

STUDIES ON THE KINETICS OF PHASE TRANSITIONS OF A MAIN CHAIN THERMOTROPIC POLYESTER

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ABSTRACT

The kinetics of phase transitions including a transition between mesophases were studied for a main-chain thermotropic polyester by means of DSC and depolarizing transmittance techniques. The isothermal process of these transitions was found to be described by the Avrami equation to high conversions. The Avrami exponents n are about 2.4, 5.3 and 2.2 for liquid crystallization, transition between mesophases and crystallization from mesophase respectively. The liquid crystallization from isotropic liquid phase occurs at very low undercoolings with high transformation rate. This behavior is explained as the results of the smaller value of the surface free energy for mesophase than that for crystallites which is evidenced by the very weak temperature dependence of liquid crystallization rate.

INTRODUCTION

Studies on the kinetics of phase transitions of polymeric liquid crystals are of great interest, as they may give insight into the structure and behavior of these materials. The transitions specific to liquid crystalline materials are the crystallization from mesophase, the transition from isotropic liquid phase to anisotropic liquid phase, or the liquid crystalline phase, which may, by analogy, be termed as the liquid crystallization transition, and also transitions between mesophases, if polymesomorphism exists.

The kinetics of transition of small molecule liquid crystals have been studied by various authors^[1-7]. The liquid crystallization from isotropic melt is characterized by very small degree of undercooling and very high rate of transformation. It was found by means of dilatometry and optical microscopy that these transitions were nucleation controlled and can be described by an Avrami equation:

$$1 - X_t = \exp(-Kt^n) \quad (1)$$

Where X_t is the fraction of polymer transformed at the time t , K is a kinetic constant of the transition process and n is a parameter dependent on the types of nucleation and growth geometry of the new phase. However studies on liquid crystal forming polymers are relatively very much limited. There are a few reports concerning the kinetics of crystallization from mesophase^[8-10]. Pracella et al.^[11] studied the liquid crystallization transition of a side-chain thermotropic polyacrylate, while Bhattacharya et al.^[12] reported their studies on the same transition for a main-chain thermotropic polyester. In a recent work we studied the liquid crystallization and crystallization transitions

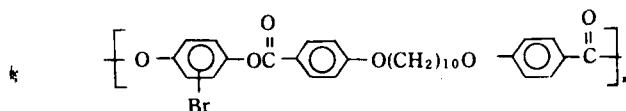
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both for fractions of a main – chain thermotropic polyester^[13]. In the present work the kinetics of transitions including a transition between mesophases for another thermotropic polyester are investigated.

EXPERIMENTAL

The thermotropic aromatic polyester that has been used in this work was derived from bromohydroquinone and 4,4' – dicarboxy – 1,10 – diphenoxydecane^[14] and has the following structure :



The intrinsic viscosity in tetrachloroethane measured at 25 °C is 0.53 dl/g. The transitions and morphology of this polymer has been studied in the previous papers^[15,16].

The kinetic measurements were performed on a differential scanning calorimeter Perkin – Elmer DSC – 4 and a depolarizing transmittance apparatus^[17]. Indium was used as thermal standard for temperature and enthalpy calibrations. Film specimens for transmittance measurements were prepared by solution cast and drying in vacuum at 60 °C.

RESULTS AND DISCUSSION

The transition behavior of the used polymer is schematically summarized in Figure 1 according to our previous studies. When the sample is cooled down from its isotropic liquid phase, it becomes nematic in a transition temperature range around

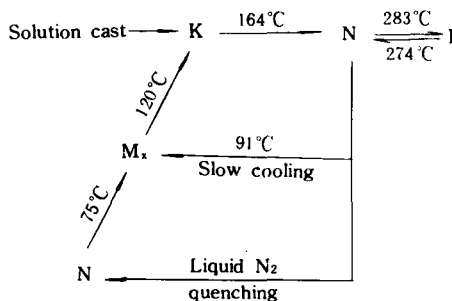


Fig. 1 Transition diagram of the polymer.

274 °. With further decreasing temperature the sample does not crystallize, but a transition between mesophases occurs, exhibiting an exothermal peak at 91 °C. It is a transition from the nematic phase to another mesophase, the Mx phase, which is more ordered than the original nematic phase in lateral packing of parallel molecules and seems to be prerequisite to crystallization from mesophase for this polymer. The kinetics of transitions from isotropic to nematic phases (the IN transition), from nematic to Mx phases (the NM transition) and from Mx to crystalline phases (the MK transition) for this polymer were investigated.

The kinetics of liquid crystallization were studied by the depolarizing

transmittance technique which is quite sensitive to the appearance of macroscopically ordered texture during the formation of the mesophase. The specimens were first heated to temperatures 15—20 °C higher than the isotropization temperature, then rapidly cooled down to the selected temperature. The intensity of depolarizing transmittance I was recorded as function of time t in the isothermal liquid crystallization experiments (Figure 2). Assuming that I_t is proportional to the fraction of polymer liquid crystallized at time t , one can analyze the kinetic behavior

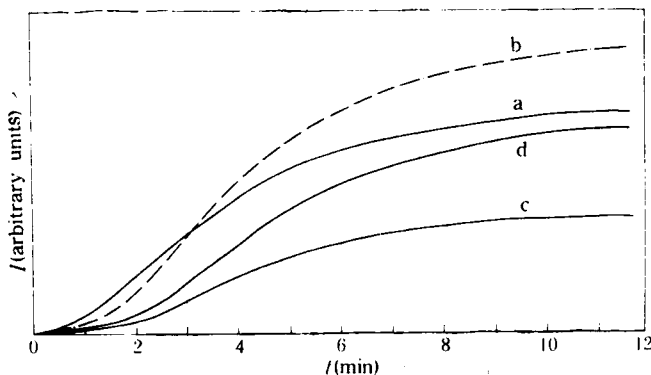


Fig. 2 Isothermal curves for liquid crystallization process from depolarizing transmittance measurements at a) 275.5 °C, b) 280 °C, c) 281.5 °C and d) 284 °C.

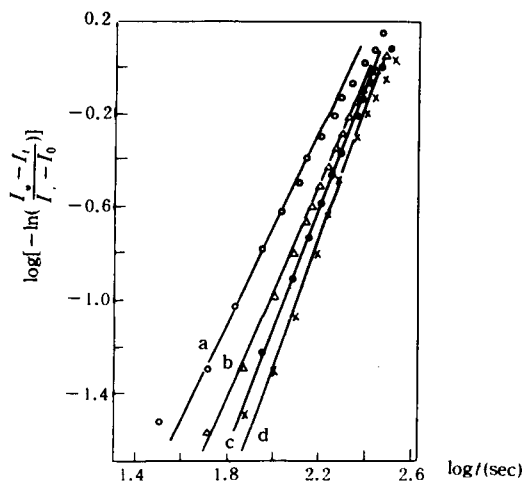


Fig. 3 Avrami plots for liquid crystallization data of the sample at a) 275.7 °C, b) 280 °C, c) 271.5 °C and d) 284 °C.

at a given temperature by means of an Avrami plot of $\lg[-\ln(I_\infty - I_t)/(I_\infty - I_0)]$ versus $\lg t$ where I_0 and I_∞ are intensity values before and after the liquid crystallization process respectively. The plots at different temperatures are given in Figure 3. Straight lines were obtained up to high conversions. The Avrami exponent n was calculated from the slope of these straight lines and is listed in Table 1. The average value of n is about 2.4, and a tendency of increasing of n with temperature was observed. The n values around 2 have been reported by Price and Wendorf^[1-5] for small molecule liquid crystals in kinetic studies of transitions from isotropic melt to mesophases. Small n values around 1 or even less were reported for some main chain thermotropic polyesters^[12, 13]. Although the parameter n is dependent on the type of nucleation and growth geometry both, the relatively small n values may

Table 1 The Avrami exponent of transitions

IN transition		NM transition		MK transition	
$T(^{\circ}\text{C})$	n	$T(^{\circ}\text{C})$	n	$T(^{\circ}\text{C})$	n
284	2.80	98	5.77	110	1.83
281.5	2.58	97	5.63	106	2.08
280	2.30	96	5.47	102	2.21
275.5	2.07	95	4.84	98	2.75
		94	4.82		

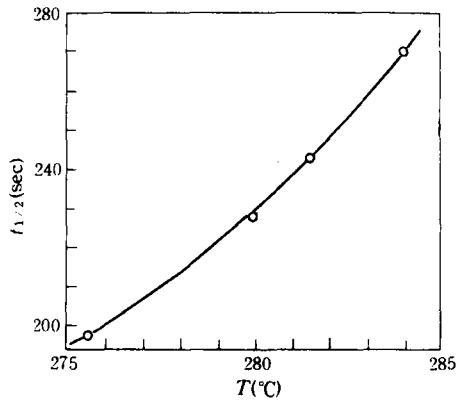


Fig. 4 Dependence of half time on the liquid crystallization temperature.

imply that the growth of the mesophase in isotropic liquid phase is not three dimensional, that is usually observed for crystallization transitions. The half-time of liquid crystallization process at different temperatures is shown in Figure 4. The $t_{1/2}$ values were found to be about 200 sec at undercoolings less than 10 $^{\circ}\text{C}$ and are comparable with data of small molecule liquid crystals^[15] and fractions of a thermotropic polyester^[13].

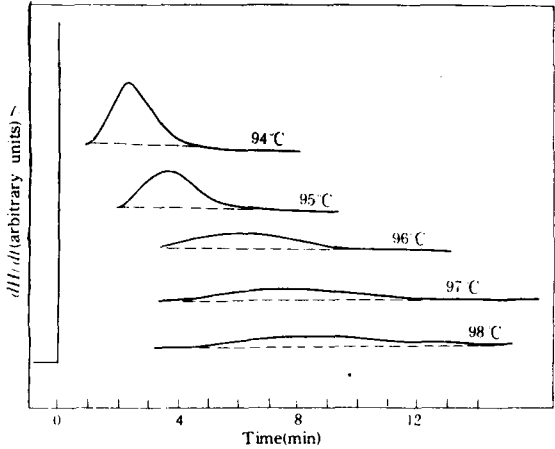


Fig. 5 Isothermal thermograms for NM transition at different temperatures.

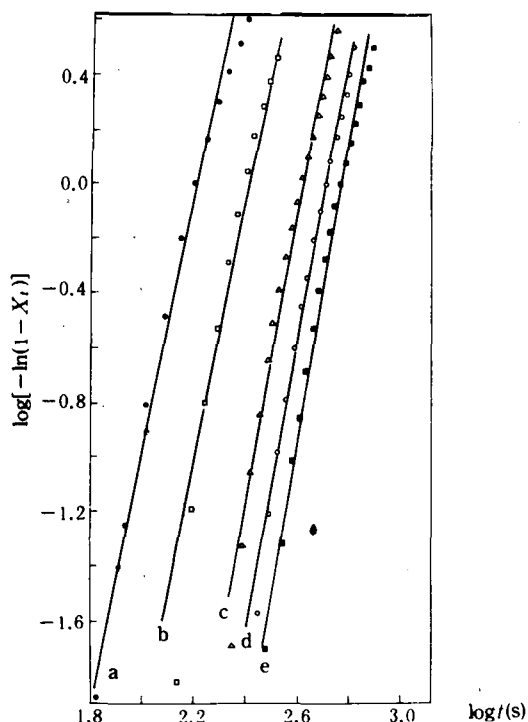


Fig. 6 Avrami plots for data of NM transition at different temperatures : a) 94 °C , b) 95 °C , c) 96 °C , d) 97 °C and e) 98 °C .

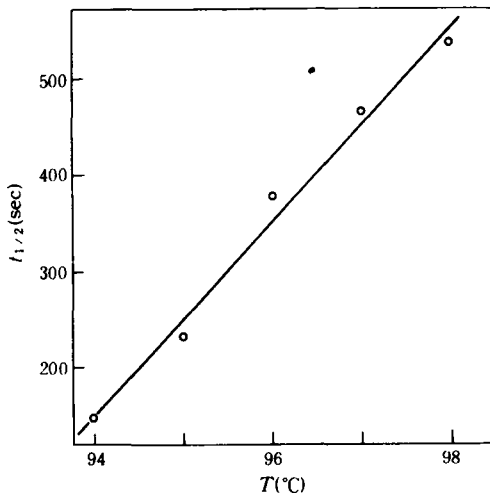


Fig. 7 Dependence of half time on temperature of the NM transition.

The kinetics of transition NM were studied by means of DSC measurements. The specimens were first heated to 190 °C, then rapidly cooled down to the selected temperatures. The isothermal DSC curves for the NM transition are given in Figure 5. From these curves the fraction of polymer X_t transformed from nematic to Mx mesophases at the time t can be determined as the ratio of the area of the exotherm at the time t to that of the overall exotherm. The data were then used for kinetic analysis on the basis of Avrami equation by plotting $\lg[-\ln(1 - X_t)]$ versus $\lg t$ (Figure 6). Results indicate that the experimental data can be described by the Avrami equation up to sufficiently high conversions. The values of the exponent n calculated from the slope of these straight lines were around 5.3 with a tendency of increasing with temperature (Table 1). The half-time $t_{1/2}$ of this transition at different temperatures is given in Figure 7. The $t_{1/2}$ values are in the range of 100—500 sec, increase rapidly, almost linearly, with temperature in the given temperature range. As the NM transition is a monotropic one, we can not estimate the degree of undercooling of these isothermal measurements.

The isothermal DSC curves for crystallization from Mx phase at different temperatures are given in Figure 8. In these experiments the specimens of nematic phase (190 °C) were rapidly cooled down to 91 °C. After staying at this temperature for 5 min they were further cooled down to 50 °C. Then the specimens were rapidly heated to the selected temperature for isothermal measurements. The plots of $\lg[-\ln(1 - X_t)]$ versus $\lg t$ at different temperatures are given in Figure 9. Straight lines were also observed for these processes to high conversions. The exponent

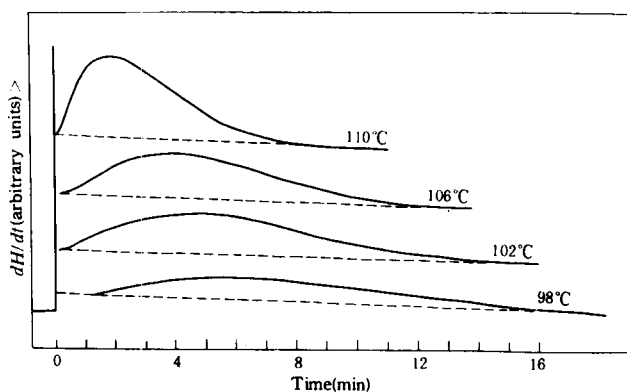


Fig. 8 Isothermal thermograms for crystallization from Mx mesophase at different temperatures.

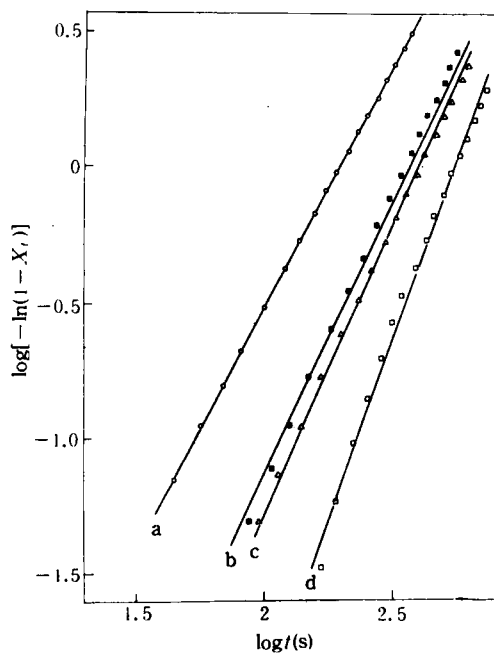


Fig. 9 Avrami plots for data of crystallization from Mx mesophase at different temperatures : a) 110 °C . b) 106 °C . c) 102 °C and d) 98 °C .

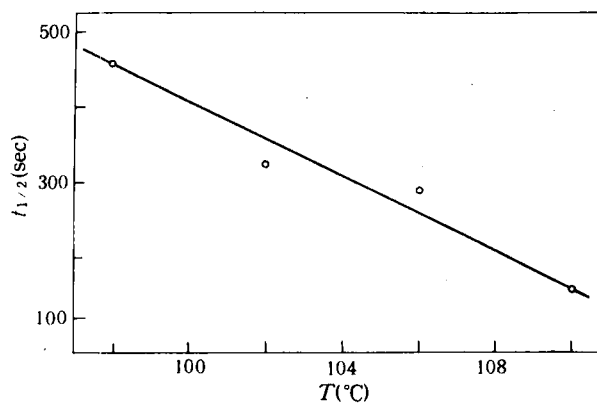


Fig. 10 Dependence of half-time on the crystallization temperature.

parameter n decreases with temperature and has an average value of about 2.2 (Table 1). The n values around 4 have been reported for crystallization from mesophases of small molecule liquid crystals^[1-7] and main-chain thermotropic polyesters with $-(CH_2)_{10}-$ flexible spacers^[9, 10, 13]. However $n=2$ has also been observed for some polymeric liquid crystals^[8, 10]. It seems that similar to crystallization from isotropic phase of conventional polymers different n values are possible for crystallization from anisotropic mesophase, and the low n value indicates an un-three-dimensional growth geometry of crystallites in the Mx mesophase of this polymer. Figure 10 shows the half time of crystallization as function of temperature. The observed isothermal crystallization processes are transitions proceeding at the low temperature side of the maximum crystallization rate temperature, so $t_{1/2}$ decreases with increasing temperature. The selected crystallization temperatures are about 60 °C higher than the glass transition temperature, and the values of $t_{1/2}$ are comparable in magnitude of order with those obtained for conventional crystallizable polymers, for example polyethylene terephthalate, at similar conditions.

The influence of temperature on the rate of transformation composed of nucleation and growth of the new phase has been discussed by many authors^[18, 19]. The overall transition rate expressed as $1/t_{1/2}$ can be correlated with temperature through a general equation:

$$\lg(1/t_{1/2}) = A - B_a T_i^0 / T(\Delta T)^a \quad (2)$$

T_i^0 is the equilibrium temperature of transformation, $a=1$ or 2 for approaches of different nucleation models. Parameter A can be considered constant at small undercoolings. B_a depends on the average surface free energy $\bar{\sigma}$ and the heat of transition ΔH of the phase formed in the transition process in the following form:

$$B_a \sim \bar{\sigma}^{a+1} / \Delta H^a \quad (3)$$

It is clear from equation (3) that B_a is a parameter characterizing the difficulty of nucleation of the new phase and can be determined from data of $t_{1/2}$ at different T according to equation (2).

As transitions NM and MK are monotropic, it is meaningless to talk about an equilibrium transition temperature for them. Besides, the $t_{1/2}$ data for MK transition are obtained at very large undercoolings. So only the data for IN transition are analyzed here. Figure 11 shows the plots of $\ln(1/t_{1/2})$ as functions of $T_{Ni}^0/T\Delta T$ and $T_{Ni}^0/T(\Delta T)^2$ respectively. The experimental data can be fit by straight lines for both plots by proper selecting the T_{Ni}^0 value. This is similar to the situation reported in the literature for crystallization analysis of conventional polymers^[18] and also for liquid crystallization of thermotropic polyesters^[13]. The B_1 and B_2 values calculated from the slopes of the straight lines shown in Figure 11 are 9.6K and 0.2K respectively. They are consistent with the values obtained for liquid crystallization process of some fractions of an aromatic polyester in our previous work^[13] and is one magnitude of order less than the corresponding B_1 , B_2 values obtained for crystallization of conventional and liquid crystal forming polymers^[13, 18]. The smaller B_a values for liquid crystallization mean that the surface free energy of mesophase domains should be much less than that of the crystallites, if the fact that ΔH for isotropization is always

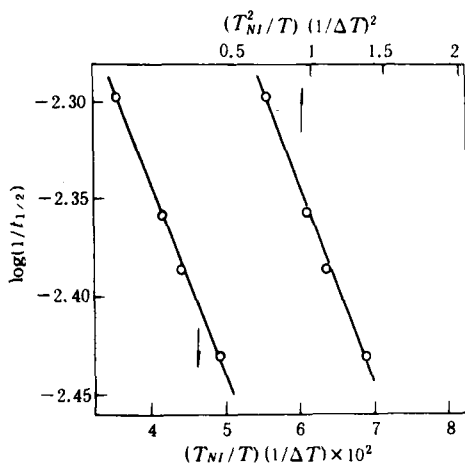


Fig. 11 Plots of $\lg(1/t_{1/2})$ versus $T_{NI}^0/T\Delta T$ and $T_{NI}^0/T(\Delta T)^2$ for data of liquid crystallization. The value of

T_{NI}^0 used is 350 °C.

less than that of fusion is also taken into account. That is the reason why liquid crystallization can proceed with high transformation rate at very small undercoolings, while crystallization only proceeds at very large undercoolings. The low surface energy of mesophase domains is also consistent with the general picture of mesophase structure. The nematic domains are liquid rather than solid as in the case of crystallites, and the molecules therein partake of the mobility characteristic of a liquid, apart from their axial orientation. Therefore the surface of the nematic domains should be very diffuse and easily changeable related with lower surface energy as compared with that of crystallites.

Keywords :

Phase transition, kinetics, thermotropic polyester.

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