

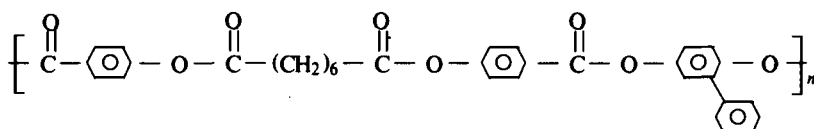
STUDY ON THE PHASE TRANSITION KINETICS OF THERMOTROPIC LIQUID CRYSTALLINE AROMATIC-ALIPHATIC COPOLYESTER

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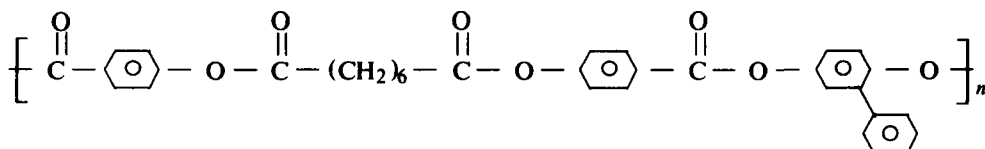
ABSTRACT

The phase transition kinetics of thermotropic liquid crystalline aromatic-aliphatic regular copolyester :



were studied by DSC. By means of Kissinger's method the kinetic equation and parameters including activation energy, rate order and preexponential factor for phase transition from nematic to isotropic were obtained. The activation energy from crystal to nematic was also presented.

The study of phase transition is one of the important subjects in the field of liquid crystalline polymer. There are only a few reports on the study of phase transition process, such as its kinetics and thermodynamics^[1]. The literature reported were mostly about the kinetics and mechanism of liquid crystallization and crystallization of liquid crystalline polymer during cooling by using Avrami equation^[2,3]. However, the kinetics of its phase transition in heating process have not been investigated yet. In this paper the phase transition kinetics of the following liquid crystalline copolyester in heating were studied by DSC :



The kinetic equation was obtained in terms of Kissinger's method for data treatment^[4-6]. The parameters including activation energy, rate order and preexponential factor were presented. And the physical meaning of activation energies in phase transition of liquid crystalline polymer was discussed.

EXPERIMENTAL

The synthesis and characterization of poly[·oxy-1, 4-(phenyl) phenyleneoxycarbonyl-1, 4-phenyleneoxy-1, 8-octanedioxyloxy-1, 4-phenylenecarbonyl] were described in another paper^[7]. The inherent viscosity of

the polymer is $\eta_{inh} = 0.479$ dl/g (30 °C, phenol/ 1,1,2, 2-tetrachloroethane mixture as solvent). The phase transition kinetic experiments of the copolyester were carried out by using DSC (Du pont) with the heating rate of 2, 5, 10, 20, 50 °C/min. separately.

RESULTS AND DISCUSSION

For any reaction or phase transition, its kinetic equation at constant temperature is :

$$-\frac{dx}{dt} = Kx^n \quad (1)$$

where n is the kinetic order of phase transition in liquid crystalline polymer and K is the rate constant which depends on temperature :

$$K = Ae^{-E/RT} \quad (2)$$

Substituting K from equation (2) into equation (1), we obtain :

$$-\frac{dx}{dt} = Ae^{-E/RT}x^n \quad (3)$$

where x is a certain property of the system, which can be the motive force of the reaction or phase transition. In phase transition the enthalpy of initial or terminal phase is the motive force. So the kinetic equation of phase transition is:

$$-\frac{dH}{dt} = Ae^{-E/RT}H^n \quad (4)$$

where H is the enthalpy of initial phase at t time ; dH/dt is the rate of phase transition ; E is the activation energy and n is the kinetic order of phase transition, or rate order.

Ozawa and Kissinger^[4,5] pointed out that the temperature at the tip of the phase transition peak in DSC thermogram (T_m) represented the maximum rate of phase transition. It can be expressed by differential equation as follows :

$$\frac{d}{dt} \left(\frac{dH}{dt} \right) T_m = 0 \quad (5)$$

The heating rate is :

$$\varphi = \frac{dT}{dt} \quad (6)$$

From equations (4), (5), (6) the following equation is deduced :

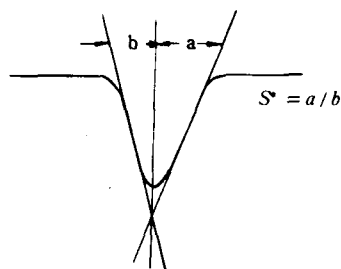
$$\frac{d(\ln \varphi / T_m^2)}{d(1/T_m)} = -E/R \quad (7)$$

Referring to Kissinger's^[6] method, we get

$$n = 1.26S^{1/2} \quad (8)$$

$$\frac{E\varphi}{RT_m^2} = A \left(1 + (n-1) \frac{2RT_m}{E} \right) e^{-E/RT_m} \quad (9)$$

where S is the shape index of the phase transition peak in DSC thermogram, and defined as the absolute value of the ratio of the slopes of tangents to the curve at the inflection points.



(10)

Equations (7), (8), (9) are the main equations for the study of the phase transition kinetics in heating process by DSC.

The DSC thermograms of the copolyester at different heating rates are shown in Figure 1 and the phase transition temperatures in Table 1.

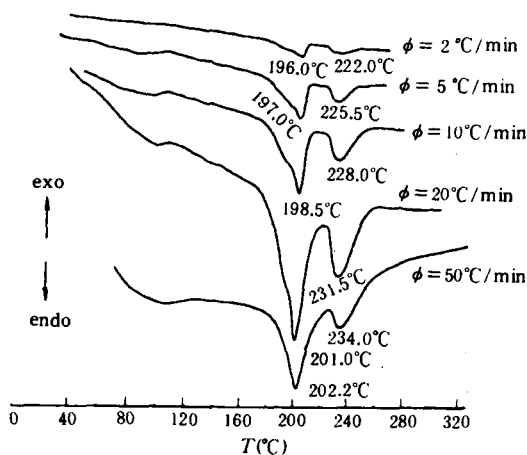


Fig.1 Thermograms of the copolyester at different heating rates

Table 1 Phase transition temperatures* at different heating rates

ϕ ($^{\circ}\text{C}/\text{min}$)	2	5	10	20	50
T_m ($^{\circ}\text{C}$)	196.0	197.0	198.5	201.0	202.2
T_i ($^{\circ}\text{C}$)	222.0	225.5	228.0	231.5	234.0

* Temperatures at the tips of phase transition peaks; m = melting, i = isotropization.

According to equation (7), the two series of points ($1/T_m$, $\ln\phi/T_m^2$), ($1/T_i$, $\ln\phi/T_i^2$) are treated with linear regressions respectively. The activation energies of the two phase transitions from crystal to nematic and from nematic to isotropic are obtained :

$$E_m = 851.6 \text{ KJ/mol}$$

$$E_i = 536.4 \text{ KJ/mol}$$

The interrelation coefficients are :

$$r_m = -0.9834$$

$$r_i = -0.9969$$

The equations of the regression lines are :

$$(\ln \phi / T_m^2) = -102.42 \cdot 10^3 (1/T_m) + 206.95 \quad (11)$$

$$(\ln \phi / T_i^2) = -64.52 \cdot 10^3 (1/T_i) + 118.57 \quad (12)$$

The regression lines and experimental points are shown in Fig.2 and Fig.3.

In terms of equations (8) and (10), the rate orders are got for each DSC thermogram in Fig.1 and then averaged.

There were multiple transitions near the melting point of the copolyester and a shoulder peak was observed before melting point (i.e. $T_m \approx 198^{\circ}\text{C}$ when $\phi = 10^{\circ}\text{C}/\text{min}$). Accordingly the shape indexes and the rate orders for phase transition from crystal to nematic are not obtained.

Finally, using equation (9) and the values of E_i , n_i above, the preexponential factor is calculated :

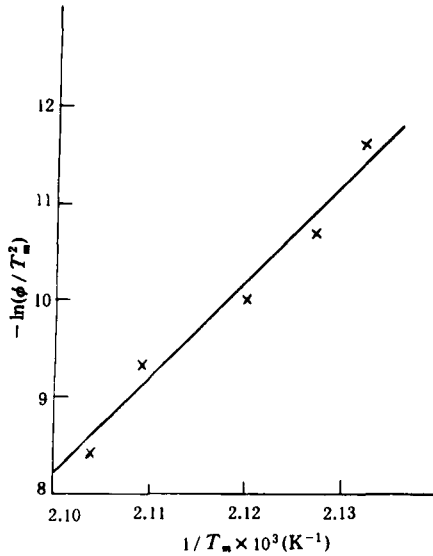


Fig.2 Regression line for activation energy of phase transition from crystal to nematic

Table 2 Values of rate order (n_i)

φ (°C/ min)	2	5	10	20	50	average
a_i (mm)	19.0	17.5	17.5	18.0	21.5	
b_i (mm)	7.0	8.0	7.5	8.5	9.5	
n_i	2.1	1.9	1.9	1.8	1.9	1.9

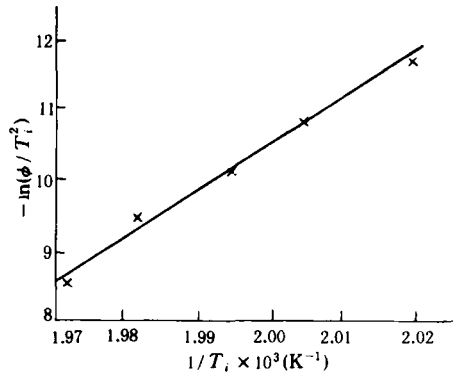


Fig.3 Regression line for activation energy of phase transition from nematic to isotropic

Table 3 Values of preexponential factor (A_i)

φ (°C/ min)	2	5	10	20	50	average
$A_i * 10^{-56}$ (SI system)	2.02	1.99	2.07	1.67	2.20	1.99

Therefore, for the two phase transitions of the copolyester, activation energy from crystal to nematic is :

$$E_m = 851.6 \text{ KJ/ mol}$$

and the other one from nematic to isotropic is :

$$E_i = 536.4 \text{ KJ/ mol}$$

The kinetic equation from nematic to isotropic is :

$$-\frac{dH_i}{dt} = 1.99 * 10^{56} \exp\left(-\frac{6.45 * 10^4}{T}\right) H_i^{1.9} \text{ (SI system)} \quad (13)$$

Activation energy is the energy barrier which has to be surmounted for phase transition. From crystal to nematic phase, there are changes from three-dimension to one-dimension order. The molecular centre of gravity, which could only vibrate near the balance position in crystal, can do translational motion when crystal is converted into nematic phase. The positional energy barrier (E_m) is overcome for the phase transition from crystal to nematic. From nematic to isotropic phase, there are changes from one-dimension order to disorder and orientational energy barrier (E_i) is surmounted. In terms of the ideas of Chandrasekhar 's theory⁽¹⁾ of phase transition, if the ratio E_i / E_m exceeds a certain critical value, then the transition from crystal to isotropic phase can go on with two steps and the middle phase is the mesophase.

Keywords :

Phase transition kinetics ; Activation energy ; Thermotropic regular copolyester ;

Rate order

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