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Molecular interactions and formation of lyotropic liquid crystals of hydroxyethyl cellulose acetate

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Summary

The relationship between the hydrogen bond (H-bond) interactions and the formation of the cholesteric liquid crystalline phase was studied by Fourier transform infrared spectroscopy (FTIR), refractometry and polarizing microscopy. It was quite evident that the H-bonding played an important role in the early stage of the formation of cholesteric liquid crystalline phase in hydroxyethyl cellulose acetate (HECA)/ dimethyl sulfoxide (DMSO) solutions and the rigidity of the HECA chains was more important to form liquid crystalline phase than molecular interactions when the concentration is very high.

INTRODUCTION

Cellulose and its derivatives are semi-rigid chain polymers and can be dissolved in many solvent systems to form cholesteric liquid crystals[1]. The force of the formation of liquid crystals for cellulose and its derivatives is attributed to both their semi-rigid backbone and molecular interactions in the systems[2]. It has been found that molecular interactions, most of them is H-bond interactions, influence no the formation of liquid crystalline phases in the system of ethyl-cyanoethyl cellulose/dichloroacetic acid (DCA) and methyl-cyanoethyl cellulose/DCA studied by Fourier transform infrared spectroscopy (FTIR)[3-4]. The formation of liquid crystalline phases and crystallization are greatly affected by the mesogenic groups for side-chain liquid crystalline polymers studied by FTIR at different temperatures[5]. Meanwhile, FTIR is widely used in studying H-bonding in many systems[6-8]. In this report, the relationship between the formation of liquid crystals and molecular interactions in hydroxyethyl cellulose acetate (HECA)/dimethyl sulfoxide (DMSO) solutions is discussed.

EXPERIMENTAL

HECA was prepared by etherifications of hydroxyethyl cellulose with ester degree of about 1.7 and acetic anhydride catalysed by zinc chloride[9]. The HECA with

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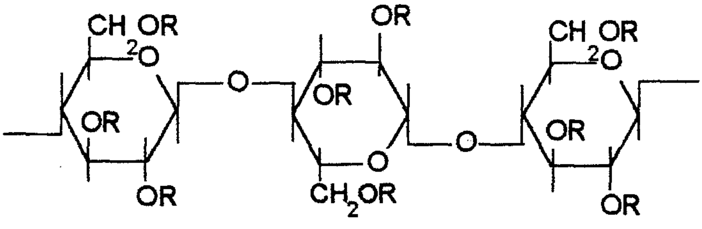
different degree of substitution for acetyl was prepared by controlling the conditions of the etherifications. The molecular weight of HECA, measured by a gel permeation chromatography (GPC) (Waters, ALC/244/GPC) with calibrating by standard polystyrene, was Mn=6.5×10^4. The content of oxygen of HECA was measured by elementary analysis, from which the degree of substitution for acetyl was calculated. The molecular formula of HECA was as follows:



R=H, CH_2CH_2OR', $COCH_3$ R'=H, $COCH_3$

The DMSO was chemically pure reagent. The HECA was mixed with the DMSO at room temperature and the mixture was sealed up in the test-tube. The solutions were heated at 40℃ for about 48 hours and then stored at room temperature for about 12 hours. Finally, the homogeneous HECA/DMSO solutions were obtained.

An Abbe' refractometer was used to measure the refractive index of the solution for determining the critical concentration of the formation of liquid crystalline phases C^*_1 and that of totally disappearance of the isotropic phase C^*_2 in the solution. The formation of liquid crystalline phases and the mesophase textures were observed by a polarizing microscope (Leitz, ORTHOPLAN-POL).

The IR spectra of the solutions were measured by a Fourier transform infrared spectrophotometer (FTIR) (RFX-65, ANALECT, U.S.A.). The solutions were placed between two KBr crystals and the spectral resolution was 2 cm^{-1}. All samples and the background were scanned 64 times to improve the signal-to-noise. The conditions and the instrument parameters were the same for all samples and the background. The peak values of the absorption bands were typed directly on the IR spectra.

RESULTS AND DISCUSSION

The IR spectra of HECA/DMSO solutions with different concentrations have been measured. It is found that some IR absorbance bands of C=O and S=O solutions shift with the variation of the concentration. There are C=O and OH groups on HECA chains and S=O group in DMSO molecules. In the HECA/DMSO solutions, therefore, there may exist H-bonds such as C=O···H-O and S=O···H-O, which lead to the shift of the C=O band and the S=O band in the IR spectra. The formation and the destruction of the H-bonding in the HECA/DMSO system can be learnt from the variation of the C=O and S=O bands in IR absorption spectra.

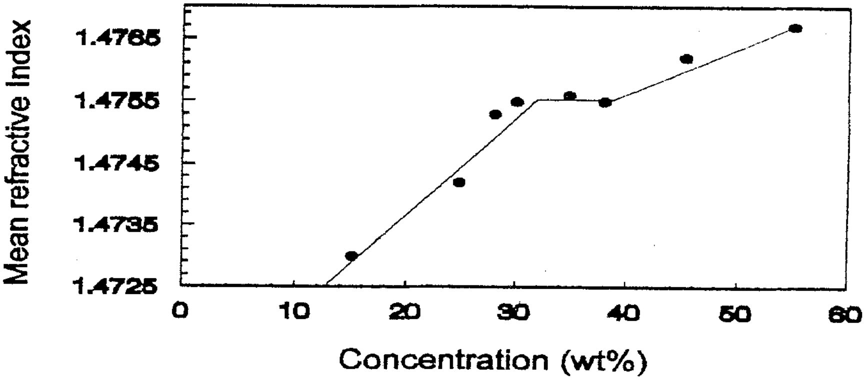


Figure 1. A plot of mean refractive index vs. the concentration of the HECA (α=2.08)/DMSO solution.

The process of the phase transformation of solutions can be learnt by using refractometry and the critical concentration of the phase transformation can be determined from the plot of the mean refractive index vs. the concentration[10]. Figure 1 is a plot of the mean refractive index vs. the concentration for the HECA/DMSO solution, in which the degree of substitution for acetyl in the HECA α is 2.08. From the Figure 1 and the observation with a polarizing microscope, it can be found that the solution is isotropic at the concentration below 30 wt% or completely anisotropic at the concentration above 38 wt%. The isotropic phase and the liquid crystalline phase coexist in the solution within the concentration region between 30-38 wt%. The HECA with different degree of substitution for acetyl shows the similar behavior in the DMSO. Table 1 gives the values of the critical concentration C_1 and C_2 for HECA/DMSO solutions with different α values.

Table 1. The values of C_1, C_2 and C_0 for HECA/DMSO solutions.

No.	a	C_1(wt%)	C_2(wt%)	C_0(wt%)
1	2.08	30	38	35
2	2.55	37	50	40
3	2.96	43	55.5	45

HECA/DMSO liquid crystalline solutions show the same texture as other cellulose derivative liquid crystals, which has the cholesteric feature. Figure 2 is a polarized micrograph of HECA/DMSO liquid crystalline solutions. It is suggested from mesophase textures that the liquid crystals in the HECA/DMSO solutions are cholesteric.

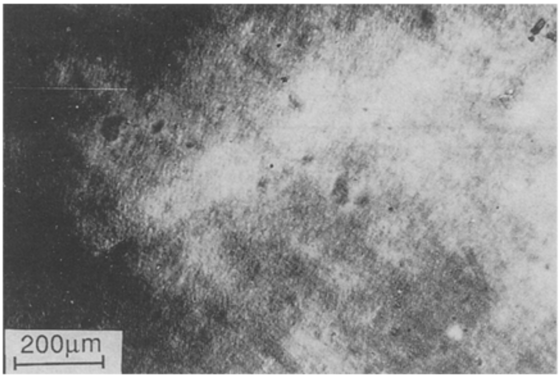


Figure 2 Polarized micrograph of HECA/DMSO liquid crystalline solutions, C=48 wt%.

The ability of the formation of H-bonding C=O···H-O and S=O···H-O increases with increasing the content of the OH group. The data in Table 1 indicate that if the ability of the formation of H-bonding is high, the ability of the formation of lyotropic liquid crystals is high and the critical concentration C_1, at which the liquid crystalline phase begins to appear, is low.

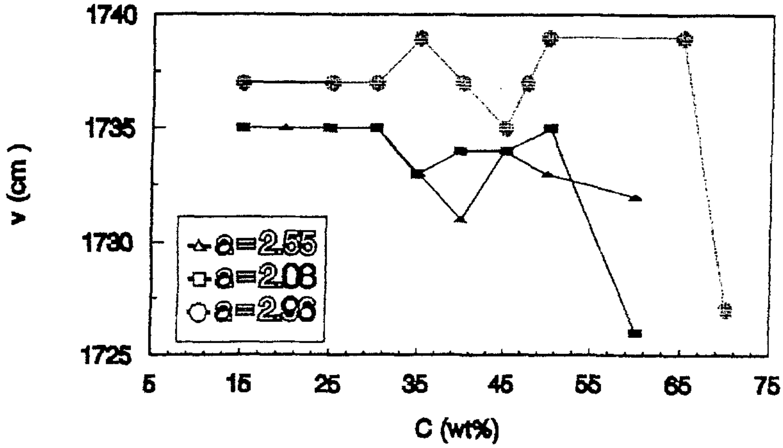


Figure 3 Frequency change observed for the C=O stretching vibration as a function of the concentration for HECA/DMSO solutions.

Figure 3 shows curves of the frequency of C=O stretching band $\nu_{C=O}$ vs. the concentration and Figure 4 shows the variation of the frequency of S=O stretching band $\nu_{S=O}$ with the concentration for HECA/DMSO solutions. It can be found that the $\nu_{S=O}$ shifts to low frequency direction with increasing concentration in very low concentration region and though the minimum value it shifts to high frequency direction. In very high concentration region, it shifts to low frequency direction again. The $\nu_{C=O}$ is nearly unchanged with increasing concentration in very low concentration region. When the concentration increases to a certain value, the $\nu_{C=O}$ shifts to low frequency direction with increasing concentration and after it reaches to the minimum value, it shifts to high frequency direction. And finally, similar to the shift of the $\nu_{S=O}$, it shifts to low frequency direction again with increasing concentration in very high concentration region.

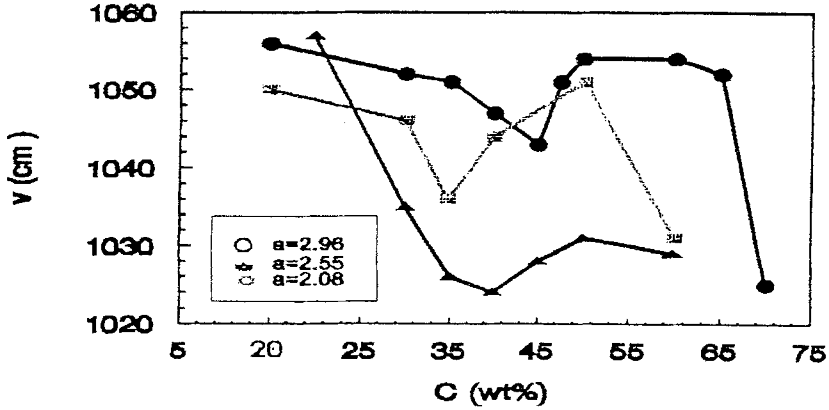


Figure 4 Frequency change observed for the S=O stretching vibration as a function of the concentration for HECA/DMSO solutions.

Table 2. The normalized width of half peak of C=O and S=O bands in IR spectra for HECA/DMSO solutions with different concentrations.

C (wt%)	10	20	30	40	45	50	60
$WHP_{C=O}$	1.0	1.0	1.0	1.20	1.32	1.14	1.11
$WHP_{S=O}$	1.0	1.0	1.08	1.08	1.25	1.13	1.03

WHP is the normalized width of half peak related to the value for the 10 wt% solution.

The variation of the $\nu_{C=O}$ and the $\nu_{S=O}$ indicates that H-bonding related with the S=O and C=O groups is changed with increasing concentration. The variation of the width of half C=O and S=O peaks (Table 2) also indicates the formation of H-bonding with increasing concentration. The width of half peak of C=O is slightly increased at the concentration above 40 wt%, at which the intermolecular H-bonding C=O···H-O forms and cholesteric liquid crystalline phase appears in the solution. It is slightly decreased at high concentration, which is corresponding to the decrease of intermolecular C=O···H-O H-bonding. The variation of width of half peak for both C=O and S=O bands with concentration is very small and the formation of only C=O ···H-O and S=O···H-O bonding is considered in the solution.

The change of the shift direction for $\nu_{C=O}$ and $\nu_{S=O}$ is corresponding to the formation of the liquid crystalline phase and the phase transformation in solutions. In the very low concentration region, the solution is isotropic and the HECA polymer chains are randomly dispersed in the DMSO. At this time, there are intermolecular H-bonding S=O···H-O between the HECA and the DMSO and intramolecular H-bonding C=O···H-O within the HECA chains. With increasing concentration, the content of the HECA increases and OH group which can form a strong H-bonds with S=O group increases. Therefore, the ability of the formation of intermolecular H-bonding S=O··· H-O increases with increasing concentration and the strength of the S=O double bond is weakened. The $\nu_{S=O}$ shifts to low frequency direction with concentration. The intramolecular H-bonding C=O···H-O can not be influenced by HECA concentration and therefore, the $\nu_{C=O}$ is nearly unchanged with increasing concentration in this very low concentration region.

In the concentration region between C_1 and C_2, the isotropic phase and the liquid crystalline one coexist in the solution. The HECA polymer chains transform from disorder state to order one with increasing concentration and the interaction between polymer chains increases. The intermolecular H-bonding C=O···H-O is formed between polymer chains, which leads to the shift of the $\nu_{C=O}$ towards the low frequency direction. At the same time, the solvent molecules, DMSO, are separated between the layers of ordered polymer chains in the liquid crystalline phase and the S=O group form H-bonds S=O···H-O with OH on polymer chains, which leads to the shift of the $\nu_{S=O}$ also towards the low frequency direction. Figure 5 shows the scheme of the H-bonds between the HECA chains and the DMSO molecules in the liquid crystalline phase. In the cholesteric liquid crystalline phase, there exist intermolecular H-bonds between HECA chains within the layers of ordered polymer chains and H-bonds S=O···H-O between DMSO molecules and HECA chains because the DMSO molecules are sandwiched between the layers of ordered polymer chains.

At the specific concentration C_0, The ability of the formation of intermolecular H-bonding between the HECA chains and the DMSO molecules is maximum. In other words, the OH group on the HECA chains which is able to form H-bonding with C=O and S=O groups has been formed the H-bonds. Figure 4 and 5 demonstrate that the $\nu_{C=O}$ and the $\nu_{S=O}$ shift to the minimum value, which suggests that strength of the double bond C=O and S=O is now weakest and the intermolecular H-bonding between HECA chains and DMSO molecules is the maximum. The values of C_0 for HECA/DMSO solutions with different α values are also listed in Table 1. The stronger the ability of the formation of liquid crystalline phases for HECA, the lower the value of C_0 is. This may be because that the formation of H-bonding C=O···H-O and S=O···H-O can be the maximum at a lower concentration if amount of OH group on HECA chains is higher.

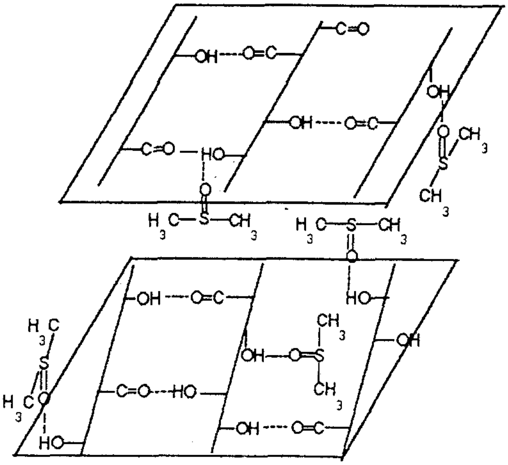


Figure 5. Scheme of the H-bonds in the cholesteric liquid crystalline phase for HECA/DMSO solutions.

When the concentration further increases, the $\nu_{C=O}$ and the $\nu_{S=O}$ shift to high frequency direction from the minimum value, which indicates that the strength of H-bonding C=O···H-O and S=O···H-O are weakened. Consequently, the influence of molecular interactions on the formation of liquid crystals in solutions decreases when the concentration is higher than C_0. The requirement of the formation of liquid crystals for polymers is anisotropic molecular interactions and rigid or semirigid backbone. HECA is a semirigid chain polymer. In HECA/DMSO solutions, when the concentration is high enough, the space of the movement for HECA chains is very small because the density of polymer chains is very high. The ability of the formation of intermolecular H-bonding decreases which may be because of steric hindrance when C=O or S=O is closing to OH groups. At this time, therefore, the rigidity of polymer chains is a key factor to influence the formation of liquid crystals. With increasing concentration at this time, the isotropic phase decreases and the liquid crystalline phase increases. The increment of the liquid crystalline phase with increasing concentration in the solution is mainly attributed to the semirigid structure of polymer chains.

When the concentration is high enough, the solution is a completely anisotropic system. the density of HECA chains increases with increasing concentration and the DMSO molecules are sandwiched between the layers of ordered HECA chains to form single molecular layers. The induced dipolar effect C=O→O-H and S=O→O-H may occur because the HECA chains and DMSO molecules are very closed, which results in the shift of the $\nu_{C=O}$ and the $\nu_{S=O}$ to the low frequency direction with increasing concentration.

CONCLUSIONS

In HECA/DMSO solutions, molecular interactions between HECA polymer chains and DMSO molecules as well as between HECA chains, that is the H-bonds C=O···H-O and S=O···H-O, play a very important role in the formation of cholesteric liquid crystalline phase at the beginning of the formation of liquid crystals. In the system with high intermolecular H-bonding, the liquid crystalline phase begins to appear at a lower concentration in solutions, i.e. the C_1 is lower. When the concentration is very high, the density of HECA polymer chains is high and the rigidity of the HECA chains plays a very important role in the formation of liquid crystalline phase.. The influence of molecular interactions on the formation of liquid crystals is small.

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