Kinetics of phase transitions for fractions of a main-chain liquid-crystalline polyester

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The kinetics of crystallization from the mesophase and liquid crystallization from an isotropic melt of fractions of an aromatic thermotropic polyester were investigated by differential scanning calorimetry and depolarizing transmittance measurements. The isothermal process of these transitions can be described by the Avrami equation. The values of the exponent n are found to be ~ 4 and ~ 1 for crystallization and liquid-crystallization transitions, respectively. The temperature dependence of the crystallization rate from the mesophase is similar to that for small-molecule liquid crystals and also to that for conventional polymers obtained from an isotropic melt. Compared to crystallization, the liquid-crystallization rate shows a very weak temperature dependence. This implies that the surface free energy of mesophase domains is much less than that of crystallites, which may explain the experimental fact that liquid crystallization from an isotropic melt can proceed with high transformation rate at very small undercoolings, whereas crystallization only proceeds at very large undercoolings.

(Keywords: phase transition; kinetics; liquid-crystalline polyester)

INTRODUCTION

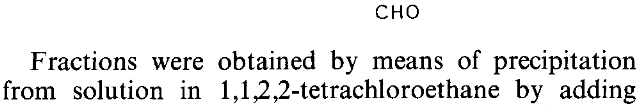
Mesophase transitions are characteristic features of liquid-crystal-forming polymers. Similar to small-molecule liquid crystals, different kinds of mesophase have been observed for polymeric liquid crystals. A lot of work has been done in recent years to study the relationship between molecular structure and the transition temperatures of these polymers.

It is of great interest to study the kinetics of phase transitions characteristic of liquid-crystalline materials. These phase transitions are: crystallization from the mesophase; transition from the isotropic liquid phase to the anisotropic liquid phase, or the liquid-crystalline phase, which may by analogy be termed liquid-crystallization transition; and also transitions between mesophases, if polymesomorphism exists. In the case of small-molecule liquid-crystalline materials, the kinetics of transitions from the isotropic liquid phase to the mesophase (cholresteric, smectic and nematic mesophases) and the kinetics of crystallization from different mesophases have been studied by various authors[1–7]. Liquid crystallization in these systems is characterized by a very small degree of undercooling and a 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-type equation. However, studies on the kinetics of liquid-crystallization[8,9] and crystallization[10–12] of polymeric liquid crystals are limited. To our knowledge, no kinetic study has been reported so far concerning the crystallization and liquid-crystallization transitions of a liquid-crystal-forming polymer and the influence of its molecular weight.

In the present work the kinetics of phase transitions, liquid crystallization and crystallization from the mesophase, of fractions of a main-chain thermotropic polyester are investigated by differential scanning calorimetry and a depolarizing transmittance method. Results are discussed in comparison with those for transitions of conventional polymers and also small-molecule liquid crystals.

EXPERIMENTAL

The aromatic polyester used was synthesized by solution polycondensation of monomers, 1,10-bis(chloroformylbenzoyloxy)decane and 2-formyl-1,4-dihydroxybenzene, and has the following structure:



$$-\!\left[O(CH_2)_{10}OOC-C_6H_4-COO-C_6H_3(CHO)-OOC-C_6H_4-CO\right]_n-$$

Fractions were obtained by means of precipitation from solution in 1,1,2,2-tetrachloroethane by adding ethanol as the precipitant. The synthesis and fractionation procedures have been described elsewhere[13]. The intrinsic viscosity of the fractions in tetrachloroethane at 40°C ranges from 0.254 to 0.591 dl g^{-1} and is given in *Table 1*.

The transition temperatures of the fractions were measured by differential scanning calorimetry in a temperature range from -20 to 220°C by using a Perkin–Elmer DSC-4, purged with nitrogen. Indium was used as thermal standard for temperature and enthalpy

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Table 1 Transition temperatures of the fractions

Fraction	$[\eta]$ (dl g^{-1})	T_{kn} (°C)	T_{nk} (°C)	T_{ni} (°C)	T_{in} (°C)
2	0.254	162	97	176	172
4	0.355	167	96(79)^a	189	184
5	0.474	166	98	189	186
6	0.591	162	71(91)^a	185	178(184)^a

^{a} Small peak shoulders

calibration. The heating and cooling rates were ±20°C min^{-1}. A main melting endothermic peak of enthalpy change ΔH_m around 20 J g^{-1} was observed for all the fractions. The isotropization endothermic peaks were very small and rather broad. The peak temperature of transitions measured in heating (T_{kn}, T_{ni}) and cooling (T_{in}, T_{nk}) processes is listed in *Table 1*.

The kinetic measurements of crystallization and liquid crystallization were made on the differential scanning calorimeter and a depolarizing transmittance apparatus[14] respectively. The specimens were first heated to temperatures 15–20°C higher than the corresponding transition temperature and then rapidly cooled down to the selected temperature. The enthalpy change and the transmittance intensity during isothermal formation of the new phase were then recorded as functions of time. The temperature range for isothermal investigation was limited from two sides. For higher temperatures the phase transformation is too slow to allow accurate measurement, while for lower temperatures the phase transformation may start before the establishment of temperature equilibrium of the specimen at the selected temperature.

RESULTS AND DISCUSSION

The isothermal d.s.c. curves for crystallization from the mesophase of fraction 5 are given in *Figure 1*. From these curves the fraction X_t of polymer crystallized at time t can be determined as the ratio of the area of the exotherm at time t to that of the overall exotherm. The data were then used for kinetic analysis on the basis of the Avrami equation:

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

where K is a kinetic constant of the transformation process, and n is a parameter dependent on the type of nucleation and crystal growth geometry[15]. The plots of $\log[-\ln(1-X_t)]$ *versus* $\log t$ at different crystallization temperatures are given in *Figures 2, 3* and *4* for fractions 2, 4 and 5 respectively. The experimental data can be described by straight lines up to sufficiently high conversions. This may imply that the mechanism of crystallization from the mesophase of the polymers is, as in the case of conventionally crystallizing polymers, nucleation followed by growth. A similar conclusion has been obtained for crystallization of main-chain thermotropic polymers[10–12]. The parameters K and n were determined according to equation (1) and the values of n are collected in *Table 2*. The exponent n remains almost constant for fractions 4 and 5 in the temperature range investigated and is around 3.9 and 3.7 respectively. An increase of n from about 3 to 5 was observed for fraction 2 with decrease of undercooling. The high value of n may indicate three-dimensional growth of crystallites in these isothermal processes. In the literature n values of 3–4 have been reported for main-chain thermotropic polyesters with $-(CH_2)_{10}-$ flexible spacers[11,12] and $n=4$ for small-molecule liquid crystals[1–7]. However $n=2$ has also been observed for some polymeric liquid crystals[10,12].

The half-time of crystallization $t_{1/2}$ of different fractions is also listed in *Table 2*, and its temperature dependence is given in *Figure 5*. The overall crystallization rate increases with decreasing molecular weight of the fractions. The value of $t_{1/2}$ is comparable with that for crystallization of conventional polymers at the same degree of undercooling[14,15]. These results may indicate that the kinetic behaviour of polymer crystallization from the mesophase is not substantially different from that of crystallization from the isotropic melt, although the two

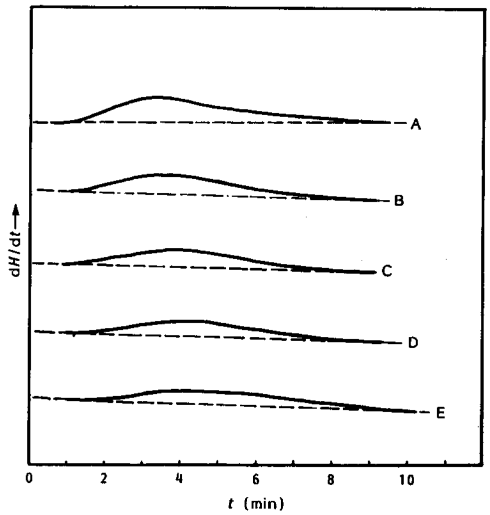

Figure 1 Isothermal crystallization thermograms of fraction 5 at 130°C (A), 131°C (B), 132°C (C), 133°C (D) and 134°C (E)

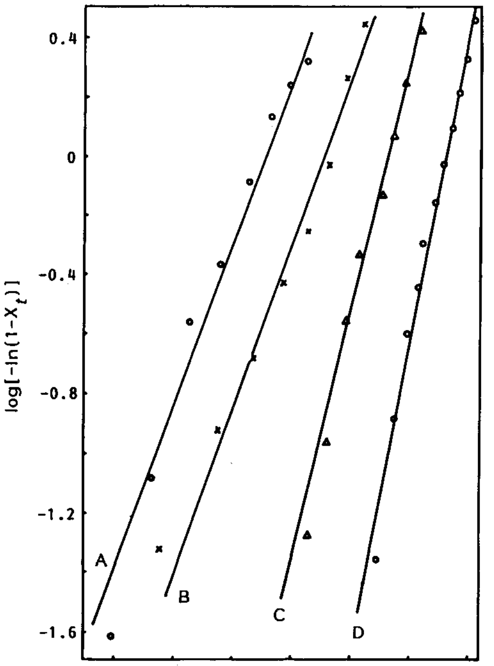

Figure 2 Avrami plots for crystallization of fraction 2 at 130°C (A), 133°C (B), 136°C (C) and 139°C (D)

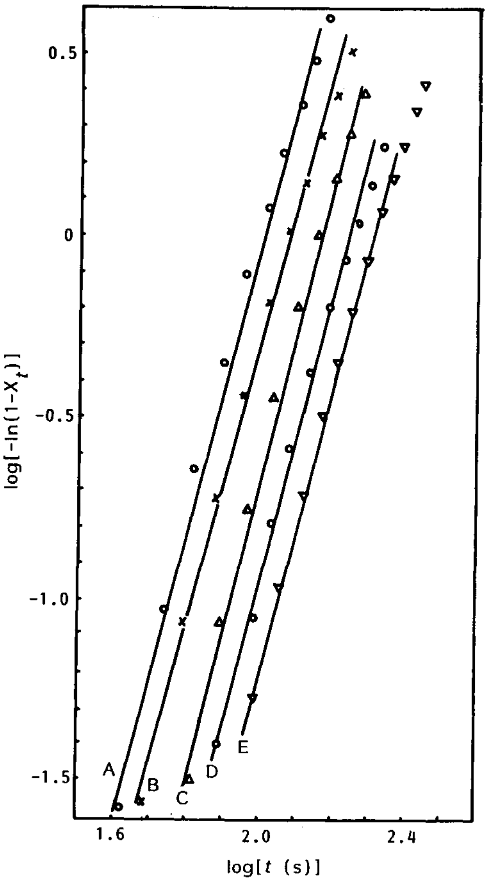

Figure 3 Avrami plots for crystallization of fraction 4 at 130°C (A), 131°C (B), 132°C (C), 134°C (D) and 135°C (E)

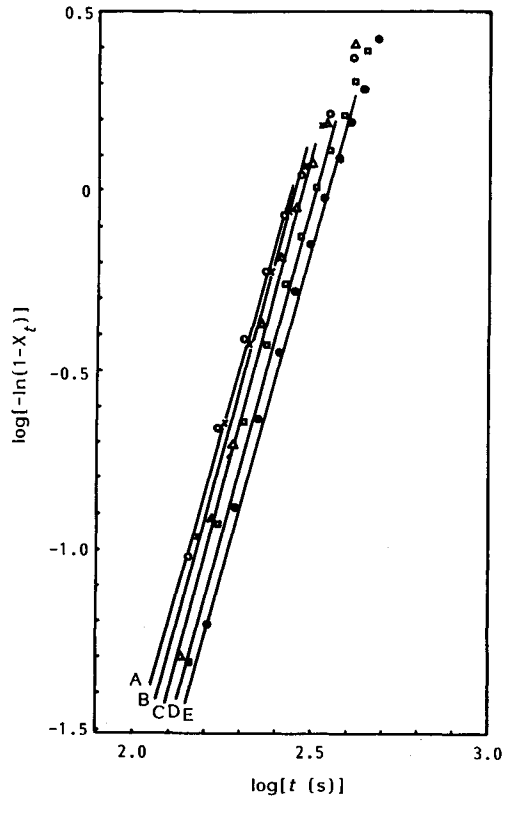

Figure 4 Avrami plots for crystallization of fraction 5 at 130°C (A), 131°C (B), 132°C (C), 133°C (D) and 134°C (E)

Table 2 Kinetic parameters for crystallization of the fractions

Fraction	Crystallization temperature (°C)	n	$t_{1/2}$ (s)	T_m° (°C)	B_1 (K)	B_2 (K)
2	130	2.71	46	166	154	5.2
	133	2.78	72			
	136	4.07	125			
	139	5.11	200			
4	130	3.88	93	170	190	7.6
	131	3.82	110			
	132	4.12	138			
	134	3.97	158			
	135	3.93	186			
5	130	3.53	248	170	90	3.7
	131	3.70	257			
	132	3.83	266			
	133	3.70	291			
	134	3.66	316			

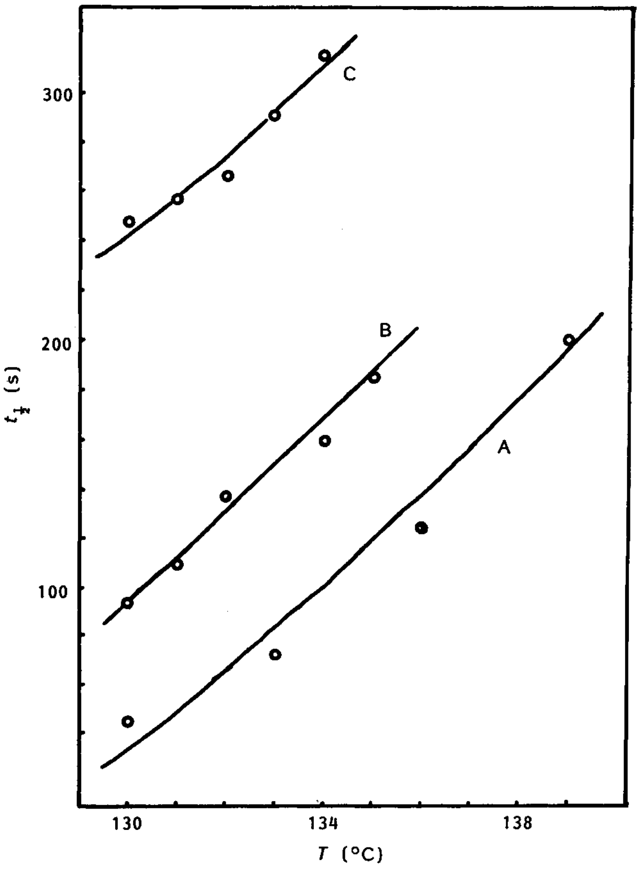

Figure 5 Dependence of half-time on crystallization temperature for fraction 2 (A), fraction 4 (B) and fraction 5(C)

initial phases are different in their order of molecular packing.

The kinetics of the liquid-crystallization process could not be studied by calorimetric measurements owing to its small exothermal effect. However, the depolarizing transmittance technique is quite sensitive to the appearance of macroscopically ordered texture during the formation of the mesophase. The intensity of depolarizing transmittance I was recorded as a function of time t in the isothermal liquid-crystallization experiments. *Figure 6* shows the plots of I *versus* t for fraction 4 at different temperatures. Assuming that I_t is

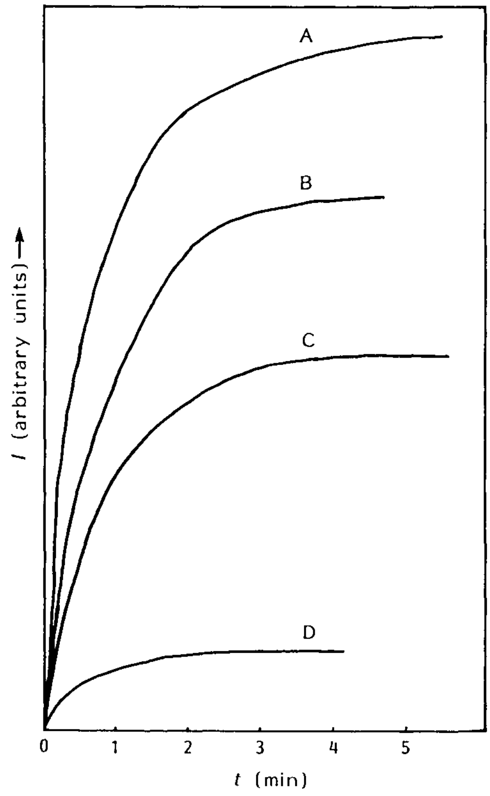

Figure 6 Isothermal curves for liquid crystallization of fraction 4 from depolarizing transmittance measurements at 185°C (A), 186°C (B), 187°C (C) and 188°C (D)

proportional to the fraction of polymer liquid-crystallized at time t, the kinetic behaviour of the liquid-crystallization process at a given temperature can be analysed by means of an Avrami plot of $\log\{-\ln[(I_\infty - I_t)/(I_\infty - I_0)]\}$ *versus* $\log t$, where I_0 and I_∞ are intensity values before and after the liquid-crystallization process, respectively. Data for different fractions are given in *Figures 7*, *8* and *9*. Straight lines were obtained up to high conversions, and kinetic parameters according to equation (1) are listed in *Table 3*. The average values of Avrami exponent n were found to be 1.06, 0.74 and 0.75 for fractions 2, 4 and 6 respectively. The small n values imply an instantaneous nucleation with rod-like growth of the mesophase in isothermal processes in the temperature ranges used. Values of n around 0.75 have been reported recently by Bhattacharya *et al.* for a main-chain thermotropic polyester from d.s.c. measurements[9]. Price and Wendorff have given n values around 2 for small-molecule liquid crystals in kinetic studies of transitions from the isotropic melt to mesophases[1–5]. Although small n values have so far been obtained in most cases, it is not clear if this is characteristic of the liquid-crystallization transition from the isotropic melt, as $n = 3$ has been reported recently for a side-chain thermotropic polyacrylate[8].

The half-times of the liquid-crystallization process for the three fractions studied are given in *Figure 10* as functions of temperature in terms of undercooling $\Delta T = T_{ni} - T$. A tendency of $t_{1/2}$ to increase with molecular weight of the fractions was observed for this polymer. The $t_{1/2}$ values were found to be about 10–100 s at undercoolings less than 10°C, which are comparable with $t_{1/2}$ values for liquid crystallization of small-molecule liquid crystals at low undercoolings (1–2°C)[1–5]. Similar results have been reported for side-chain thermotropic polyacrylate[8]. Very large $t_{1/2}$ values of about 70–200 min at small undercoolings have been given[9]. It is doubtful if one should attribute these large $t_{1/2}$ values simply to a liquid-crystallization process, as a positive temperature coefficient of the transition rate was reported at very small undercoolings.

The influence of temperature on the rate of a transformation composed of nucleation and growth has been discussed by many authors[15,16], and the overall transition rate expressed as $1/t_{1/2}$ can be correlated with temperature through a general equation:

$$\ln(1/t_{1/2}) = A - B_k (T_t^\circ)^k / T(\Delta T)^k \qquad (2)$$

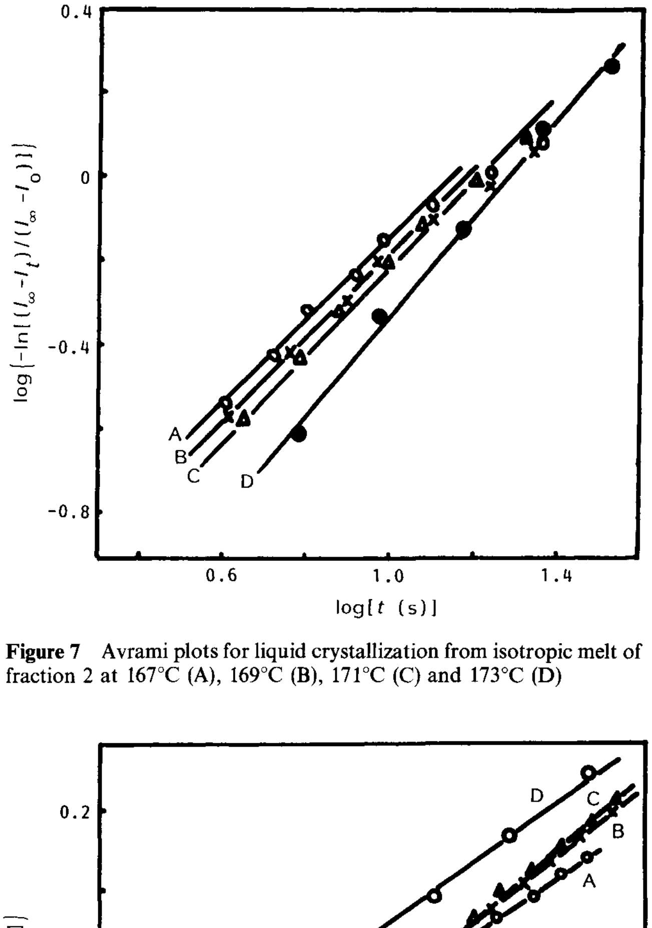

Figure 7 Avrami plots for liquid crystallization from isotropic melt of fraction 2 at 167°C (A), 169°C (B), 171°C (C) and 173°C (D)

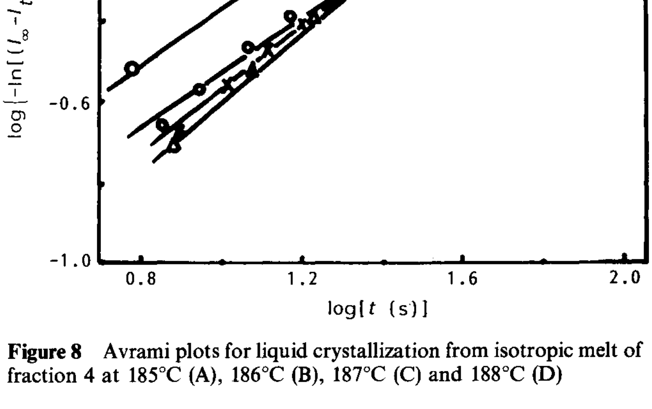

Figure 8 Avrami plots for liquid crystallization from isotropic melt of fraction 4 at 185°C (A), 186°C (B), 187°C (C) and 188°C (D)

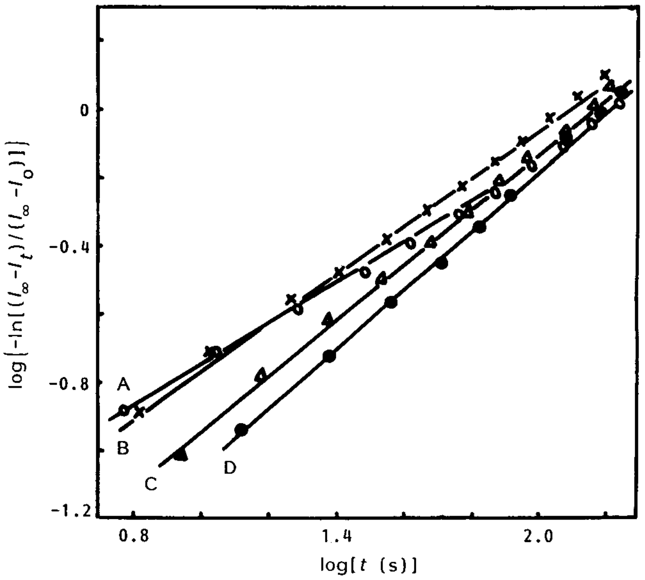

Figure 9 Avrami plots for liquid crystallization from isotropic melt of fraction 6 at 178°C (A), 180°C (B), 181.5°C (C) and 183°C (D)

Table 3 Kinetic parameters for liquid crystallization

Fraction	Liquid-crystallization temperature (°C)	n	$t_{1/2}$ (s)	T_t° (°C)	B_1 (K)	B_2 (K)
2	167	0.98	10.8	–	–	–
	169	1.0	12			
	171	1.06	9			
	173	1.19	13.5			
4	185	0.67	22.5	–	–	–
	186	0.73	34.2			
	187	0.84	33			
	188	0.71	25.5			
6	178	0.58	81	196	25	0.4
	180	0.72	78			
	181.5	0.82	93			
	183	0.88	111			

T_t° is the equilibrium temperature of transformation, and $k=1$ or 2 for different nucleation models. A depends on the density of nucleation and on the energy of transport of molecules, and can be considered constant at small undercoolings. B_k 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 way:

$$B_k \sim (\bar{\sigma})^{k+1}/\Delta H^k \qquad (3)$$

It is clear from equation (3) that B_k is a parameter characterizing the difficulty of nucleation of the new phase.

Data on crystallization and liquid crystallization of all the fractions were analysed according to equation (2). *Figures 11, 12* and *13* show the plots of crystallization data of the fractions. The same plots for liquid crystallization of fraction 6 are given in *Figure 14*. In all cases the experimental data can be fitted by straight lines for plots of $\ln(1/t_{1/2})$ vs. $T_t^\circ/T\Delta T$ and $\ln(1/t_{1/2})$ vs. $(T_t^\circ)^2/T(\Delta T)^2$ by proper selection of the T_t° values. This is similar to the results for crystallization rate given in the literature[15]. The slope B_k and T_t° values of the fractions are listed in *Tables 2* and *3*. The B_1 and B_2 values for crystallization from the mesophase are found to be consistent with those reported for crystallization of conventionally crystallizing polymers[15,16]; while the B_1 and B_2 values for liquid crystallization of fraction 6 are about one order of magnitude less than those for crystallization. The B_k values of liquid crystallization seem to decrease with decreasing molecular weight. The half-time $t_{1/2}$ for liquid crystallization of fractions of lower molecular weight remains almost constant with variation of temperature. The smaller B_k value for liquid

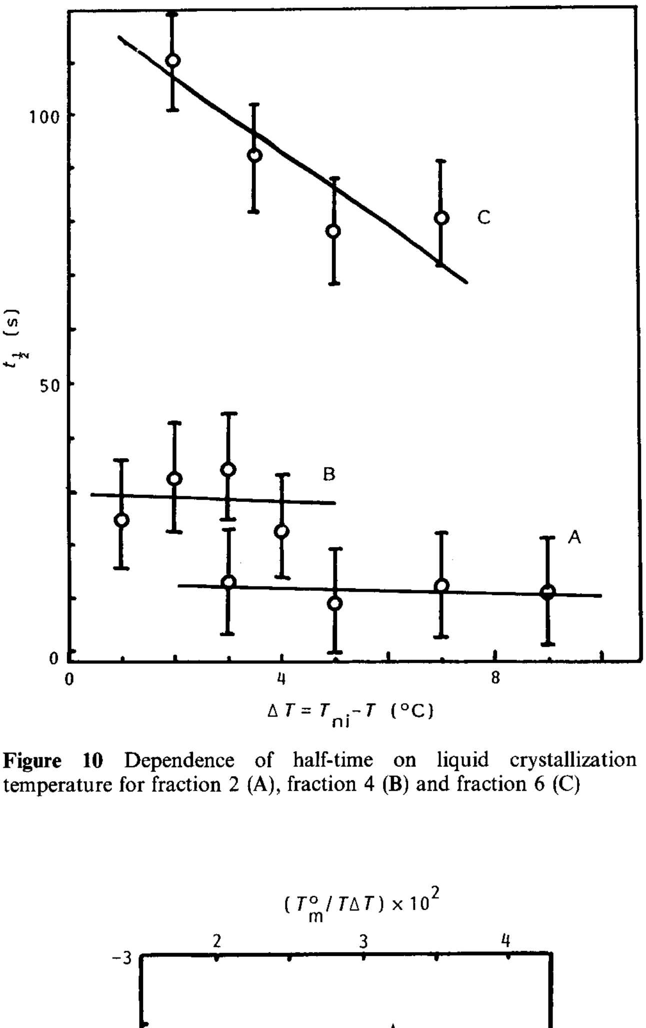

Figure 10 Dependence of half-time on liquid crystallization temperature for fraction 2 (A), fraction 4 (B) and fraction 6 (C)

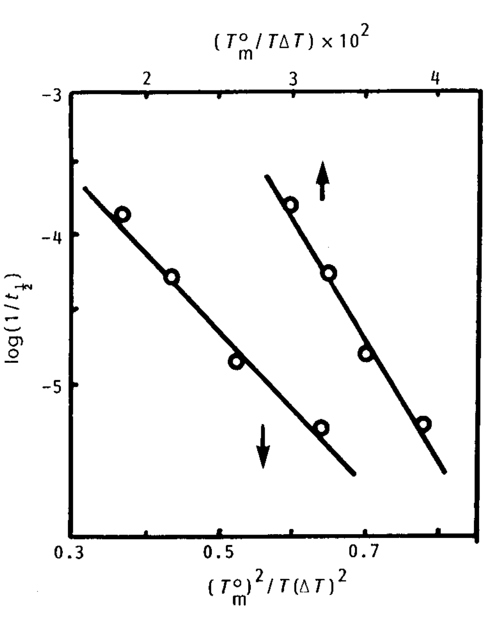

Figure 11 Plots of $\ln(1/t_{1/2})$ *versus* $T_m^\circ/T\Delta T$ and $(T_m^\circ)^2/T(\Delta T)^2$ for fraction 2

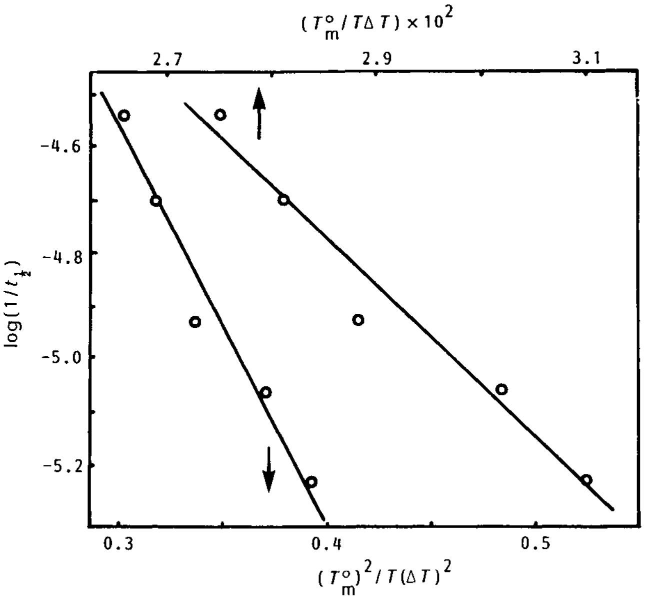

Figure 12 Plots of $\ln(1/t_{1/2})$ *versus* $T^\circ_m/T\Delta T$ and $(T^\circ_m)^2/T(\Delta T)^2$ for fraction 4

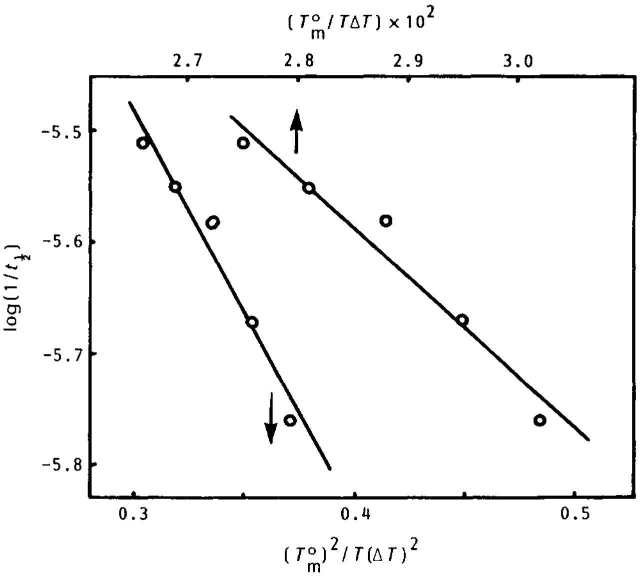

Figure 13 Plots of $\ln(1/t_{1/2})$ *versus* $T^\circ_m/T\,\Delta T$ and $(T^\circ_m)^2/T(\Delta T)^2$ for fraction 5

crystallization means 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 less than that of fusion is also taken into account. These results may explain the experimental phenomena that liquid crystallization can proceed with high transformation rate at very small undercoolings, whereas crystallization only proceeds at very large undercoolings.

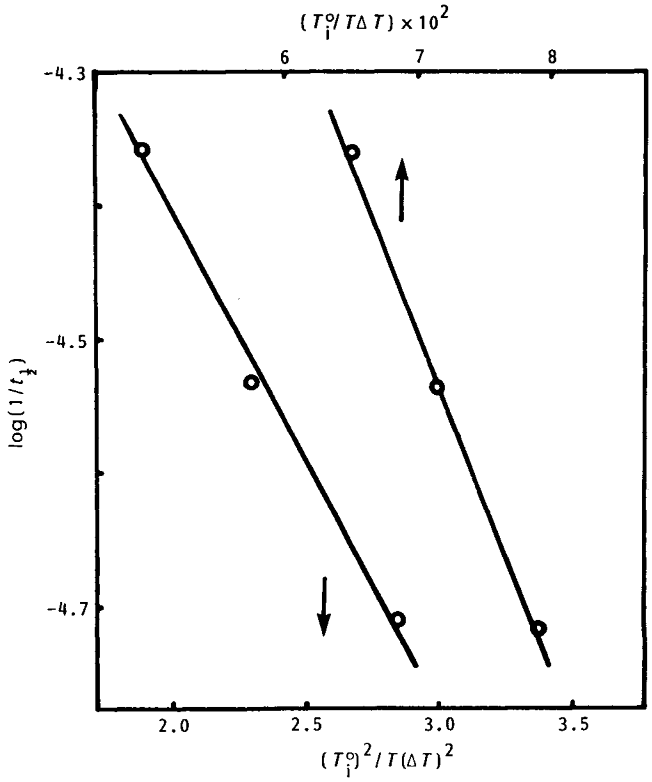

Figure 14 Plots of $\ln(1/t_{1/2})$ *versus* $T^\circ_i/T\Delta T$ and $(T^\circ_i)^2/T(\Delta T)^2$ for fraction 6

CONCLUSIONS

The isothermal processes of crystallization from the mesophase and liquid crystallization from the isotropic melt are composed of nucleation and growth of the new phase and can be described by the Avrami equation. The Avrami exponent n was found to be ~ 4 and ~ 1 for crystallization and liquid-crystallization transitions respectively. The difference in the n values implies a difference in growth geometry of new phases during the two transitions. The temperature dependence of the crystallization rate from the mesophase is similar to that for small-molecule liquid crystals and also that for conventional polymers from the isotropic melt. Compared to crystallization, the liquid-crystallization rate shows a very weak temperature dependence. This implies that the surface free energy of mesophase domains is much less than that of crystallites, which may explain the experimental fact that liquid crystallization from the isotropic melt can proceed with high transformation rate at very small undercoolings, whereas crystallization only proceeds at very large undercoolings.

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