

Influence of Thermal History on the Formation of Liquid Crystalline Phase of Hydroxyethyl Cellulose Acetate

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ABSTRACT: The influence of thermal history on the formation of HECA liquid crystalline phase was studied by DSC. It was found that the degree of ordering in the liquid crystalline phase was heterogeneous, and the multiphase transformation appears when the liquid crystalline phase transformed to the isotropic one. When HECA was annealed in the liquid crystalline state, the parts with the lower degree of ordering could transform to ones with the higher degree of ordering, and the temperature and the enthalpy of the phase transformation from the liquid crystalline phase to the isotropic phase increased. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1137–1142, 1998

Key words: hydroxyethyl cellulose acetate; thermal history; formation of liquid crystalline phase; degree of ordering; heterogeneous

INTRODUCTION

Cellulose and its derivatives are semirigid chain polymers and can be dissolved in many organic or inorganic solvents to form lyotropic liquid crystals.¹ Some of cellulose derivatives can form both lyotropic liquid crystals and thermotropic liquid crystals.² Hydroxyethyl cellulose acetate (HECA) is a cellulose derivative that can form both lyotropic liquid crystals³ and thermotropic liquid crystals.⁴

The formation of liquid crystalline phases is influenced by both the molecular structure and the thermal history. It has been reported that the kinetic ability of the formation of liquid crystalline phases of HECA is influenced by its molecu-

lar weight.⁴ Feijoo et al. have reported that the phase transformation from the liquid crystalline phase to the isotropic phase varies with the variation of the thermal history.⁵ The thermal history, therefore, is one of the important factors influencing the formation of the liquid crystalline phase and its structure. In this report, the influence of thermal history on the formation of the HECA liquid crystalline phase is studied by DSC, and the structure of the liquid crystalline phase is also discussed.

EXPERIMENTAL

The preparation of hydroxyethyl cellulose acetate (HECA) has been described elsewhere,⁴ and its molecular formula is shown in Figure 1.

The molecular weight of HECA, measured by gel permeation chromatography (GPC) (Waters, ALC/244/GPC), calibrated by standard polystyrene, was $M_n = 6.5 \times 10^4$. The degree of ether

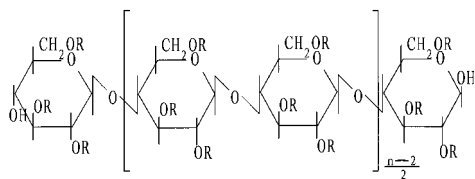
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R = H (0.1), CH₂CH₂OOCCH₃ (1.65), CH₃CO (1.25)

Figure 1 Molecular formula of HECA.

substitution of hydroxyethyl was about 1.65, and of ester substitution of acetyl was about 2.9.

The thermal treatment and the measurements of the phase transformation from the liquid crystalline phase to the isotropic one for HECA were carried out by using a differential scanning calorimeter (DSC) (Perkin-Elmer DSC-2C). The weight of specimen was 17.5 mg, and nitrogen was used in the measurements to protect the specimen from oxidation. Temperature and energy were calibrated with a standard substance—indium. First, the thermal history of HECA samples had to be eliminated before thermal treatment and DSC measurement. The sample of HECA was heated at 80 K/min to 473 K, and held at this temperature for 5 min. Subsequently, it was quickly cooled to 323 K, and the sample without thermal history was obtained. Then, the sample of HECA was thermally treated with different procedures and finally, the phase transformation from the liquid crystalline phase to the isotropic one was measured by DSC.

RESULTS AND DISCUSSION

HECA becomes a liquid crystalline fluid in the temperature region between 400 to 460 K. Figure 2 shows the DSC curves of HECA on both heating and cooling. It is clear that a phase transformation occurs when HECA is heated and subsequently cooled. HECA is a liquid crystalline glass at room temperature, which is confirmed by X-ray diffraction.⁴ With increasing temperature, HECA transforms from a liquid crystalline glass to a liquid crystalline fluid at about 400 K and to the isotropic phase from 420 to 460 K [Fig. 2(a)]. It is a totally isotropic fluid at temperatures above 460 K. On cooling, the phase transformation of HECA from isotropic fluid to liquid crystalline begins at about 430 K [Fig. 2(b)]. From observation with a polarizing microscope, the mesophase texture shows that the HECA liquid crystalline phase is a

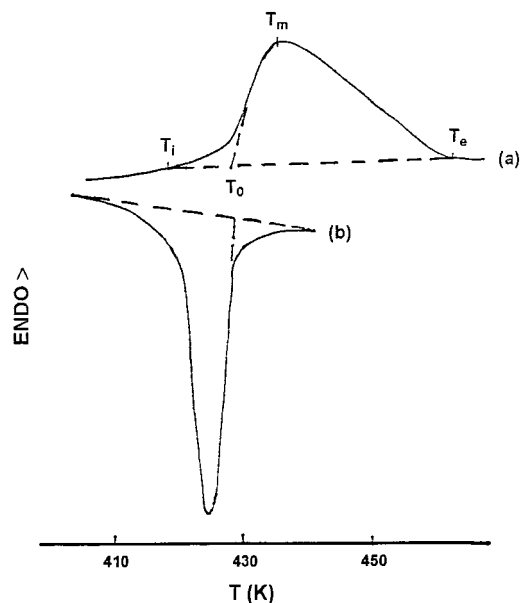


Figure 2 DSC curves of HECA on heating (a) and cooling (b) at 10 K/min.

cholesteric liquid crystal (Fig. 3), which is also confirmed by X-ray diffraction.⁴

To understand the relationship between thermal history and the formation of the HECA liquid crystalline phase, four procedures were suggested to thermally treat HECA samples and, subsequently, their phase transformation was measured.

In Procedure One, HECA was heated at 40 K/min to 428 K, and subsequently annealed at this temperature for different periods, from 2 to 300 min. Finally, it was heated again from the annealing temperature to 473 K at 10 K/min and the DSC curves were recorded (Fig. 4). When

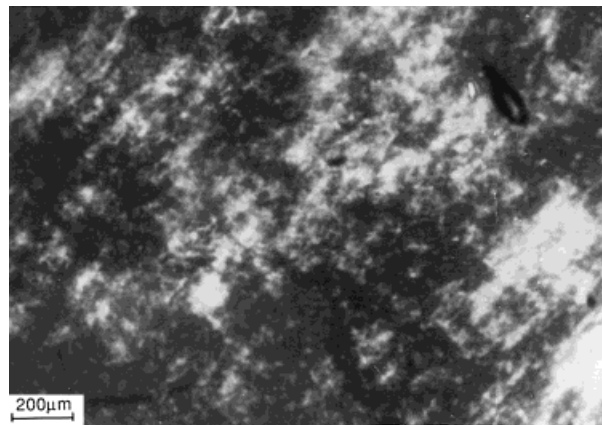


Figure 3 Polarizing micrograph of HECA at 415 K.

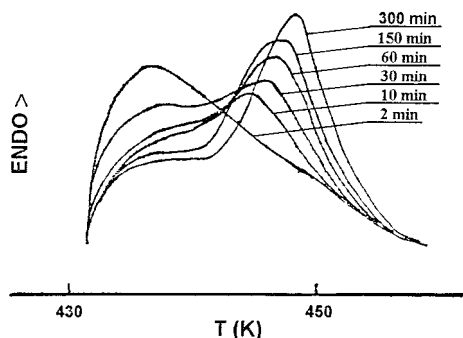


Figure 4 DSC curves of HECA in Procedure One.

HECA was annealed at 428 K, a liquid crystalline phase was formed from the liquid crystalline glass. The DSC curves in Figure 3 indicate that the phase transformation of HECA from a liquid crystalline fluid to the isotropic phase is closely related to the annealing period. There is only one peak at about 435 K on the DSC curve when annealing time is 2 min. When annealing time is 10 min, however, another peak appears on the DSC curve at about 442 K, and this peak increases and shifts to higher temperature with increasing annealing time, which means that a multiphase transformation appears. The original peak at about 435 K, however, decreases with annealing period. Table I lists the data of the phase transformation of HECA from the liquid crystalline to isotropic after it is thermally treated with Procedure One.

In general, it is believed that the multiphase transformation implies heterogeneity in structure or degree of ordering in the system. The measurements of X-ray diffraction indicate that the structure of the liquid crystalline phase is unchanged with increasing annealing time (Fig. 5). There is a

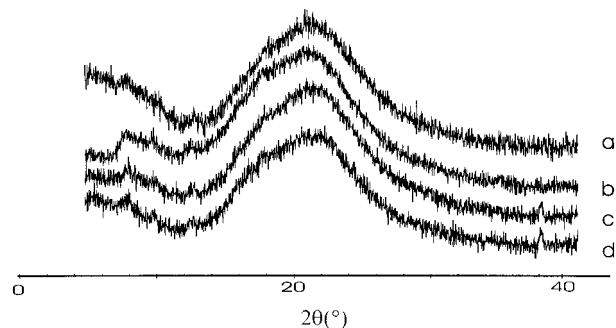


Figure 5 Spectra of X-ray diffraction of HECA annealed at 428 K for (a) 0 min, (b) 30 min, (c) 120 min, and (d) 1440 min.

diffraction peak of the cholesteric phase at the diffraction angle of about $2\theta = 9^\circ$, and it does not shift with increasing the annealing period. It is suggested, consequently, that multiphase transformation results from heterogeneity in degree of ordering of the liquid crystalline phase instead of the difference of the liquid crystalline structure. Appearance of two peaks on DSC curves in Figure 4 suggests the existence of the liquid crystalline phases with different degrees of ordering. The parts with the lower degree of ordering transform to the isotropic phase at the lower temperature, and those with the higher degree of ordering transform to the isotropic fluid at the higher temperature. In Table I, ΔH_l decreases and ΔH_h increases with increasing annealing time, although the total enthalpy of the phase transformation $\Delta H_l + \Delta H_h$ is nearly unchanged. The increase of the peak at the higher temperature and the decrease of the peak at the lower temperature suggest that the liquid crystalline phase with the lower degree of ordering transforms to that with the higher degree of ordering with the annealing

Table I The Phase Transformation Temperatures and Enthalpies of HECA from Liquid Crystalline Fluid to the Isotropic after Thermal Treatment with Procedure One

Period (min)	T_l^a (K)	T_h^b (K)	ΔH_l (cal/g)	ΔH_h (cal/g)	$\Delta H_l + \Delta H_h$ (cal/g)
2	435.16		0.99		0.99
10	435.46	442.05	0.40	0.64	1.06
30	435.8	444.8	0.40	0.64	1.06
60	436.4	445.67	0.47	0.65	1.12
150	435.5	447.16	0.37	0.75	1.12
300	435.8	447.5	0.28	0.64	0.92

^a l represents the peak at the lower temperature region.

^b h represents the peak at the higher temperature region.

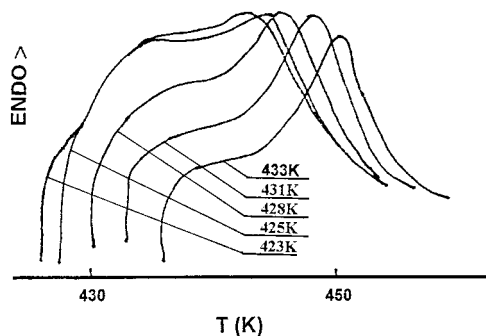


Figure 6 DSC curves of HECA in Procedure Two.

period when HECA is annealed in the liquid crystalline state. But the fraction of the liquid crystalline phase in the system is unchanged with time when the annealing temperature is unchanged. The shift of T_h toward the high-temperature direction suggests that the degree of ordering in the liquid crystalline phase also increases with increasing annealing time.

In Procedure Two, HECA was heated at 40 K/min to different annealing temperatures, from 423 to 433 K, and subsequently annealed at each temperature for 1 h. Then, it was heated again from the annealing temperature to 472 K at 10 K/min, and the DSC curves were recorded (Fig. 6). It can be seen that there are double peaks on DSC curves after HECA is annealed at the lower temperature, in which it transforms from liquid crystalline glass to liquid crystalline fluid. The peak at the lower temperature decreases with increasing annealing temperature, and finally disappears when annealing temperature is above 430 K. The peak at the higher temperature increases and shifts in the high temperature direction. Consequently, the degree of ordering in the liquid crystalline phase increases with increasing annealing temperature. Table II presents the data

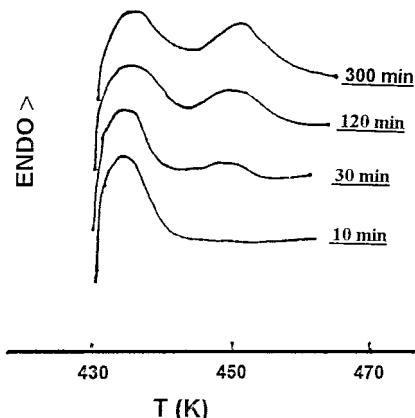


Figure 7 DSC curves of HECA in Procedure Three.

of the phase transformation of HECA from the liquid crystalline phase to the isotropic one after it is annealed at different temperatures. The enthalpy of the phase transformation in Figure 6 decreases with increasing the annealing temperature, which implies a decrease of the fraction of the liquid crystalline phase in the system. Moreover, the decrease of ΔH_l with increasing the annealing temperature is much faster than that of ΔH_h , which demonstrates that the degree of ordering in the liquid crystalline phase increases with increasing the annealing temperature.

In Procedure Three, HECA was heated quickly to 473 K and subsequently cooled to 428 K at 10 K/min. HECA was annealed at 428 K for different periods and then heated again to 473 K at 10 K/min and DSC curves were recorded (Fig. 7). In this procedure, HECA is transformed from the isotropic phase to the liquid crystalline phase in annealing. When annealing time is 10 min, there is only one peak at about 435 K on the DSC curve, where the phase transformation from the liquid crystalline phase to the isotropic one occurs.

Table II The Phase Transformation Temperatures and Enthalpies of HECA from Liquid Crystalline Fluid to Isotropic after Thermal Treatment with Procedure Two

T (K)	T_l^a (K)	T_h^b (K)	ΔH_l (cal/g)	ΔH_h (cal/g)	$\Delta H_l + \Delta H_h$ (cal/g)
423	433.0	442.5	0.74	0.68	1.42
425	435.5	443.9	0.58	0.69	1.27
428	436.4	445.7	0.47	0.65	1.12
431		448.1		0.51	0.51
433		450.0		0.45	0.45

^a l represents the peak at the lower temperature region.

^b h represents the peak at the higher temperature region.

Table III The Phase Transformation Temperatures and Enthalpies of HECA from Liquid Crystalline Fluid to Isotropic after Thermal Treatment with Procedure Three

Period (min)	T_l^a (K)	T_h^b (K)	ΔH_l (cal/g)	ΔH_h (cal/g)	$\Delta H_l + \Delta H_h$ (cal/g)
10	434.4		0.42		0.42
30	434.9	447.9	0.44	0.11	0.55
120	435.2	449.6	0.41	0.26	0.67
300	435.5	450.8	0.37	0.31	0.68

^a l represents the peak at the lower temperature region.

^b h represents the peak at the higher temperature region.

When the annealing time is 30 min, however, a new peak at about 448 K appears on the DSC curve, and the enthalpy ΔH_h increases with increasing the annealing time (Table III). In other words, the phase transformation from the liquid crystalline phase to the isotropic one changes from single to double with increasing the annealing time. The double peaks on the DSC curves indicate that the degree of ordering is heterogeneous in the liquid crystalline phase formed in annealing.

From Table III it can be seen that when the annealing time is longer than 120 min, the total enthalpy of the phase transformation $\Delta H_l + \Delta H_h$ is nearly unchanged with annealing time. The enthalpy of the phase transformation at the lower temperature ΔH_l decreases, and that at the higher temperature ΔH_h increases with increasing the annealing time, which demonstrates that the liquid crystalline phase with the lower degree of ordering transforms to one with the higher degree of ordering in annealing. It can be concluded, therefore, that the liquid crystalline phase with the higher degree of ordering of HECA increases with increasing annealing time.

Feijoo et al. have observed the increase of T_i and ΔH_i when the sample is thermally treated in the liquid crystalline state,⁵ and they have suggested that annealing in the nematic state results in the decrease of defects in the liquid crystalline phase and domains become larger and larger.⁶ The results in Procedures One to Three not only demonstrate the increase of the phase transformation temperature and enthalpy from the liquid crystalline phase to the isotropic one, but also directly reveal the heterogeneity of the degree of ordering in the liquid crystalline phase.

In Procedure Four, HECA was quickly heated from room temperature to 428 K, and subsequently annealed at 428 K for 1 h. Then, the

sample was heated again from 428 to 473 K at 10 K/min, and the DSC curve was recorded [Fig. 8(a)]. If the sample was heated at 10 K/min to 473 K, after it was cooled from 428 K quickly to 323 K, another DSC curve was recorded [Fig. 8(b)]. On the DSC curves in Figure 8, T_L , T_M , and T_H represent the peaks at the low, middle, and high temperatures, which are 427.4, 436.0, and 446.0 K, respectively. In Figure 8, the parts of T_M and T_H on curve b are totally overlapped with curve a. This suggests that the parts of T_M and T_H are responsible for the phase transformation from the liquid crystalline phases, which are formed in annealing at 428 K, to the isotropic phase. The part of T_L is attributed to the phase transformation of the liquid crystalline phase, formed in quick cooling from 428 to 323 K, in which the degree of ordering is lower than that formed at 428 K. Consequently, the temperature of the formation of liquid crystalline phases is higher, the degree of ordering in the liquid crystalline phase is higher, and the temperature of the phase transformation to the isotropic phase is higher.

CONCLUSIONS

The formation of a HECA liquid crystalline phase is dependent on its thermal history, and the de-

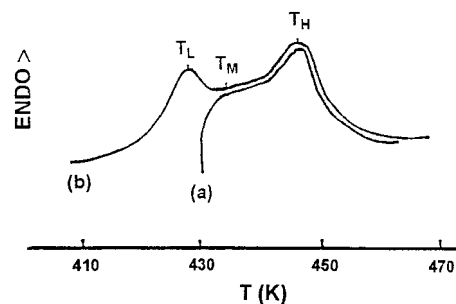


Figure 8 DSC curves of HECA in Procedure Four.

gree of ordering is heterogeneous in the liquid crystalline phase. In the phase transformation from the liquid crystalline glass to the liquid crystalline fluid, or from the isotropic phase to the liquid crystalline one, the part with the lower degree of ordering gradually changes to that with the higher degree of ordering with increasing annealing time or annealing temperature when HECA is annealed in the liquid crystalline state. The liquid crystalline phase with the higher degree of ordering transforms to the isotropic phase at the higher temperature.

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