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Formation of lyotropic liquid crystals and molecular interactions in maleyl ethyl cellulose/acetic acid system

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A novel cellulose derivative, maleyl ethyl cellulose (MAEC), was synthesized. MAEC could be dissolved in acetic acid (AA) and formed cholesteric liquid crystalline solutions. The critical concentration of the phase transformation from the isotropic phase to the liquid crystalline one decreased with increasing the degree of substitution of maleic acid. MAEC formed complexes with the rare earth metal ion Eu^{3+}, which resulted in fluorescence in the system. The fluorescent spectrum of the system was influenced by the complexion state of Eu^{3+} with MAEC and AA. The variation of the molecular interactions between polymer chains and between the polymer chains and the solvents in the formation of the liquid crystalline phase, and the phase transformation with the variation of the concentration in the solutions, were reflected by the variation of $R = I_{613}/I_{591}$ in fluorescent spectra. It was found that the interactions between polymer chains are enhanced in the initial stage of the formation of the liquid crystalline phase. But the interaction between polymer chains decreased when the concentration was very high and, at this time, the rigidity of the polymer chains plays a principal role in the formation of the liquid crystalline phase. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: fluorescence; rare-earth metal ion; lyotropic liquid crystal)

INTRODUCTION

Polymers with rigid or semi-rigid main chains can form liquid crystalline states in suitable conditions. Cellulose and its derivatives are semi-rigid chain polymers and can form lyotropic liquid crystals in appropriate solvents[1]. The driving force of the mesophase formation depends on not only the semi-rigid polymer backbone, but also the molecular interactions of polymer chains in the solutions[2]. It has been reported that the molecular interactions, most of which are hydrogen bonding, affect the formation of the liquid crystalline phase[2,3].

Many methods, such as *FT*-i.r.[2,3], n.m.r.[4,5] and d.s.c.[6] have been used to study the molecular interactions in lyotropic liquid crystalline systems. Fluorescence can also be used in this field to detect molecular interactions in polymer solutions because of its high sensitivity to the variation of the molecular interactions. In synthetic polymers, especially in the systems with aromatic rings, the formation of excimers changes their fluorescent spectra[7]. In cellulose and its derivatives, the chromophores along the chains are not in a suitable geometry to form excimers, or the chromophores are far apart from each other because of the semi-rigid cellulose backbone, which results in very weak interactions between polymer chains[8].

Investigations of cellulose and its derivatives by fluorescent spectra began in the 1950s[9]. Many cellulose derivatives can emit fluorescence by themselves. However, there is little reported about the relationship between fluorescent spectra and molecular structures, and it is difficult to obtain directly information about the molecular interactions between polymer chains from the fluorescent spectra of cellulose derivatives because no fundamental relationship between the fluorescence and the molecular structure has been set up.

Many rare-earth metal ions can produce fluorescence and can form complexes with some functional groups in both small molecules and polymers. The fluorescent properties of the rare-earth metal ions in the complexes with small molecules or polymers are influenced by their complex structures. Consequently, the fluorescent spectra of the rare-earth metal ions can be used to determine the variation of the molecular interactions in polymer solutions. In this paper, the rare-earth metal ion Eu^{3+} is used as a fluorescent probe to study the process of the phase transformation and the variation of the molecular interactions between maleyl ethyl cellulose (MAEC) chains and solvent molecules in MAEC/AA solutions. The influence of the degree of substitution by maleyl on the formation of the liquid crystalline phase in the solutions is also discussed.

EXPERIMENTAL

MAEC was prepared by reacting ethyl cellulose (EC), of which the degree of substitution for ethyl was 2.1, with maleic anhydride. The preparation procedure was as following: EC (3 g) was dissolved in 40 ml of acetic acid, and then 12 g of maleic anhydride as reacting reagent and a measured amount of zinc chloride as catalyst were added to the solution with stirring. The solution was heated to 40°C and stirred for 16 h. The solution was then poured into distilled water and the precipitate was removed by

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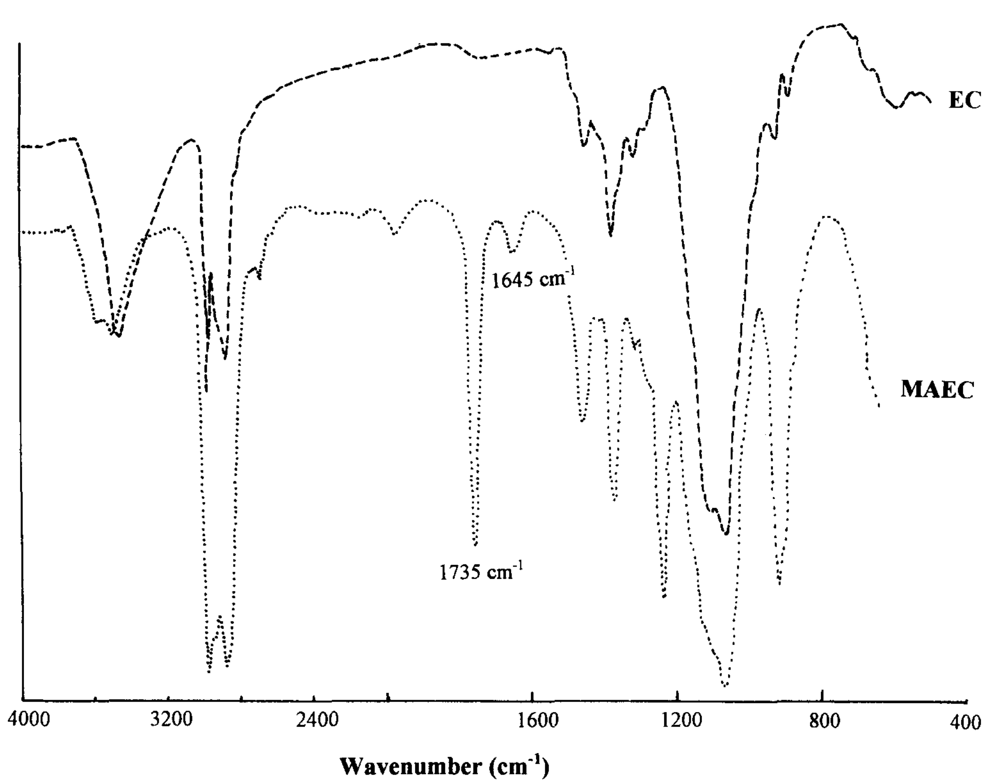
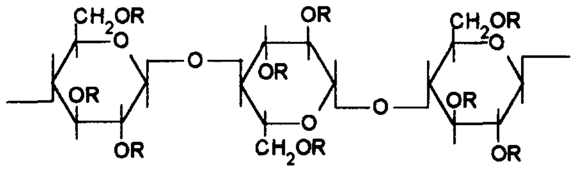


Figure 1 Infrared spectra of EC and MAEC ($\alpha = 0.28$)



R=H, CH_2CH_3, COCH=CHCOOH

Figure 2 Molecular formula of MAEC

decantation. The precipitate was washed by distilled water several times until the washings remained neutral and then was dried. The MAEC with different degrees of substitution (D.S.) by maleyl groups were prepared by using different amounts of $ZnCl_2$.

The esterification reaction of the EC and the maleic anhydride was characterized by determining the changes of –C=C– and –C=O– vibration bands in the infrared spectra. MAEC was dissolved in THF and then formed into a film. The emergence and changes of –C=C– and –C=O– vibration bands were determined by measuring the MAEC films via *FT*-i.r. (Model RFX-65, Analect Co., USA). The degree of substitution by maleyl groups was determined by elementary analysis.

Eu_2O_3 (0.1 g), which was a spectrum-pure reagent, was dissolved in concentrated hydrochloric acid and then evaporated to dryness. Needle-like $EuCl_3{\cdot}2H_2O$ crystals were obtained when ethanol was added. The solution of $EuCl_3$ in ethanol was mixed with 200 ml MAEC/THF solution (5 wt.%) and stirred at room temperature for 30 h so that Eu^{3+} formed complexes with the –COOH group of the MAEC. The solution was poured into distilled water and the product was precipitated. After being washed and dried, the product was re-dissolved and precipitated twice and finally dried. The Eu content of the MAEC was assumed to be equal to the amount added.

MAEC was dissolved in a measured amount of acetic acid (AA) at room temperature and the solution was sealed into test tubes. The solution was heated at 40°C until it became homogeneous and then it was matured at room temperature for at least 48 h.

An Abbé refractometer was used to measure the refractive index of the solution for determining the critical concentration of the formation of liquid crystalline phase, C_{1*}, and that of total disappearance of the isotropic phase in the solution, C_{2*}. The formation of the liquid crystalline phase in the solution and the mesophase textures were also observed by a polarizing microscope (Leitz, Orthoplan-Pol, Germany).

The solutions were put onto quartz glass slides to form solution films with thicknesses of 30–50 nm. The fluorescent spectra were measured by a fluorescence spectrophotometer (Model 970MC, Shanghai No. 3 Analytical Instrument Factory, Shanghai, China). In the measurements, the plane of the quartz slide was held at an angle of 50° to the exciting beam.

RESULTS AND DISCUSSION

Lyotropic liquid crystalline properties of MAEC/AA solutions

The reaction of maleic anhydride with hydroxyl groups on EC chains can be characterized by infrared spectra. From infrared spectra, it can be observed that the maleic acid ester group is present on the polymer chains after the esterification reaction of the EC with maleic anhydride (*Figure 1*). Two new vibration bands at 1645 and 1735 cm^{-1}, which are attributed to the vibration of the –C=C– and –C=O– groups, appear in the i.r. spectrum of the product. The molecular structure of MAEC is shown in *Figure 2*.

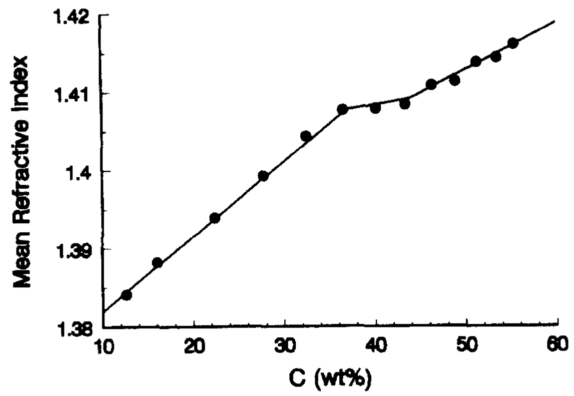


Figure 3 A plot of mean refractive index *versus* the concentration of MAEC ($\alpha = 0.28$)/AA solutions at 30°C

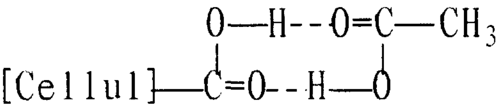
Figure 4 Polarized optical micrograph of the MAEC ($\alpha = 0.28$)/AA liquid crystalline solution, $C = 43.4$ wt.%, 30°C

Table 1 The values of C_{1*} and C_{2*} for MAEC/AA solutions with differenct D.S.

D.S. for maleyl (α)	C_{1*} (wt.%)	C_{2*} (wt.%)
0.28	37	44
0.17	41	49
0.12	42	51

The phase transformation from isotropic to anisotropic phase of the solutions can be determined by refractometry, and the critical concentration of the phase transformation can be measured from the plot of the mean refractive index *versus* the concentration[10]. *Figure 3* gives a plot of the mean refractive index *versus* the concentration of the MAEC/AA solutions, in which the D.S. for maleyl groups in the MAEC (α) is 0.28. It can be seen from *Figure 3*, and by observations with a polarizing microscope, that the solution is isotropic when the concentration is lower than 37 wt.% and completely anisotropic when the concentration is higher than 44 wt.%. The isotropic phase and the liquid crystalline phase coexist in the solution in the concentration of range 37 to 44 wt.%. *Figure 4* is a polarized optical micrograph of the MAEC/AA liquid crystalline solution and the mesophase texture is totally the same as that of other cellulose derivative cholesteric liquid crystalline solutions. The liquid crystalline phase shows vivid colours when the concentration is higher than 44 wt.%, which means that the liquid crystalline phase selectively reflects visible light. This is one of the typical features of cholesteric liquid crystals and it is suggested, therefore, that the liquid crystalline phase in the MAEC/AA solutions is cholesteric.

MAEC/AA solutions in which the MAEC has different D.S. for maleyl show similar behaviour. The liquid crystalline phase is formed when the concentration is higher than a critical value. *Table 1* gives the values of the critical concentration of the MAEC/AA solutions, C_{1*} and C_{2*}. With increasing D.S. for maleyl of MAEC, the critical concentration C_{1*} decreases, which means that ability to form the liquid crystalline phase in the solution is increased. The formation of the liquid crystalline phase in the lyotropic liquid crystals is concerned with the molecular interactions in the system[11]. The polymers with the stronger interactions between polymer chains and between the polymer chain and the solvent molecule more easily form an ordered arrangement and, consequently, they have a higher ability to form a liquid crystalline phase and the critical concentration at which the liquid crystalline phase begins to appear in the solution is lower. The critical concentration of liquid crystalline solutions of cellulose derivatives decreases with increasing molecular interactions between polymer chains and solvent molecules[12]. There is a –COOH group on MAEC chains when part of the –OH group on the EC chains is substituted and hydrogen bonds C=O···HO may be formed between the polymer chains and solvent molecules in the solution, which is shown as follows:



$$\begin{array}{l} \qquad\qquad\;\; \mathrm{O{-}H{\cdots}O{=}C{-}CH_3} \\ \mathrm{[Cellul]{-}C{=}O{\cdots}H{-}O} \end{array}$$

The hydrogen bonding interaction between two carboxyl groups to form a doubly hydrogen bonded cyclic system is energetically much more stable than that between carboxyl and alcoholic hydroxyl. Hence, MAEC should be dissolved by acetic acid through formation of cyclic hydrogen bonding complexes between the acetic acid and the maleyl carboxyl groups. In EC polymer chains, the degree of substitution by ethyl is 2.09. The ability of the formation of hydrogen bonding will increase with increasing amounts of –COOH groups on polymer chains, which results in an increase in the ability to form the liquid crystalline phase in the system and a decrease of the critical concentration at which the liquid crystalline phase begins to appear.

Analysis of fluorescent spectra

Eu^{3+} has a strong fluorescence and its fluorescent spectrum is influenced by the molecular interaction. *Figure 5* shows the fluorescent spectra of the MAEC/AA/$EuCl_3$ solution. MAEC and AA have no fluorescent behaviour in the region of 550–650 nm, but Eu^{3+} shows fluorescence. It has been observed that when the exciting wavelength is 394 nm, the solution produces an orange-red light in its emission spectrum. In *Figure 5B* there are two peaks located at wavelengths of 591 and 613 nm, respectively. The emission peak at 591 nm corresponds to the $^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+}, which is a magnetic dipole transition and is insensitive to the variation of the crystalline field of the complexes. The emission peak at 613 nm corresponds to the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}, which is an electric dipole transition and is sensitive to the variation of the crystalline field of the complexes. Therefore, the intensity of the peak at 613 nm is changed with the variation in the structure of $Eu(L_4)Cl_3$ but of the peak at 591 nm is not[13].

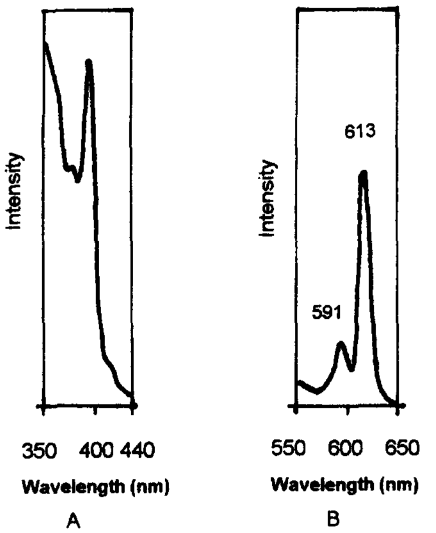


Figure 5 Fluorescent spectra of the MAEC ($\alpha = 0.28$)/AA solution with Eu^{3+}, $C = 10$ wt.%. (A) Excitation spectrum, $\lambda_{em} = 613$ nm and (B) emission spectrum, $\lambda_{em} = 394$ nm

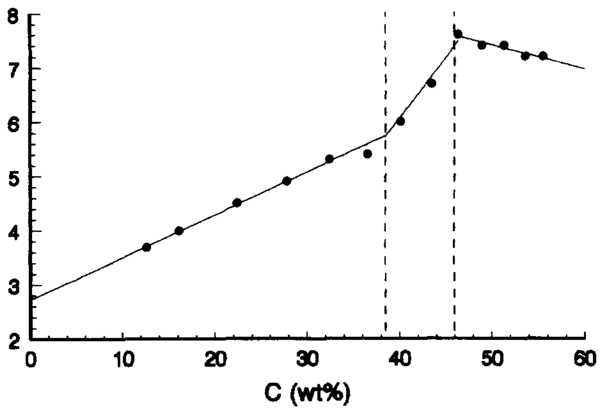


Figure 6 A plot of the R value *versus* the concentration of the MAEC ($\alpha = 0.28$)/AA solutions at 30°C

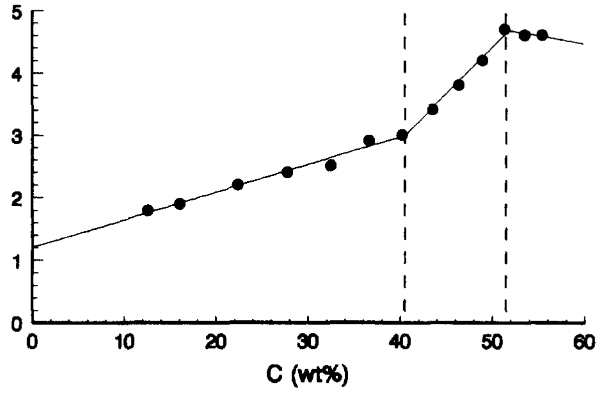


Figure 7 A plot of the R value *versus* the concentration of the MAEC ($\alpha = 0.17$)/AA solutions at 30°C

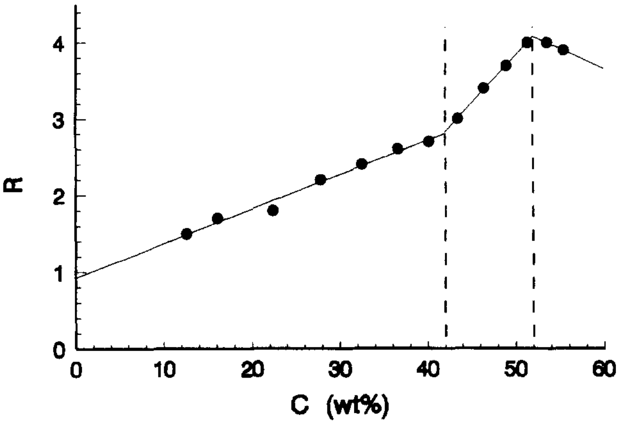


Figure 8 A plot of the R value *versus* the concentration of the MAEC ($\alpha = 0.12$)/AA solutions at 30°C

Eu^{3+} can form complexes with the –COOH group, and the intensity of the emission peak at 613 nm in fluorescent spectra is influenced by the variation in the Eu^{3+} complex structures. Ligands of small molecules can form symmetric complex structures with Eu^{3+} and polymeric ligands can form asymmetric complexes with Eu^{3+}. The fluorescent intensity of the complex with polymeric ligands is stronger than that with small molecular ligands when the number of ligands is constant. Therefore, the intensity of the emission peak at 613 nm decreases with increasing small molecular ligands, but increases with increasing polymeric ligands. The variation of the intensity of the emission peak at 613 nm reflects the variation in the structure of the Eu^{3+} complex with the –COOH group on polymer chains and of small molecules. The ratio of the fluorescent intensity of the emission peaks at 613 and 591 nm, $R = I_{613}/I_{591}$, can be used to characterize the structure of Eu^{3+} complexes, because the intensity of the emission peak at 591 nm is not changed with the variation of the Eu^{3+} complex structure. The small molecular ligands decrease and the polymeric ligands increase with increasing the value of R. The interactions between polymer chains will be strengthened when the Eu^{3+} complexes with –COOH groups on different polymer chains are formed. Consequently, the variation of R actually reflects the molecular interactions between polymer chains in the solutions.

Figure 6 is a plot of the R value *versus* the concentration of the MAEC/AA solutions. It can be seen that extrapolation of the relationship between R and the concentration back to $C = 0$ in *Figure 6* gives the fluorescence when europium is complexed only with the solvent acetic acid. The value of R in the binary complex (cation/polymer) is smaller than that in the ternary complex (cation/polymer/solvent), which confirms that the fluorescent intensity of the complex with polymeric ligands is stronger than that with small molecular ligands when the number of ligands is constant.

The variation of R with the concentration in *Figure 6* can be divided into three regions, and it is a linear variation in each region but the slope is different in different regions. The value of R increases with increasing concentration in the low concentration region, but it increases more quickly in the higher concentration region. When the concentration is very high, it decreases with further increasing concentration. Therefore, two critical concentrations C_1 and C_2 exist, at which the slope of plot of R *versus* the concentration is changed. Other MAEC/AA solutions with different D.S. for maleyl (α) in MAEC exhibit similar behaviour (*Figures 7 and 8*). *Table 2* gives the concentrations C_1 and C_2 of the MAEC/AA solutions with different α values obtained from *Figures 6–8*. It can be seen that C_1 and C_2 decrease with increasing α value. It has been found by comparison of the data in *Table 2* with those in *Table 1* that C_1 and C_2 are nearly equal to C_{1*} and C_{2*}, which means that C_1 and C_2 also represent the critical concentrations at which the liquid

Table 2 The critical concentration for MAEC/AA solutions (via fluorescent measurement)

D.S. for maleyl (α)	C_1 (wt.%)	C_2 (wt.%)
0.28	38.5	46.0
0.17	40.5	51.5
0.12	42.0	52.0

crystalline phase begins to appear, and the isotropic phase totally disappears, respectively. It is suggested that the variation of the phase transformation is associated with the molecular interactions between polymer chains and the three regions in *Figures 6–8* correspond to the isotropic state, the biphasic state and the liquid crystalline state.

As we know, the solution is isotropic in the low concentration region and Eu^{3+} can be complexed with –COOH both on polymer chains and in AA molecules. There is an equilibrium between Eu^{3+} complexing with AA molecules and polymer chains:

$$[\text{Cellul}] - \text{COOH} \rightarrow \text{Eu}^{3+} \Leftrightarrow \text{CH3COOH} \rightarrow \text{Eu}^{3+}$$

The polymer chains increase in the MAEC/AA solutions with increasing concentration, and the number of small molecular ligands around Eu^{3+} decreases but the number of polymeric ligands increases. Therefore, the fluorescent intensity at 613 nm and the value of R increase with increasing concentration.

When the concentration is increased to C_{1*}, the liquid crystalline phase begins to appear in the solution and the MAEC polymer chains begin to transform from a disordered state to an ordered one. In the liquid crystalline phase, the polymer chains have orientation and ordering arrangements and it is easy for –COOH groups on different polymer chains to complex with the same Eu^{3+}. Then, the polymeric ligands in Eu^{3+} complexes are much more in the liquid crystalline state than in the isotropic phase, because the polymer chains are more closely packed in the liquid crystalline phase. The turning point in the curves of R *versus* the concentration appears at the concentration of C_{1*}. *Figures 6–8* show that R increases more quickly with increasing concentration when the concentration is higher than C_1. This suggests that the molecular interactions between polymer chains are enhanced after the liquid crystalline phase appears in the solution, which has been confirmed by the enhancement of the hydrogen bonding between polymer chains when the liquid crystalline phase appears in ethyl-cyanoethyl cellulose/dichloroacetic acid solutions[3].

When the concentration is increased to C_{2*}, the isotropic phase in the solution totally disappears. Another turning point in the curves of R *versus* concentration appears and the R increases with increasing concentration to the maximum. When the concentration is further increased, R begins to decrease, which means that the polymeric ligands in Eu^{3+} complexes decrease and small molecular ligands increase. Therefore, the complexing interactions between polymer chains are weakened with increasing concentration after C_{2*}. The density of the polymer chains in the liquid crystalline phase is unchanged with increasing concentration when the solution is biphasic ($C < C_{2*}$) but increases when the solution is totally anisotropic ($C > C_{2*}$). Consequently, the space for the movement of polymer chains in the liquid crystalline phase becomes smaller. The formation of Eu^{3+} complexes with –COOH on polymer chains is restrained by steric hindrance and lack of the suitable geometry to form the complexes of Eu^{3+} with the polymer chains. Therefore, the number of polymeric ligands in Eu^{3+} complexes decreases with further increasing concentration, which means the molecular interactions between polymer chains are weakened, and the small molecular ligands increase.

We know that the driving force to form a liquid crystalline phase may be the molecular interactions or the rigidity of the chains or both. In the MAEC/AA system, the molecular interactions, that is, the complexing interactions, between polymer chains play a very important role in the formation of the liquid crystalline phase when the concentration is lower than C_{2*}, but the rigidity of the polymer chains plays a principal role when the concentration is higher than C_{2*}.

CONCLUSIONS

MAEC can form cholesteric liquid crystalline solutions with AA. The extent of C=O···H–O hydrogen bonding formation between polymer chains and solvent molecules increases with increasing D.S. for maleyl on polymer chains and the liquid crystalline phase is formed more easily in the system with more hydrogen bonding between polymer chains and the solvent.

The variation of the complexing interactions between polymer chains can be reflected by the variation of the fluorescent spectra when the rare-earth metal ion Eu^{3+} is used as a fluorescence probe. The formation of the liquid crystalline phase in the solution is associated with the enhancement of molecular interactions between polymer chains when the concentration is lower than C_{2*}. The critical concentration of the phase transformation, C_{1*} and C_{2*}, can be obtained from the curves of the $R = I_{613}/I_{591}$ *versus* the concentration.

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