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ISOTHERMAL CRYSTALLISATION KINETICS OF LIQUID CRYSTAL SEMIFLEXIBLE POLYESTERS *

M. LAUS and P. FERRUTI

Dipartimento di Ingegneria Meccanica, Università di Brescia, 25060 Brescia (Italy)

D. CARETTI and A.S. ANGELONI

Dipartimento di Chimica Industriale e dei Materiali, Università di Bologna, 40136 Bologna (Italy)

G. GALLI and E. CHIELLINI

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, 56100 Pisa (Italy)

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ABSTRACT

The isothermal crystallisation from the nematic phase of five thermotropic liquid crystalline TR*m* polyesters formed from two mesogenic *p*-oxybenzoyl diads alternately flanked by a trioxyethylene segment and a polymethylene spacer of variable length ($m = 6–10$) was investigated.

The melting behaviours, thermodynamic melting temperatures and crystallisation kinetic parameters are discussed in terms of the polymer structure. The activation energy for the formation of critical nuclei proved to be dependent on the inherent flexibility and parity of the spacer.

INTRODUCTION

The investigation of the thermal behaviour and relevant thermodynamic parameters of thermotropic liquid crystalline polymers containing rigid groups and flexible spacers in the main chain has attracted great interest on both fundamental and technological grounds. Much work [1] has been done on the molecular design and mesomorphic properties in the melt of thermotropic polymers, whereas there have been very few studies [2–5] on the kinetics of the phase transformations between the mesomorphic state and the semicrystalline solid. Calorimetric techniques, optical microscopy and small-angle light-scattering analysis have indicated that for this class of semiflexible polymer, the crystallisation mechanism is consistent with

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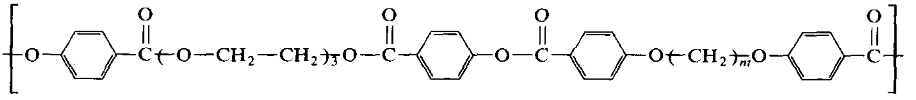
nucleation followed by crystal growth, and that the lamellar crystallites are organised in spherulitic superstructures [3].

To elucidate the influence of structural factors on the propensity of thermotropic polymers to crystallise from the mesophase, differential scanning calorimetry was used to investigate the melting behaviour and kinetics of isothermal crystallisation from the nematic phase of a series of liquid crystalline polyesters [6,7] with the following general structure



TR*m* ($m = 6-10$)

The polymer repeating unit contains two mesogenic *p*-oxybenzoyl diads alternately separated by a segment derived from triethylene glycol and a polymethylene spacer of variable length ($m = 6$–10). According to the nomenclature previously adopted [7], these polymers are designated TR*m* where *m* indicates the number of methylene units in the spacer.

Monitoring the melting process and isothermal crystallisation permitted determination of the Avrami crystallisation exponents and kinetic rate constants, and evaluation of the energy of formation of nuclei of critical dimensions as functions of the length of the spacer.

EXPERIMENTAL

TR*m* polymers were synthesised as previously described [7]. Calorimetric analyses and crystallisation experiments were carried out under a dry nitrogen flow with a Perkin–Elmer DSC 7 apparatus equipped with a 3700 data station, using Delta and Delta Isothermal standard programs respectively. Polymer samples of 5–10 mg were employed. The temperature scale was calibrated against the melting temperatures of benzoic acid and indium. Indium was used as a standard material for the determination of enthalpy of fusion. Glass transition temperatures were taken at the temperature of half devitrification with a heating rate of 10 K min^{-1}. The transition temperatures of the bulk-crystallised samples were taken as corresponding to the maximum in the enthalpic peaks obtained with a heating rate of 10 K min^{-1}.

Isothermal crystallisation procedure

The samples were first melted for 20 min at an isotropic melt annealing temperature T_{ia} (Table 1), chosen 20 K above the isotropisation temperature to avoid any traces of crystallinity. The samples were subsequently cooled at 50 K min^{-1} to a nematic melt annealing temperature T_{na} (Table 1) chosen

TABLE 1

Isotropic and nematic melt annealing temperatures for TR*m* polyesters

Sample	*m*	T_{ia} (K)	T_{na} (K)
TR6	6	477.2	451.2
TR7	7	427.2	388.2
TR8	8	455.2	423.2
TR9	9	431.2	396.2
TR10	10	448.2	408.2

from within the range over which the nematic phase exists on cooling. After 20 min, the samples were rapidly cooled at 200 K min^{-1} to the predetermined crystallisation temperature, and the exothermic crystallisation curve was recorded as a function of time. The time at which the crystallisation exotherm began was taken as the crystallisation zero-time. The weight fraction X_t of crystallised material at time t is the ratio of the area at time t and the area of the whole exotherm.

RESULTS AND DISCUSSION

Liquid crystalline properties

The liquid crystalline properties of TR*m* polyesters were studied, as described elsewhere [6,7], by DSC, polarising microscopy and, in some cases, by X-ray diffraction.

The phase-transition parameters and glass transition temperatures are collected in Table 2. Each polyester has one enantiotropic nematic mesophase, as clearly shown by X-ray analysis and observations of unequivocal schlieren and threaded optical textures. Both isotropisation temperatures and entropies zigzag in function of the length of the spacer, even members of the series possessing remarkably higher values than odd members. The pronounced even–odd alternation of the thermodynamic parame-

TABLE 2

Physicochemical and thermal properties of TR*m* polyesters

Sample	*m*	$[\eta]$ [a] (dl g^{-1})	T_g (K)	T_m (K)	T_i (K)	ΔH_i (kJ mol^{-1})	ΔS_i (J mol^{-1} K^{-1})
TR6	6	0.83	299.5	447.2	457.2	4.52	9.9
TR7	7	0.72	305.0	400.2	407.2	1.55	3.8
TR8	8	0.76	290.0	418.2	435.2	6.66	15.3
TR9	9	0.53	300.2	397.2	411.2	1.97	4.8
TR10	10	0.80	289.0	415.2	428.2	8.13	19.0

[a] In chloroform, at 30 ° C.

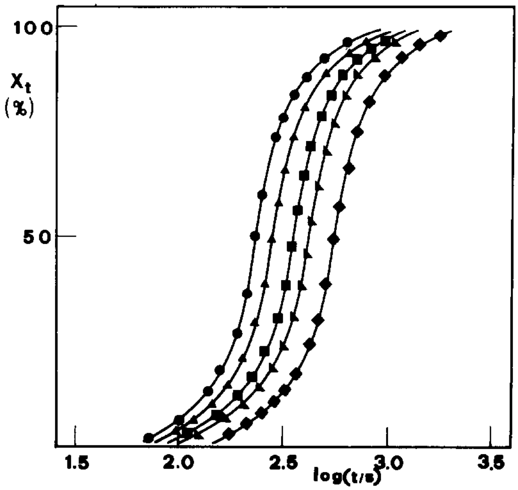


Fig. 1. Crystallisation isotherms from the nematic phase for TR6 polyester at various crystallisation temperatures: ●, 398.2 K; ▲, 400.2 K; ■, 401.2 K; ◣, 402.2 K; and ◆, 403.2 K.

ters of the nematic–isotropic transition demonstrates the fundamental role of the spacer in the ordering process in the nematic state [8].

Isothermal crystallisation kinetics

Isothermal crystallisation from the nematic phase was studied by DSC. As a typical example, the plot of the weight fraction X_t of the crystallised material at time t for TR6 polyester as a function of time at different crystallisation temperatures T_c is reported in Fig. 1. The isotherms have a characteristic sigmoid shape shifted along the time scale. The crystallisation half-times $t_{1/2}$ were calculated (Table 3). The crystallisation rate becomes much faster as the temperature is lowered, indicating a very strong negative temperature coefficient.

The kinetics of isothermal crystallisation was quantitatively analysed using the Avrami equation [9]

$$1 - X_t = e^{-K_n t^n} \tag{1}$$

where K_n is the kinetic rate constant and n is the Avrami exponent indicating the type of nucleation and geometry of the growing crystals [10]. The Avrami plots of $\log[-\ln(1 - X_t)]$ versus $\log t$ for TR6 polymer at five crystallisation temperatures (Fig. 2) are initially linear and then level off for conversion degrees above 70–75% due to secondary crystallisation. The n and K_n values for TRm polyesters were determined from the slope and intercept of the initial linear part (Table 3). The average values $\bar{n}$ (2.7–4.2) are indicative of thermal and/or athermal nucleation followed by a three-dimensional growth. Indeed, for spherulitic growth and athermal nucleation $\bar{n}$

TABLE 3

Equilibrium melting temperature T_m^o, Avrami exponent n (average $\bar{n}$), half-time of crystallisation $t_{1/2}$, and $-\frac{1}{3}(\log K_n)$ as functions of the crystallisation temperature T_c for TR*m* polyesters

Sample	m	T_m^o (K)	T_c (K)	$t_{1/2}$ (s)	n	$\bar{n}$	$-\frac{1}{3}(\log K_n)$
TR6	6	445.5	398.2	250	3.06	2.7	2.24
			399.2	280	2.84		2.29
			400.2	295	2.75		2.31
			401.2	356	2.71		2.38
			402.2	420	2.65		2.45
			403.2	562	2.41		2.56
TR7	7	399.4	367.2	21	3.27	2.9	2.34
			368.2	286	3.46		2.46
			369.2	382	2.87		2.58
			370.2	574	2.58		2.76
			371.2	693	2.52		2.84
TR8	8	419.2	393.2	379	3.80	4.2	3.65
			396.2	732	4.37		4.05
			397.2	946	4.30		4.21
			398.2	1212	4.33		4.36
			399.2	1564	4.18		4.51
TR9	9	407.7	369.2	282	2.84	2.8	2.36
			370.2	300	2.89		2.38
			371.2	332	2.80		2.42
			372.2	351	2.79		2.45
			374.2	383	2.79		2.48
TR10	10	415.9	393.2	244	3.64	3.7	2.96
			394.2	327	3.84		3.11
			395.2	413	3.68		3.24
			396.2	536	3.51		3.37
			397.2	695	3.58		3.51

is expected to be 3 [10]. In the case of thermal nucleation, it is expected to be 4. However, complications in the Avrami analysis often arise because several assumptions, not necessarily applicable to polymer crystallisation, are involved in the derivation [10].

Thermodynamics of melting transition

The melting behaviour of isothermally crystallised TR*m* samples is quite complex. In the DSC heating curves, TR6 polymer shows one defined melting endotherm independent of crystallisation temperature. In contrast, at lower temperatures, a set of endothermic and exothermic peaks is present whose temperatures and intensities are dependent on the crystallisation

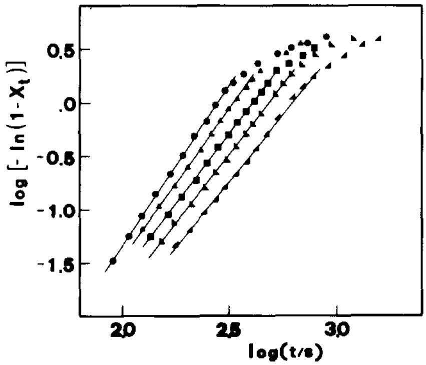


Fig. 2. Avrami plots for TR6 polyester at various crystallisation temperatures: ●, 398.2 K; ▲, 400.2 K; ■, 401.2 K; ◣, 402.2 K; and ◢, 403.2 K.

conditions. The structuring of the melting process is probably due to successive melting and recrystallisation of regions of imperfect crystallinity [11,12].

In the case of TR7 polymer, one broad melting peak is observed which is preceded by a shoulder. The temperature of the former endotherm is practically independent of any thermal treatment. In contrast, the temperature of the latter transition increases with increasing crystallisation temperature. TR8, TR9 and TR10 polymers display similar DSC melting profiles consisting of two distinct endothermic transitions. In some cases, a recrystallisation exotherm located between the two melting peaks is also observed. The temperature of both melting endotherms increases with increasing crystallisation temperature, the increase being more pronounced for the lower temperature component. The enthalpy of the lower temperature peak

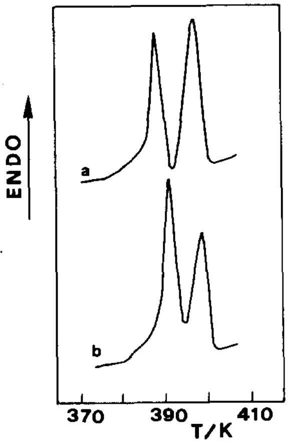


Fig. 3. DSC melting endotherms for TR9 polyester: a, isothermally crystallised at 370.2 K; b, isothermally crystallised at 374.2 K.

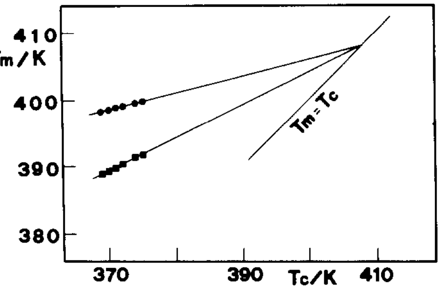


Fig. 4. Temperatures of the melting endotherms (T_m) vs. the crystallisation temperatures (T_c) for TR9 polyester.

increases with increasing crystallisation temperature, while the enthalpy of the higher temperature peak decreases (Fig. 3). This dual melting behaviour may result from reorganising processes consistent with partial melting of the initial crystallites, followed by recrystallisation and then final melting [11,12]. The equilibrium melting temperatures T_m^o for the polymers examined were determined by plotting the peak temperatures corresponding to the actual melting of the isothermally grown crystals against the crystallisation temperatures and extrapolating to infinite thickness of the lamella ($T_m = T_c$), following the method suggested by Hoffmann et al. [13] (Fig. 4). Accordingly, when multiple peaks were observed in the melting process, the evaluation of T_m^o (Table 3) was performed by considering the lower temperature endotherm only.

Analysis of the overall crystal growth rate

According to classical crystallisation theory [14,15], in the case of spherulitic crystal growth the overall rate constant K_n can be expressed by the equation

$$\tfrac{1}{3}\log K_n + \frac{\Delta F^\star}{2.3kT_c} = A_0 - \frac{\Delta\Phi^\star}{2.3kT_c} \tag{2}$$

where $\Delta F^\star$ is the free energy of activation for the transport of units across the phase boundary and $\Delta\Phi^\star$ is the free energy of activation for the formation of a critical size nucleus; A_0 is taken as a constant, to a first approximation, which implies that the spherulite nucleus density is independent of time, melting temperature and crystallisation temperature [10], and k is the Boltzman constant. We equate the transport term, $\Delta F^\star$ to the activation energy for viscous flow obtained from the Williams–Landel–Ferry (WLF) equation [16]

$$\Delta F^\star = \Delta F_{\mathrm{WLF}} = \frac{C_1 T}{C_2 + T - T_g} \tag{3}$$

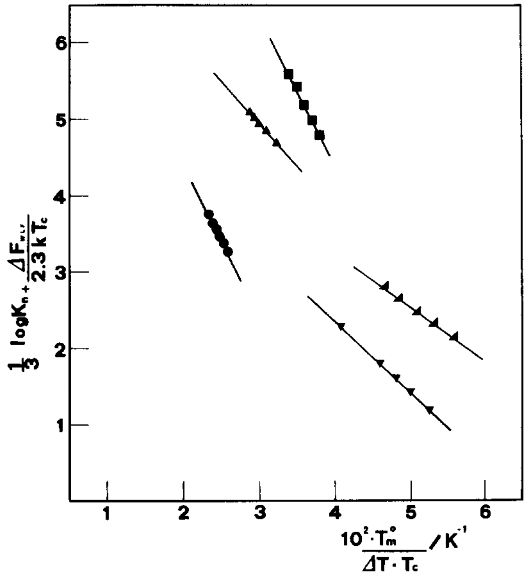


Fig. 5. Plot of $\frac{1}{3}$ log $K_n + (\Delta F/2.3kT_c)$ against $(T_m^o/\Delta T T_c)$ for TRm polyesters: ●, TR6; ▲, TR7; ■, TR8; ▼, TR9; and ◢, TR10.

where C_1 and C_2 are constants equal to 4.12 kcal mol^{-1} and 51.5 K respectively, and T_g is the glass transition temperature of the polymer. It should be observed that the reported values of C_1 and C_2 in the WLF equation are typically found in isotropic glasses. However, it has been pointed out that nematic and isotropic glasses of thermotropic side-chain polymers at a given temperature possess the same amount of free volume [17], which ultimately controls the transport properties.

The free energy of formation of a nucleus of critical dimensions is given by [10a]

$$\Delta\Phi^\star = \frac{4b_0\sigma\sigma_e T_m^o}{\Delta_m H \Delta T} \tag{4}$$

where σ and σ_e are the surface free energies per unit area parallel and perpendicular to the chain axis respectively, b_0 is the distance between crystallographic planes of growth, $\Delta_m H$ is the enthalpy of melting, T_m^o is the equilibrium melting temperature, and $\Delta T = T_m^o - T_c$ is the degree of supercooling. According to eqns. (2) and (4), plots of $[\frac{1}{3}\log K_n + (\Delta F/2.3kT_c)]$ versus $(T_m^o/\Delta T T_c)$ give straight lines (Fig. 5), whose slopes (Table 4) enable the energy of formation of a nucleus of critical dimensions $\Delta\Phi^\star$ to be calculated.

The trend of $\Delta\Phi^\star$ at a constant degree of supercooling as a function of the number m of methylene units of the spacer is illustrated in Fig. 6.

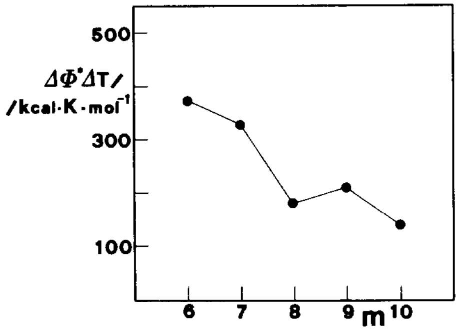


Fig. 6. Trend of the activation energy for the formation of critical nuclei, $\Delta\Phi$ *, at constant supercooling ΔT for TR*m* polyesters as a function of the number *m* of methylene units in the polymethylene spacer.

TABLE 4

Numerical values for the slopes of the straight lines in Fig. 5 for TR*m* polyesters

Sample	*m*	Slope [a]
TR6	6	183.3
TR7	7	180.3
TR8	8	94.6
TR9	9	111.0
TR10	10	73.0

[a] The value of the slope corresponds to the quantity $(4b_0\sigma\sigma_e/2.3k\Delta_m H)$.

The energy of formation of a nucleus of critical dimensions decreases with a slightly pronounced zigzag as the series is ascended. The downward trend of $\Delta\Phi^\star$ is a result of the increasing flexibility of the repeating unit, which favours the packing possibility of the macromolecular chains from the nematic phase. These results are consistent with those of previous isothermal crystallisation experiments from the smectic phase of polyesters containing the mesogenic 4,4′-(terephthaloyloxydioxy) dibenzoate unit and alkylene spacers [4]. In addition, at constant supercooling the values of $\Delta\Phi^\star$ for odd members appear to be higher than those expected for a simple diluting effect.

CONCLUSIONS

The kinetics of isothermal crystallisation from the nematic phase of a series of TR*m* polyesters is controlled by nucleation, and the crystals essentially grow according to a spherulitic geometry. The melting behaviour of isothermally crystallised samples is influenced by the chemical structure of the polymer and may involve multiple transitions. The equilibrium melting temperatures have been determined. They are influenced by the even–odd character of the spacer.

The overall crystallisation rate can be described in accordance with existing crystallisation theories. The activation energy for the formation of critical nuclei is found to be dependent upon the inherent flexibility of the spacer with an apparent even–odd fluctuation.

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