Macromolecules 1992, *25*, 4392–4398

Kinetics of Three-Dimensional Ordering in the Thermotropic Liquid Crystal Poly(decamethylene-4,4′-diphenoxy terephthalate)

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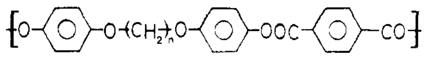
Received October 31, 1991; Revised Manuscript Received March 11, 1992

ABSTRACT: Differential scanning calorimetry has been used to study the isothermal kinetics of three-dimensional ordering from the liquid crystalline and isotropic states in poly(decamethylene-4,4′-diphenoxy terephthalate). Different transformation rates were obtained for different conditioning temperatures from both the mesophase and the isotropic state, indicating that the mesophase has a strong influence on the kinetics. The isotherms obtained follow the Avrami relation with an exponent of $n = 2$ for the kinetic studies from the isotropic melt, and exponents $n = 2$ and 3 for the studies from the mesophase. A nucleation and growth process was assumed in the determination of the temperature coefficient of the transformation. A break in this coefficient for the transformation from the mesophase has been identified for the first time and has been related to changes in the Avrami exponent.

Introduction

Polyesters prepared from series of (4,4′-dihydroxydiphenoxy)alkanes and terephthalate acid with the general structure



have been described by Lenz et al.[1-3]

Due to the possibility of changes of the molecular spacers between linear and symmetrically or asymmetrically side-group-substituted polymers, the properties, and particularly the thermal transitions, in these systems can be dramatically modified.

In a general project on the study of these properties, we previously analyzed the behavior of the linear polymer with $n = 10$, poly(decamethylene-4,4′-diphenoxy terephthalate) (PDDPT), with particular emphasis on the influence of thermal treatment on the transitions and on the nature of the mesophase.[4] In these studies, PDDPT was shown to be a semicrystalline polymer which exhibits thermotropic behavior, with several interesting features which have not been previously reported. A variety of thermal transitions were determined, including a glass transition temperature at 67 °C, a crystal–liquid crystal transition with a maximum at ~241 °C, a mesophase–mesophase transition at temperature slightly higher than 241 °C, and, finally, a mesophase–isotropic transition at 290 °C.

Two main points must be emphasized. First, contrary to the results found for other thermotropic polyesters,[5,6] different thermal treatments do not affect the range of the transition temperatures. Second, although it was considered that PDDPT has a nematic texture,[2,3] this polymer exhibits a mesophase (1)–mesophase (2) transition. A number of experimental techniques (thermoptical analysis, X-ray diffraction, and small-angle light scattering) have been used in order to examine and understand the nature of this transition, which corresponds to a smectic C–nematic transition.[4]

However, studies on the kinetics of the mesophase formation and of the three-dimensional ordering, or crystallization, from the mesophase or from the isotropic state are very scarce in thermotropic polyesters. Only in some systems such as polyphosphazenes,[7,8] polysiloxanes,[9] and a few thermotropic polyesters[10-13] and copolyesters[14,15] have the kinetics of these processes been analyzed. Most of these studies have been carried out using approaches derived for the analysis of the crystallization of polymers. It is well-known that this process is described by a nucleation and growth mechanism,[16,17] and the strong temperature coefficient observed in the transformation is explained in terms of the temperature coefficient of these two processes. Moreover, the development of crystallinity, or the degree of transformation, has been described by the free growth[18] and Avrami approximations.[19]

Therefore, the ordering kinetics of liquid crystalline polymers has generally been analyzed by assuming a nucleation-controlled process and by using the Avrami equation, in spite of the differences between the formation of a mesophase from the isotropic state and the transformation of a mesophase to a three-dimensional array. Moreover, the experimental data are mainly related to the transformation of the mesophase, since the major limitation for studies of ordering from the isotropic state is that most of these systems present a degradation temperature very close to the isotropization temperature.

The general results present some controversial points about the mechanism of the transformation and the resulting parameters. In some polyphosphazenes, the Avrami exponents have been found to be 2 for the isotropic–mesogenic transformation, and for the mesophase–crystalline transformation,[7] and in others,[8] a value of $n = 3$ has been found. In a similar way, polyesters containing different mesogenic units with glycols of different length have been analyzed[10,11] in order to study the nucleation and growth from the mesomorphic state, and the Avrami equation was fit with different exponents depending on the glycol and the mesogenic unit. Thermotropic random rigid copolyesters, which frequently display a nematic mesophase,[14] have also been studied, and in some cases extremely low values of n have been found.[15]

Besides these changes, other points of interest are the influence of the conditioning temperature on the kinetics of the transformation from the mesomorphic state and the comparison of the transformation rates from the isotropic and the mesomorphic states because, in principle, the anisotropic organization of the mesophase may play an important role in the kinetics.

Considering all of these reasons, the main aim of this work is to analyze the kinetics of crystalline formation

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from the isotropic and from the mesomorphic states in PDDPT, after extensive analysis of the phase transition carried out previously by several techniques.[4] A previous report indicated that crystallization kinetic data on this polymer could not be obtained.[11]

This analysis may be generalized and applied to other semiflexible polyester liquid crystals, with the same or different mesogenic units, at present being studied in our laboratory.

Experimental Section

Synthesis and Characterization. The monomer α,ω-bis(hydroxyphenoxy)decamethylene (DHDFD) was synthetized as described by Griffin and Havens[20] from hydroquinone and α,ω-dibromodecamethylene. Poly(decamethylene-4,4′-diphenoxy terephthalate) (PDDPT) was prepared by the method described by Lenz et al.[2]

Characterization of both DHDFD and PDDPT was carried out by elemental analysis, IR, ^{1}H NMR, and ^{13}C NMR methods, as previously described.[4] According to the experimental analysis from these methods, the structure of the polymer corresponds to the predicted theoretical structure. The existence of the monofunctional premonomer has been eliminated from intensity ratios in the ^{13}C and ^{1}H NMR results.

The inherent viscosity of the polymer solution was measured in a Ubbelohde viscosimeter at a concentration of 0.2 g·dL^{-1} in *p*-chlorophenol at 45 °C. The value obtained was $\eta_{\text{inh}} = 0.45$ dL·g^{-1}.

Kinetics. Prior to the kinetic analysis, the thermal stability of the polymer was studied by thermogravimetry. A Perkin-Elmer TGA7 apparatus was used with nitrogen as the purge gas and with a heating rate of 10 °C·min^{-1}. In another experiment, the isothermal curve at 300 °C was recorded for more than 1 h. The polymer was shown to be stable up to 300 °C for at least 60 min, and only a 10% loss was obtained at 425 °C in the dynamic experiment.

The kinetic studies were carried out using calorimetric techniques, the general principles having been described elsewhere.[21] All the differential scanning calorimetry measurements were made on a Perkin-Elmer DSC 7 instrument. Automatic calibration was carried out with indium (T_m = 156.6 °C, ΔH_m = 28.45 J·g^{-1}) and zinc (T_m = 419.47 °C, ΔH_m = 108.37 J·g^{-1}) as standards.

For the kinetic experiments, the size of the samples was between 8 and 10 mg. In some cases, the samples were heated to 10 °C above the corresponding isotropization temperature for 5 min. Subsequently, the samples were undercooled at a rate of 32 °C·min^{-1} until the desired temperature was reached, and the corresponding exotherms were scanned as a function of time until no change in the DSC energy axis was observed. Partial areas corresponding to a given percentage of the total transformation were determined from the data points stored for each isothermal run on a PE 7700 computer by using DSC 7 kinetics software.

In other cases, the samples were heated from room temperature to a temperature, T_a, between the crystal–liquid crystal transition temperature (T_1) and the isotropization temperature (T_i), where $T_1 < T_a < T_i$. From the T_a temperature, the sample was undercooled at a rate of 32 °C·min^{-1} until the crystallization temperature, T_c, was reached ($T_c < T_1$). The corresponding exotherms were scanned and the partial areas calculated as was described above for the first case.

After completion of the kinetic process, the transition temperatures were determined by heating the samples at a rate of 10 °C·min^{-1}. T_1 and T_i were obtained from the maximum of the endothermic peaks.

Morphology. Wide-angle X-ray diffractograms were obtained using a Philips Geiger counter X-ray diffractometer with an Anton Paar 300 temperature camera. Samples for analysis were prepared from the original powder or from samples thermally treated as recorded in each case. The diffractograms were recorded in a 2θ range between 3° and 32° at a rate of 2°·min^{-1}, using Ni-filtered Cu Kα radiation. Pinhole collimation and a flat-plate camera were also used with a Siemens K710 generator to obtain photographic diffraction patterns through Polaroid plates.

Microscopy studies and thermoptical analysis were carried out using a Reichert polarizing microscope, Zetopan Pol, equipped with a Mettler FP80 hot stage and Nikon FX 35A camera.

Small-angle light scattering studies were carried out with an instrument similar to that described by Stein[22] using a He–Ne, λ = 6328 nm, laser. The scattering patterns were recorded on Polaroid plates.

Results and Discussion

The kinetics of the transformation of liquid crystals can be considered for three different situations: (a) crystallization from the isotropic state to a crystallization temperature below the temperature at which the liquid crystal–crystal transition (T_1) takes place, (b) transformation from the isotropic state to the mesomorphic ordered state at a temperature T ($T_1 < T < T_i$), and (c) three-dimensional ordering from the mesomorphic state at a temperature below T_1.

Case a will be possible only if the chemical structure and the kinetic and thermodynamic conditions allow one to obtain three-dimensional order. Consequently, this case will be limited to semicrystalline liquid crystals. In order to get reproducible data, the isotropization temperature must be below the descomposition temperature. This condition constrains the possibilities of analyzing the kinetics because in many liquid crystals these two temperatures are very close. Moreover, the transformation from the isotropic melt to three-dimensional order seems to take place, in many polymers, throughout the mesophase formation.[7] Only in those cases in which the isotropic melt–liquid crystal transition is very slow can the rate of the three-dimensional ordering be measured. If this is not the case, the overall transforming rate will be a combination of isotropic melt–liquid crystal and liquid crystal–crystal transition.

In case b, there are different possibilities of ordering during the transformation. The mesomorphic type must be considered, since several different types can exist, and the possibility of smectic–nematic transitions must be recognized. The enthalpy changes for these processes are, in general, very small and the usual calorimetric measurements do not detect the isothermal ordering that occurs in many liquid crystals, only a few degrees below T_i. In some cases the enthalpy values associated with the isotropization are larger than those for the crystal–liquid crystal transition due to the fact that the difference in order between the crystalline and mesophase forms is smaller than that between the mesophase and the isotropic state. This situation, reported for thermotropic polyethers,[23] is very favorable for experimental analysis of the kinetics.

Case c is the more generally studied transformation, but the temperature of the mesomorphic state at which the system is maintained prior to undercooling may play an important role.

PDDPT is a semicrystalline polymer, and its thermal transitions and thermodynamical parameters have been reported before.[2–4] The isotropization temperature T_i = 300 °C is below the decomposition temperature. Therefore, it is a good candidate to study and perform experiments following cases a and c. The formation of the mesophase from the isotropic state has not been studied because the enthalpic changes under isothermal conditions are very small compared with the enthalpic change in the crystal–liquid crystal transition (ΔH_1).

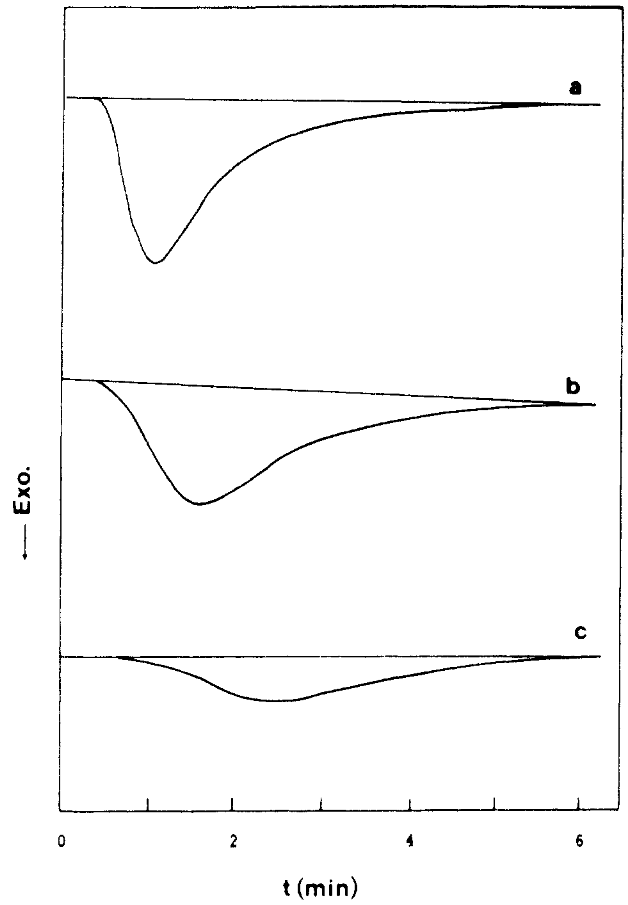

Figure 1. Experimental isothermal curves of PDDPT at three different temperatures: (a) 237, (b) 238, and (c) 238.5 °C, crystallized from the isotropic state.

(A) Kinetics of Formation of Three-Dimensional Order from the Isotropic State. The crystallization kinetics of PDDPT from the isotropic state was quantitatively analyzed from data obtained in the temperature interval from 237 to 240 °C. At higher temperatures the rates were too slow to be measured by DSC in a reasonable time period, and at lower temperatures the process was so rapid as to preclude accurate measurements. In Figure 1, typical experimental curves are shown, and in Figure 2, the isotherms are plotted for several crystallization temperatures. The shape of the isotherms and their superimposability indicate that the mechanism controlling the tranformation is the same in the temperature range which has been considered.

The total crystallinity of PDDPT could not be obtained from the DSC experiments. However, from independent WAXS measurements, crystallinities of ~50% have been estimated. From the values of crystallinities obtained for samples crystallized from solution, slowly cooled, and quenched in liquid nitrogen, and the corresponding values of the enthalpies determined by DSC, it is possible to extrapolate the enthalpy corresponding to the melting of 100% crystalline PDDPT, $[\Delta(H_1)_{100\%} = 60 \pm 5\ \mathrm{J{\cdot}g^{-1}}]$. Therefore, with this value, crystallinities after isothermal crystallization could be calculated. They are practically independent of the crystallization temperature and are significantly lower than those obtained after crystallization under nonisothermal conditions. The reason for this result must be related to the crystallization of lower molecular weight species at the highest undercooling.

Moreover, the half-time $\tau_{0.5}$ (time to reach 50% of the total transformation) is very dependent on the crystallization temperature, and it increases exponentially with temperature (see Figure 7 in part B). This behavior is once again a strong confirmation that the crystallization, like the bulk crystallization of polymers, proceeds via a nucleation mechanism.[17]

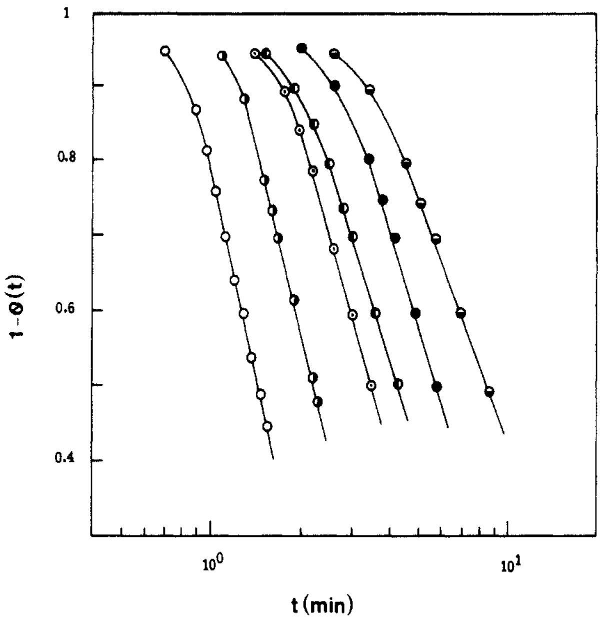

Figure 2. Logarithmic plot of $1 - \Theta(t)$ against time for PDDPT crystallized from the isotropic state at indicated temperatures: (○) 237, (◑) 238, (⊙) 238.5, (◐) 239, (●) 239.5, and (⊖) 240 °C.

Isothermal development of crystallinity in polymers has been described by the Avrami[19] and Göler–Sachs[18] approximations. The Avrami equation is given by

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

where θ is the fraction of crystallized material at time t, k is a constant, and n defines the mode of nucleation and growth. Values of n are 2, 3, or 4 for one-, two-, or three-dimensional growth geometries, respectively. Other values have been proposed for different situations in the nucleation and growth processes.[24]

In spite of the simplifications introduced in the Avrami equation, it is a convenient method to represent experimental data, and the analyses of many polymers show good adherence to the equation for the initial part of the crystallization process. Values of n can be obtained from the slope of the double-logarithmic plot, ln $(1 - \theta)$ against log t. Integral values of n have been obtained for low extents of transformation, and only at long crystallization times do deviations from the theory occur.

For PDDPT, a linear relation was obtained for the initial part of the transformation in the Avrami plot (Figure 3). The slope corresponds to an integral value of $n = 2$. This value is related either to homogeneous nucleation and one-dimensional growth or to heterogeneous nucleation and two-dimensional growth. A value of $n = 3$ seems to fit the linear part of the plot only at the lowest crystallization temperature.

Crystallization kinetics of thermotropic polyesters have been studied mostly from the mesophase to the crystalline order, and this case will be commented on in the next section. To our knowledge, the only case in which the kinetics of isotropic three-dimensional-order transformation has been previously reported is poly[(bis(4-ethylphenoxy)phosphazene].[8] The Avrami analysis gives a value $n = 4$. It is important to emphasize that in this case no formation of the mesophase is observed when the sample is quenched from the isotropic melt.[8] This indicates that the mesophase formation rate is very low for this particular

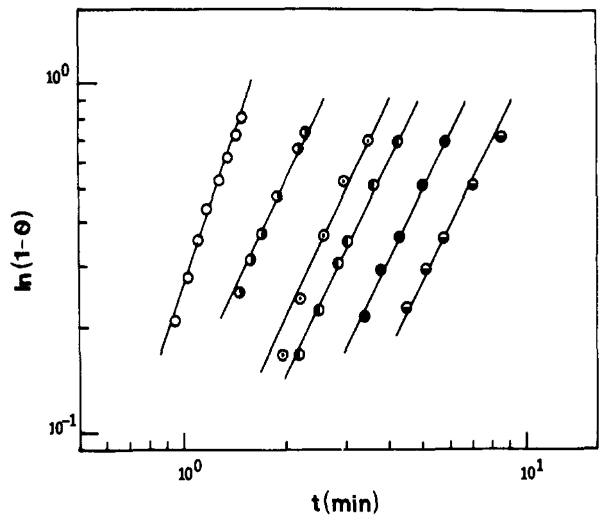

Figure 3. Double-logarithmic plot of $1 - \Theta(t)$ against time for PDDPT at indicated temperatures: (○) 237, (◑) 238, (⊙) 238.5, (◐) 239, (●) 239.5, and (⊖) 240 °C.

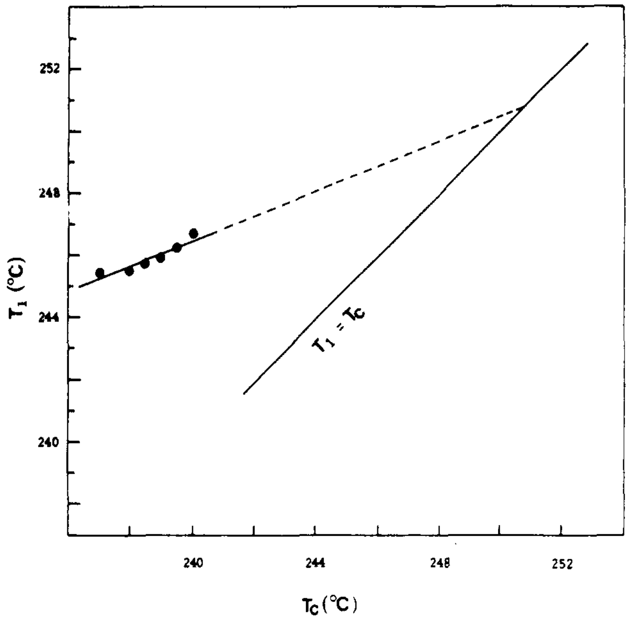

Figure 4. Plot of T_l after crystallization at several T_c.

case, and the crystallization process is very similar to that found in other semicrystalline polymers.

On the other hand, in order to analyze the crystallization data, it is important to study the crystal–liquid crystal transition temperature, T_l, after the isothermal crystallization. Here again, it is necessary to consider two different situations: the ordering from the isotropic state and the ordering from the mesophase. With reference to the first case, T_l depends on the crystallization temperature, as shown in Figure 4. The higher the crystallization temperature, the higher are the T_l temperatures, which range from 245.5 to 246.7 °C.

The slope of the relation $T_l - T_c$ corresponds to 0.5, similar to the value obtained in the relationship for semicrystalline polymers.[24-26] A value of T_l extrapolated at the line $T_l = T_c$ gives a value of $T_l = 250 \pm 2$ °C. In spite of the similarity to the behavior of semicrystalline polymers, and the method to determine the equilibrium melting temperature, the meaning of the extrapolated T_l is quite different, because it is not a transition to a random melt. It is in fact the maximum temperature at which T_l is independent of T_c.

A way of analyzing the crystallization data is to consider the temperature coefficient of the crystallization rate. It is well established that the steady-state nucleation rate $\dot{N}$ in a condensed system for all types of nuclei is given by[27]

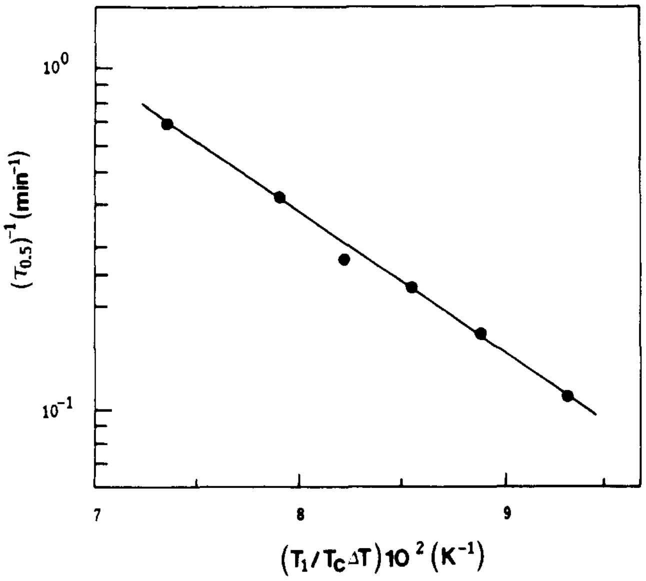

Figure 5. Plot of log $(\tau_{0.5})^{-1}$ against $T_l/T_c\Delta T$.

$$\dot{N} = \dot{N}_0 \exp[-E_d/RT - \Delta G^*/RT] \qquad (2)$$

where $\dot{N}_0$ is a constant, E_d is the energy of transport in the solid–liquid interface, and ΔG^* the free energy of forming a stable nucleus.

The values of ΔG^* have been obtained for both three-dimensional homogeneous nucleation[16,17,28] and coherent two-dimensional nucleation.[16,17,29]

For instance, in the latter case, which involves the unimolecular deposition of chain sequences, from the critical conditions at the limit of high molecular weights, the value of ΔG^* is given by

$$\Delta G^* = 4\sigma_e\sigma_u/\Delta G_u = 4\sigma_e\sigma_u T_m/\Delta H_u \Delta T \qquad (3)$$

where σ_e and σ_u are the interfacial free energy per sequence as it emerges from the basal plane of the nuclei and the lateral interfacial free energy, respectively, ΔG_u is the free energy of fusion per repeat unit of the infinite chain, ΔH_u is the melting enthalpy, and ΔT is the undercooling ($T_m - T_c$).

The nucleation rate can be incorporated into the expression for the overall rate of the process. This rate is expressed by the equation

$$\ln\,(\tau_{0.5})^{-1} = \ln\,(\tau_{0.5})^{-1}{}_0 - K_2 T_m/T_c\Delta T \qquad (4)$$

in which $K_2 = 4\sigma_e\sigma_u/R\Delta H_u$ and $(\tau_{0.5})^{-1}{}_0$ is a constant, including the transport term.

After analysis of the influence of the crystallization temperature on the isotherms, it can be assumed that the ordering takes place according to a nucleation-controlled process followed by a growth process. Although the transformation is not the same situation as the isothermal crystallization from the melt, we can use the same formulation given in eq 4 to analyze and to compare the experimental results. For this purpose, it is necessary to establish a melting temperature in order to calculate the undercooling of the system. In principle, if we use the extrapolated value of T_l ($T_l = 250 \pm 2$ °C), a plot of log $(\tau_{0.5})^{-1}$ against $T_l/T_c\Delta T$ gives, according to eq 4, a straight line with slope equal to K_2 (Figure 5). From the value of the slope, the product $\sigma_e\sigma_u$ can be obtained and is given by 4.9×10^6 (J·mol^{-1})^2 [2.8×10^5 (cal·mol^{-1})^2]. This value will be discussed in the next section. Nevertheless, these values are comparable with those corresponding with

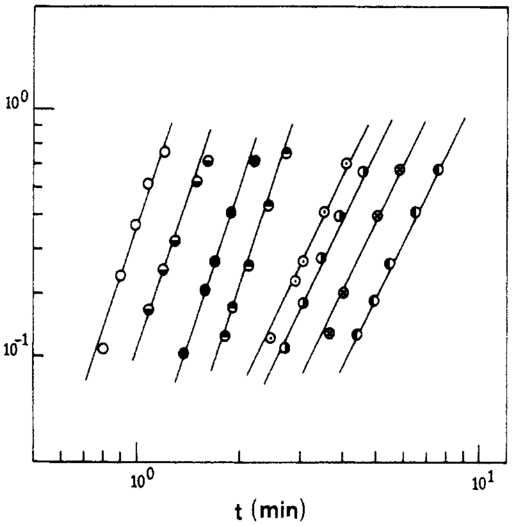

Figure 6. Double-logarithmic plot of $1 - \Theta(t)$ against time for PDDPT at indicated temperatures: (○) 237, (⊖) 238, (●) 238.5, (◒) 239, (◎) 239.5, (◑) 240, (⊛) 240.5, and (◐) 241 °C.

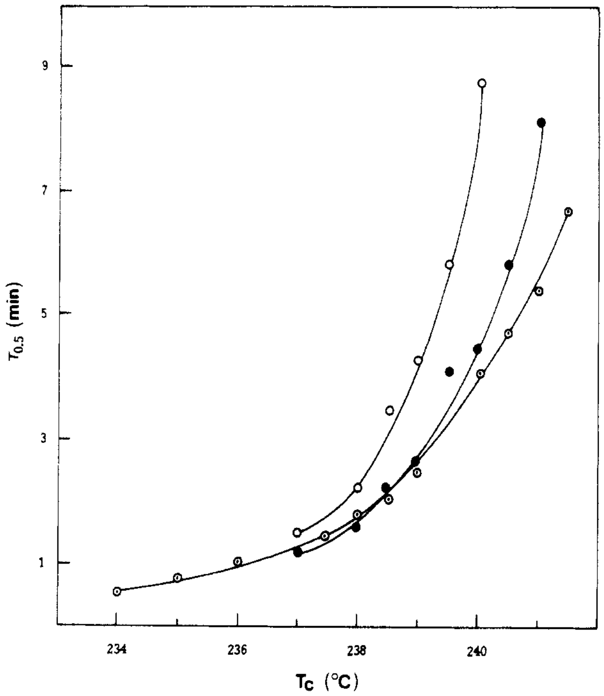

Figure 7. Plot of $\tau_{0.5}$ against crystallization temperature for indicated conditioning temperatures: (○) 300, (●) 280, and (◎) 265 °C.

crystallization of polymers from the melt.[17,30] It is obvious that σ_e and σ_u cannot be independently determined from this set of data.

(B) Kinetics of Three-Dimensional Order from the Mesophase. The isothermal crystallization from the mesophase of PDDPT has been analyzed in the crystallization temperature range between 234 and 241.5 °C. As reported for other polymer liquid crystals,[7] the transformation from the mesophase to the crystalline state occurs within a small temperature range below T_1. However, the transformation process has been studied on cooling from temperatures at which the nematic phase is stable.[4] It was established[4] that this polymer presents a crystal–smectic mesophase transition at 240 °C and, at 250–260 °C, transition from smectic C to nematic, before the isotropic transition at 290 °C. Morphological analysis by optical microscopy and SALS experiments have shown that when PDDPT is quenched only a marbled structure can be observed. However, it is possible to distinguish the transition bars and the striated texture corresponding to the transition smectic C–nematic. In this mesophase, only a blurred Schlieren texture was observed. SALS H_v diagrams in the temperature range in which the mesophases are stable present circular spots in both cases, as expected for smectic C mesophases and nematic mesophases. A four-leaf clover H_v pattern typical of smectic A, B states or spherulites was not observed at any temperature. Moreover, in the case of PDDPT, this point is more important, because the nematic mesophase is the most stable and the formation of three-dimensional order from this nematic mesophase is studied here.

Before the isothermal experiments are conducted, an interesting point to note is the analysis of the influence of the initial conditioning temperature on the rate of transformation, because this temperature may influence the polymer mobility and cause variations in the rate of the transformation.[31] Therefore, two conditioning temperatures, T_a, were used, 265 and 280 °C.

Quantitative kinetic data were obtained from calorimetric measurements. As in the case of crystallization from the isotropic state, the isotherms for a given crystallization temperature were reproducible but they could not be superimposed one other by shifting in the time scale as a consequence of changes in the exponent, which will be considered below. Figure 6 shows the isotherms at several temperatures after conditioning the sample at 280 °C.

It is important to point out the strong influence of the conditioning temperature in the subsequent crystallization rates. For the same crystallization temperatures, the higher the value of $\tau_{0.5}$ the higher was T_a, or, in other words, the rate of the transformation was smaller at the higher T_a. Figure 7 shows the values of $\tau_{0.5}$ plotted against the crystallization temperature for two values of T_a, which have been used for the mesophase–crystalline transformation, together with the results obtained from the isotropic state. It is clearly shown that the slowest process is this last one. However, in spite of the importance of the conditioning temperature, this factor has not, to our knowledge, been considered in the analysis of thermotropic polyesters. Only in the case of polyphosphazenes has it been studied.[8,31] It has been reported that changes in T_a cause variations in the rate of the transformation, and this effect has been related to the mobility of the mesophase.

If the experimental data are analyzed according to the Avrami equation, the exponent after crystallization at $T_c \geq 239.5$ °C corresponds to $n = 2$. However, at $T_c < 239.5$ °C, an exponent $n = 3$ is found.

Values of $n = 2$ and $n = 3$ have been found[7,8] for the mesophase–crystalline transformation in polyphosphazenes. In the case of polyesters, values of 2 and between 3 and 4 have been indicated.[32,33] For poly(alkyl terephthaloyl–bis(4-oxybenzoate)s,[10,11] values of $n = 2$ and $n = 3$ have also been reported. More recently, the nematic–crystalline transformation of polyesters with two mesogenic *p*-oxybenzoyl diads separated by a segment derived from triethylene glycol and a variable polymethylene spacer has been analyzed. Values of n between 2.7 and 4.2 have been found.[13] Moreover, isothermal kinetic studies of thermotropic copolyesters with different 1,4-dihydroxybenzoic acid and 2,6-dihydroxynaphthoic acid compositions have been carried out, and extremely low values of n (0.2–0.8) have been reported.[14] The explanation for these low values has been related to a modification of the Avrami treatment when the crystals do not grow with constant radial growth rate.[15]

Table I
Avrami Exponents for the Kinetics of Some Polymer Liquid Crystals

transformation	polymer	mesophase	Avrami exp	ref
isotropic–mesophase	polyester	nematic	0.68–0.85	12
	poly(azomethines)	nematic	0.1–0.6	34
	polyphosphazenes		2	7
	polyester		1	39
	polyethers	smectic	2.5–3.0	23
mesophase–three-dimensional order	copolyesters	nematic	0.24–0.73	14, 15
	copolyesters	nematic	2, 0.15–0.38	40, 41
	polyphosphazenes		2	7
	polyphosphazenes		3,4	8
	poly(azomethines)	nematic	2.4–3.8	34
	polyesters	nematic	2.7–4.2	13
	polyesters		2	32
	polyester		3–4	33
	polyester (spacer 10CH$_2$)	smectic	3–4	10
	polyester (spacer 3CH$_2$)	smectic	2	10
	polyester (spacer 6CH$_2$)	nematic	2	11
	polyester (spacer 10CH$_2$)	smectic	2.89–3.22	11
	polyester		4	39
	PDDPT	nematic	2 at $T_c > 239$ 3 at $T_c < 239$	*a*
isotropic–three-dimensional order	polyphosphazene		4	8
	PDDPT	nematic	2	*a*

[a] This work.

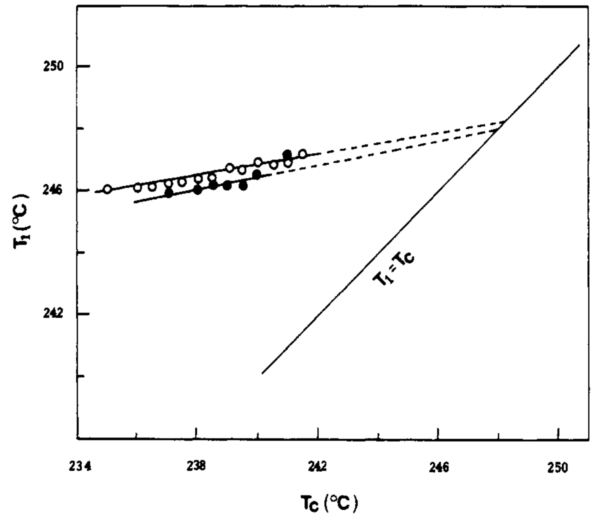

Figure 8. Plot of T_i after crystallization at several T_c, for indicated conditioning temperatures: (●) 280 and (○) 265 °C.

Poly(azomethine) with one ethylene glycol flexible spacer has also been investigated. Values of n, changing with T_c from 3.8 at 247 °C to 2.4 at 259 °C, have been reported.[34]

In Table I, Avrami exponents for the kinetics of transformation of some polymer liquid crystals are summarized. The variations in the n values are, to some extent, quite suprising and limit any possibility of generalization.

In conclusion, the differences in n cannot be explained by a general mechanism and require further analysis. They must correspond to different processes closely related to morphological changes which in most cases have not been observed or analyzed. A high sensitivity to variations in the preparation of the polymers and in the experimental techniques cannot be excluded.

On the other hand, after crystallization, T_i was obtained as a function of T_c. This analysis showed that T_i does not change significantly, as was previously indicated. Values of T_i = 250 ± 2 °C are found when two different conditioning temperatures (265 and 280 °C) are used (Figure 8).

Analysis of the temperature coefficient according to eq 4 has been carried out by taking T_i = 250 °C, in order to estimate the undercooling. It is quite clear, and has been previously pointed out,[8] that the transformation from the mesophase is not the same situation as isothermal crystallization from the isotropic melt.

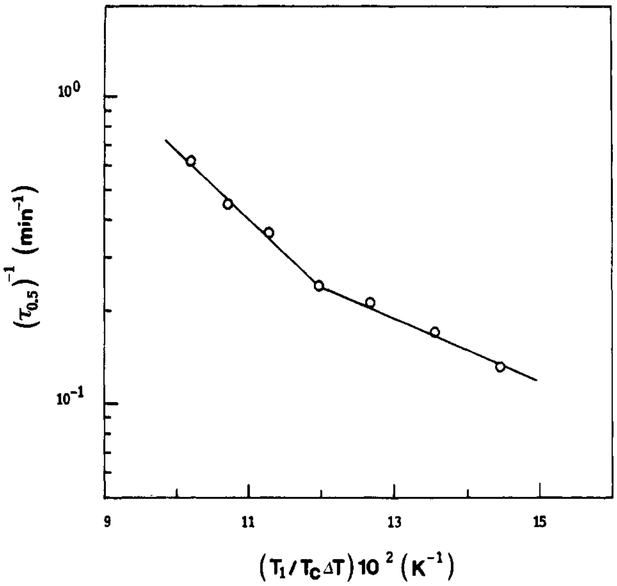

Figure 9. Plot of log $(\tau_{0.5})^{-1}$ against $T_i/T_c\Delta T$.

A plot of log $(\tau_{0.5})^{-1}$ against $T_i/T_c\Delta T$ results in two straight lines with different slopes (Figure 9). This change in slope has been found for the first time in the analysis of the temperature coefficient of the nematic–crystalline transition in polyesters. It is important, however, to point out that this type of break in the temperature coefficient has been reported in the analysis of the crystallization of several homopolymers[16,35–38] and has been theoretically interpreted to be due to changes in nucleation and lateral growth rates.[35,36,38]

In order to consider the origin of this break, it is important to analyze the ratio between the slopes of the two straight lines in the temperature coefficient plot, and the influence of changes in the Avrami exponent, which can give breaks in the temperature coefficient plot. It can be easily demonstrated that changes in the exponent from n to n' lead to ratios of the temperature coefficient slopes equal to n/n'. The temperature at which the change in slope appears ($T = 239.5$ °C) is the one at which the system changes from $n = 2$ to $n = 3$.

In order to analyze the breaks in the slope, the undercooling has been calculated by taking $T_1 = 250$ °C and by considering the two regions in which the exponent of the Avrami equation is 2 and 3. At the lowest undercooling, in which $n = 2$, the slopes are independent of the mesophase conditioning temperature. The product $\sigma_e\sigma_u$ corresponds to 2.4×10^6 $(\text{J}\cdot\text{mol}^{-1})^2$ $[1.4 \times 10^5$ $(\text{cal}\cdot\text{mol}^{-1})^2]$. However, at high undercooling, the crystallization from the mesophase takes place with a change in the Avrami exponent, giving a quite higher slope in the analysis of the temperature coefficient. The values $\sigma_e\sigma_u$ obtained from these slopes [4.9×10^6 and 3.5×10^6 $(\text{J}\cdot\text{mol}^{-1})^2$ [(2.8×10^5 and 2.0×10^5 $(\text{cal}\cdot\text{mol}^{-1})^2$], for $T_a = 280$ °C and $T_a = 265$ °C, respectively] are close to the value obtained previously from the analysis of the crystallization from the isotropic state. In principle, this seems to indicate that the mechanism of crystallization at high undercooling is the same for crystallization either from the isotropic state or from the mesophase. Furthermore, the values obtained for $\sigma_e\sigma_u$ are in the range of values found for other thermotropic polyesters[10,39] and polyphosphazenes.[8] The values of the experimental ratios of the slopes are in the range from 0.5 to 0.7. This range agrees reasonably with the ratio 2/3 corresponding to the values found to the Avrami exponents.

Conclusions

The kinetics of formation of three-dimensional order from the mesomorphic and the isotropic states for poly(decamethylene-4,4′-diphenoxy terephthalate) has been studied. After analysis of the influence of the crystallization temperature, it can be assumed that the ordering takes place according to a nucleation-controlled process followed by a growth process, as observed in the bulk crystallization of polymers.

An important influence of the conditioning temperature on the rate of transformation from the mesomorphic state has been observed, as well as differences in transformation rates from the isotropic and the mesomorphic states due to the anisotropic organization of the mesophase. A change in the Avrami exponent has been found in the ordering process from the mesophase. The change is reflected in a break in the slope of temperature coefficient of this process. The temperature coefficient of the transformation process has also been determined, and the values obtained for the product of the interfacial free energies showed values comparable with those found for other semicrystalline polymers.

Acknowledgment. Financial support for the work by CICYT, Madrid, Project MAT 91-0505, is gratefully acknowledged. I.C. thanks the Ministerio de Educación y Ciencia for providing a postgraduate grant.

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Registry No. PDDPT (copolymer), 78644-17-4; PDDPT (SRU), 78666-26-9.