NOTE

Effect of Molecular Weight on the Birefringence of Lyotropic Liquid Crystalline Ethyl Cellulose and Hydroxypropyl Cellulose

INTRODUCTION

Recently, refractometry of the lyotropic liquid crystalline solution ((LCS) of cellulose derivatives has been reported by many investigators.[1-9] Determination of the birefringence for the LCSs with an Abbe refractometer is useful to estimate the order parameter S for those LCSs.[2,9] Refractometry seems to yield satisfactory results of S. However, this is an approximate method because the birefringence for the perfectly ordered sample is unknown.[2,7] Very recently, Siekmeyer and Zugenmaier[10] showed that S determined with refractometer was independent of molecular weight (MW) for the liquid crystalline cellulose tricarbanilate/diethylene glycol monoethyl ester system. However, the birefringence data for cellulosic liquid crystals, which were basically needed for estimating S, are still insufficient to establish the MW dependence of S.

In this note, the birefringence of four kinds of ethyl cellulose (EC) and of hydroxypropyl cellulose (HPC) concentrated solutions was determined by means of an Abbe refractometer and the MW dependence of the birefringence was discussed.

EXPERIMENTAL

Samples

Commercial reagent grade four different ECs and HPCs (Tokyo Kasei Kogyo Co. Ltd.) were used without further purification. EC and HPC powders were dried *in vacuo* at 60°C for about 24 h before use. The MW and distribution of MW (DMW) are summarized in Table I. Those data were determined in THF at 25°C by GPC. The molecular weight vs. elution volume curve prepared with standard polystyrene samples was used without correction. The following is worthy of note: DMW for EC-A or HPC-D is different from that for the others. Commercial reagent grade dimethylacetamide (DMAc) and *m*-cresol (Wako Pure Chemical) were purified by distillation at reduced pressure prior to use.

Preparation of Concentrated Solution

Approximately 50 g of EC or HPC were mixed with given amounts of *m*-cresol or DMAc in a glass-stoppered flask. The concentrations of EC/*m*-cresol system were 33 and 40 wt % and those of HPC/DMAc system were 45, 50, and 55 wt %. The mixtures were stored in the dark at room temperature for about 3–6 months which were dependent on the concentration and MW of polymers.

Refractometry

An Abbe refractometer (Shimazu Seisakusho Ltd., Bausch & Lomb 3L type) with a rotatable polarizer mounted on the eyepiece was used for determining two principal refractive indices: extraordinary refractive index n_e and ordinary refractive index n_0. The birefringence Δn was defined as the difference between n_e and n_0. The sample solutions relatively low MW could be spread out over the measuring prism with ease; however, the sample solutions of relatively high MW (especially, in the case of the HPC-D system) could not be done with ease and were allowed to equilibrate for about 2 h because of those high viscosities. As the equilibrium refractive indices, the measured values were independent of the direction of wiping the prism surfaces and of the shear effect.[2,6] The sample solution was renewed at each temperature to minimize the effect of thermal history on the refractive indices. A more detailed description of the refractometry is given elsewhere.[6,8]

TABLE I
Molecular Weights for EC and HPC

	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
EC-A	115,000	27,100	4.25
EC-B	123,000	37,800	3.26
EC-C	137,000	43,100	3.17
EC-D	187,000	58,600	3.12
HPC-A	112,000	52,900	2.12
HPC-B	192,600	89,600	2.14
HPC-C	812,000	327,200	2.48
HPC-D	1195,000	268,000	4.45

RESULTS AND DISCUSSION

EC / m-Cresol System

Figure 1 shows typical temperature dependence of two principal refractive indices for 40 wt % solution of EC-D in m-cresol. At relatively low temperatures, the difference between n_e and n_0 was distinct and was almost constant; n_e was greater than n_0 and the birefringence Δn was negative. The absolute values of Δn will be shown in the following figures. Hereinafter, we omit the absolute value and refer simply to Δn. Above a critical temperature, Δn began to decrease gradually and finally disappeared. The critical temperature at which Δn begins to decrease or disappears is T_c' (isotropization begins) or T_c (clearing temperature; isotropization finishes). In our experimental range, T_c' for the EC/m-cresol system could not be determined clearly.

Figures 2(a) and 2(b) show the temperature dependence of Δn for 33 wt % solutions of EC-B, EC-C, and EC-D, and for 40 wt % solutions of EC-A, EC-C, and EC-D, respectively. Δn decreased with temperature for each solution. At a given temperature, Δn increased with $\overline{M}_w$. In the same figures, Δn (full mark) was plotted as a function of reduced temperature T^* ($= T/T_c$). The rate of increase in Δn with decreasing T^* became greater as $\overline{M}_w$ increased and this was more pronounced as the concentration of the solution was higher. At a constant T^* for each solution, Δn increased with $\overline{M}_w$ as shown in Figure 3. There appeared to be a critical MW (ca. 16×10^4), above which Δn for 33 wt % solution tended to reach a constant value. This behavior was similar
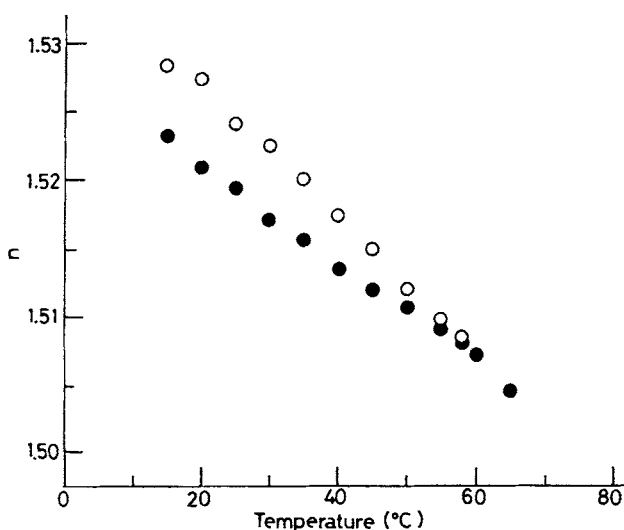

Fig. 1. Temperature dependence of refractive indices for 40 wt % solution of EC-D in m-cresol: (○) extraordinary refractive index; (●) ordinary refractive index.
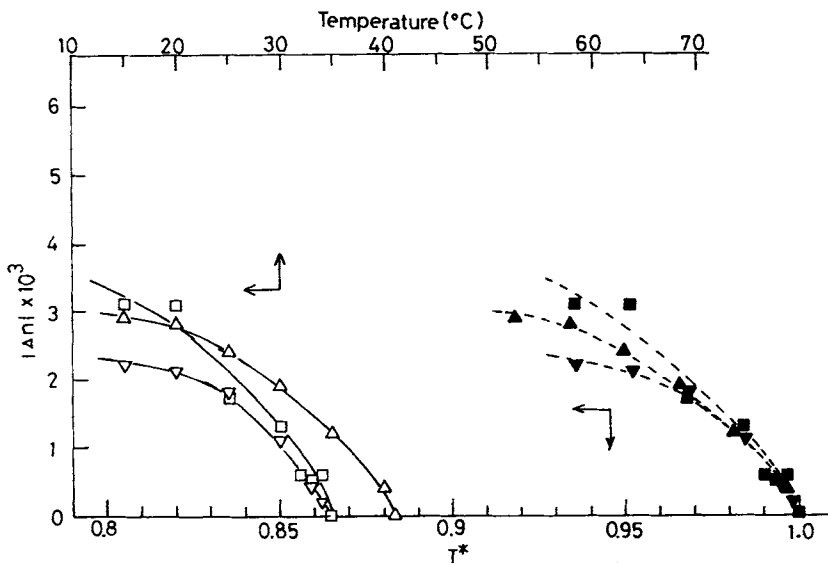
Fig. 2(a). Temperature dependence of birefringence for 33 wt % solution of each EC in
m-cresol: (▽,▼) EC-B; (△,▲) EC-C; (□,■) EC-D.

to the dependence of T_c on MW of cellulose derivatives.[10-13] Furthermore, an isotropization
temperature determined by viscometry exhibited a similar behavior with T_c as did Δn.[14] The
critical MW for the 40 wt % solutions seemed to be greater than that for 33 wt %.

HPC / DMAc System

Figures 4(a), 4(b), and 4(c) show the dependence of Δn on T^* for 45, 50, and 55 wt % solutions
of HPC in DMAc for each MW. Δn decreased with T^* and the rate of increase in Δn with

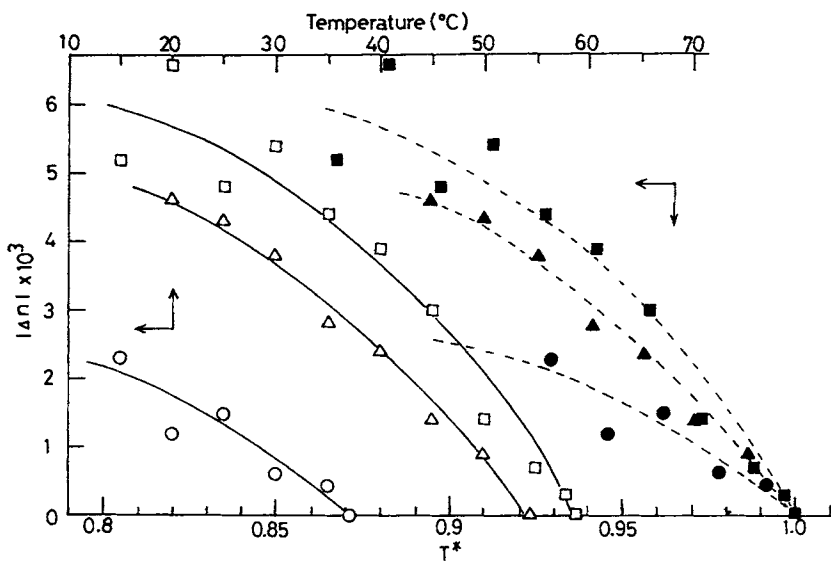

Fig. 2(b). Temperature dependence of birefringence for 40 wt % solution of each EC in
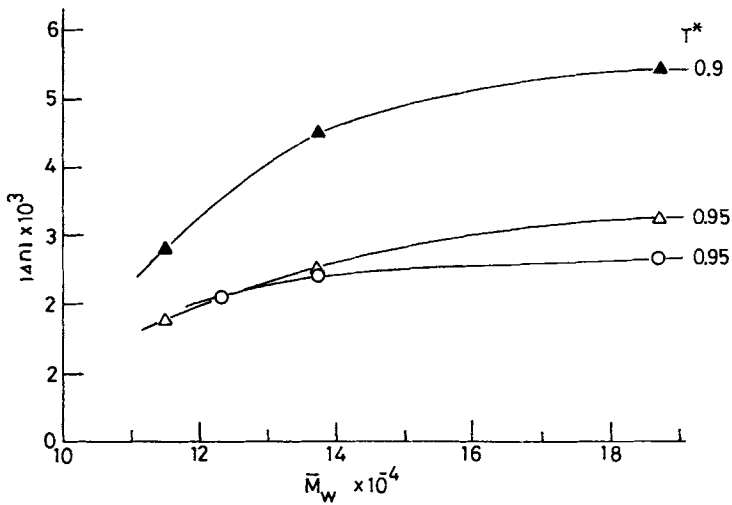m-cresol: (○,●) EC-A; (△,▲) EC-C; (□,■) EC-D.

Fig. 3.   Molecular weight dependence of birefringence at given temperature for EC solution in m-cresol. Concentration: (O) 33 wt %; (△, ▲) 40 wt %.

decreasing T^* was greater as MW of HPC increased. Figures 4(b) and 4(c) clearly show that below a critical T^*, Δn is almost constant. The constant value of Δn (here defined as Δn_{equil}) was dependent on MW of HPC; Δn_{equil} increased as MW increased. Not only T_c but also T_c' could be determined for HPC-C and HPC-D. Figure 5 shows the MW dependence of Δn at $T^* = 0.95$. Δn increased with MW and tended to attain a constant value. Strictly speaking, Δn for 55 wt % solution continued to increase. Seurin et al.[15] have reported that the isotropization temperature for bulk HPC did not tend to an asymtotic value and continued to increase with MW up to 100×10^4. Thus, there is generally a critical MW above which Δn does not depend on MW for a given concentration of polymer. This critical MW increases with polymer concentration.
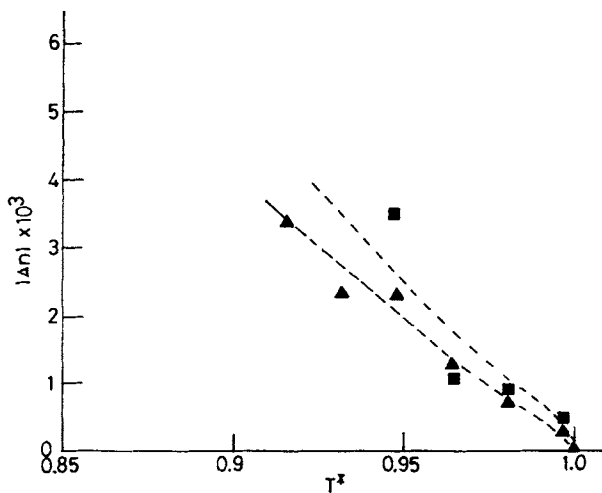

Fig. 4(a).   Reduced temperature dependence of birefringence for 45 wt % solution of HPC in DMAc: (▲) HPC-C; (■) HPC-D.
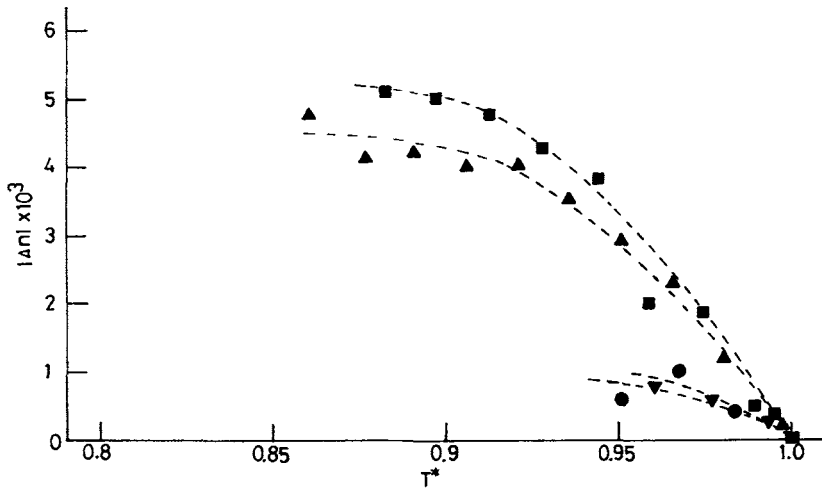
Fig. 4(b).   Reduced temperature dependence of birefringence for 50 wt % solution of HPC in DMAc: (●) HPC-A; (▼) HPC-B; (▲) HPC-C; (■) HPC-D.

At a given $\overline{M}_w$, Δn was greater as the polymer concentration became higher. When the behavior of the HPC/DMAc system was compared with that of EC/m-cresol system, the following results were the same for both systems: (1) At a given temperature (T or T^*) Δn increased with MW and tended to reach a constant value; this suggests there is a critical MW; (2) Δn increased with decreasing temperature and came to equilibrium at relatively low T^*; the equilibrium value of Δn increased with MW. These behaviors became more pronounced as the polymer concentration increased. The critical MW for HPC was found to be greater than that for EC.

Our findings strongly suggest that the effect of MW on Δn for cellulosic LCSs is dependent on the MW range of polymer used: in relatively lower MW range (lower than a critical MW), the
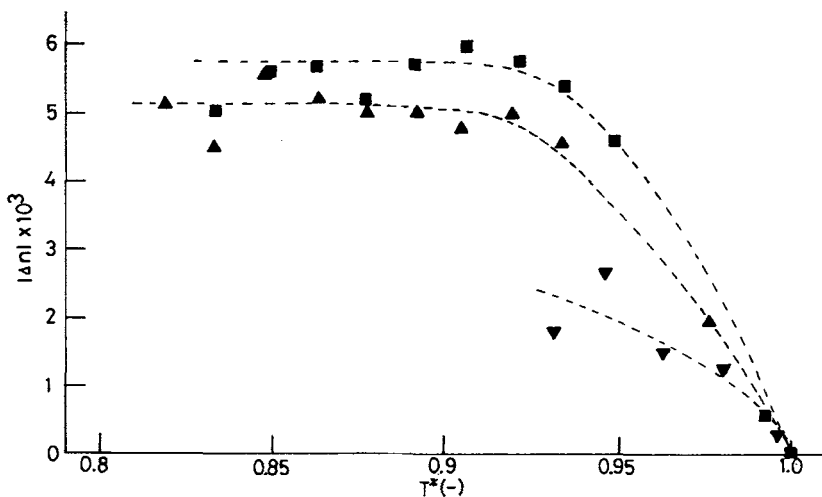

Fig. 4(c).   Reduced temperature dependence of birefringence for 55 wt% solution of HPC in m-cresol: (▼) HPC-B; (▲) HPC-C; (■) HPC-D.
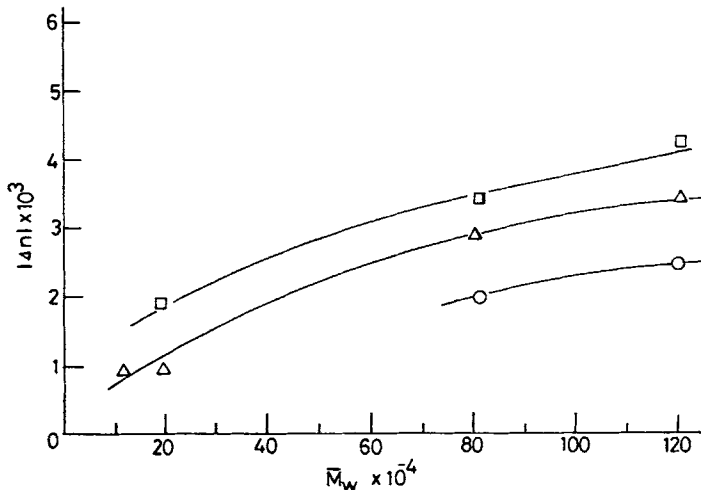
Fig. 5. Molecular weight dependence of birefringence at $T^* = 0.95$ for HPC solution in DMAc. Concentration (wt %): (○) 45; (△) 50; (□) 55.

effect is significant, whereas, in relatively higher MW range (higher than a critical MW), the effect is not significant.

Finally it is interesting to note that the MW dependence of Δn for cellulosic LCSs (cholesteric type) resembles that of the order parameter S for nematic liquid crystal.[16, 17]

CONCLUSIONS

(1) Δn at a given temperature increased with MW and tended to level off. This suggests there is a critical MW which depends on the polymer concentration and the liquid crystal system.

(2) Δn increased with decreasing temperature and approached a constant value at a relatively low temperature. The equilibrium value of Δn increased with MW.

(3) The behaviors described in (1) and (2) became more pronounced as the polymer concentration increased.

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