Crystallization and melting behaviour of a semirigid liquid-crystalline polyester

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Differential scanning calorimetry has been used to investigate the thermal behaviour of a mesogenic polyester built up of a flexible spacer of eight methylene units and a rigid aromatic ester triad. Non-isothermal crystallizations at different cooling rates and isothermal crystallizations at various temperatures have been carried out; the variations of the melting temperatures and enthalpies as a function of the crystallization parameters have been investigated. The melting profiles of the treated samples reveal two endotherms at T_m^1 and T_m^2,which cannot be interpreted as usually reported for conventional polymers. A new model of crystallization has been proposed, taking into account that a certain registry of neighbouring chains persists in the nematic state above T_m, and becomes poorer and poorer on increasing the temperature and time; this persistent registry can be regarded as potential nuclei of crystallization, responsible for the high-temperature endotherm. Therefore, the presence of multiple endotherms in the melting profile of thermotropic polymers crystallized from the liquid-crystalline state appears to be a consequence of the annealing conditions in the nematic phase.

(Keywords: crystallization; melting behaviour; polyester; liquid crystals; differential scanning calorimetry)

INTRODUCTION

Full understanding of the crystallization mechanism of melt-processable liquid-crystalline polymers appears to be of great interest in order to control the effect of processing conditions on the final properties of the material. When these polymers are cooled from the nematic melt, both a crystalline structure and a nematic glassy state can be obtained. Good mechanical properties, however, require that the material become partially crystallized.

Many papers have been published in the last decade dealing with the crystallization behaviour of a number of thermotropic nematic copolyesters having rigid backbones[1–12]. It has been generally found that: (i) massive structural rearrangements do not occur during crystallization and the structure of the solid crystal closely resembles that of the liquid crystal[1]; (ii) the nematic to solid transition occurs with negligible volume change[7]; and (iii) random copolymers can display an ordered solid phase, as demonstrated by X-ray scattering[10], thermal analysis[6,8,12] and electron microscopy studies[13,14], despite the random distribution of comonomer units along the backbone and the marked difference in their geometry. Most available information arises from the investigation of random copolyesters of *p*-hydroxybenzoic acid (HBA) and 2,6-hydroxynaphthoic acid (HNA), which form non-periodic layer crystallites[13]. The chains are rotationally disordered in the crystal[7]; as a consequence the thermodynamic parameters of the crystal–nematic transition exhibit small changes, and annealing below this temperature increases the degree of crystallinity but affects the heat of fusion very little[7,12]. Similar rotationally disordered phases have been observed in related homopolymers, such as poly(*p*-phenylene terephthalate) and Xydar[15]. Copolyesters obtained from terephthalic acid and phenyl hydroquinones have been shown to form well ordered three-dimensional structures with unusually large heats for the crystal–nematic transition[12,16].

Segmented liquid-crystal polymers, having flexible spacers in the main chain, have been extensively investigated because of their accessible transition temperatures and improved solubility. A widely observed phenomenon is the occurrence of crystallization on cooling from the liquid-crystal phase. However, very little research has been carried out on the detailed crystallization and melting behaviour of these systems[17,18].

This work addresses the phenomenon of crystallization in a mesogenic segmented polymer exhibiting a wide range of stability of the nematic phase. A polarizing microscope equipped with a hot stage and a differential scanning calorimeter have been used to investigate the thermal behaviour; non-isothermal crystallizations at different cooling rates and isothermal crystallizations at various temperatures have been carried out. A new model of crystallization is proposed, which could explain the unusual thermodynamic and kinetic behaviour observed at the nematic–solid transition of main-chain liquid-crystal polymers.

EXPERIMENTAL

Materials

The polymer used in this investigation was a segmented thermotropic polyester obtained by joining together an

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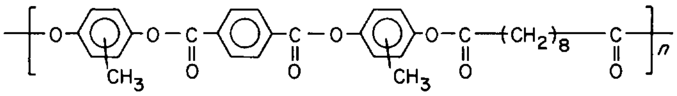
aromatic ester trimer with a flexible spacer of eight methylene units, i.e.



The preparation of the polyester is described in detail in ref. 19. It was characterized by its intrinsic viscosity in 1,1,2,2-tetrachloroethane at 25°C (1.74 dl g^{-1}) and its thermal behaviour (a nematic phase existed between 186 and 320°C). A more detailed thermal analysis of this sample revealed a glass transition temperature T_g at about 50°C and the appearance of multiple endotherms in a second heating cycle. On cooling from the nematic state a fast crystallization occurs. Tests of thermal stability, carried out under a nitrogen atmosphere with a Perkin–Elmer TGS2 analyser, indicate that the polymer is stable up to 450°C.

Thermal analysis

The analysis was performed with a computer-interfaced Mettler TA 3000 system with a DSC 30 measuring cell. The thermodynamic parameters were evaluated by using the software Graphware TA72; partly superimposed peaks were resolved into their component curves using a deconvolution method[20]. All the experiments were performed in a nitrogen atmosphere, using high-purity standards for calibration, and sample pans were always filled with the same quantity of polymer (10 ± 1 mg). Before each treatment the samples were heated to the nematic state (230°C) and kept at this temperature for 15 min; it has been observed that reproducible results were obtained by changing the time at 230°C from 5 to 30 min. This temperature was higher than the extrapolated metastable equilibrium melting temperature T_m° derived, as described by Cheng[8], on the basis of the relationship between T_m and crystallization time at different temperatures (see *Figure 11*).

The non-isothermal crystallization samples were cooled from the nematic state to 20°C at different cooling rates, ranging between 1 and 40°C min^{-1}.

The isothermal crystallization samples, after the treatment at 230°C, were cooled to the predetermined crystallization temperature T_c (ranging from 100 to 170°C) as quickly as possible and kept there for different time periods T_c (from 1 to about 1000 min). The samples were then heated again to the nematic melt and the d.s.c. heating traces recorded. Peak temperatures for both heating and cooling traces were used. T_m^1 and T_m^2 corresponded to the positions of the first and second endothermic peaks of the final heating cycle, and ΔH_m^1 and ΔH_m^2 are the associated heats of transition. In the annealing experiments, samples non-isothermally crystallized at a cooling rate of 10°C min^{-1} were heated in the d.s.c. from 20°C to the chosen annealing temperature T_a (ranging between 174 and 182°C). The samples were kept at this temperature for different times t_a (from 5 to 1000 min) and then reheated directly from T_a.

In a few experiments the samples were maintained in the nematic state at 270 and 300°C for 5 min or heated to the isotropic state at 350°C before being kept at 230°C for 15 min and finally crystallized. In addition the effect of a long permanence (1000 min) at 230°C has been investigated.

Optical microscopy

The optical textures of the polymer at different temperatures were investigated by means of a Polyvar Pol Reichert polarizing microscope equipped with a Mettler FP82 hot stage (control unit FP 80).

Wide-angle X-ray scattering

WAXS experiments were carried out at room temperature with a Philips PW 1050/71 powder diffractometer (Cu Kα Ni-filtered radiation) in reflection mode, continuous scanning angle 2θ. Annealed and crystallized specimens were subjected to X-ray scattering. Annealing was achieved by heat treatment of the dry polymer at 182°C for 1000 min, crystallization by rapid cooling of the nematic melt to 165°C and leaving for 1000 min.

RESULTS AND DISCUSSION

Non-isothermal experiments

In non-isothermal crystallizations the exothermic peaks appear quite narrow at all the rates used and the peak temperature T_p varies to a certain extent with the cooling rate. T_p, the width of the exothermic peak at half peak height and the associated enthalpy are reported in *Table 1* for different cooling rates. The shift of the peak position is small when compared with conventional polymers[21] and the crystallization process is not suppressed even at high cooling rate. Moreover, the width of the exothermic peak changes very little over the whole range used. These effects are due to the high rate of the transition process.

The d.s.c. fusion curves, at constant heating rate (20°C min^{-1}), of samples that have been non-isothermally crystallized are reported in *Figure 1*. For all cooling rates the samples exhibited two melting endotherms.

Table 1 Non-isothermal crystallization properties of the polyester

Cooling rate (°C min^{-1})	T_p (°C)	$\Delta T_p(\frac{1}{2})$ (°C)	ΔH_p (kJ mol^{-1})
1	154.8	4.5	4.13
3	148.6	4.6	4.08
5	145.0	4.9	4.35
10	141.4	4.9	4.78
20	135.9	7.0	4.56

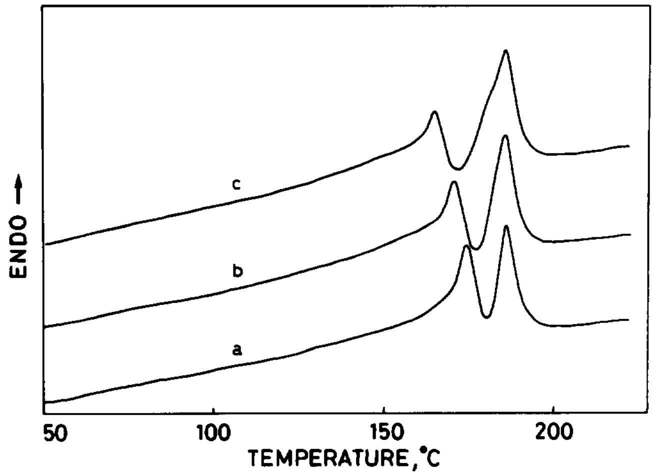


Figure 1 Melting profiles measured at 20°C min^{-1} of samples crystallized non-isothermally at different cooling rates: (a) 1°C min^{-1}, (b) 3°C min^{-1}, (c) 20°C min^{-1}

Double melting peaks have been seen with many other polymers[21] and the reason for such behaviour has been attributed to the presence of different crystal structures[22–24], to crystal reorganization[25–29] or to different components of the morphology formed in two stages of crystallization[6,30].

The formation of two kinds of crystal structure can lead to a double peak in the d.s.c. thermogram, but will also be evident from the X-ray diffraction pattern. The WAXS experiments (described below) are consistent with the presence of one crystalline form only.

When crystal reorganization during heating[25–29] occurs, the lower endotherm is due to the melting of the crystallites produced at the crystallization temperature and the higher one to crystal reorganization processes on melting. The first melting point and the size of the second melting endotherm are more strongly dependent on heating rate[29]. As the heating rate increases, the amount recrystallized decreases; this results in a reduction of the second endotherm and an increase of the first one, which shifts towards higher temperatures. At high heating rates, the two distinct melting endotherms coalesce into a single peak since, under these conditions, the heating rate is fast enough to minimize reorganization. Since the lower melting point is correlated to the original crystals present, it strongly depends on the crystallization conditions and therefore, in non-isothermal treatments, on the cooling rate. The lower the cooling rate, the larger is the time available for the crystals to form a more perfect structure and so they exhibit a higher melting point. Therefore, samples crystallized non-isothermally and reheated at constant rate should exhibit d.s.c. traces that correlate with the cooling rate. For heating rates lower than the cooling one, recrystallization on heating is still possible and a double melting endotherm will still be present. On increasing the ratio between heating and cooling rate, the possibility of crystal reorganization diminishes and finally a single peak should be observed.

The d.s.c. traces of our samples (see *Figure 1*) always exhibited a double melting endotherm. Samples crystallized at a cooling rate as low as 1°C min^{-1} and heated at 20°C min^{-1} show two very large melting endotherms not ascribable to a reorganization process. This appears for the sample heated at a rate comparable with the cooling rate (*Figure 1*, trace c); in this case the shoulder in the higher-melting endotherm could arise from the melting of crystals formed during a recrystallization process. Therefore for our samples the presence of two melting endotherms cannot be interpreted either as a double structure or as a reorganization process, but rather as the presence of different components of the morphology[6,30] arising from a crystallization that occurs in two stages and leads to crystals of different size. This behaviour will be treated in more detail later.

Isothermal experiments

The results reported refer to the melting behaviour of isothermally crystallized samples. This procedure appeared to be adequate to clarify the nature of the heating profiles. Samples crystallized isothermally between 100 and 120°C showed two separate endothermic peaks, practically independent of t_c. At 130, 140 and 150°C a similar behaviour was observed, the only difference being a more noticeable variation in the temperature and heat of transition associated with the first endotherms. D.s.c. traces of samples crystallized at 140°C are reported in *Figure 2*. The exothermic peak and the shoulder between the melting endotherms indicate the occurrence of some recrystallization; however, this does not imply that the peak at T_m^2 originates essentially from the melting of the recrystallized morphology.

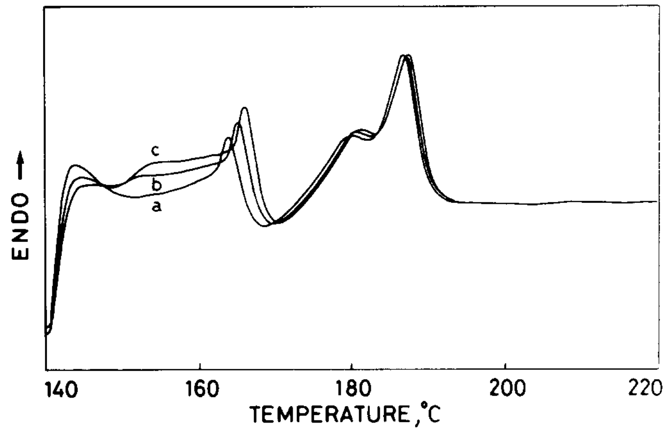


Figure 2 D.s.c. heating traces measured at 10°C min^{-1} on samples crystallized at 140°C for different times t_c: (a) 1 min, (b) 120 min, (c) 935 min

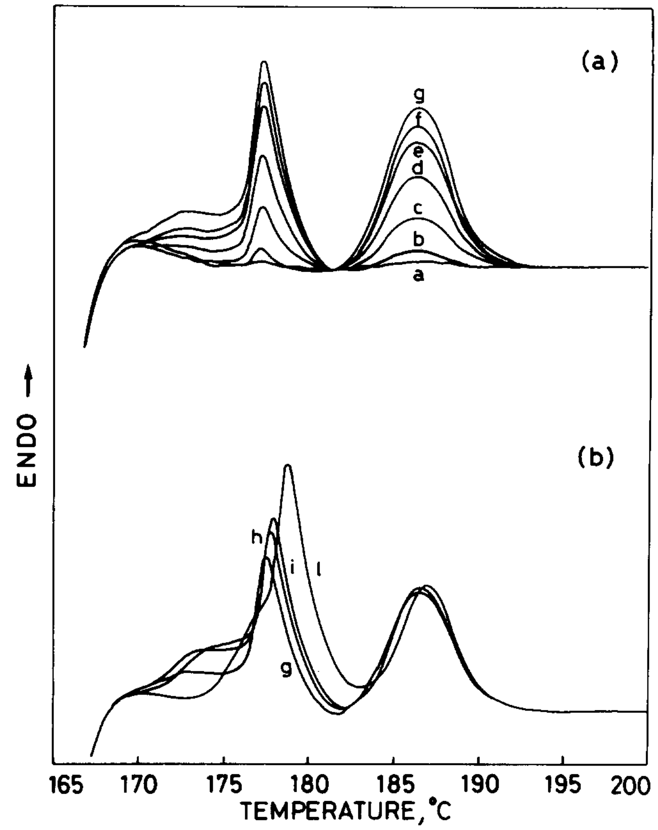


Figure 3 D.s.c. heating profiles measured at 10°C min^{-1} on samples crystallized at 165°C for different times t_c: (a) 5 min, (b) 7 min, (c) 10 min, (d) 13 min, (e) 16 min, (f) 18 min, (g) 20 min, (h) 60 min, (i) 120 min, (l) 1042 min

The situation starts to change at 155°C, where the heats of the transition characteristic of the two endotherms both increase with the crystallization time. Similar results have been obtained at 160 and 165°C. D.s.c. heating profiles of samples crystallized at 165°C are shown in *Figure 3a* (for crystallization times t_c ranging between 5 and 20 min) and in *Figure 3b* (t_c from 20 to 1042 min). The high-temperature transition corresponds

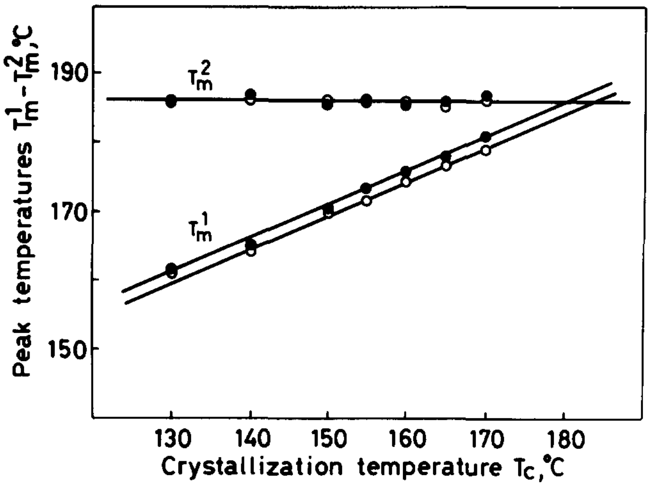


Figure 4 Variation of the melting temperatures T_m^1 and T_m^2 with the crystallization temperature T_c at two different dwell times: (○) 30 min, (●) 950 min

to a process of crystal formation that appears to be complete in a few minutes (4, 8 and 20 min at 155, 160 and 165°C respectively). The low-temperature melting peak exhibits heats of transition that increase continuously with the crystallization time and seems to be still rising after times of about 1000 min. Slight variations of the peak temperatures T_m^1 are also evident. The shoulder in the higher-melting endotherm, appearing in the heating profiles of samples crystallized at lower temperature, disappears at 165°C where two well resolved endotherms are evidenced. For crystals obtained at 170°C both processes are more strongly time-dependent and the heats of transition of the low- and high-temperature endotherms continue to increase after crystallization times of about 1000 min.

The results are summarized in *Figures 4* and *5*, where the peak temperatures and enthalpies of the low-temperature ($T_m^1, \Delta H_m^1$) and high-temperature ($T_m^2, \Delta H_m^2$) endotherms are reported as functions of the crystallization temperature and time. This suggests the presence of two distinct processes leading to crystals of different size.

Nematic melts cooled to the crystallization temperature T_c undergo a process of crystallization, characterized by the peak temperature T_m^2, which is practically independent of the crystallization temperature and time (see *Figure 4*). This step is generally complete in a few minutes; the heat of the transition ΔH_m^2 increases with the logarithm of the crystallization time at constant T_c and reaches a plateau value of about 2.3 kJ mol^{-1}, which is almost constant at every crystallization temperature (see *Figure 5*). The crystallization conditions affect T_m^1, which increases linearly with the crystallization temperature and exhibits a weak dependence on t_c (*Figure 4*). Its peak value is generally no more than 25°C higher than the crystallization temperature. Apparently it corresponds to a structure characteristic of the crystallization conditions, unstable with respect to slight temperature increases and able to give rise to a crystal reorganization process, evidenced by the small exotherm and the shoulder preceding the endotherm at T_m^2, when crystallization is carried out at low enough temperature. The heat of the transition characteristic of this peak, ΔH_m^1, is a function of both the crystallization temperature and time (broken curves of *Figure 5*); this second step of crystallization needs very long times to be complete. However, it improves substantially the degree of crystallinity of the sample, as evidenced by the ratio $\Delta H_m^1/\Delta H_m^2$, in the order of 2–3 after crystallization times of about 1000 min.

Annealing experiments

Figure 6 shows the d.s.c. traces of samples annealed for 1020 min at different temperatures, ranging between 174 and 182°C. The melting curves exhibit one or two peaks depending on the annealing treatment. For annealing times up to about 1000 min, two peaks are present for $T_a < 182$°C and only one if $T_a = 182$°C. The higher melting temperature of the double endotherm is roughly constant (about 186°C), while the lower one increases with both annealing time (see *Table 2*) and temperature. According to the presence of different morphologies in the system, the first endotherm must be related to the melting of smaller crystallites and the second to the melting of larger more perfect crystals. On increasing the annealing temperature, a recrystallization of the material in a more perfect form is observed and T_m^1 increases until superimposed onto T_m^2.

X-ray scattering and optical microscopy

In order to clarify the origin of the multiple endotherm, WAXS measurements have been carried out on two samples suitably treated such that one d.s.c. trace exhibited double peaks (after crystallization at 165°C for 1000 min; see *Figure 3*) and the other only one (after annealing at 182°C for 1000 min; see *Figure 6*). The WAXS powder spectra of the two samples were similar, with seven strong reflections superimposed on an amorphous halo. The intensity profile is shown in *Figure 7*. As a consequence the different thermal behaviours cannot be ascribed to the presence of two crystal structures.

Polarized optical microscopy showed a threaded texture characteristic of the nematic phase. Crystallization appeared as a darkening of certain regions, which reduced the overall transmission, without the occurrence of large-scale reorganization.

ADDITIONAL EXPERIMENTS AND CONCLUSIONS

A structural model for crystallization of the fully aromatic copolyesters has recently been introduced by Butzbach *et al.*[6]; these authors suggest a mechanism of crystallization that occurs with different rates at different places within the sample. On cooling from the nematic melt, crystallization occurs in two steps: the former is rapid and takes place independently of the cooling conditions and continues until the sample is physically crosslinked; the latter, which accounts for the transformation of the remaining part of the sample into an ordered structure, is controlled by a slow diffusional process. This two-step process, introduced to describe the behaviour of

Table 2 Effect of annealing at $T_a = 174$°C for different times t_a

t_a (min)	T_m^1 (°C)	T_m^2 (°C)	ΔH_m^1 (kJ mol^{-1})	ΔH_m^2 (kJ mol^{-1})
5	180.0	186.0	2.55	2.34
30	180.3	185.9	3.04	2.39
120	180.9	186.3	3.21	2.34
1020	181.2	186.2	3.80	2.39

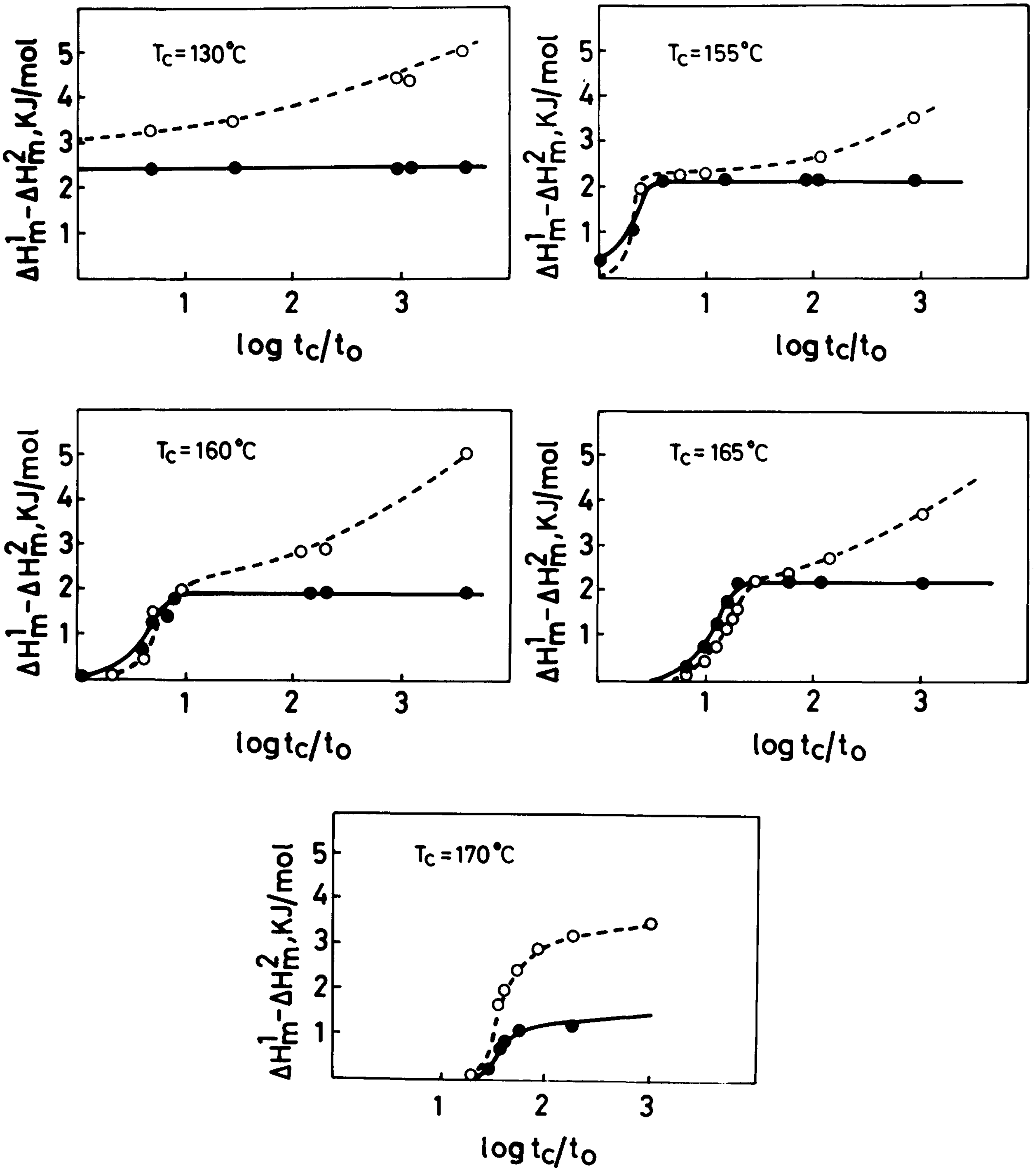


Figure 5 Variation of the melting enthalpies ΔH_m^1 (broken curves) and ΔH_m^2 (full curves) with the crystallization time t_c ($t_0 = 1$ min) for different crystallization temperatures T_c

HBA/HNA copolymers[6], can justify in a first approximation the results reported on HTR, a polymer made by Granmont[12], even if in the latter case some differences in the evolution of ΔH_m with annealing time have been attributed to a solid-state post-polymerization, simultaneously present with crystal perfectioning[12].

The two transitions at T_m^1 and T_m^2, observed in our samples crystallized at $T_c < 150$°C, seem to agree qualitatively with the above model. In this temperature range both the transitions appear to be fast. However, the greater flexibility of polymer chains could act in varying the timescale of the process; for rigid polymers the first step is complete in a few seconds, whereas the second one needs very long transformation times[6]. For semiflexible systems the second step could be faster and less affected, at constant T_c, by the crystallization time. However, the behaviour of samples treated at $T_c > 150$°C indicates that some other effects must be taken into account, since under these conditions both steps are slow, the only difference being the attainment of a plateau value for ΔH_m^2.

For a better understanding of the phenomenon, additional experiments have been carried out. Samples crystallized at 165°C for 60 min have previously been maintained in the nematic range under different conditions. The resulting d.s.c. melting profiles are compared in *Figure 8* with the reference curve h of *Figure 3b*. In another experiment, before the usual treatment at 230°C for 15 min, a very quick heating to the isotropic state has been carried out; *Figure 9* shows the melting of a sample crystallized for 1000 min at 165°C (the reference curve of *Figure 3b* is also drawn). The transition at T_m^2 appears to be a function of the annealing conditions in the nematic phase; it can be completely cancelled going to the isotropic state or probably choosing appropriate conditions of treatment in the nematic range.

It is well known that liquid-crystal copolyesters, after a long permanence in the nematic state or annealing at high temperature, may undergo post-polymerization processes as well as reorganization of chain sequences[12,31–33]. All these processes vary the thermal behaviour of the polymer, raising T_m if the sample is subjected to post-polymerization[12] or strongly affecting the thermal profile in the case of reorganization[31–33]. In order to interpret our d.s.c. curves correctly, the thermal stability of our polymer has been verified. For this purpose a sample was kept at 230°C for 1000 min and then dissolved in chloroform. In this way the thermal history of the treated polymer was cleared and, after precipitating and drying, it could be compared to the as-polymerized material. The d.s.c. curve of this sample was similar to the first fusion of the original polymer and showed that the above-mentioned chemical processes have little or no influence on the thermal behaviour of the polymer.

The dependence of the melting temperature and the associated enthalpy on the thermal treatment of the

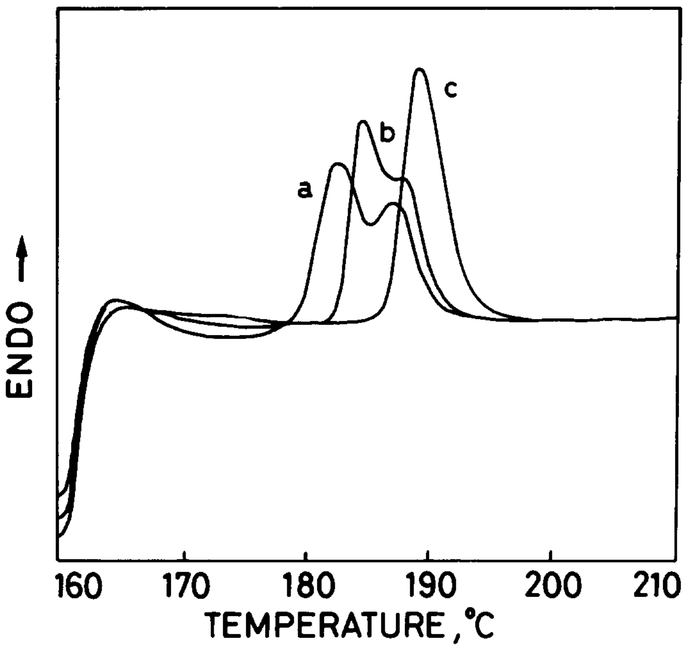


Figure 6 D.s.c. melting traces measured at 10°C min^{-1} on samples annealed for 1020 min at different temperatures T_a and quickly cooled to 160°C: (a) 174°C, (b) 178°C, (c) 182°C

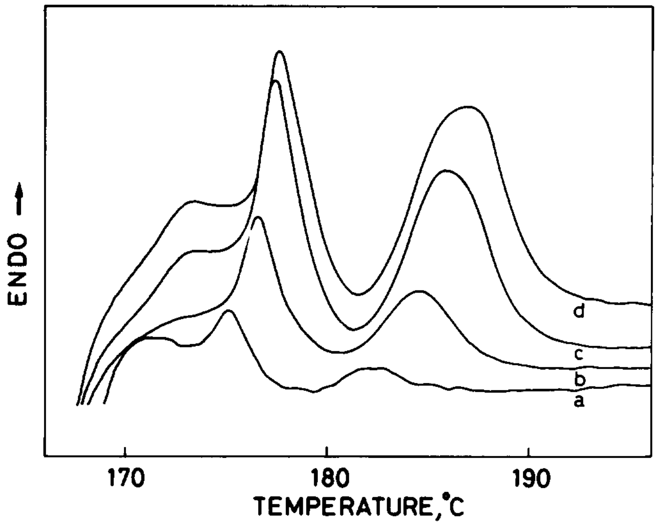


Figure 8 Melting profiles measured at 10°C min^{-1} on samples crystallized at 165°C for 60 min after different thermal treatments: (a) 230°C for 1000 min; (b) 300°C for 5 min, 230°C for 15 min; (c) 270°C for 5 min, 230°C for 15 min; (d) 230°C for 15 min, reference curve h of *Figure 3b*

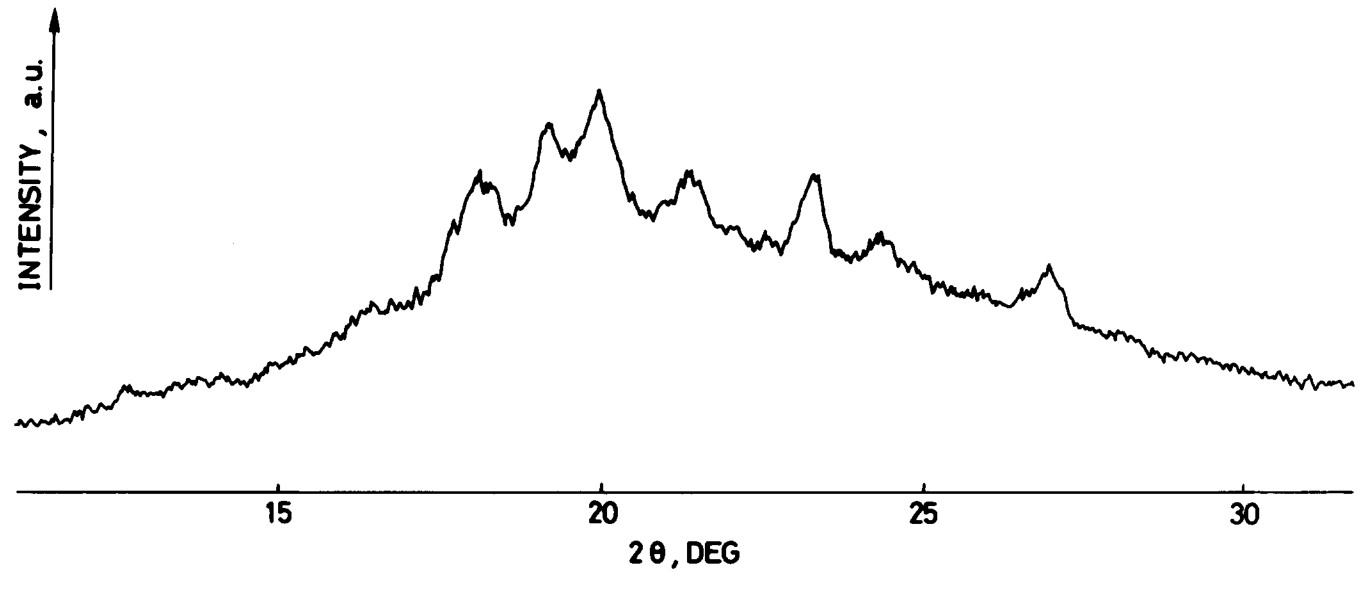


Figure 7 X-ray diffraction pattern of a sample crystallized at 165°C for 1000 min

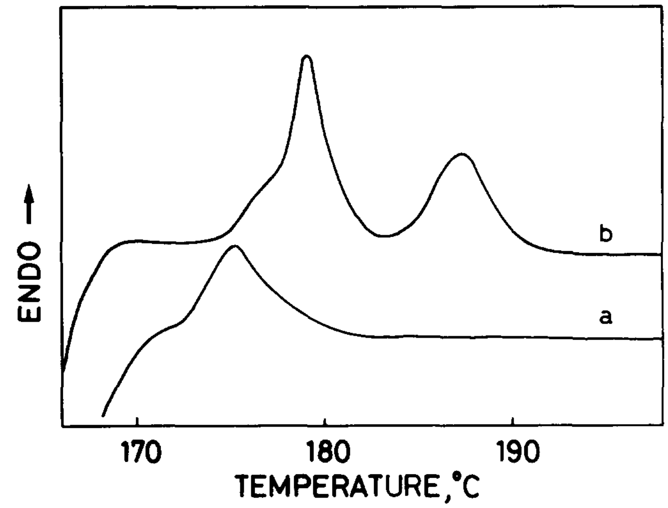


Figure 9 Melting profiles measured at 10°C min^{-1} on samples crystallized at 165°C for 1000 min after different thermal treatments: (a) sample heated very quickly to 350°C, before being maintained at 230°C for 15 min; (b) sample kept at 230°C for 15 min, reference curve 1 of *Figure 3b*

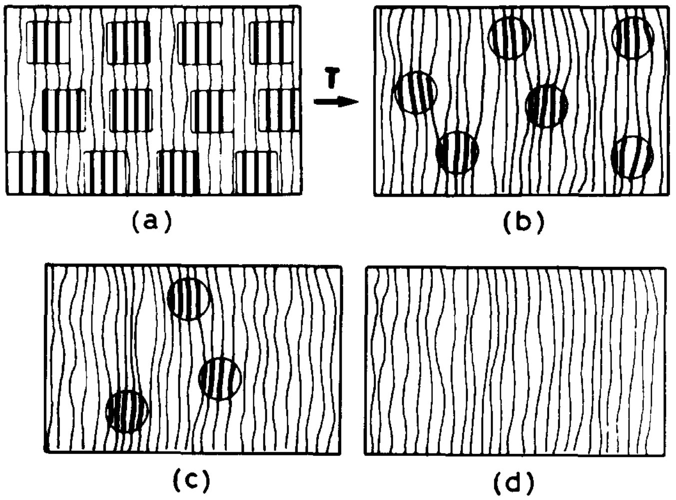


Figure 10 Scheme of crystallization proposed: (a) crystal structure below T_m; (b) nematic state with a certain registry of neighbouring chains; (c) the registry becomes poorer on increasing temperature or time; (d) homogeneous nematic phase

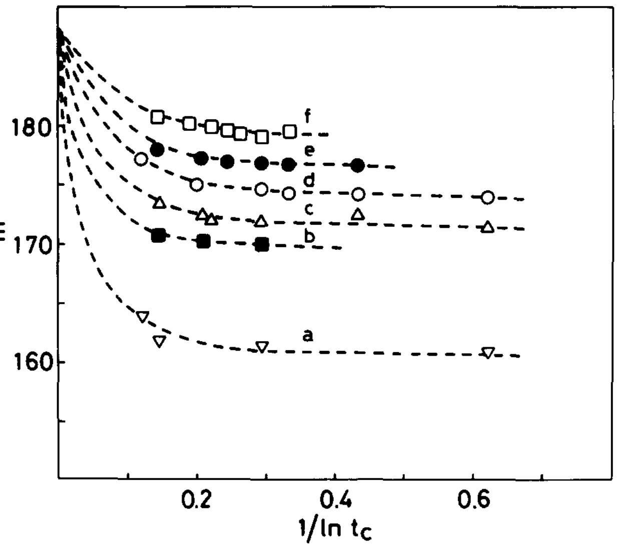


Figure 11 Extrapolation of the metastable equilibrium melting temperature T_m° at different temperatures T_c, according to Cheng[8]: (a) 130°C, (b) 140°C, (c) 155°C, (d) 160°C, (e) 165°C, (f) 170°C

nematic melt suggests the existence of non-equilibrium states of liquid crystallinity. This is in contrast with the usual behaviour of low-molecular-weight liquid crystals[34] and side-chain polymers[35]. Time-dependent effects have been recognized by Feijoo *et al.*[36,37] on the nematic–isotropic transition and on the short-range order parameter of a family of segmented copolyethers. These authors report that the equilibrium state is achieved in minutes in the isotropic phase, but takes hours in the nematic phase.

Therefore, to explain the crystallization behaviour, a new scheme can be proposed, taking into account that a certain registry of neighbouring chains persists in the nematic state above T_m which becomes poorer and poorer on increasing temperature and time (*Figure 10*) and finally disappears when the equilibrium state is attained. We are not dealing with conventional nuclei of crystallization; in fact the temperature of 230°C, chosen to treat the samples in the nematic state before crystallization, is high enough to prevent this possibility. Following the procedure reported by Cheng[8] we have tried to extrapolate the metastable equilibrium melting temperature T_m° (*Figure 11*), which appears to be substantially lower than 230°C. We can consider the persistent registry of neighbouring chains as potential nuclei of crystallization, responsible for the high-temperature endotherm; this peak is due to the melting of crystals, which maintain a certain memory of their arrangement in the original sample. As a consequence the real structure arising from nematic ordering must be related to the low melting endotherm.

These results lead to the conclusion that the presence of multiple endotherms in the melting profile of thermotropic polymers can be a consequence of the annealing conditions in the nematic state. Since data obtained from different heating and cooling runs cannot be representative of equilibrium situations, some determinations of melting temperature and enthalpy must be reconsidered, as already suggested by Percec *et al.*[38] on the basis of a different argument. The attainment of equilibrium conditions could depend on the chemical nature of the polymer, on its molecular weight and on the flexible spacer length, as suggested by some new results on other segmented polyesters[39,40] under current investigation.

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