Colloid & Polymer Science Colloid Polym Sci 272:1501–1507 (1994)

Original Contributions

Crystallization and melting behavior of a main-chain thermotropic copolyester

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Abstract: The crystallization and melting behavior of a main-chain thermotropic copolyester has been investigated by differential scanning calorimetry (DSC). The effect of annealing time and temperature on the transition temperatures and enthalpies has been evidenced. Two melting peaks are observed and the first one clearly develops on annealing. Hypotheses are suggested about the crystallization mechanism.

Key words: Thermotropic liquid crystalline copolyester – annealing – crystallization – differential scanning calorimetry

Introduction

Stiff long chain molecules tend to exhibit a liquid crystalline melt, usually a nematic one, intermediate between a partially ordered solid and an isotropic fluid state [1–4]. From a molecular structural viewpoint liquid crystalline polymers can be classified into two groups, i.e., those with the mesogenic units in the main chain and those with the mesogenic units present as side chains [5, 6]. In both cases the formation of a mesophase is due to the high anisotropy of the polarizability of rigid components such as aromatic rings. In the case of main chain polymers the most diffuse are aromatic polyesters. Nevertheless, the homopolyesters derived from terephtalic acid and hydroquinone or from hydroxybenzoic acid alone melt at about 600 °C [6], therefore, they cannot be processed. There are several ways to depress the melting point of such rigid polymers to temperatures such as they are stable enough to be processed [2]. One of the most successful methods consists of the replacement of one or more hydrogens in an aromatic ring by other elements or radicals. The so-obtained polymers can be very easily oriented in the molten state and keep their orientation in the solid state, which results in materials with very high mechanical and thermal properties. It is, therefore, very important to control their transitions, which play a key role in the processing and use conditions of these materials. Differential scanning calorimetry (DSC), often associated with optical microscopy to identify the nature of the mesophase, can be successfully used to determine phase transitions in thermotropic liquid crystalline systems, as well as for polymers, in general.

Nevertheless, few papers are present in the literature about the crystallization and melting behavior of thermotropic polymers. Butzbach et al. [10] propose, for the crystallization of a thermotropic polyester, a two-step crystallization mechanism consisting of a rapid step until the sample is physically crosslinked, followed by a slow step due to a crystallization occurring only through a diffusional process in regions which have not been transformed during the first step.

Hedmark et al. [11] for a thermotropic liquid crystalline polyester containing *p*-hydroxybenzoic acid (HBA) suggest the occurrence of two types of crystallization: the formation of large HBA-rich crystals of high melting point, likely due to a transesterification reaction induced crystallization – as previously proposed by Lenz [12] – and the formation of thin HBA-rich crystals due to a normal cold crystallization.

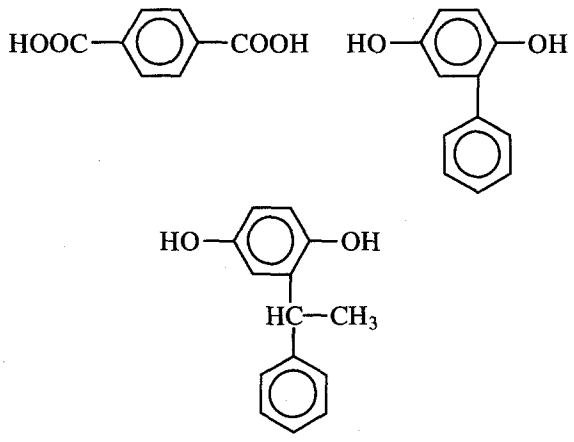
In this paper, we study the crystallization and melting behavior of a main chain thermotropic

copolyester, Granlar supplied by Montedison S.p.A. (Italy) in form of pellets.

Experimental

Materials

The polymer studied is a copolyester based on



with molar ratio 0.5:0.25:0.25 and was supplied by Montedison S.p.A.

Thermal analysis

A thermal gravimetric analyzer (TGA) DuPont 951 was used to investigate the thermal stability range of the material, using a scanning rate of 10 °C/min.

The thermal properties were investigated by using a differential scanning calorimeter (DSC 7, Perkin Elmer) equipped with a 1020 Personal Integrator. All runs were performed on 10 ± 0.5 mg samples in a nitrogen atmosphere. Before the measurements the samples were taken at 370 °C and kept at this temperature for 1 min. The annealing was performed in the DSC apparatus, in nitrogen atmosphere for times ranging from 1 to 360 min.[1])

The transition temperatures correspond to the maxima (or the minima) of the peaks and their uncertainty is ± 0.3 °C. The heats of transition have been evaluated using a program for computing the partial areas, and their uncertainty is ± 0.05 J/g.

Optical analysis

An optical microscope (Polyvar, Reichert Jung) with cross polarizers was used in order to observe the texture of the mesophase. The instrument was equipped with a hot stage (TMS 90/TH 600, Linkam). The samples for the optical analysis were prepared with heating to 350 °C and squeezing a small amount of material between two glass slides in order to obtain thin sections (0.1 mm thick). The specimens were cooled to 150 °C, then heated to 325 °C at 10 °C/min and the texture was observed.

Results

From the thermal gravimetric analysis the polymer was found to be stable up to 375 °C, therefore we limited the thermal analysis up to 370 °C.

The optical analysis performed up to 325 °C at 10 °C/min revealed textures characteristic of a nematic phase (Fig. 1).

The DSC curve of the as-supplied sample is reported in Fig. 2. A gradual increase of the specific heat at about 150 °C is easily attributable to the glass transition, while an endothermic, broad and complex peak at about 328 °C is likely to correspond to the melting (solid state – nematic state).

In Fig. 3 the melting curves recorded at different heating rates are reported. Two melting peaks are always present. The lower temperature melting peak strongly develops on increasing the heating rate, passing from 25.8% of the total area at 20 °C/min to 59.3% at 80 °C/min; correspondingly, the higher temperature melting peak is reduced.

On cooling from the nematic state an exothermic peak (crystallization) is observed (Fig. 4A), whose shape and location are strongly dependent on the cooling rate. In fact, with a cooling rate of 20 °C/min only one exothermic peak is observed

[1]) Longer annealing times were not used as at the higher annealing temperatures the samples were found to be not stable.

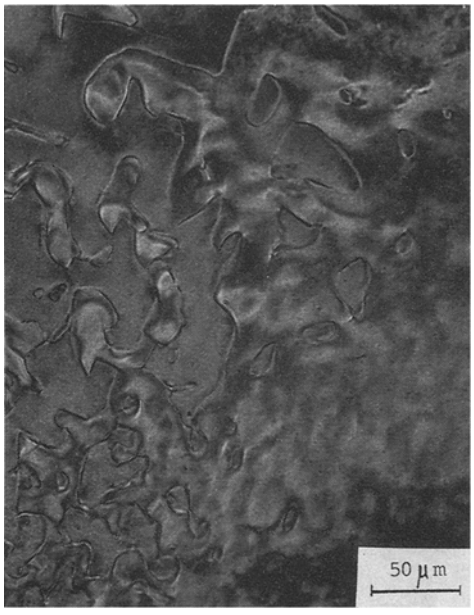


Fig. 1. Optical micrograph of the sample between crossed polarizers at 325 °C

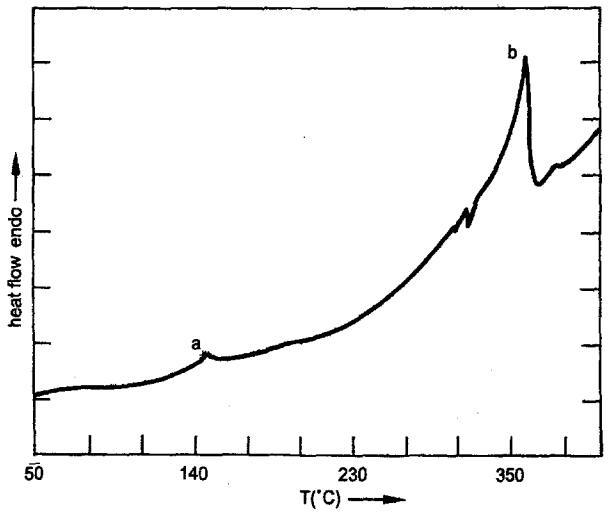


Fig. 2. DSC heating curve at 20 °C/min for the as-supplied sample. The glass-transition (a) and the solid state-nematic state transition (b) are shown. The heat flow scale is 15 mW

at about 290 °C, with 10 °C/min a shoulder appears at higher temperatures (about 297 °C), with 3 °C/min a well-evident double exothermic peak occurs, with the minima located at about 290° and 300 °C; finally, with 1.5 °C/min the two peaks are still observable but tend to coalesce. In Fig. 5 the location of the exothermic peaks is reported as

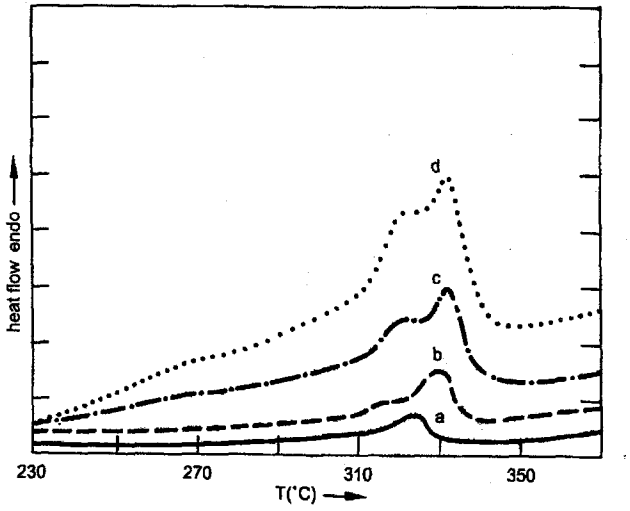


Fig. 3. DSC curves from 230° to 370 °C recorded at the following heating rates: a) 10, b) 20 c) 50 and d) 80 °C/min. The heat flow scale is 30 mW

function of the cooling rate. The position of the lower-temperature peak is not influenced by the cooling rate, while that of the second one is slightly influenced in that the peak temperature tends to decrease on decreasing the cooling rate. Figure 4B shows the DSC curves obtained heating (at 10 °C/min) the samples cooled at different scanning rates. The variation of the cooling rate affects the shape of the curve as well as the peak temperatures and the heat of transition. In fact, for the "quenched" sample (cooled from the nematic state at 200 °C/min) a very small melting peak at 297 °C and a large one at 325 °C are observed. On reheating samples cooled at lower scanning rates the first of the two peaks increases (and also its temperature moves towards higher values) and after heating the samples cooled at 3 and 1.5 °C/min only one melting peak is present.

In order to better investigate the crystallization process, the samples were submitted to isothermal annealing in the range from 200° to 300 °C, for times going from 1 to 360 min. In Fig. 6 the DSC curves recorded on reheating at 10 °C/min the annealed samples are reported in the cases of $T_a = 270$ and 280 °C. Two endothermic peaks are always present, nevertheless, the first one, which is very small for lower annealing temperatures and/or times, strongly develops on annealing. Prolonged and/or higher-temperature annealings cause this peak to become more intensive and shifted to higher temperatures. In Fig. 7 the

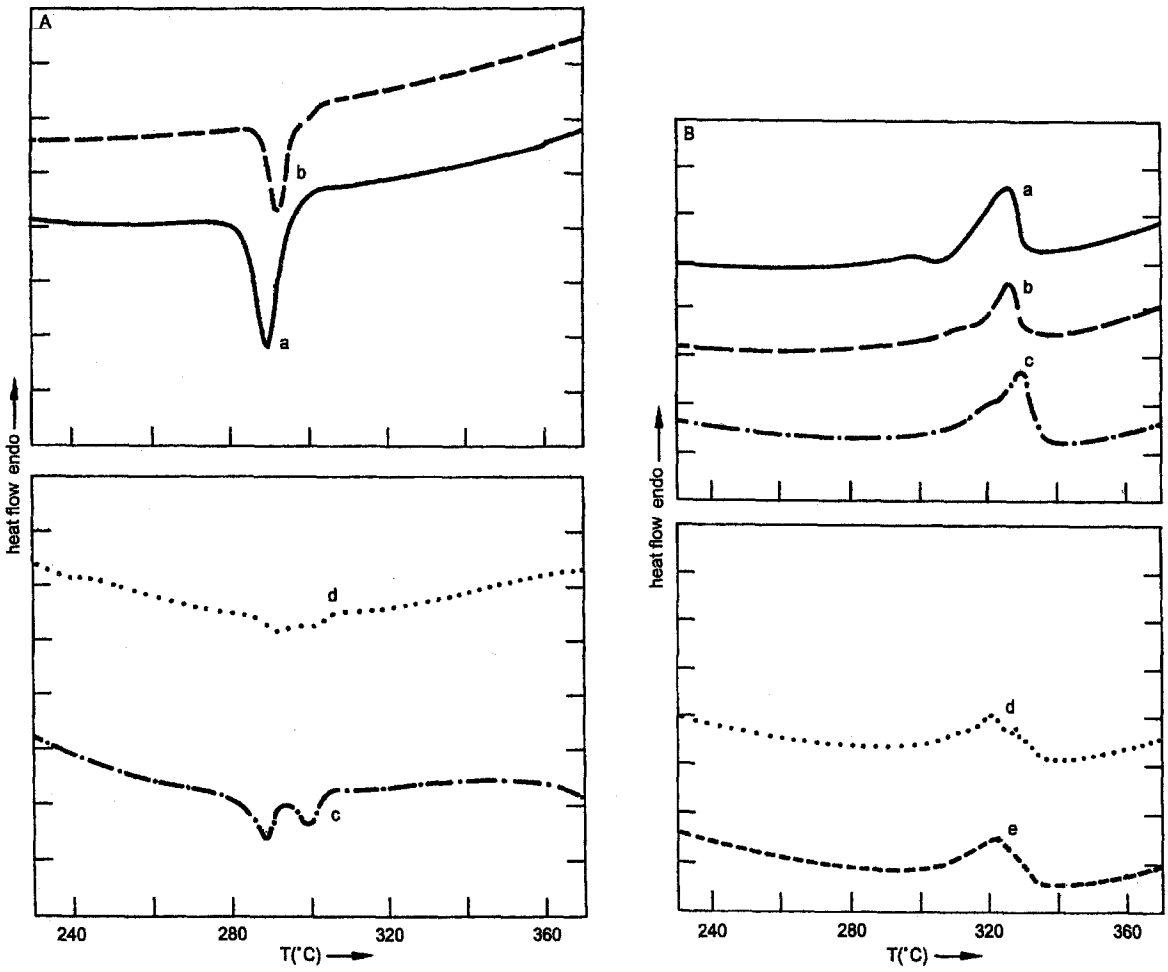


Fig. 4. A) DSC curves recorded on cooling the nematic phase at the following scanning rates: a) 20 °C/min; b) 10 °C/min; c) 3 °C/min; d) 1.5 °C/min. The heat flow scale is 20 mW for a) and b), and 5 mW for c) and d). B) DSC curves recorded on reheating at 10 °C/min the samples cooled at the following scanning rates: a) 200°C/min ("quenched"); b) 20 °C/min; c) 10 °C/min; d) 3 °C/min; e) 1.5 °C/min. The heat flow scale is 10 mW for a), b) and c), and 5 mW for d) and e)

heat of transition associated with the whole process $\Delta_t H$, and the heats of transition associated with the lower and higher temperature peaks, ΔH_1 and ΔH_2, respectively, are reported as function of the logarithm of the annealing time, t_a, for samples annealed at different temperatures. $\Delta_t H$ and ΔH_1 increase in a non-linear manner, without any leveling-off tendency. In contrast, ΔH_2 tends to decrease versus the logarithm of t_a: the decrease is more rapid at higher annealing temperatures. As far as the peak temperatures are concerned it is worthy noting that T_1 strongly increases as t_a increases, in a non-linear manner, while T_2 is about constant. Both T_1 and T_2 are always higher than T_a.

In order to shed further light on the crystallization behavior, standard Avrami analysis according to $\ln[-\ln(1-\Delta H/\Delta H^0)] = \ln k + n \ln t_a$ [13] (where ΔH^0 is the heat of fusion of a 100% crystalline sample, k is constant and n is the Avrami exponent) was performed on the kinetic data relative to the peak at T_1.

Figure 8 presents the linear Avrami plots obtained at $T_a = 200°$, 270°, 280°, 290° and 300 °C. The values of the kinetic data calculated by the Avrami analysis are reported in Table I and are calculated on the basis of $\Delta H^0 = 30$ J/g, the value reported in the literature for the crystal -nematic transition of polyesters [7–9]. The evaluation is just indicative as this value corresponds to

polyesters with different chemical structure. However, $\Delta H^0 = 30$ J/g is the value used for the Avrami analysis of other liquid-crystalline copolyesters [11] and, on the other side, n and k are not particularly sensitive to the choice of ΔH^0 value. The values of n are very low, always less than 0.5. The trend of k as a function of the temperature shows that the temperature of maximum crystallization rate is 290 °C.

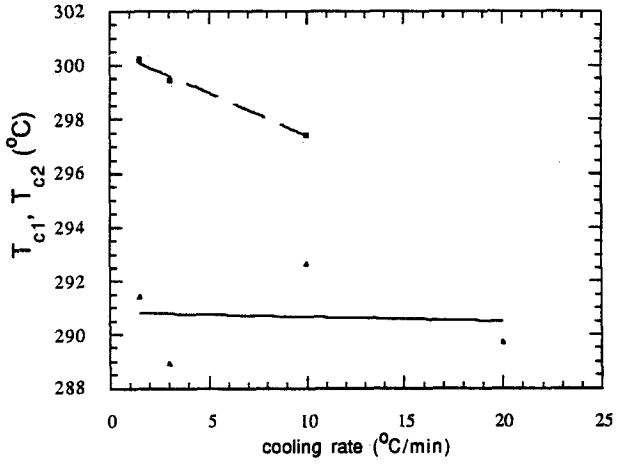


Fig. 5. Location of the exothermic peaks as function of the cooling rate. T_{c1} (▲) and T_{c2} (■) indicate the transition temperatures of the lower and the higher temperature peaks, respectively

Discussion

The most important features stemming from the described calorimetric study are the reduction of the higher temperature peak and the corresponding increase of the lower temperature one occurring: a) on reheating samples cooled at decreasing cooling rates, b) on reheating samples submitted to prolonged annealing and/or to higher temperature annealing, c) on heating samples at increasing scanning rates. All these results may be interpreted on the basis of what occurs for the melting of polyethylene- and polytetramethyleneterephtalate [13], i.e., only the lower temperature melting peak corresponds to the melting of crystals actually present in the sample before the analysis, while the higher temperature melting peak is relative to the melting of more perfect crystals formed during the heating. The observed increase of the lower temperature melting peak and the reduction of the higher one in the previously described conditions may be tentatively explained by admitting that more defectous crystals (i.e., crystals obtained on annealing at lower T_a and/or t_a) during the subsequent heating are able to experience a recrystallization process. Instead, more perfect crystals (i.e., those obtained on annealing at higher T_a and/or t_a) are not able to further perfect during the subsequent heating. In the same way the behavior observed

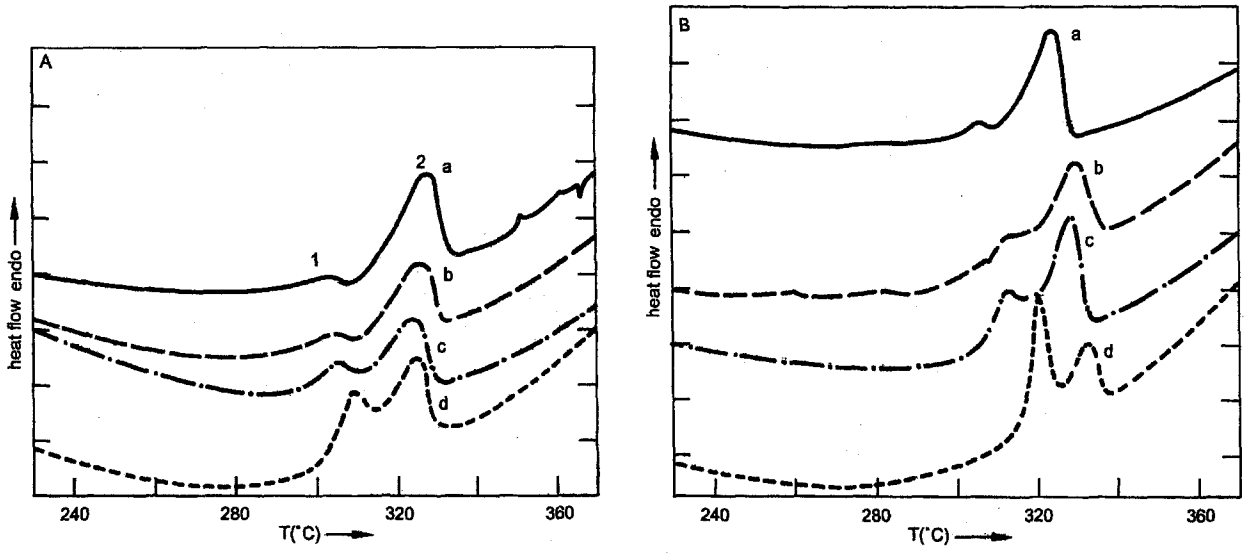


Fig. 6. DSC curves recorded on heating at 10 °C/min the samples annealed at A) 270 °C and B) 280 °C for ta = 1 (a); 30 (b); 60 (c) and 180 (d) minutes. Peaks 1 and 2 are shown.

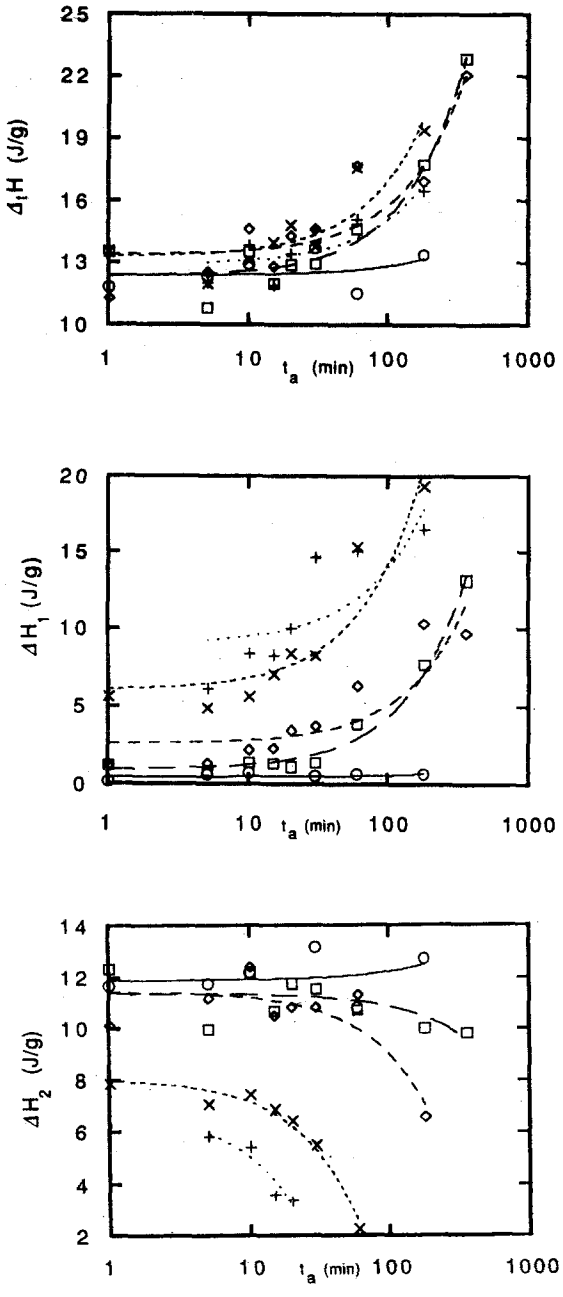


Fig. 7. Total heat of transition ΔtH, heats of transition associated to peak 1 ΔH_1 and to peak 2 ΔH_2 as a function of the annealing time for different annealing temperatures. (T_a = 200 °C (○), 270 °C (□), 280 °C (◇), 290 °C (+) and 300 °C (×))

on reheating samples cooled at decreasing scanning rates and on heating samples at increasing scanning rates can be explained.

Our results are, however, also interpretable by admitting that, during the annealing, the initially

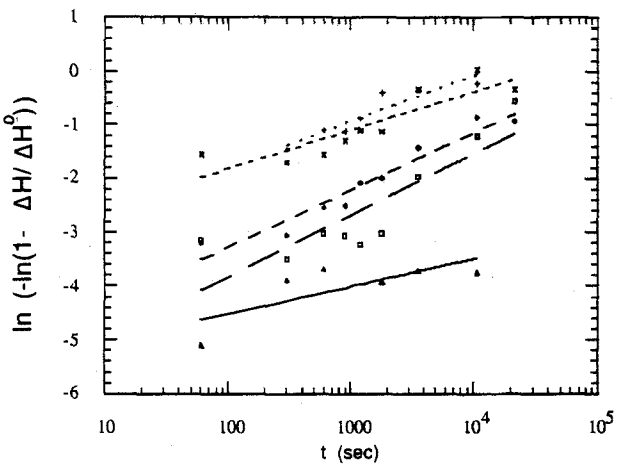


Fig. 8. Linear Avrami plots obtained at the different annealing temperatures based on DSC data corresponding to peak 1. (Ta = 200 °C (▲), 270 °C (+), 280 °C (×), 290 °C (●) and 300 °C (□))

Table 1. Kinetic data for peak 1 calculated by Avrami analysis

Annealing temperature (°C)	n	k
200	0.22	7×10^{-3}
270	0.50	2.5×10^{-3}
280	0.46	7×10^{-3}
290	0.30	5×10^{-2}
300	0.37	7×10^{-3}

random copolyester can be reorganized to a blocky structure by the process called "crystallization induced reaction" [12]. In this last case, as proposed by Hedmark et al. [11], the two melting peaks could be due to two kinds of crystals of different size. In particular, the high-temperature melting peak may be due to larger crystals constituted of homopolymer blocks formed during the annealing and then crystallized, and the low temperature melting peak to lower dimension crystals, the formation of which follows the characteristic behavior of a crystallization occurring during the annealing.

Our results do not seem to be interpretable on the basis of the two-step mechanism proposed by Butzbach [10]. In fact, the trends of $\Delta_t H$ vs $\log t_a$ does not suggest the occurrence of a two-step mechanism. Moreover, the higher temperature peak in our case is not independent from the annealing conditions, as required in the mechanism proposed by Butzbach.

Lastly, we want to remind that the Avrami exponents obtained from the analysis of the kinetic data of the lower temperature peak are very low, ranging from approx. 0.2 to 0.5. This suggests the occurrence of a highly restricted, one-dimensional crystal growth, as expected on the basis of the rigid-rod character of the molecules in the nematic mesophase [11, 13].

Acknowledgements

Financial support from Consiglio Nazionale delle Ricerche (Italy) is gratefully acknowledged.

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Received November 15, 1993;
accepted March 3, 1994

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