Journal of Thermal Analysis, Vol. 53 (1998) 35-47

KINETICS OF ISOTHERMAL CRYSTALLIZATION OF THE THERMOTROPIC POLYESTER POLY(ETHYL ETHYLENE-4,4-DIPHENOXYTEREPHTHALATE)

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(Received July 16, 1997; in revised form December 1, 1997)

Abstract

Differential scanning calorimetry was used to study the isothermal kinetics of three-dimensional ordering formation from the mesophase of the thermotropic polyester poly(ethyl ethylene-4,4-diphenoxyterephthalate). An Avrami exponent of 4 was found and the measured rates of transformation were related with the efficiency of packing. A nucleation and growth process was assumed in the determination of the temperature coefficient, and the interfacial free energies are discussed in terms of the chain flexibility.

Keywords: DSC, isothermal crystallization, thermotropic polyester

Introduction

The thermotropic polyesters based on a mesogenic unit constituted from 4,4-terephthaloyldioxydibenzoic acid and a flexible spacer form a significant family of main chain liquid crystal polymers, whose synthesis, characterization, thermal stability, thermal transitions and mechanodynamic and dielectric behaviour have been the subject of special attention during recent years [1–16]. Three-dimensional ordering and liquid crystalline phases usually coexist in these materials, some showing mesomorphism or polymorphism, depending on the chemical structure and thermal treatment [17–19]. Studies of the kinetics of three-dimensional ordering formation, both from the mesophase and from the isotropic state, have been reported, but these analyses are limited to thermotropic copolyesters [20, 21] or thermotropic polyesters with linear flexible spacers [22–28].

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1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The main aim of the present work, which forms part of a general project on the study of structure-property relationships in poly[alkyl terephthaloyl-bis(4-oxybenzoate)]s, is to analyse the kinetics of the three-dimensional ordering formation from the liquid crystalline phase in the branched thermotropic polyester poly(ethyl ethylene-4,4-diphenoxyterephthalate) (PTOBEE), in order to determine the kinetic parameters and to correlate them with those corresponding to the thermotropic polyesters with the same mesogenic unit and linear flexible spacers.

Experimental

Synthesis and characterization

This thermotropic polyester was synthesized by polycondensation of 4,4-(terephthaloyldioxydibenzoyl chloride) and a racemic mixture of 1,2-butanediol in 1-chloronaphthalene at 200°C for 3 h in a N_2 atmosphere, according to the method described by Bilibin [29]. The product of the polycondensation reaction, PTOBEE, was precipitated in toluene, and the fraction dissolved in the resulting transparent solution was obtained by recrystallization at room temperature, (–)PTOBEE.

The structure of this material was confirmed by ^1H and ^{13}C NMR in $(CD_3)_2SO$, with a Varian 300 MHz spectrometer.

The inherent viscosity was estimated in an Ubbelhode viscosimeter at a concentration of 0.5 g dl^{-1} in *p*-chlorophenol at 45°C.

Optical rotatory dispersion (ORD) was evaluated in a Perkin Elmer 241 MC polarimeter with λ_{Na}=589 nm, using a 5 mm slit, an integration time of 5 s and E=40 μA, at a concentration of 0.0056 mol l^{-1} in toluene.

Thermal properties

Thermogravimetric analysis was performed with a Mettler TA4000/TG50 thermobalance at a heating rate of 10°C min^{-1} with a N_2 purge. Thermal transitions were determined by differential scanning calorimetry (DSC), using a Mettler TA4000/DSC30 calorimeter coupled to a computer with TA72 thermal analysis software. The heating rate was 10°C min^{-1}. The peak maxima were taken as the transition temperatures and the mid-points as the glass transition temperatures.

Thermooptical analysis was carried out in a Reichert Zetopan polarizing light microscope equipped with a Mettler FP80HT hot stage and a Nikon FX35A camera. The sample was prepared by heating to 220°C between two microscope slides.

Crystallization kinetics was examined with a Perkin Elmer DSC 7/Unix differential scanning calorimeter.

Automatic calibration was carried out with indium (T_m=156.5°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 samples were heated for 5 min at 180°C, a temperature above the crystalline-mesophase transition. These conditions ensured the complete crystal–liquid crystal transformation of the sample and excellent reproducibility. Subsequently, the samples were undercooled at a rate of 64°C min^{-1} until the desired crystallization temperature, T_c, and the corresponding exotherms were scanned as a function of time until no change was observed in the DSC baseline. The crystallization isotherms were obtained from the data points stored for each crystallization, and the partial areas corresponding to a given percentage of the total transformation were determined on a Perkin Elmer 7700 computer, using DSC7 kinetic software. After the kinetic process had reached completion, the crystal–liquid crystal transition temperatures were determined by heating the samples at a rate of 10°C min^{-1}.

X-ray diffraction

X-ray diffractograms of samples subjected to different thermal treatments were obtained by using a Rigaku Geigerflex-D/max diffractometer with a Rigaku RU-200 rotating anode generator. The diffractograms were recorded in the range $2\theta=3°$ to 30° at a rate of 2°C min^{-1}, using Ni-filtered CuK_α radiation.

Results and discussion

(–)PTOBEE is a thermotropic polyester with an ORD given by $[\alpha]_{589}^{25}=-2.33$; its inherent viscosity in *p*-chlorophenol at 45°C was 0.10 dl g^{-1}.

This polymer is thermally stable up to 280°C and only a 10% mass loss is observed at 310°C. (–)PTOBEE is a semicrystalline polymer whose thermal transitions have been reported elsewhere [30]. In brief, it shows a glass transition, T_g, at 50°C, and a very sharp endothermic transition at 146°C, with an apparent enthalpy of 42 J g^{-1}, interpreted as the crystal-mesophase transition, T_1. At higher temperatures, it was not possible to determine other transitions by DSC. The clearing point associated with the mesophase-isotropic transition could be estimated by thermooptical analysis at 230°C, which is below the decomposition temperature.

Polarizing light microscopy analysis does not reveal a well-defined crystalline morphology in the temperature range where the three-dimensional order exists. In contrast, at temperatures between 160 and 220°C, this polymer displays a range of morphologies, such as Grandjean steps, Schlieren, oily streaks and myelinic-striated textures, which can correspond to a planar-cholesteric mesophase [31].

Wide-angle X-ray diffractograms demonstrate two main crystalline reflections at $2\theta=19°$ and 28°, which disappear at 150°C, together with another two at $2\theta=16°$ and 24°, associated with the mesomorphic state.

In this liquid crystal polyester, three-dimensional ordering formation, from either the mesophase or the isotropic state, was not possible during cooling, independently of the cooling rate. However, (–)PTOBEE could be crystallized from the mesophase under isothermal conditions.

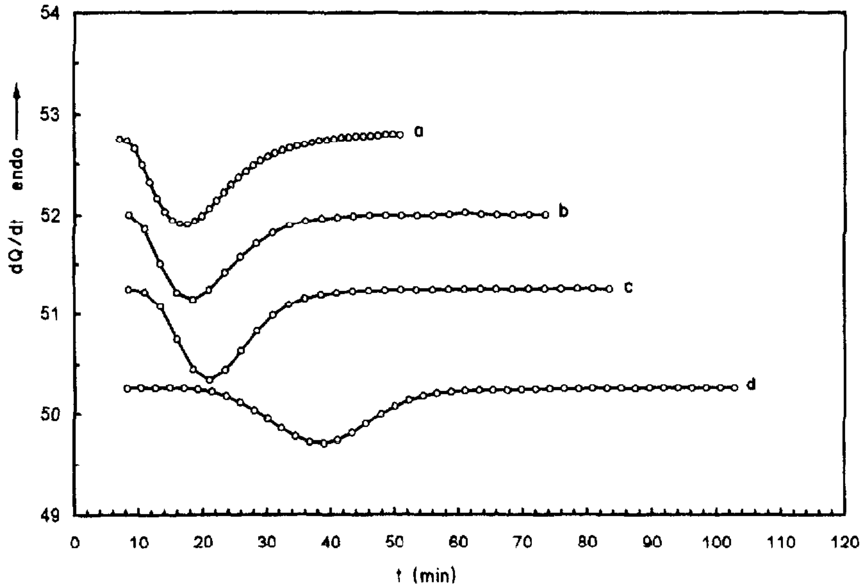

Fig. 1 Experimental isothermal curves of (–)PTOBEE crystallized from the mesophase at T_c=102°C (a), 108°C (b), 114°C (c) and 122°C (d)

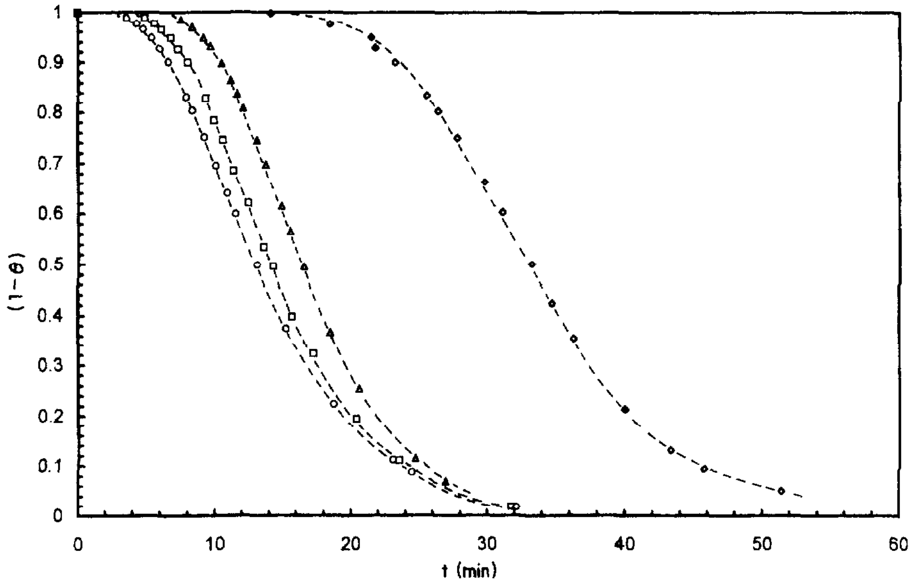

Fig. 2 Plots of (1–θ) *vs.* time for (–)PTOBEE crystallized from the mesophase at T_c=102°C (○), 108°C (□), 114°C (△) and 122°C (◊)

Isothermal crystallization from the mesophase of (–)PTOBEE was studied in the crystallization temperature range from 102 to 122°C. The crystallization times in this temperature range are between 25 and 100 min. Figure 1 depicts several experimental crystallization curves, and Fig. 2 shows typical transformation-time plots for several crystallization temperatures. The shapes of the isotherms are qualitatively very similar to those reported for conventional polymers and other thermotropic polyesters [26–28].

The apparent enthalpy associated with the isothermal crystallization process reaches a value of 22 J g^{-1} and does not change with the crystallization temperature. The crystallinity level obtained after isothermal crystallization could be calculated from X-ray diffraction measurements and tended towards a limiting value of 18%. This is lower than found for (–)PTOBEE recrystallized from toluene, which gave 42 J g^{-1} and 34%, respectively. The reason for this result must be related to the fact that the crystallization of lower molecular weight species is hindered during the isothermal process.

The value extrapolated for the enthalpy corresponding to 100% crystalline phase (–)PTOBEE was ΔH_u=122 J g^{-1}; this was determined from the apparent enthalpies of different samples crystallized either from solution in toluene or under isothermal conditions, and the corresponding crystallinities determined from independent X-ray measurements, using the same methodology as reported for other thermotropic polyester [26–28].

In order to analyse the isotherms, and assuming the mutual impingement of growing centres upon one another, the Avrami approximation was used [32]. In this case, the process is given by the equation

$$1-\theta=\exp(-kt^{n}) \tag{1}$$

where θ is the fraction of material crystallized at time t, k is a rate constant, and n defines the mode of nucleation and growth. Several values of n have been proposed for homogeneous and heterogeneous nucleation and different growth geometries, and the values of n are specifically 2, 3 or 4 for one, two or three-dimensional growth, respectively [33]. In spite of the many simplifications introduced in the Avrami equation, numerous polymers [34] display excellent adherence to this relation in the first part of the transformation, at least up to 10–20% of the process. An integral value of n=4 was obtained for (–)PTOBEE; this is related to homogeneous nucleation and three-dimensional growth and is connected with the mechanism of the mesophase–crystal transformation. It is important to point out here that this value coincides with the Avrami exponent previously reported for the crystal–mesophase transformation kinetics of other members of the poly[alkyl terephthaloyl-bis(4-oxybenzoate)] family with 6, 7 and 10 methylene groups in the flexible spacer [26], and low molecular weight cholesteric aliphatic esters of different lengths [35–37]. As mentioned earlier, analysis of the crystalline superstructure of (–)PTOBEE does not afford any morphological information directly related with the Avrami exponent value, as reported for other thermotropic polyesters [26].

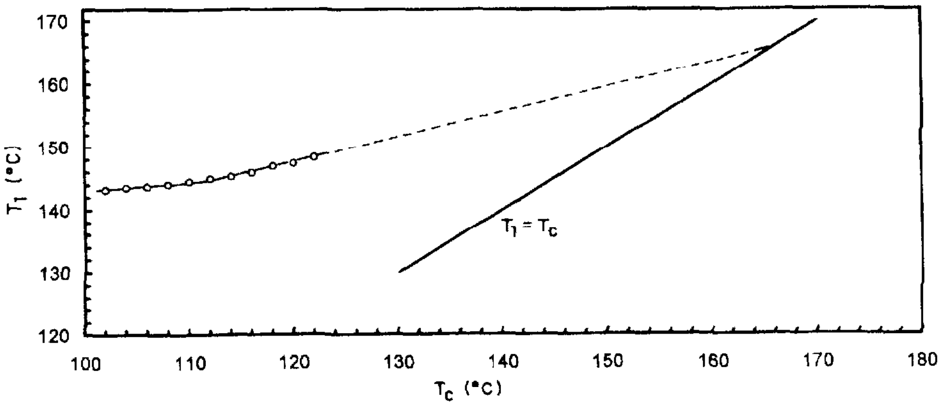

Fig. 3 Plot of T_l *vs.* T_c after isothermal crystallization of (–)PTOBEE

On the other hand, in order to analyse the crystallization behaviour of thermotropic polyester, (–)PTOBEE, the variation in the crystal–liquid crystal transition temperature, T_l, after isothermal crystallization was studied. The relation between this transition temperature and the crystallization temperature (Fig. 3) demonstrates that the higher the crystallization temperature, the higher the values of T_l. The slope of the relation T_l/T_c is 0.42, and the value extrapolated to $T_l=T_c$ corresponds to 164°C. This slope is very close to the value of 0.5 found for semicrystalline polymers [38–40]. However, it has been pointed out [27] that this similarity to the behaviour of semicrystalline polymers does not have any formal

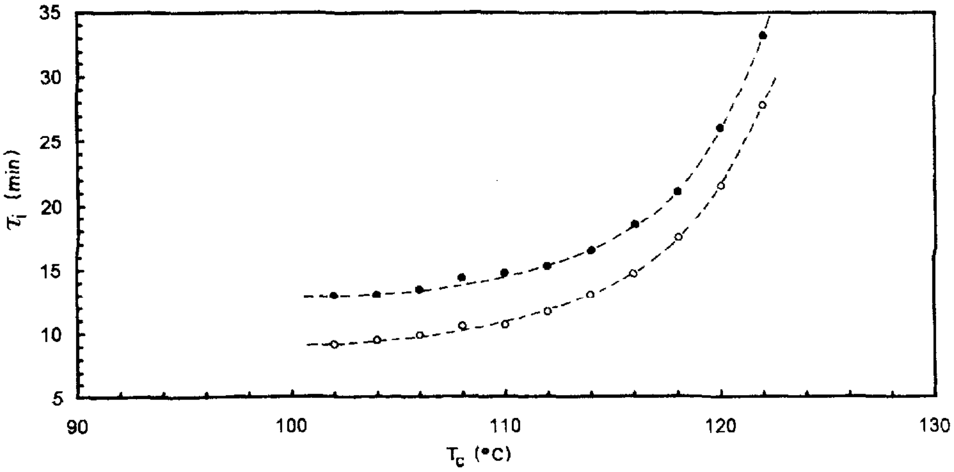

Fig. 4 Plots of $\tau_{0.25}$ (○) and $\tau_{0.50}$ (•) *vs.* crystallization temperature, T_c, of (–)PTOBEE

support. The meaning of the extrapolated T_1 is quite different, because it is not a transition to a random melt, and therefore is not an equilibrium melting temperature. This extrapolated value of 164°C represents the maximum temperature at which the crystal–liquid crystal transition temperature is independent of the crystallization temperature, and it is used in this work to determine the undercooling of the system.

Another important observation is related to the influence of the crystallization temperature on the time scale of the crystallization process. Figure 4 shows plots of the times necessary to reach 25% and 50% of the transformation, $\tau_{0.25}$ and $\tau_{0.50}$, respectively, *vs.* the crystallization temperature. The crystallization times increase as the crystallization temperature increases. That is to say, the crystallization rate depends on the crystallization temperature in the temperature range analysed.

As indicated above, the crystallization rates display a negative temperature coefficient, which is suggestive of a nucleation-controlled process. Additional information could be obtained from the *k* values in the Avrami equation. This rate constant is a composite rate constant, including nucleation and growth of the crystallites, and can be calculated from the half-transformation time $\tau_{0.5}$ via the expression [41]

$$k = \frac{\ln 2}{(\tau_{0.5})^{n}} \tag{2}$$

Figure 5 shows a plot of different *k* values *vs.* the crystallization temperature. The temperature dependece of *k* is negative and very slight, and its trend in the high undercooling region seems to indicate the proximity of the maximum crystallization rate of this thermotropic polyester.

On the other hand, when we compare the crystallization rates of (–)PTOBEE with those of other thermotropic polyesters in the same series, with the same mesogenic unit and different spacer length, several observations can be made. To this end, in Fig. 6 the variations in the crystallization rate constant values, corresponding to several members of the poly[alkyl terephthaloyl-bis(4-oxybenzoate)] series [26], are plotted *vs.* the undercooling. The transformation at the same degreé of undercooling, ΔT~40°C, is slower in the case of (–)PTOBEE than for PHXTOB and PDTOB. Moreover, the temperature dependence of *k*, deduced from the corresponding slopes, is greater for the thermotropic polyesters with 6 and 10 methylene groups in the flexible spacer. The reason for this behaviour can be related with the existence of strong steric hindrance in the packing of the molecular chains, which is reflected not only in a strong depression in the transition temperatures, but also in the crystallization rates at the same crystallization undercooling.

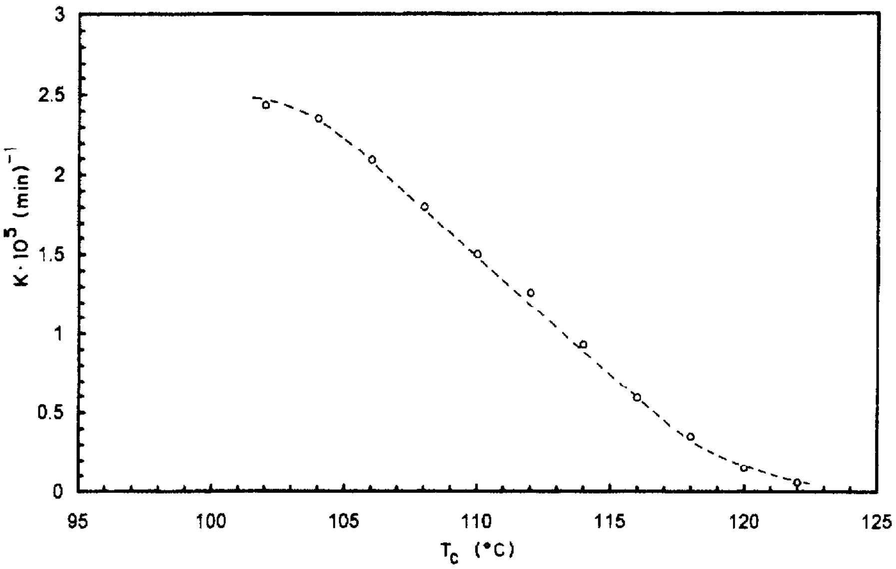

Fig. 5 Plot of rate constant k for (–)PTOBEE, calculated by using Eq. (2), *vs.* crystallization temperature T_c

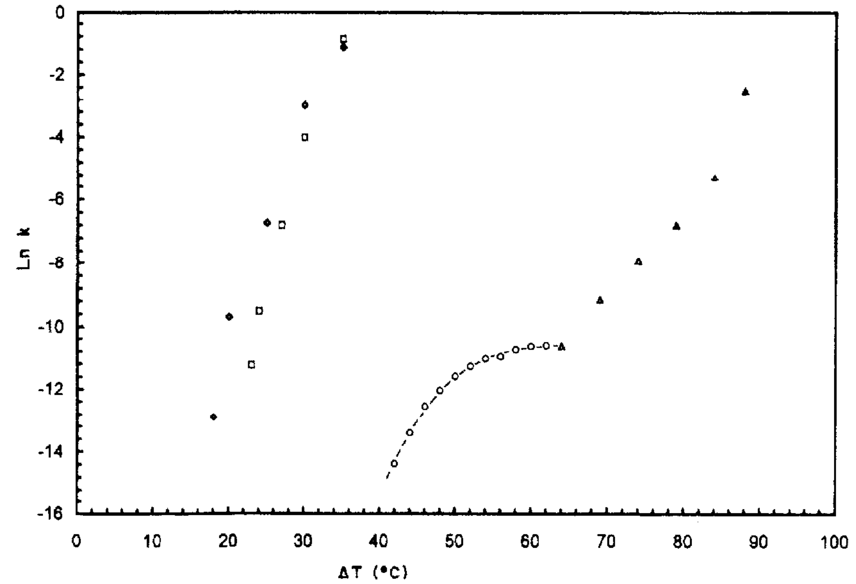

Fig. 6 Comparative plots of rate constants for (–)PTOBEE (o), PHXTOB (□), PHTOB (△) and PDTOB (◊), *vs.* undercooling ΔT

Analysis of the crystallization temperature coefficient can be carried out by calculating the rate constant, expressed in terms of $(\tau_{0.25})^{-1}$, for the steady-state nucleation rate, given by the equation [34]

$$\ln(\tau_{0.25})^{-1} = \ln(\tau_{0.25})_o^{-1} - \frac{k}{T_c}\left(\frac{T_l^o}{\Delta T}\right)^n \tag{3}$$

where $(\tau_{0.25})_o^{-1}$ is a constant including the transport term, T_l^o is the extrapolated crystal–liquid crystal transition, and ΔT is the undercooling given by $T_l^o - T_c$. The value of the exponent n depends on the mode of nucleation and growth and has a value of two for three-dimensional homogeneous nucleation since the Avrami exponent in the crystallization is 4. The constant k is given by the expression

$$k = \frac{8\pi\sigma_e\sigma_u^2}{R}\Delta H_u \tag{4}$$

where σ_e is the interfacial free energy per sequence as it emerges from the basal plane of the crystalline nuclei, σ_u is the lateral free energy, and ΔH_u is the melting enthalpy of the 100% crystalline polymer. Although the liquid crystal–crystal transformation does not reflect the same situation as the isothermal crystallization from the melt of a semicrystalline polymer, it has been demonstrated that expression (3), can be used, in principle, to analyse and compare the experimental results.

Hence, and according to Eq. (3), a plot of $\ln(\tau_{0.25})^{-1}$ *vs.* $(T_l^o/\Delta T)^2(1/T_c)$, where T_l^o corresponds to the extrapolated value of 164°C, results in two straight lines with different slopes, with a change in the trend at a crystallization temperature of 114°C (Fig. 7). This type of break in the temperature coefficient has been observed in the analysis of the crystallization of several homopolymers and has been interpreted theoretically to be due either to changes in the Avrami exponent [27] or to the existence of different crystallization regimes in consequence of changes in nucleation and lateral growth rates [42].

In the first case and as mentioned earlier, there is no change in the Avrami exponent in the range of crystallization temperatures analysed. Therefore, the break observed in the temperature coefficient cannot be related to a change in the crystalline growth model.

On the other hand, the slope ratio associated with the change in the temperature coefficient is 0.46. This value is very similar to those reported for the slope ratio of regime II/regime I in low molecular weight fractions of polyethylene [43], which have been interpreted with characteristic nucleation rates that do not necessarily correspond to an integral change in crystallite thickness. However, when the large undercoolings used in the isothermal crystallization of this thermotropic polyester were taken into account, the influence of the transport term

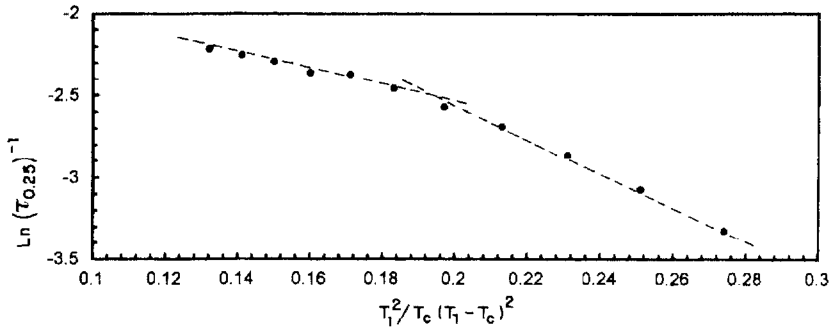

Fig. 7 Plot of $\ln(\tau_{0.25})^{-1}$ *vs.* $T_1^2/T_c(\Delta T)^2$ for (–)PTOBEE

on the crystallization kinetics was also considered. In this respect, the overall crystallization rate can be described by the general equation

$$\ln(\tau_{0.25})^{-1}+\frac{E_D}{RT_c}=\ln(\tau_{0.25})_0^{-1}-\frac{k}{T_c}\left(\frac{T_1^0}{\Delta T}\right)^n \tag{5}$$

where E_D is the activation energy for transport across the crystal-liquid interface. This term has been defined by either using arbitrary values or has been calculated using different approximations [44–47]. When the Williams-Landel-Ferry approximation is considered, E_D is given [44] by

$$\frac{E_D}{RT_c}=\frac{C_1}{R}(C_2+T_c-T_g) \tag{6}$$

where C_1 and C_2 are constants, with the universal values 17.24 kJ mol^{-1} and 51.6 K, respectively. A conventional plot with these constants fits the experimental kinetic points to a straight line in the higher crystallization temperature region, but it shows a slight curvature at lower crystallization temperatures (Fig. 8). This fit does not allow the determination of a correct slope value and therefore an accurate $\sigma_e\sigma_u^2$ product value.

Another of the most usual expressions for E_D is given by the widely-used approximation

$$\frac{E_D}{RT_c}=\frac{U}{R}(T_c-T_\infty)=\frac{U}{R}(T_c-T_g+C_2) \tag{7}$$

where U is a variable parameter, T_∞ is the temperature at which the viscosity is infinite and C_2 is a constant of 50 K [45, 47]. Plots of Eq. (7) using a set of U values ranging from 4.180 to 16.720 J mol^{-1} are shown in Fig. 9; it is clear that the introduction of the transport term modifies the temperature coefficient behaviour. Slope changes, hypothetically related with the regime I–regime II transi-

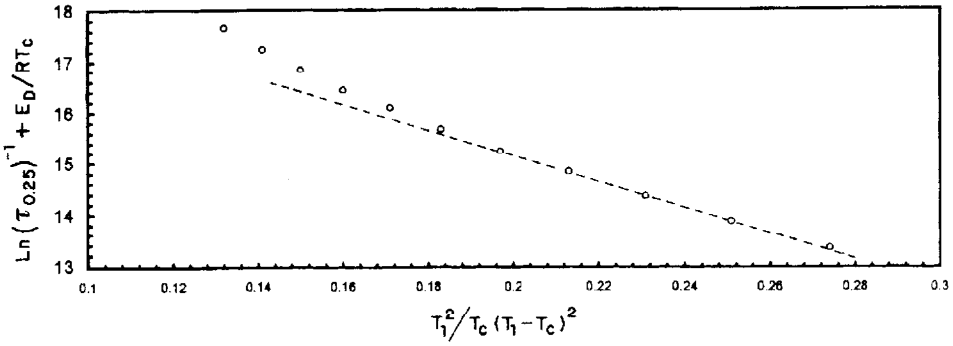

Fig. 8 Plot of Eq. (5) using the universal values of WLF parameters

tion, were not observed. On the other hand, whereas fits with values of 8.360 or 16.720 J mol^{-1} show a very slight curvature associated with the lower crystallization region, the fit with a U value of 4.180 J mol^{-1} produces excellent linearity. From this last fit, a value of $\sigma_e\sigma_u^2$ of 36·10^8 (J mol^{-1})^3 has been determined. This value is higher than those obtained in the poly[alkyl terephthaloyl-bis(4-oxybenzoate)] series for 6, 7 and 10 methylene groups in the flexible spacer, which have the same crystalline growth mode [26]. In other words, the product of the free energies decreases when the flexibility of the chain increases. This seems to confirm, as previously reported [26], the fact that the length of the

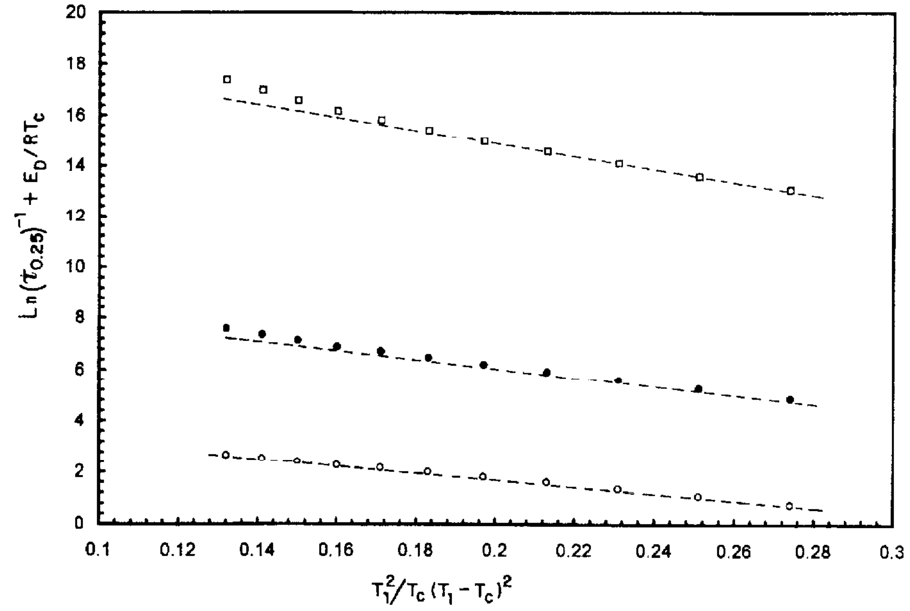

Fig. 9 Plots of Eq. (5) using the values C_2=50 K and U=4.180 (○), 8.360 (•) and 16.720 J mol^{-1} (□)

spacer plays an important role in the distortion of the crystalline interphase. Additionally, the steric hindrance caused by bulky substituents in the spacer will increase the separation of the mesogenic units in adjacent polymer chains, and should lead to a reduction in the formation of the three-dimensional ordering.

Conclusions

The kinetics of three-dimensional ordering formation from the mesophase in poly(ethyl ethylene-4,4-diphenoxyterephthalate) has been analysed for the first time. Although this thermotropic polyester does not crystallize during cooling from the mesophase, independently of the cooling rates, it is possible to generate the crystalline order by isothermal crystallization at high undercooling. Under these conditions, the Avrami exponent n=4 coincides with the corresponding values for other members of the same series with linear flexible spacers, indicating the same crystalline growth mode.

However, the rate of the crystallization process in the same undercooling range is lowered, and it seems to be affected by the steric hindrance increment due to the existence of branching in the spacer. Finally, the higher value of the product of the interfacial free energies of (–)PTOBEE is in agreement with the reduction in the flexibility of the chain.

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Financial support from the research project MAT95-0819 is gratefully acknowledged.

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