Thermotropic Behavior of Hydroxyethyl Cellulose Acetate

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SYNOPSIS

Thermotropic behavior of hydroxyethyl cellulose acetate (HECA) was studied by polarizing microscopy, DSC, and X-ray diffraction. It was found that HECA was an anisotropic liquid between the temperature from 130 to 185°C on heating, and when the temperature was over 185°C, it became isotropic. In cooling, however, mesophase began to form at about 165°C. The transformation temperature decreased with decreasing molecular weight and the temperature region of transformation decreased with decreasing the distribution of the molecular weight for HECA. The kinetic ability of transformation appeared the maximum with molecular weight. The HECA liquid crystal is cholesteric and the distance between layers of ordered molecular chains was enlarged when HECA was transformed from liquid crystalline glass to the liquid crystalline state. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Cellulose and many of its derivatives can form liquid crystals in appropriate solvents[1] and show lyotropic behaviors. Thermotropic cellulose derivatives have also been prepared by introducing some appropriate flexible substituents. Derivatives of hydroxypropyl cellulose, e.g., can form thermotropic liquid crystals.[2-4] Some cellulose esters and ethers with long flexible substituents have also been found to be thermotropic[5] and form cholesteric liquid crystals. Recently, the cellulose derivative that can form the smectic mesophase has been reported.[6] However, some of questions about thermotropic cellulose derivatives remain unanswered and the problems such as the effect of molecular weight and distribution of molecular weight on thermotropics and the role of the substituent in the formation of the thermotropic mesophase are still obscure. In this report, thermotropic hydroxyethyl cellulose acetate (HECA) is prepared and its thermotropic behaviors are studied. The effect of molecular weight on thermotropics is also discussed.

EXPERIMENTAL

Preparation and Fractionation of HECA

Hydroxyethyl cellulose with the degree of ether substitution of 1.5–1.8 was used as a starting material to prepare HECA. The preparation of HECA is as follows: 48 g zinc chloride was dissolved in 192 mL acetic acid. Then, 24 g hydroxyethyl cellulose was added and stirred mildly at 50°C for 1.5 h. Finally, 240 mL acetic anhydride was added to the solution, and the reaction was carried out at 50°C for 24 h under stirring. Then, the mixture was poured into a large amount of distilled water, and the precipitate was filtered and repeatedly washed with fresh distilled water until the pH value was about 6. The absence of the OH absorption band in the IR spectra confirms complete etherification and the degree of sterification, calculated from the content of oxygen of 2.6–3.0.

HECA was fractionated to three fractions by fractional precipitation of the whole polymer with acetone as a solvent and petroleum ether as a precipitant. The molecular weight and the distribution of molecular weight of HECA was measured by a gel permeation chromatograph (GPC) (Waters ALC/244/GPC), calibrated by standard polysty-

Table I   Molecular Weight and Oxygen Content of HECA

Sample	0#	1#	2#	3#
$\bar{M}_n \times 10^4$	6.5	10.0	8.8	3.9
$\bar{M}_w \times 10^4$	15.1	16.2	11.8	6.7
$\bar{M}_w/\bar{M}_n$	2.338	1.618	1.340	1.728
0%	42.77	42.72	42.87	42.65

Sample 0# is the HECA without fractionating.

rene. The content of oxygen of HECA was measured by elementary analysis. The molecular weight, the distribution of molecular weight, and the content of oxygen of HECA are given in Table I. The same content of oxygen demonstrates that the degree of ester substitution is same for all fractions of HECA.

Thermotropy and Phase Transformation of HECA

The thermal properties of HECA were studied by differential scanning calorimetry (DSC) (Perkin-Elmer DSC-2C) and polarizing microscopy. The phase transformation was observed when heating and cooling by a polarizing microscope with a hot stage (Leitz, ORTHOPLAN-POL). A Perkin-Elmer DSC-2C was used to measure the phase-transformation temperatures and transformation enthalpy at the heating and cooling rate of 20 K/min. The variation of structure of HECA was measured by an X-ray spectrometer (D/max-1200, RIGAKU) on heating.

RESULTS AND DISCUSSION

HECA is a thermotropic material. Figure 1 shows its DSC thermograms. On heating, an endothermic peak appears from 130 to 160°C, and on cooling, an exothermic peak appears from 150 to 105°C. The same DSC thermograms were obtained in the second cycle and thereafter. This indicates that the phase transformation occurs in both heating and cooling. By observing under a polarizing microscope it can be found that the HECA is solid below 130°C. After the specimen is heated to 130°C, the HECA transforms from a solid to an anisotropic fluid and it totally becomes an isotropic fluid at about 185°C. When the specimen is cooled from the isotropic fluid, the mesophase begins to appear at about 165°C. These results demonstrate that the HECA is thermotropic and a liquid crystalline state exists in the temperature region from 130 to 185°C on heating

and it transforms to isotropic state gradually with increasing temperature. The endothermic peak in DSC thermogram on heating corresponds to this transformation.

HECA is first pressed into a thin film between two glass slides at about 180°C observed using a polarizing microscope. Then, the specimen is heated at 5 K/min on a hot stage and becomes an isotropic melt at 185°C. It is to be heated to 195°C and kept at this temperature for 5 min. Then, it is cooled at 1 K/min and the anisotropic phase appears at about 165°C. The transformation is finished at about 142°C. Mesophase textures do not vary with decreasing temperature from 142°C. Figure 2 gives the results observed using the polarizing microscope when the specimen is cooled from 195°C.

The isothermal transformation from isotropic to anisotropic phases of HECA can be observed using the polarizing microscope when the HECA is quickly cooled from 195°C to a given temperature. Figure 3 presents the variation of mesophase textures with time at 145°C. The formation of the mesophase is very fast when the transformation temperature is lower than 145°C. The mesophase texture does not vary with both temperature and time after it forms, even when temperature decreases to room temperature, i.e., the mesophase texture can be retained in the HECA solid state when it cooled from an isotropic melt. Therefore, the variation of mesophase textures observed under the polarizing microscope and the transformation peak in DSC thermograms demonstrate that there is only one transformation when HECA is cooled from an isotropic melt and that the solid state with liquid crystalline order is formed.
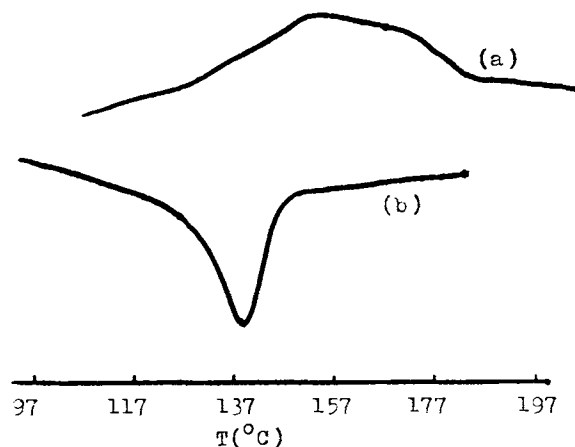

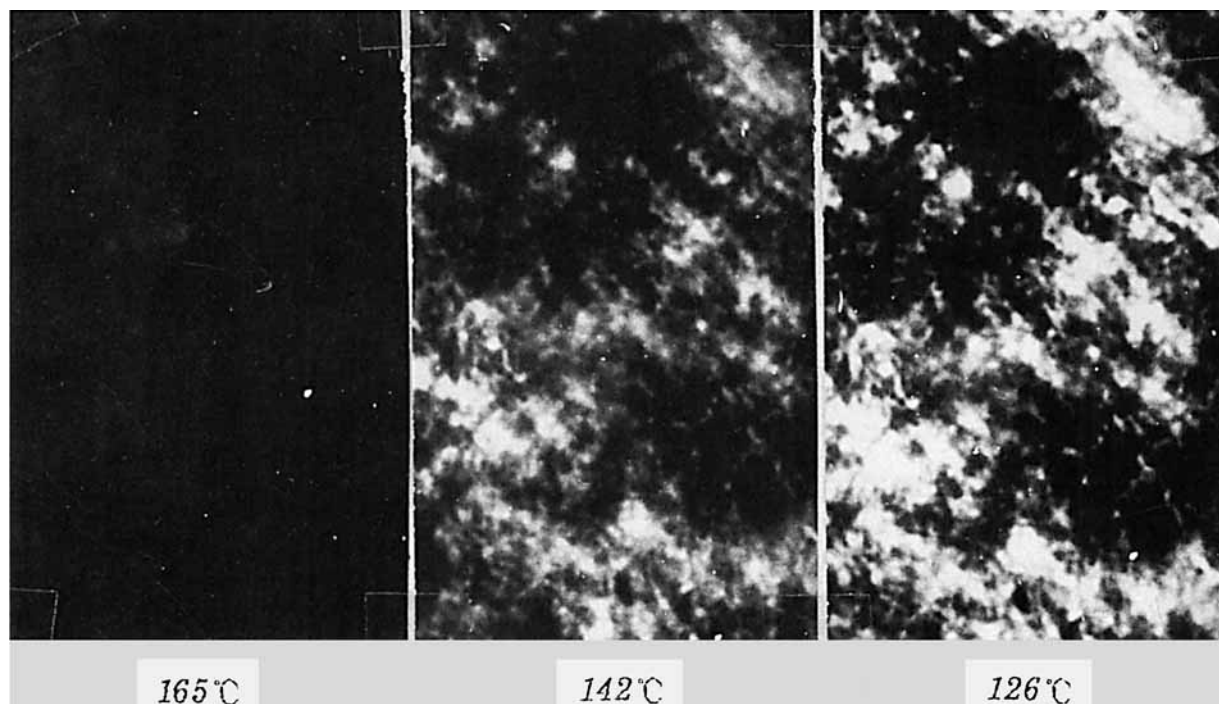**Figure 1**   The DSC thermograms of HECA on (a) heating and (b) cooling.

Figure 2 Polarized micrographs of HECA when cooling at 1 K/min from 195°C.

The molecular weight of HECA influences its thermotropics. HECA is fractionated to three fractions by fractional precipitation of the whole polymer with acetone as a solvent and petroleum ether as a precipitant. Figures 4 and 5 give DSC thermograms for every fraction on heating and cooling.
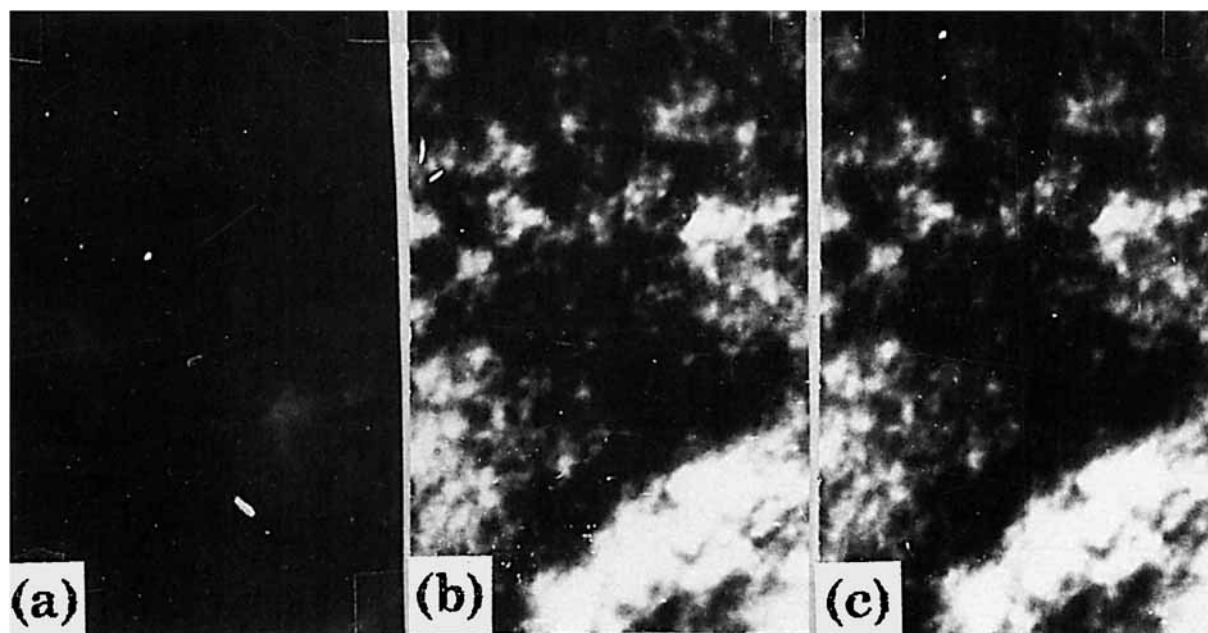

Figure 3 Polarized micrographs of HECA after quickly cooling from 195 to 145°C for (a) 0 min, (b) 3 min, and (c) 20 min.
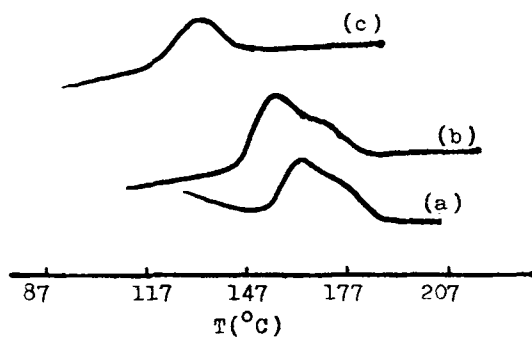
Figure 4 DSC thermograms of HECA with different molecular weights on heating: (a) specimen 1#, (b) specimen 2#, and (c) specimen 3#.

Table II   Transformation Temperatures and Enthalpy of HECA

Sample	0#	1#	2#	3#
T_{c-i} (°C)	153	163	155	131
T_{i-c} (°C)	138	150	147	127
ΔH (J/g)	4.10	3.64	5.23	2.01
ΔH^* (J/g)	−3.26	−3.56	−4.39	−2.18

The transformation temperature is the value at top of peak. T_{c-i}: transformation from mesophase to isotropic phase; T_{i-c}: transformation from isotropic phase to mesophase; ΔH: from mesophase to isotropic phase; ΔH^*: from isotropic phase to mesophase.

In comparison with the thermograms of HECA without fractionating in Figure 1, the transformation occurs in the temperature region of that without fractionating in Figure 1 and the temperature region of transformations for every fraction is narrow. These phenomena indicate that the transformation of HECA without fractionating is composed of transformations of all fractions with different molecular weights and the transformation of every fraction occurs at the specific temperature region. Therefore, the HECA with a wide polydispersity of molecular weight should have a wide transformation temperature region. It is also shown in Figures 4 and 5 that the transformation temperature increases with increasing molecular weight. The transformation temperatures and transformation enthalpy for all fractions are presented in Table II.
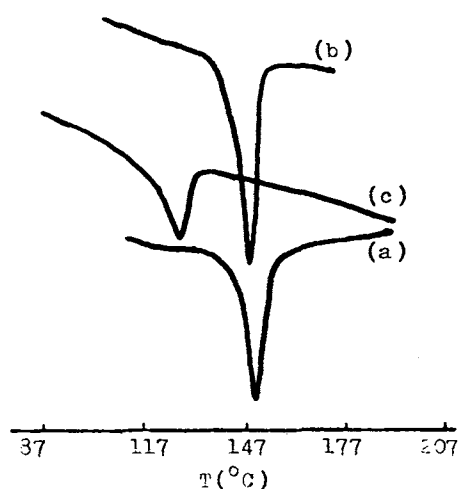

Figure 5 DSC thermograms of HECA with different molecular weights on cooling: (a) specimen 1#, (b) specimen 2#, and (c) specimen 3#.

The transformation enthalpy ΔH of the fraction with the middle molecular weight is largest in both heating and cooling. Jeziorny[7] suggested a method to evaluate the kinetic ability of crystallization, i.e., the kinetic ability of crystallization in nonisothermal crystallization is related with the cooling rate and crystallity. It increases with the crystallity in a constant cooling rate. Similarly, in the transformation from isotropic to anisotropic phases, the enthalpy ΔH is related to the fraction of transformation and reflects the level of kinetic ability of transformation in a constant cooling rate. Therefore, the values of ΔH in Table II imply that the kinetic ability of transformation becomes weaker when the molecular weight is too large or too small and the ability of the mesophase formation from the isotropic phase becomes smaller. HECA, with the middle molecular weight, has the maximum kinetic ability of the transformation from isotropic to anisotropic phases.

The changes of structures in the transformation can be revealed by X-ray diffraction. HECA is pressed into a plate at about 200°C and cooled to room temperature. Therefore, the specimen is a liquid crystalline glass and is placed into the hot stage in the X-ray spectrometer. Then, it is heated at 5 K/min to measuring temperatures and kept at these temperatures for 5 min, and, finally, the X-ray diffraction patterns are measured. The spectra of X-ray diffraction for HECA at different temperatures are presented in Figure 6. At room temperature, two diffraction peaks appear at the diffraction angle 2θ = 7.9–8.3° and 19.8–20.8°. The intensity of the peak at the higher diffraction angle decreases with increasing temperature, but that at the lower diffraction angle increases at temperatures below 150°C. When the temperature is 150°C, however, the latter also decreases with temperature and it almost disappears at about 180°C. The variation of the X-ray
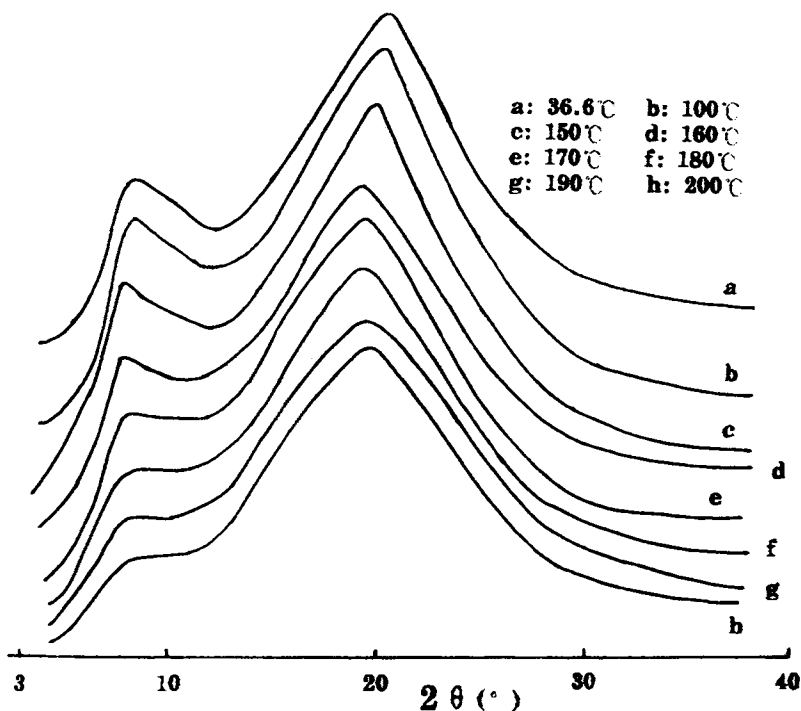
Figure 6 X-ray diffraction spectra of HECA (sample 0#) at different temperatures.

diffraction with temperature corresponds to the phase transformation known from the results of DSC and the polarizing microscopy. Consequently, the results from the X-ray diffraction suggest that the diffraction peak at the lower angle is related to the mesophase structures. Its intensity increases with increasing mesophase when HECA transforms from the solid to the liquid crystalline state and decreases with decreasing mesophase when HECA transforms from the mesophase to the isotropic phase, and, finally, the peak disappears when HECA becomes a wholly isotropic system. From the X-ray diffraction patterns, therefore, it is believed that the

HECA liquid crystal is cholesteric. The diffraction is attributed to the layers of ordered polymer chains at $2\theta = 7.8$–$8.3°$ and to the distance between polymer chains at $2\theta = 19.8$–$20.8°$.

Table III presents the X-ray diffraction data for HECA at different temperatures. The diffraction angle 2θ of the peak at the lower angle is $8.3°$ at the temperature below $150°C$ and does not vary with increasing temperature. When the specimen is heated to $150°C$, however, it shifts to $7.9°$ and nearly does not change again when temperature is further increased. This means that the interplanar distance increases from 1.0644 to 1.1182 nm when HECA

Table III   Diffraction Angles and Intensity of HECA at Different Temperatures

	T (°C)							
	36.6	100	150	160	170	180	190	200
Peak 1								
Angle 2θ (°)	8.3	8.35	7.9	8.1	8.1	8.0	7.8	8.1
Intensity (cps)	186	202	209	165	158	136	117	114
Peak 2								
Angle 2θ (°)	20.9	20.5	20.0	19.4	19.3	19.7	20.5	21.3
Intensity (cps)	327	305	342	294	290	278	264	255

transforms from liquid crystalline glass to the liquid crystalline state, while the diffraction angle shifts back to about 8.8° and the intensity of diffraction increases when HECA is cooled from 200 to 25°C, in which it transforms from an isotropic melt to an anisotropic one and, finally, to liquid crystalline glass. The results mentioned above suggest that the distance of layers of ordered polymer chains is smaller in liquid crystalline glass than that in the mesophase.

CONCLUSIONS

HECA is thermotropic and transforms from the solid to the liquid crystalline state at 130°C on heating. It becomes wholly isotropic at about 185°C and transforms from an isotropic melt to an anisotropic one at 165°C on cooling. The molecular weight and the distribution of molecular weight influence the thermotropics. The transformation temperature decreases with decreasing molecular weight and the transformation temperature region decreases with decreasing the polydispersity. The kinetic ability of the transformation decreases when the molecular weight is very high or very low. The aggregating

density of polymer chains in liquid crystalline glass is larger than that in liquid crystalline melt.

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