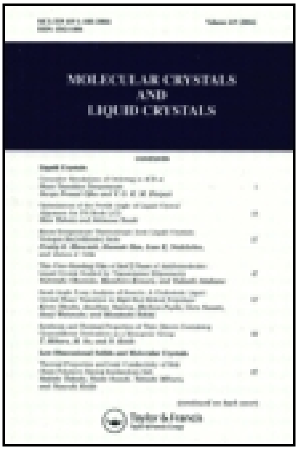

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Kinetics of Nonisothermal Transformations of Thermotropic Hydroxyethyl Cellulose Acetate

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Kinetics of Nonisothermal Transformations of Thermotropic Hydroxyethyl Cellulose Acetate

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The kinetics of non-isothermal transformation from isotropic to anisotropic phases of hydroxyethyl cellulose acetate (HECA) was studied by DSC at different cooling rates. It was found that the modified Avrami equation could be used in study and the exponent n was closed to 1. The rate of transformation increased with decreasing temperature and the apparent activation energy E was about 2.641 KJ/mol. The half-time of transformation $t_{1/2}$ was smaller than that of polymer crystallization and increased with temperature. The rate of transformation appears the maximum with temperature and the temperature at the largest rate of transformation shifted towards the low temperature with increasing cooling rate and the kinetic ability of transformation was also enlarged.

Keywords: Hydroxyethyl, cellulose acetate, nonisothermal kinetics, Avrami equation, liquid crystals.

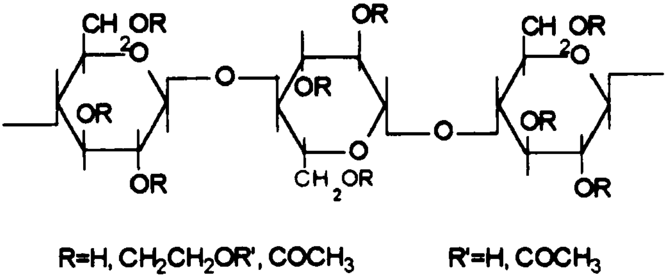
INTRODUCTION

In recent years, the kinnetics of the phase transformation of liquid crystalline polymers is an interesting topic.[1–7] Bhattacharya *et al.*[1] and Lui *et al.*[2] have studied the kinetics of mesophase formation of main-chain thermotropic polyesters by DSC and found that the Avrami exponenet is about 1. This means that the mesophase grows in one dimension. Hans and Zugenmaier[3] have studied the transition from isotropic to smectic phases of a side-chain liquid crystalline polymer by polarizing microscopy and found that the n is close to 1.8–1.9, which means two-dimensional growth of the mesophase. Pracella *et al.*[4] have studied the transformation from isotropic to smectic phases of another side chain liquid crystalline polymer with DSC and found the value of n is about 3 which indicates the growth of mesophase is three dimensional. The other workers[5–7] have also reported their results in this field and indicated that the mesophase formation is controlled by the mechanism of nucleation and the Avrami equation can be used in study for transformation from isotropic to anisotropic phases. However, all reports mentioned about are in isothermal transformation. By means of DSC, it is difficult to study the kinetics of isothermal transformation for the systems with low transition enthalpy and the high rate of transformation.

Recently, nonisothermal transformation is used for study in kinetics by some researchers because of the simple and fast operation, and it is similar to the actual processe. The study of transformation in nonisothermal conditions can be used in many systems especially in the case of mesophase formation with very low enthalpy and high transformation rate. Hydroxyethyl cellulose acetate (HECA) is thermotropic[8] However, there is no obvious isothermal transformation peaks in DSC curves because the transformation enthalpy is very low. Therefore, in this report the kinetics of nonisothermal transformation from isotropic to anisotropic phases is studied by DSC and some kinetic parameters are discussed.

EXPERIMENTAL

Thermotropic hydroxyethyl cellulose acetate (HECA) was synthesised in our laboratory. The degree of subsitution for hydroxyethyl was about 1.65 and for acetate was 2.8. The molecular weight, measured by the gel permeation chromatograph (GPC) (Waters ALC/244/GPC) with calibrating by standard polystyrene, was $M_n = 8.8 \times 10^4$ and $M_w = 11.8 \times 10^4$. The distribution of the molecular weight was about 1.34. The content of oxygen of HECA was measured by elementary analysis, from which the degree of substitution for acetyl was 2.80. The molecular formula of HECA was as follows:



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

On heating, mesophase appeared at about 403K and mesophase totally dis-appeared at about 458 K. On cooling, the transformation from isotropic to liquid crystalline phases began at about 438 K. The mesophase texture of HECA was observed by a polarizing microscope (Leitz, ORTHOPLAN-POL) with a hot stage. The differential scanning calorimetry (DSC) measurement was carried out with a Perkin-Elmer DSC-2c. In the measurement, the weight of the HECA was 24 ± 0.1 mg and nitrogen was used to protect the specimen from oxidization. The specimen was heated at 10 K/min to 478 K and then kept at this temperature for 5 min and finally cooled at 2.5, 5.0, 10.0 and 20 K/min to room temperature. Temperature and energy were calibrated with a standard substance—indium at the same heating or cooling rate before measurement. The DSC curves were recorded.

RESULTS AND DISCUSSION

Avrami equation for isothermal crystallization has been extended to nonisothermal process with the constant heating rate by Zhang *et al.*[9] Similarly, it can also be extended to nonisothermal process with the constant cooling rate.

For the isothermal crystallization, Avrami equations is

$$1 - \mathrm{Cr} = \exp(-kt^n) \tag{1}$$

where Cr is crystallity, k is a transformation rate constant. By the first derivative of the equation (1) with respect to t, the following equations can be obtained:

$$[1/(1 - \mathrm{Cr})]d\mathrm{Cr} = knt^{n-1}\,dt \tag{2}$$

For the cooling process with the constant cooling rate of β, there is $T = T_0 - \beta t$, that is $dT/dt = -\beta$. Where T_0 is the temperature at which transformation begins and T is the temperature of transfromation.
So the follwoing equations can be derived from Equation (2):

$$[1/(1 - \mathrm{Cr})]d\mathrm{Cr} = [k(T)(T_0 - T)^{n-1} n/\beta^n]dT \tag{3}$$

where $k(T)$ is the transformation rate constant as a function of temperature. Assuming n is not vaired with temperature, by integrating Equation (3), it can be obtained:

$$\ln(1 - \mathrm{Cr}) = -(n/\beta^n)\int_{T_0}^{T} k(T)(T_0 - T)^{n-1}\,dT = -F(T)/\beta^n \tag{4}$$

$$\ln[-\ln(1 - \mathrm{Cr})] = \ln F(T) - nLn\beta \tag{5}$$

where

$$F(T) = n\int_{T_0}^{T} k(T)(T_0 - T)^{n-1}\,dT$$

or

$$dF(T)/dT = n(T_0 - T)^{n-1}k(T) \tag{6}$$

If ploting $\ln[-\ln(1-\mathrm{Cr})]$ against $\ln\beta$, there is a straight line with the slope of $-n$ and the length of $\ln F(T)$. $k(T)$ can be obtained from $F(T)$ at different temperature and $t_{1/2}$ can also be calculated from the equation

$$t_{1/2} = [\ln 2/k(T)]^{1/n} \tag{7}$$

The kinectic ability of transformation Gc can be given by using the Jeziorny's method[10]:

$$\mathrm{Gc} = (1/\beta)\int_{T_0}^{T} k(T)\,dT = (1/\beta)(\pi/\ln 2)^{1/2} k_{\max} D/2 \tag{8}$$

where

$$k_{max} = [1/[1-Cr(t_{max})]dCr/dt]|_{t=t_{max}} = -[\beta/[1-Cr(T_{max})]dCr/dT|_{T=T_{max}} \quad (9)$$

k_{max} is a maximum of K, D is the half-width of the transformation peak in DSC curves and T_{max} is the temperature at which the transformation is fastest. dCr/dT can be evaluated from DSC curves.

If Cr is defined as a ratio of transformation from isotropic phase to liquid crystalline state, the equations mentioned above may be used in the liquid crystalline transformation.

HECA is a thermotropic material. Figure 1 shows its DSC thermograms. On heating, a endothermic peak appears from 403 K to 433 K and on cooling a exothermic peak appears from 423 K to 378 K. 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 403 K. HECA is a liquid crystalline glass at room temperature according to the X-ray diagram.[8] After the specimen is heated to 403 K, the HECA transforms from solid to anisotropic fluid and it totally becomes isotropic fluid at about 435 K. When the specimen is cooled form isotropic fluid, mesophase begins to appear at about 423 K. Figure 2 gives the results in observing by the polarizing microscope when the specimen is cooled from 468 K. These results demonstrate that the HECA is thermotropic and liquid crystalline state exists in the temperature region from 403 K to 435 K on heating and from 423 K to 378 K on cooling. The endothermic peak on heating and the exothermic peak on cooling in DSC thermogram corresponds to this transformation between the liquid crystalline phase and the isotropic one. The mesophase texture in Figure 2 indicated that HECA thermostropic liquid crystalline state is cholesteric.

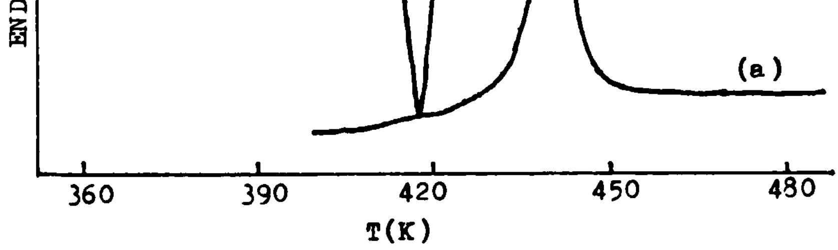


FIGURE 1 The DSC thermograms of HECA on (a) heating and (b) cooling.

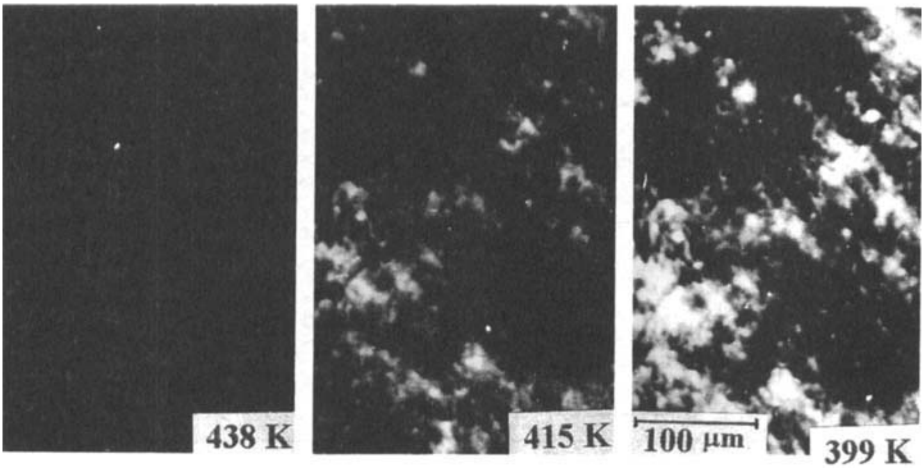


FIGURE 2 Polarized mocrograph of HECA when cooling at 1 K/min from 468 K.

HECA was cooled from isotropic melt at the constant cooling rate in this study. The ratio of transformation from isotropic to anisotropic phases Cr and 1 − Cr at any temperature can be given from DSC curves in cooling. The values of 1 − Cr are plotted as a function of T, for some of the cooling rate β investigated, in Figure 3. All the curves have the same shape and are superimposable on each other by an appropriate shift along the temperature axis. The plots of $\ln[-\ln(1-Cr)]$ vs. $\ln\beta$, at different temperature, are presented in Figure 4, The experiemental data may be described by straight lines, which is required by Avrami equation. The slop of the lines in Figure 4 suggusts that the Avrami exponent n does not vary with temperature within the temperature

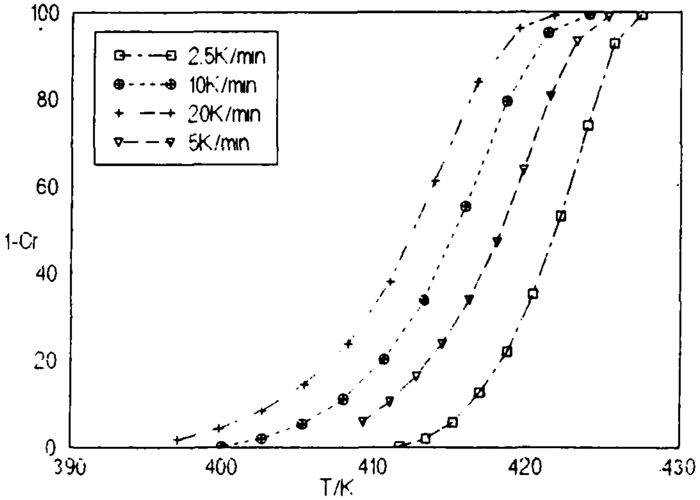


FIGURE 3 The curves of 1 − Cr vs. T for HECA in nonisothermal transformation.

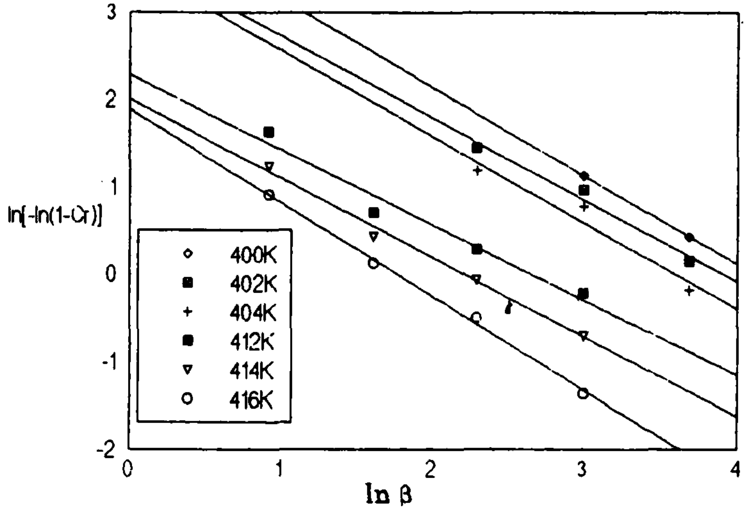


FIGURE 4 The curves of $\ln[-\ln(1-Cr)]$ vs. $\ln\beta$ for HECA is nonisothermal transformation.

region of 400–420 K. The value of n and $\ln F(T)$ from the straight lines in Figure 4 are listed in Table 1. The value of n is genegally close to 1 from 400 K to 420 K.

The plot of $\ln F(T)$ vs. T is presented in Figure 5, which shows a straight line and its linear equation is

$$\ln F(T) = -0.137T + 58.6$$

So

$$F(T) = \exp(-0.137T + 58.6)$$

and

$$dF(T)/dT = -0.137\exp(-0.137T + 58.6)$$

It has been shown above that the relationship between $k(T)$ and $dF(T)/dT$ is descripted by Equation (6). Then, $k(T)$ at any temperature can be calculated from equation above and the half-time of transformation $t_{1/2}$ can also be obtained from the Equation (7).

TABLE 1

The values of n and $\ln F(T)$ of HECA in nonisothermal transforamtion

T(K)	400	402	404	406	408	410	412	414	416	418	420
n	1.03	0.88	0.85	0.85	0.84	0.84	0.86	0.88	0.88	1.03	1.29
$\ln F(T)$	4.14	3.50	3.23	3.03	2.77	2.43	2.13	1.85	1.52	1.35	1.12

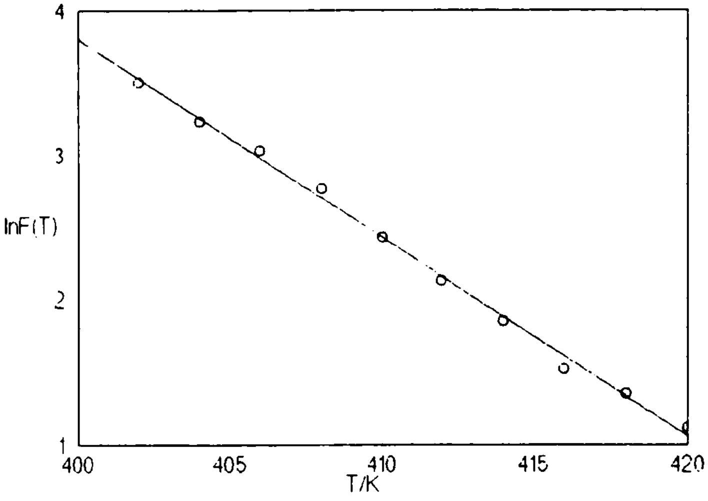


FIGURE 5 The plot of $\ln F(T)$ vs. T for HECA is nonisothermal tranformation.

The values of $k(T)$ and $t_{1/2}$ are collected in Table 2. The values of the half-time of transformation are 0.1–3.0 min, which generally much lower than those obtained for the crystallization of high polymers.[11] Consequently, the mesophase formation of liquid crystalline polymers is much faster than crystallization of polymers. This is probably because of very low surface energy of mesophase. Papkov *et al.*[6] have reported that the value of the surface energy for a mesomorphic lamella is about 2–5 $\mathrm{erg}^2/\mathrm{cm}^4$, but corresponding values for polymer crystal lamella are often 100–1,000 $\mathrm{erg}^2/\mathrm{cm}^4$. This is the one of the reasons why the enthalpy of transformation from isotropic to anisotropic phases is very low. In this system, for example, the enthalpy of mesophase formation is only about 1.6–3.2 J/g.

By using Arrhenius equation:

$$k(T) = A\exp(-E/RT) \tag{10}$$

where A is constant. The apparent activation energy $-E$ can be calculated from the values of $k(T)$ in Table 2. The plot of $\ln k(T)$ vs. $1/RT$ is a straight line in Figure 6 and its slope is equal to the values of $-E$. Therefore, the apparent activation energy of the transformation from isotropic to anisotropic phases for HECA is about 2.641 kJ/mol.

TABLE 2

The values of $k(T)$ and $t_{1/2}$ for HECA in nonisothermal transformation

T(K)	403	405	407	409	413	415	417	419	421
k(min^{-n})	3.75	2.88	2.21	1.69	1.00	0.76	0.59	0.45	0.35
$t_{1/2}$(min)	0.15	0.20	0.27	0.36	0.66	0.99	1.20	1.58	2.18

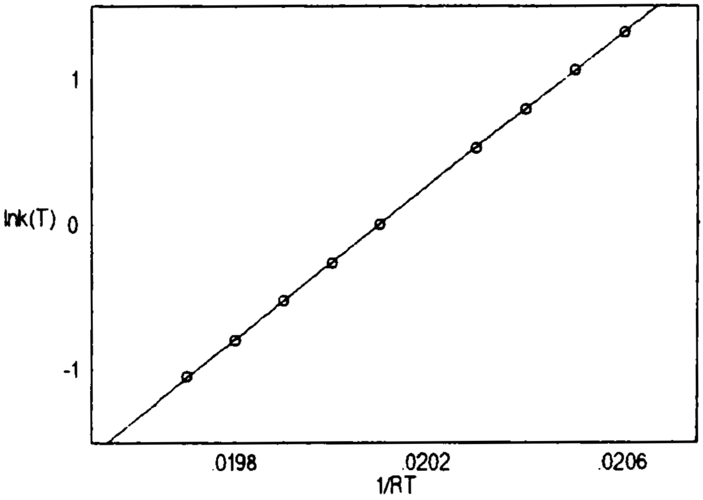


FIGURE 6 The plot of $\ln k(T)$ vs. $1/RT$ for HECA in nonisothermal tranformation form isotropic to anisotropic phases.

The presentation of the rate of transformation is different by using $t_{1/2}$ and dCr/dT. $t_{1/2}$ presents the half periodicity of transformation and demonstrates the rate of transformation only when the Cr is the same at the end of transformation. dCr/dT shows the variation of the ratio of mesophase formation with temperature and indicates the rate of mesophase formation at temperature of T in nonisothermal trnasformation. The plots of dCr/dT vs. T are presented in Figure 7. All plots of dCr/dT vs. T (the cooling rate from 2.5 K/min to 20 K/min) appear maximum. The rate

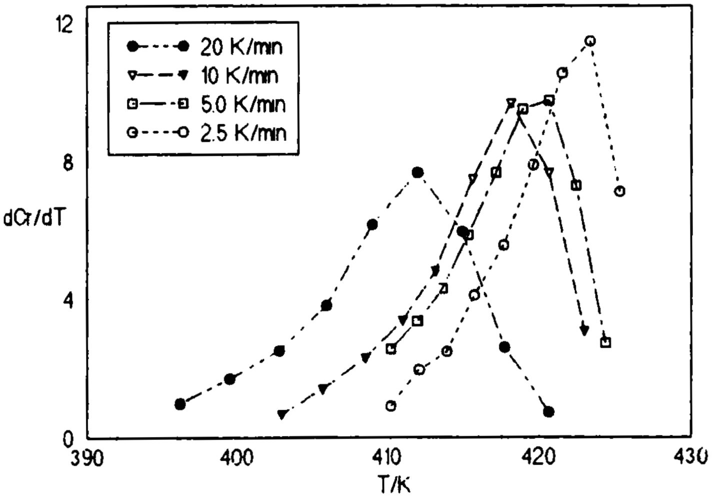


FIGURE 7 The curves of dCr/dT vs. T for HECA in nonisothermal transformation.

TABLE 3

Kinetic parameters of HECA in nonisothermal transformation

β(K/min)	t_{max}(min)	D(K)	K_{max}(min^{-1})	G(K/min)	Gc
2.5	2.72	8.00	0.0234	0.199	0.0796
5.0	1.54	9.20	0.0626	0.613	0.123
10.0	0.87	8.35	0.270	4.401	0.240
20.0	0.55	11.5	0.980	12.0	0.600

of mesophase formation increases with decreasing temperature in the first stage of transformation till to the maximum and then decreases. Moreover, the temperature at which the rate of mesophase formation is highest decreases gradually with increasing cooling rate. The values of T_{max}, t_{max} and D can be obtained from the curves in Figure 6 and consequently, the K_{max} and Gc can be calculated by using Equation (8) and (9). All of these data are presented in Table 3. For the thermotropic HECA, the rate mesophase formation is increased and the kinetic ability of the transformation from isotropic to anisotropic phases is enlarged by increasing cooling rate.

CONCLUSIONS

The modified Avrami equation can be used in nonisothermal transformation from isotropic to anisotropic phases for HECA and the Avrami exponent n is close to 1. The transformation rate constant is the function of temperature and decreases with increasing temperature. In the general, the mesophase formation is much faster than crystallization, which is probably because of the very low surface energy of mesophase. The apparent activation energy of tranformation from isotropic phase to mesophase is about 2.641 kJ/mol. The variation of the ratio of mesophase formation with temperature $d\mathrm{Cr}/dT$ appears a maximum value and it shifts towards the lower temperature with increasing cooling rate. The kinetic ability of transformation from isotropic to anisotropic phases is enlarged by increasing cooling rate and the rate of mesophase formation increases.

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