] The order of the Δn_{ch} for our systems was similar to that of the other cellulosic liquid crystals[22-24] and polybenzylglutamate,[21,25] but was smaller than that of
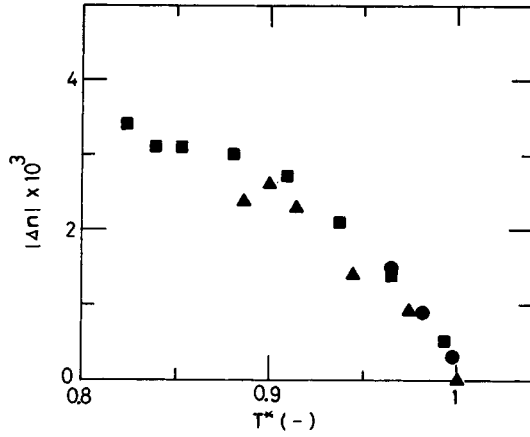
Fig. 2(A). Birefringence as a function of reduced temperature for HPC/DMSO system; concentrations as in Figure 1(A).
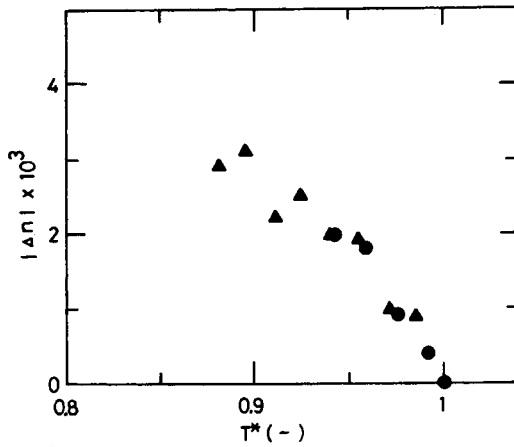

Fig. 2(B). Birefringence as a function of reduced temperature for EC/benzyl alcohol system; concentrations as in Figure 1(B).
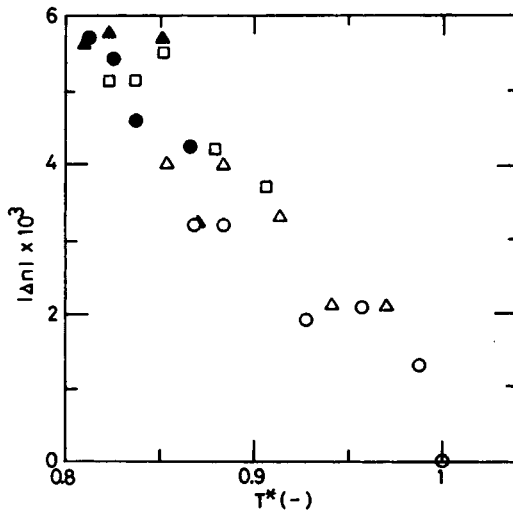

Fig. 2(C). Birefringence vs. reduced temperature for HPC/acetic acid system at different concentrations (wt %): (○) 35; (△) 38; (□) 45; (●) 50; (▲) 60.
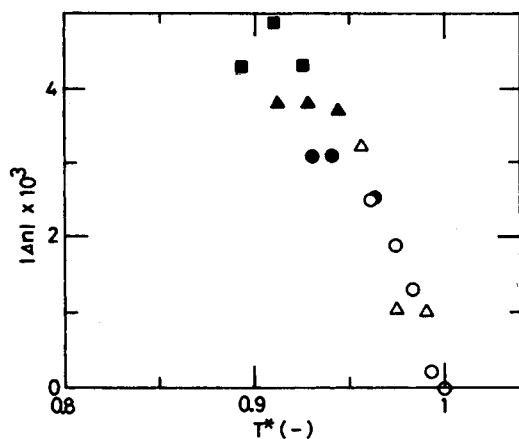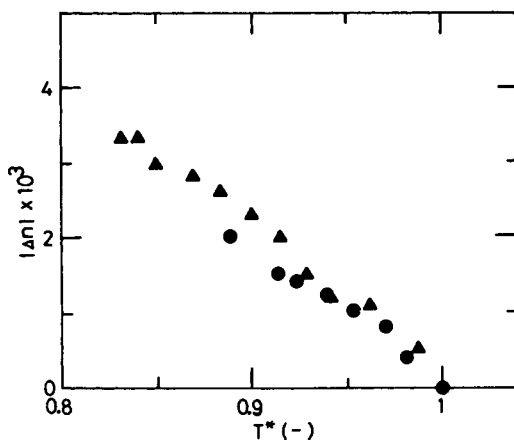
Fig. 2(D).   Birefringence vs. reduced temperature for HPC/water system at different concentrations (wt %): (O) 40; (△) 45; (●) 50; (▲) 55; (■) 60.

Fig. 2(E).   Birefringence vs. reduced temperature for HPC/DMF system at different concentrations (wt %): (●) 50; (▲) 52.8.
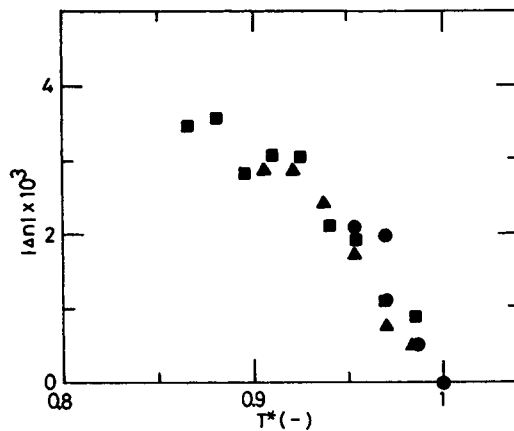

Fig. 2(F).   Birefringence vs. reduced temperature for HPC/DMAc system at different concentrations (wt %): (●) 50; (▲) 55; (■) 57.
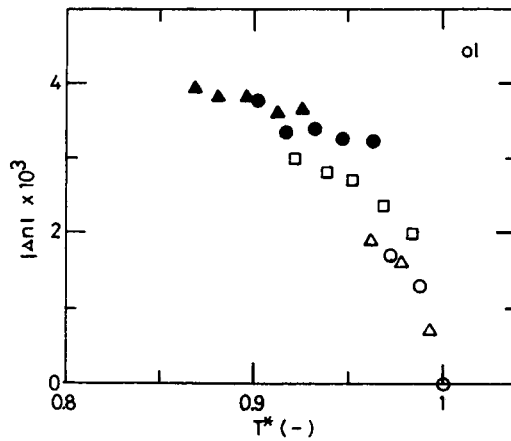
Fig. 2(G). Birefringence vs. reduced temperature for EC/m-cresol system at different concentrations (wt %): (○) 35; (△) 36.4; (□) 41.7; (●) 44.8; (▲) 50.1.

nematic liquid crystals. Generally, the following relation is given[24]:

$$\Delta n_n = -2\,\Delta n_{ch}$$

Therefore, our results for Δn_{ch} is typical of cholesteric liquid crystals.

We have reported in a previous paper[26] that Δn_{ch} for each concentration could be generalized by a master curve when Δn_{ch} was plotted against the reduced temperature. Then, the data in Figures 1 are plotted in Figures 2,
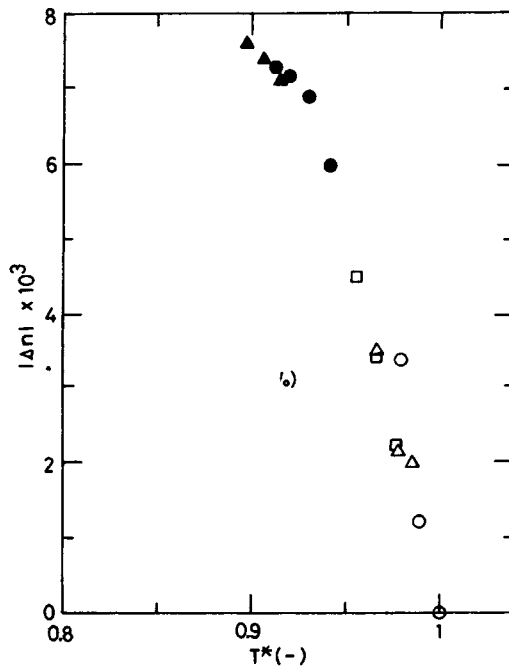

Fig. 2(H). Birefringence vs. reduced temperature for EC/chloroform system at different concentrations (wt %): (○) 27.2; (△) 30.1; (□) 33.2; (●) 35.3; (▲) 40.
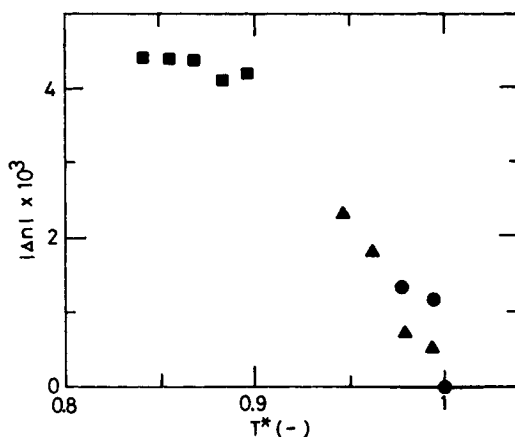
Fig. 2(I).   Birefringence vs. reduced temperature for EC/acetic acid system at different concentrations (wt %): (●) 47.2; (▲) 49.9; (■) 61.1.
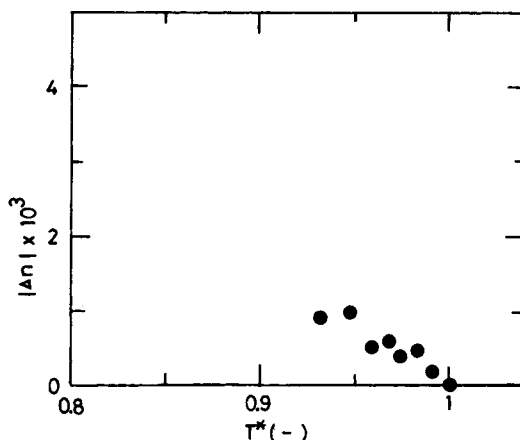

Fig. 2(J).   Birefringence vs. reduced temperature for EC/dioxane at 55 wt % concentration.

with the Δn_{ch} as the ordinate and reduced temperature T^* as the abscissa; $T^* = T/T_c$. From those figures it is evident that the concentration dependence of Δn_{ch} is relatively simple and Δn_{ch} plotted against T^* is independent of concentration. This generalization could be valid for all systems in this study.

Another feature of Figures 2 is that the Δn_{ch} is greatly dependent on solvents.[25] Chloroform resulted in larger Δn_{ch} than the others for EC systems and water and acetic acid did for HPC systems. It is well known that the critical concentration C_a depends greatly on solvent,[10] and that the solvent dependence of the C_a can be explained in terms of the axial ratio of a polymer molecule[27,28]; the axial ratio varies with the different extent of polymer–solvent interaction. We attempted to compare the C_a with the Δn_{ch} at $T^* = 0.9$ for each solvent system, but no relation between them could be found, as shown in Table II. The Δn_{ch} at $T^* = 0.9$ was not a suitable parameter for the comparison, because the parameter was not the equilibrium
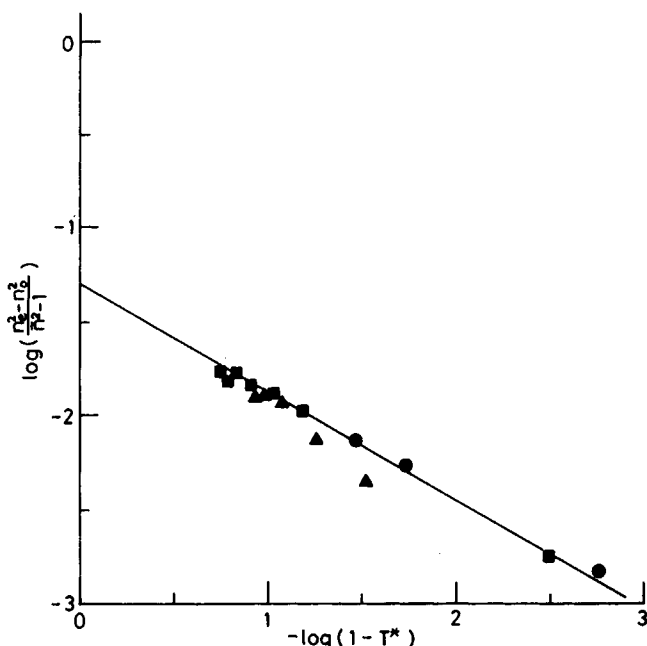
Fig. 3(A).   Haller plot for HPC/DMSO system; concentrations as in Figure 1(A).

one, and the increment of the Δn_{ch} with decreasing temperature was greatly different from solvent to solvent. The solvent effect will be discussed again in the order parameter section below.

Order Parameter S

Typical examples for the so-called Haller's plots are shown in Figures 3. Data for three concentrations were plotted for the HPC/DMSO system, and the data for two concentrations were done for EC/benzyl alcohol system. For two systems the linear line (least squares fit) were yielded as expected from eq. (3) despite the data showed some scatter at higher temperatures. This scattering of the data seems to be typical for Haller's method.[17] To eliminate this implicit problem, another reduced temperature was empirically used[12]: $T^{*\prime} = T/T'$, where T' is chosen as an empirical parameter to obtain the linear Haller's plots at higher temperatures; generally T' is larger than T_c by ca. 5°C. However, such an alternative approach was not considered here, because there were not such large differences between the values extrapolated to zero using two approaches. For the other systems which were not shown here, there was good agreement with eq. (3). The value extrapolated to zero and the slope of the linear plots [B of eq. (3)] greatly depend on the solvents.

Finkelmann et al.[19] have revealed that below the glass transition temperature T_g the macroscopic texture freezes in and no longer changes with temperature: A bend in the linear curve of Haller's plots occurs at T_g. However, the clear bend did not occur for our systems. The T_g's for HPC film and for EC film used were determined by refractive index of variation with temperature and found to be ca. 30°C for HPC[29] and ca. 40°C for EC. The
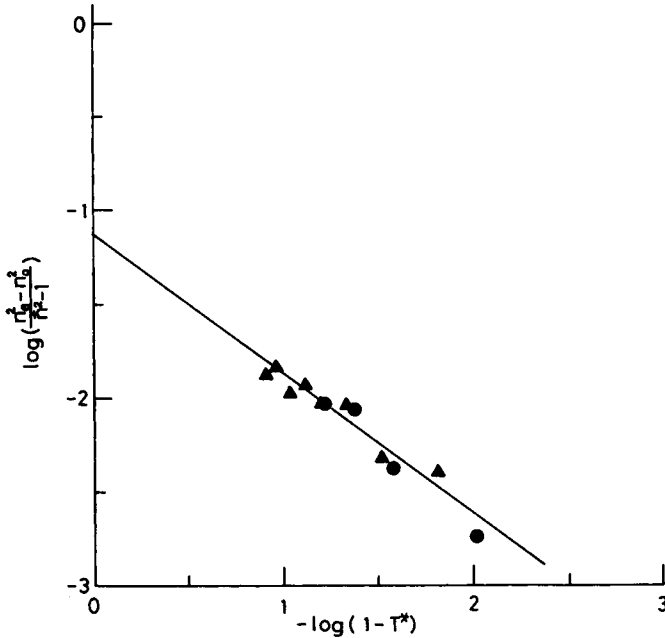
Fig. 3(B).   Haller plot for EC/benzyl alcohol system; concentrations as in Figure 1(B).

value of T_g for EC film used is quite smaller than that reported by Chen et al.,[30] 123°C. No significant transition was observed from DSC thermogram between 110 and 150°C, at least for the sample examined. Then, we predicted the T_g of ca. 40°C for EC film used. T_g of the solutions should be smaller than that of bulk samples. Consequently, it appears that all the measurements in this study were made at temperatures above the T_g of the HPC and EC solutions.

Figures 4 show the macroscopic order parameter S estimated using Haller's method as a function of reduced temperature T^* for each system. S at a given
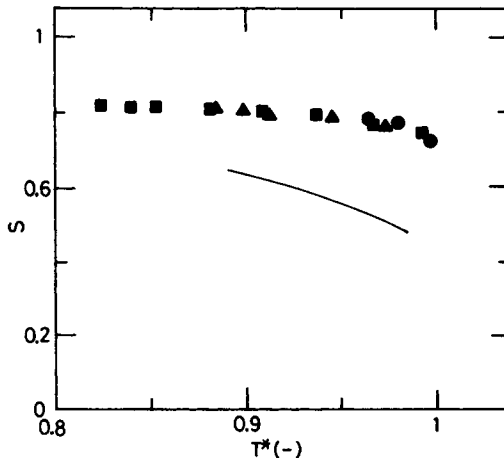

Fig. 4(A).   Order parameter S vs. reduced temperature for HPC/DMSO system; concentrations as in Figure 1(A): (—) theoretical prediction by Doi theory [eq. (6)].
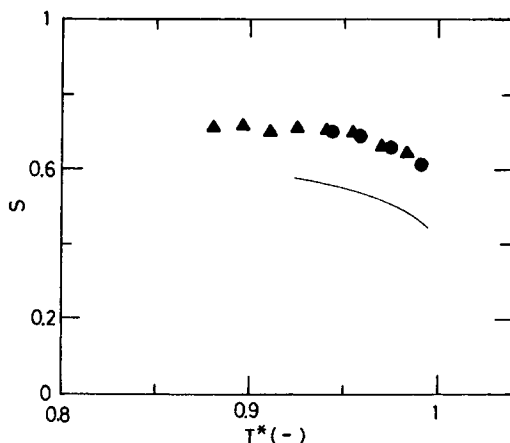
Fig. 4(B). Order parameter S vs. reduced temperature for EC/benzyl alcohol system; concentrations as in Figure 1(B): (—) theoretical prediction by Doi theory [eq. (6)].
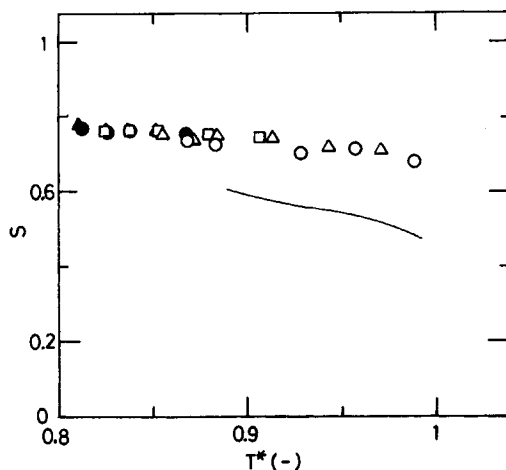

Fig. 4(C). order parameter S vs. reduced temperature for HPC/acetic acid system; concentrations as in Figure 2(C): (—) theoretical prediction by Doi theory [eq. (6)].

temperature T increased with polymer concentration; however, S was independent of polymer concentration when plotted against T^*, and first increased rapidly, then increased slightly, and finally became to be constant with decreasing temperature. S is strongly influenced by varying the nature of the solvent for a given polymer. The values of the S at $T^* = 0.85$ (almost constant) for HPC systems ranged from 0.56 for water and DMAc, through 0.72 for DMF, 0.76 for acetic acid, and 0.82 for DMSO. For EC systems, S ranged from 0.52 for chloroform, through 0.69 for acetic acid, 0.71 for benzyl alcohol, 0.75 for m-cresol, and 0.77 for dioxane. We attempted to find a correlation between the values of the S and C_a for HPC and EC systems, but failed as noted previously. This result suggests that the effect of solvent, hence, to a different extent of the polymer–solvent interaction, on the phase
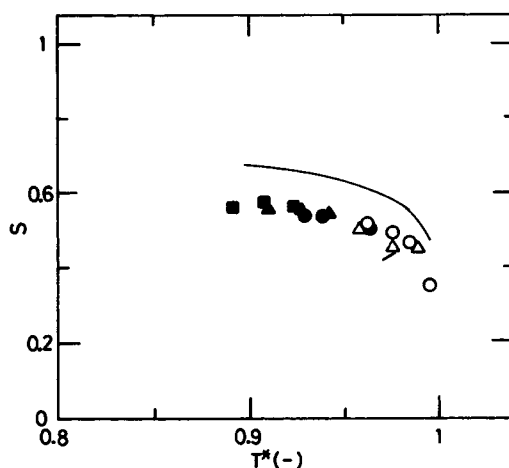
Fig. 4(D).   Order parameter S vs. reduced temperature for HPC/water system; concentrations as in Figure 2(D): (—) theoretical prediction by Doi theory [eq. (6)].
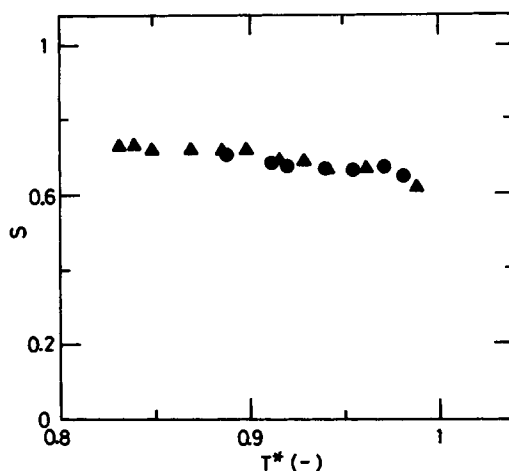

Fig. 4(E).   Order parameter S vs. reduced temperature for HPC/DMF system; concentrations as in Figure 2(E).

transition differs from that on the ordering of molecules in the liquid crystalline state.

Some order parameter for semirigid polyesters (nematic liquid crystals) have been reported and the values of the S varied from ca. 0.3 to 0.75.[31] However, unfortunately, there were very few data on S for cellulosic liquid crystals. Dayan et al.[32] showed the very low value of S for cellulose acetate solutions in trifluoroacetic acid and noted that was due to the semirigidity of the polymer. Our finding in this study is quite different from that by Dayan et al. and is quite similar to that reported for the semirigid nematic polyesters[31] in spite of the different type of liquid crystals. The serious discrepancy of S between Dayan et al. and us may be due to the effects of thermal history and rubbing prisms. As noted in the Experimental section, when the sample
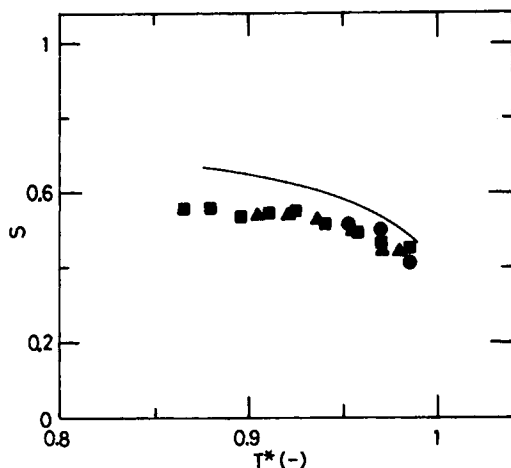
Fig. 4(F).   Order parameter S vs. reduced temperature for HPC/DMAc system; concentrations as in Figure 2(F): (—) theoretical prediction by Doi theory [eq. (6)].
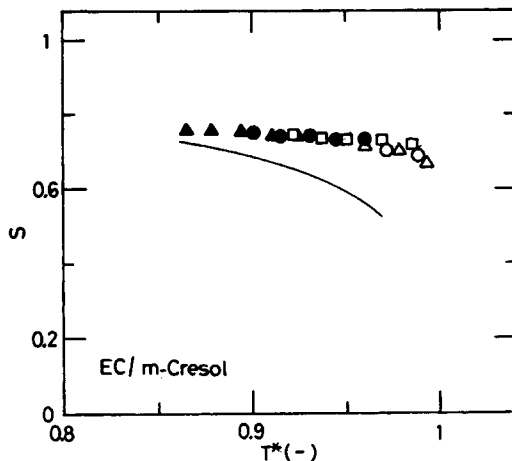

Fig. 4(G).   Order parameter S vs. reduced temperature for EC/m-cresol system; concentrations as in Figure 2(G).

solution was used throughout measurement from low to high temperature, Haller's plots were quite different from those shown in Figures 3; the values extrapolated to zero and the slopes of the plots were smaller than those in this study. Consequently, S was quite small and was found to be the order of 10^{-2}–10^{-3}, the same order as that reported by Dayan et al.[32] Therefore, for the determination of S from refractometry, we need to (1) rub carefully the prisms and (2) renew the sample solutions at each temperature.

Next we compare our data with theoretical ones as Cifferi et al.[8] did. They analyzed Flory's theory[33] and Doi's theory[34] and found the values using Flory's theory were always much larger than experimental ones. Therefore, the theoretical S was predicted only by Doi's theory in this study. According
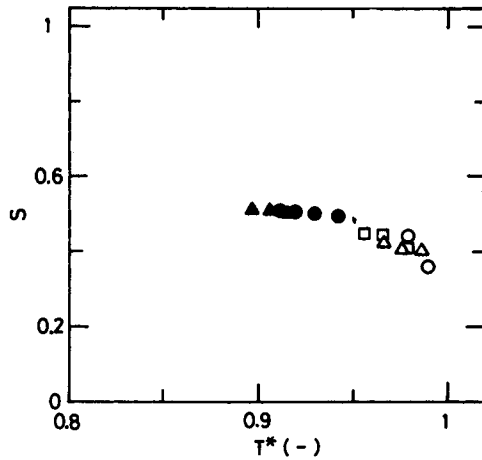
Fig. 4(H).   Order parameter S vs. reduced temperature for EC/chloroform system; concentrations as in Figure 2(H).
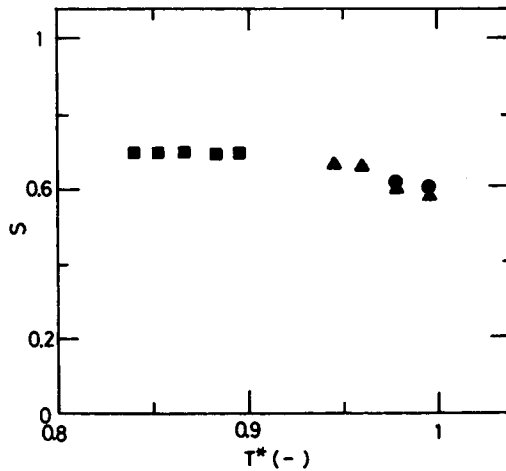

Fig. 4(I).   Order parameter S vs. reduced temperature for EC/acetic acid system; concentrations as in Figure 2(I).

to Doi's theory, the S for solutions of rigid rodlike polymer is given by[34]

$$S = 0, \qquad\qquad V < V^*$$

$$= \frac{1}{4} + \frac{3}{4}\left(1 - \frac{8V^*}{9V}\right), \quad V > \frac{8}{9}V^* \qquad (6)$$

where V is volume fraction of polymer concentration and V^* is that of critical polymer concentration. V^* was calculated from the corresponding C_a by using the densities of the HPC and EC films and solvents and assuming additivity:
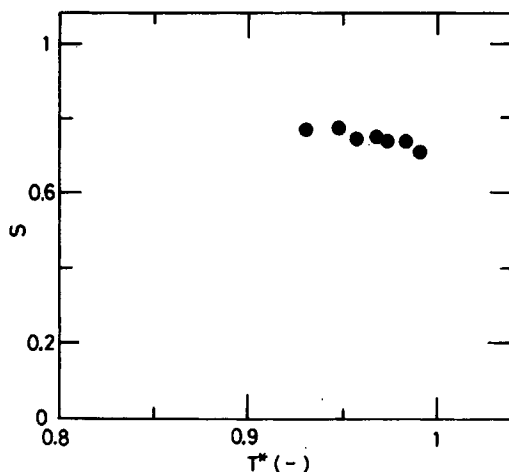
$$d(T) = d_1 w_1 + d_2(T)w_2$$

Fig. 4(J). Order parameter S vs. reduced temperature for EC/dioxane at 55 wt % concentration.

where d_1 and d_2 are densities of film and solvent, respectively, and w_1 and w_2 are weight fractions of film and solvent. The densities of solvents were measured with Anton Parr Digital Density Meter (DMA 40 type) at given temperatures, and the density of EC film was measured pycnometrically at 25°C and found to be 1.11 g/cm^3. The density of the HPC film used was the literature value, 1.17 g/cm^3.[35] We also assumed that the densities of the films were independent of temperature. In a strict sense, the assumption was unreasonable, but the temperature dependence of the density of solid film should be negligibly small for comparison with that of the density of solvent.

Theoretical values of S for each system were presented by a solid line in Figures 4. S for the EC/dioxane system could not be estimated because only one concentration prepared had exhibited the birefringence and could not show the phase diagram. From Figures 4, it was apparent that the experimental values of S were larger than theoretical ones of S except for HPC/DMAc and HPC/water systems. However, the difference between them was not so serious as was expected, and the temperature dependence of theoretical S was in line with that of the experimental one. Then, we feel that our data of the S for cellulosic liquid crystals were quantitatively reasonable. Consequently, the use of Haller's method seems to be valid for determining S of the liquid crystalline solutions of HPC and EC.

Another approach for estimating S is that the use of shear viscosity data at low shear rates: Doi's theory for shear viscosity gives following equation[34]:

$$\frac{\eta}{\eta^*} = \left(\frac{V}{V^*}\right)^3 \frac{(1-S)^4(1+S)^2(1+2S)\left[1+\left(\frac{3}{2}\right)S\right]}{(1+S/2)^2} \tag{7}$$

where η^* is the maximum viscosity at the critical concentration V^*, and η is shear viscosity at concentration V. Navard and Haudin[36] recently applied this

approach to estimating S for the HPC/acetic acid system (cholesteric liquid crystal) and noted very low S, less than 0.3. However, Doi's theory seems to be not applicable to the viscometric behavior for the singlely anisotropic solutions.[37] Therefore, the estimated value of S from eq. (7) may not be adequate.

In a strict sense, it is not ascertained whether eq. (6) can be applicable to our semirigid polymer systems at rest state or not, because Doi's theory is for rigid rodlike polymer at a very low shear rate. However, Doi's theory [eq. (6)] is fruitful for quantitatively estimating S of cellulosic liquid crystalline solutions.

CONCLUSIONS

The experimental values of S for liquid crystalline solutions of HPC and EC lay in the range of 0.4–0.8 and showed quantitatively good agreement with the theoretical ones estimated from Doi's theory. This result suggests that Haller's approach is applicable to the determination of S for cellulosic liquid crystals.

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