Polymer Bulletin 34, 203–210 (1995)

Polymer Bulletin

Molecular structure and cholesteric liquid crystalline behavior of ethyl-cyanoethyl cellulose

Y. Huang[1], **S. H. Jiang**[2], **J. R. Shen**[3]

[1] Laboratory of Cellulose and Lignocellulosics Chemistry, [2] National Laboratory of Polymer Materials and Engineering, Guangzhou Institute of Chemistry, Academia Sinica, P.O. Box 1122, Guangzhou 510650, People's Republic of China
[3] Department of Polymer Material Science, South China University of Technology, Guangzhou 510641, People's Republic of China

Received: 19 August 1994/Revised version: 19 September 1994/Accepted: 11 October 1994

Summary

Ethyl-cyanoethyl cellulose [(E-CE)C] can form lyotropic cholesteric liquid crystals in acrylic acid (AA) and the liquid crystalline behavior is influenced by the concentration and (E-CE)C molecular structure. The critical concentration C_1 increases with increasing (E-CE)C molecular weight and is also influenced by the degree of substitution for cyanoethyl. The C_1 is lowest when the degree of substitution for cyanoethyl is 0.26. The pitch of cholesteric phase decreases with increasing both the (E-CE)C concentration and the degree of substitution for cyanoethyl and can not be influenced by the molecular weight of (E-CE)C in the molecular weight region of 6×10^4 - 5×10^5.

INTRODUCTION

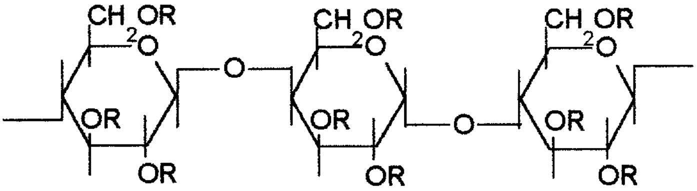
Many cellulose derivatives can form a lyotropic liquid crystalline state with various solvents or a thermotropic liquid crystal[1]. Ethyl-cyanoethyl cellulose [(E-CE)C] is a cellulose derivative with two kinds of ester groups and can be dissolved in many organic solvents. (E-CE)C can form lyotropic liquid crystals when the concentration is higher than the critical one[2]. In some of solvent systems, (E-CE)C solutions exhibit vivid colors in a certain concentration regions because of the selective reflection of the cholesteric liquid crystalline phase in the solution for visible light. The maximum wavelength of selective reflection is closely related with the pitch of cholesteric liquid crystals P and can be described by the equation[3]: λ_{max} =nP, where n is the mean refractive index of the system. The pitch of cholesteric phase is greatly influenced by the temperature and the concentration of the system and the molecular structure, such as molecular weight, the substituent groups on the molecules, etc.

(E-CE)C can be dissolved in acrylic acid (AA) and formed cholesteric liquid crystalline solutions at the concentration above 35 wt%. The (E-CE)C/AA cholesteric liquid crystalline solutions can selectively reflect visible light in the concentration between 42-52 wt% and exhibit vivid colors[4]. (E-CE)C/polyacrylic acid (PAA) composite films that perfectly retain the cholesteric order in the solutions can be prepared by the photopolymerization of the AA[5]. This kind of composite films generally show the thermal and mechanical stability and can be used in some optical devices, such as circular polarizers, bandpass filters, notch filters and reflective displays.

In this report, (E-CE)C is fractionated and the samples with different molecular weights and the degree of substitution for cyanoethyl are obtained. The influence of the molecular weight, the degree of substitution for cyanoethyl and the concentration of (E-CE)C in the (E-CE)C/AA solutions on the lyotropic behavior and the pitch of cholesteric phase is discussed.

EXPERIMENTAL

(E-CE)C was prepared by the reaction of ethyl cellulose, of which the degree of substitution for ethyl was about 1.9, and acrylonitrile. The molecular formula of the (E-CE)C is as following:



R=H, CH_2CH_3, CH_2CH_2CN

(E-CE)C was fractionated by two methods. One was by fractional precipitation of the whole polymer with acetone as a solvent and water as a precipitant. The other was by extraction with ethanol at 5℃, 28℃ and 52℃. The molecular weight of the fractions was measured by a gel permeation chromatography (GPC) (Waters ALC/244/GPC), which was calibrated by standard polystyrene. The content of nitrogen of (E-CE)C was measured by elementary analysis, from which the degree of substitution for cyanoethyl was calculated.

The critical concentration of (E-CE)C/AA solutions, at which the cholesteric liquid crystalline phase began to appear, was determined by refractometry[6] and observing with polarizing microscopy. The cholesteric pitch of (E-CE)C/AA liquid crystalline solutions was measured by spectrometry and transmission electron microscopy (TEM). In the spectrometry, the (E-CE)C/AA liquid crystalline solution was placed in a sample pool ($0.3\times15\times20$ mm). The maximum wavelength of the selective reflection of the solution, where the apparent absorbance was maximum in the spectra, was recorded by an UV-VIS spectrophotometer (SPECORP UV-VIS, Ziess, Germany) after the solution was stored at room temperature for about 24 hours. The cholesteric pitch P of the liquid crystalline solution was calculated according to the equation $\lambda_{max} = nP$, where n is the mean refractive index of the solution. In the observation with TEM, the (E-CE)C/AA liquid crystalline solutions with 2 wt% benzoin ethyl ether (with respect to the solvent AA) which was an initiator of the photopolymerization were stored in darkness for one week and sandwiched between two glass slides to form solution films with 0.3mm in thickness. The solution films were inserted into the ultraviolet chamber with 250 Watt high-intensity mercury arc lamp until complete polymerization and the (E-CE)C/polyacrylic acid (PAA) composite films with cholesteric order were obtained. A Transmission electron microscope (TEM) (TEM - 100CX/II, JEOL, Japan) was used to observed the periodical lamellation in the (E-CE)C/PAA composite films which were sectioned to super-thin films and the periodicity of the lamellation was equal to a half pitch of cholesteric order[5].

RESULTS AND DISCUSSION

Table 1 gives the molecular weight, the distribution of molecular weight, the degree of substitution for cyanoethyl of the different fractions of (E-CE)C obtained from the fractional precipitation. The interaction parameter χ of the different fractions with the AA and the critical concentration C_1 of (E-CE)C/AA solutions, at which the liquid crystalline phase begins to appear, are also given in Table 1. Both the molecular weight and the degree of substitution for cyanoethyl are different from the different fractions. The solubility of the (E-CE)C is gradually changed with variation of the ratio between the solvent and the precipitant. The cyanoethyl group in (E-CE)C is a polar group and consequently, the solubility of the (E-CE)C is related with not only the molecular weight but also the degree of substitution for cyanoethyl. The fractions from the fractional precipitation, therefore, give different molecular weights and different degrees of substitution for cyanoethyl. The distribution of molecular weight for each fraction is wide due to the influence of the distribution of substitution for cyanoethyl.

It can be found from Table 1 that the critical concentration of the formation of liquid crystalline phase C_1 generally decreases with increasing molecular weight of (E-CE)C. But there is an abnormal phenomenon between the fraction b and c. The molecular weight of the fraction b is almost same as that of the fraction c but the C_1 for fraction b is higher than that for fraction c. In Table 1, the degree of substitution for cyanoethyl decreases from fraction a to e and the molecular interaction parameter between the (E-CE)C and the AA χ decreases from fraction a to c and increases from c to e. The value of χ is the minimum for fraction c. The smaller the value of χ, the stronger the molecular interaction between the (E-CE)C and the solvent and the lower the critical concentration of the formation of liquid crystalline phase is[2]. The same result of the variation of C1 with χ for other cellulose derivative liquid crystalline systems has also been reported by Aharoni[7]. For the (E-CE)C/AA solutions, the critical concentration of the formation of liquid crystalline phase is influenced by both the molecular weight and the degree of substitution for cyanoethyl. In comparison fraction a with b, the molecular weight is much larger and the value of χ is much smaller for fraction b than for fraction a, both of which lead to decreasing the critical concentration. Therefore, the value of C_1 for fraction b is lower than that for fraction a. The molecular weight for fraction b and c is almost the same, however, the value of χ for fraction c is much smaller than that for fraction b. So, the critical concentration for fraction c is lower than that for fraction b. The molecular weight increases from fraction c to e, but the molecular interaction decreases gradually. The variation of molecular weight leads to lowering the critical concentration but the change of the molecular interaction results in the increment of the C_1. The influence of molecular weight on the C_1 is larger than that of the variation of molecular interaction and therefore, the C_1 slowly decreases from fraction c to e. Generally speaking, the preparation of the (E-CE)C/AA cholesteric liquid crystalline solution with low critical concentration requires high molecular weight and a suitable degree of substitution for cyanoethyl, which is about 0.26 in the (E-CE)C/AA system.

Table 1. The molecular weight, the distribution of molecular weight, the degree of substitution for cyanoethyl of the fractions from fractional precipitation, the C_1 of (E-CE)C/AA solutions and the χ of the (E-CE)C with AA.

No.	a	b	c	d	e
M_W	58000	146000	140000	300000	464000
DMW	3.56	4.02	3.89	4.25	5.52
C_1 (wt%)	38.8	37.6	35	34.4	34
DS for cyanoethyl	0.39	0.31	0.26	0.22	0.17
$\chi \times 10^3$	1.02	0.12	0.001	0.30	0.55

DMW: The distribution of molecular weight
DS: The degree of substitution

In the liquid crystalline polymer/solvent lyotropic system, the relationship between the concentration and the cholesteric pitch can be described as following[8]:

$$M_A(1-\omega_A)/2Pd\omega_A=(N\beta_A M_B/M_A-2N\beta_{AB})\omega_A+2N\beta_{AB}$$

$$d=d_B/[1+(d_B/d_A-1)\omega_A$$

Where M_A and M_B are molecular weight of the polymer and the solvent respectively, ω_A is weight fraction of the polymer, N is Avogadadro' number and P is the cholesteric pitch. d_A and d_B are the density of the polymer and the solvent respectively. β is the interaction parameter - " molecular twisting power", which is related with the molecular structure, the molecular weight and the temperature of the system. From the equation, the relationship between $(1-\omega_A)Pd\ \omega_A$ and ω_A must be linear.

The cholesteric pitch of the (E-CE)C/AA liquid crystalline solutions is generally in the region 100-500 nm and the fingerprint texture can not be directly observed with polarizing microscopy. Then, the cholesteric pitch can not be measured directly by using a polarizing microscope. According to the formula $\lambda_{max}=nP$, the cholesteric pitch can be calculated after the wavelength of the maximum reflection for the solution is recorded by a UV-VIS spectrophotometer when the wavelength of the selective reflection is in the visible light. If the wavelength of the selective reflection of the solution is out of the visible light, a transmission electron microscope (TEM) is used to measure the cholesteric pitch. The AA in the (E-CE)C/AA cholesteric liquid crystalline solutions is photopolymerized and the (E-CE)C/PAA composites with cholesteric order are obtained. The periodical lamellation can be observed in the (E-CE)C/PAA composites by TEM after the composites are sectioned to super-thin films and it has been confirmed that the periodical lamellation in the composite is attributed to the cholesteric structure and the periodicity of the lamellation is equal to the half pitch[5]. Table 2 gives the cholesteric pitch of the (E-CE)C/AA liquid crystalline solutions with different concentrations. It can be seen from Table 2 that the cholesteric pitch decreases with increasing concentration. The same result has been found in ethyl-acetyl cellulose/ dichloroacetic acid liquid crystalline system[9].

From the data in Table 2, the curve of $(1-\omega_A)Pd\ \omega_A$ vs. ω_A for the (E-CE)C/AA cholesteric liquid crystalline solutions is plotted (Fig.1) and it is clear that the variation of $(1-\omega_A)Pd\ \omega_A$ with ω_A is linear and the relationship between the cholesteric pitch and the concentration can be described by the equation mentioned above for the (E-CE)C/AA liquid crystalline solutions.

Table 2. The pitch of (E-CE)C/AA cholesteric liquid crystalline solutions with different concentrations

(E-CE)C wt%	40	44	45	47.5	50
p(nm)	332	232	216	182	157

By using the fractional precipitation and the extraction with ethanol at different temperatures, the (E-CE)C is fractionated to many fractions with different molecular weight and degree of substitution for cyanoethyl. Some of them have nearly same molecular weight but much different degree of substitution for cyanoethyl and some of them have nearly same degree of substitution for cyanoethyl but much different molecular weight.

The fractions with different molecular weight and degree of substitution for cyanoethyl are used to form lyotropic liquid crystals in AA and Table 3 gives the cholesteric pitch of 45 wt% (E-CE)C/AA liquid crystalline solutions. It can be found that the molecular weight of fraction d and B is nearly the same but the degree of substitution for cyanoethyl of the fraction B is larger than that of the fraction d, and the cholesteric pitch is smaller for fraction B than that for fraction d. The degree of substitution for cyanoethyl of fraction d is the same as that of fraction A but the molecular weight of fraction d is much different from that of fraction A. The cholesteric pitch for the fraction d and A, however, is nearly the same. It is suggested that the variation of the cholesteric pitch for (E-CE)C/AA liquid crystalline solutions is mainly influenced by the degree of substitution for cyanoethyl of the (E-CE)C in the region of molecular weight and degree of substitution for cyanoethyl studied in this report. It has been reported[8] that the pitch of the cholesteric phase of cellulose tricarbanilate rapidly changes at small molecular weight and remains constant at a certain high molecular weight.

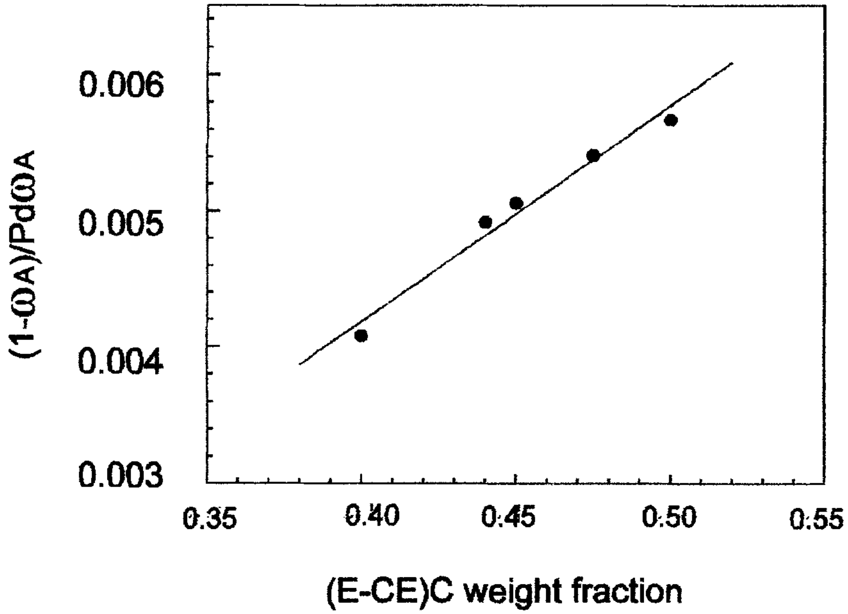


Fig. 1 Relationship between $(1-\omega_A)Pd\,\omega_A$ and ω_A to (E-CE)C in AA.

Table 3. Mw, degree of substitution for cyanoethyl and the pitch of the 45 wt% (E-CE)C/AA cholesteric liquid crystalline solutions with different fractions.

No.	a	b	c	d	e	A*	B*
Mw	58000	146000	140000	300000	464000	189000	303000
DS for cyanoethyl	0.39	0.31	0.26	0.22	0.17	0.23	0.29
P(nm)	143	185	223	244	261	241	197

*: A and B are the fractions from extraction with ethanol at 5°C and 28°C respectively

Fig.2 gives the plot of the cholesteric pitch vs. the degree of substitution for cyanoethyl to (E-CE)C/AA liquid crystalline solutions. The variation of the pitch with the degree of substitution for cyanoethyl is linear and the pitch of the (E-CE)C/AA cholesteric liquid crystalline solutions decreases with increasing the degree of substitution for cyanoethyl in the (E-CE)C.

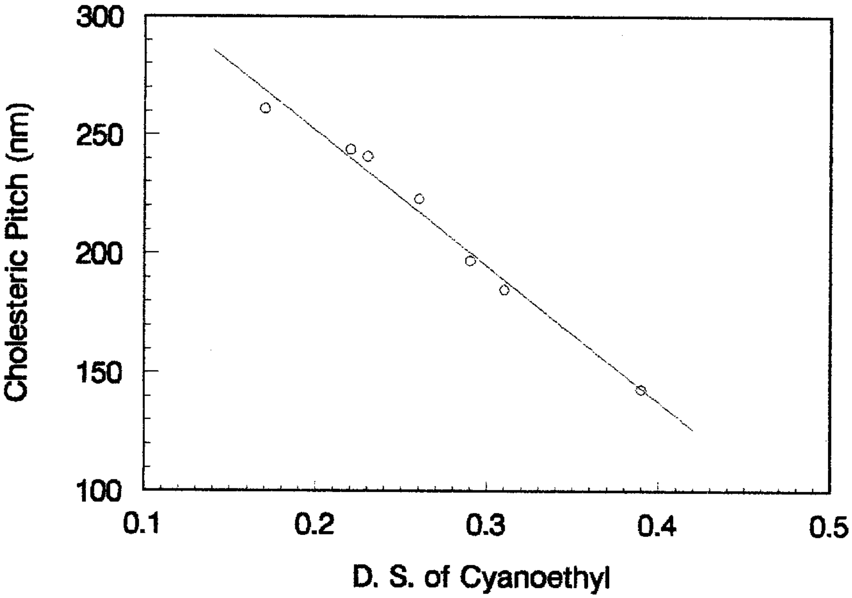


Fig.2 The plot of the pitch vs. the degree of substitution for cyanoethyl of the (E-CE)C/AA cholesteric liquid crystalline solutions.

CONCLUSIONS

The (E-CE)C can form lyotropic cholesteric liquid crystals in the AA and the critical concentration C_1, at which the liquid crystalline phase begins to appear, decreases with increasing the molecular weight of (E-CE)C. The C_1 is also influenced by the degree of substitution for cyanoethyl in the (E-CE)C and is lowest when the degree of substitution for cyanoethyl is about 0.26. Both increment and decrement of the degree of substitution for cyanoethyl lead to increase of the C_1.

(E-CE)C/AA cholesteric liquid crystalline solutions can selectively reflect visible light and the wavelength of the selective reflection is controlled by the cholesteric pitch of the solutions. The pitch decreases with increasing both the (E-CE)C concentration and the degree of substitution for cyanoethyl. It can not be influenced by the molecular weight of (E-CE)C in the molecular weight region of 6×10^4 - 5×10^5. The (E-CE)C/AA solutions, which can selectively reflect visible light with different wavelength and exhibit different colors, can be prepared by controlling the degree of substitution for cyanoethyl and the concentration of (E-CE)C.

Acknowledgement: The financial support by National Basic Research Project - Macromolecular Condensed State and National Natural Science Foundation of China is greatly appreciated.

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