Crystallization and melting behaviour of segmented thermotropic polymers: 3. Analysis of two polyesters based on 4,4′-(alkanedioyldioxy)dibenzoyl dichlorides and hydroquinones

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A differential scanning calorimeter has been used to investigate the crystallization and melting behaviour of two segmented nematic polyesters based on 4,4′-(alkanedioyldioxy)dibenzoyl dichlorides and hydroquinones. Isothermal crystallizations from the nematic melt have been carried out on both samples. The results are discussed in terms of variation of the successive melting profiles as a function of various parameters, such as the crystallization temperature and time and, in more detail, the conditions of the preliminary treatment in the nematic state. The complex melting behaviour evidenced by the polyesters can be justified on the basis of a new scheme, introduced in our previous paper, which accounts for the slow evolution of the nematic melt towards its thermodynamic equilibrium. Above the crystal–nematic transition a certain registry of neighbouring chains persists in the melt, which becomes poorer and poorer upon increasing temperature and time and eventually disappears when equilibrium is attained. These results raise some fundamental questions on the ability of thermotropic polymers to crystallize from the nematic melt and underline that a careful adjustment of the process parameters must be achieved to obtain reproducible results and to control the final properties of the material.

(Keywords: segmented thermotropic polymers; crystallization; melting; polyesters; differential scanning calorimetry)

INTRODUCTION

The crystallization process of random copolymers with rigid chain molecules, which usually display nematic melts, has recently attracted the attention of several groups of scientists[1–6], since the structures formed at the nematic–solid transition are basically different from crystals of flexible polymers. On the other hand, only a few papers have dealt with a detailed investigation of the crystallization and melting behaviour of segmented thermotropic polymers having flexible spacers in the main chain[7–9].

Recently we have proposed a new model to explain the crystallization behaviour of thermotropic polymers[10], which accounts for the unusual thermodynamic and kinetic properties observed at the nematic–solid transition. Non-equilibrium effects in these systems can justify the complex melting behaviour of samples crystallized from the nematic melt.

In this paper we consider the crystallization and melting behaviour of two segmented nematic polyesters of similar chemical nature, containing polymethylene spacers of different length and unsubstituted or substituted mesogenic moieties. Our aim is to verify that the proposed model[10] applies to various systems and can therefore be considered of general validity. To this purpose, in a previous paper[11], the behaviour of a poly(ether ester) of low isotropization temperature is considered.

Isothermal and non-isothermal crystallizations from the nematic melt have been carried out on both samples; the results are discussed in terms of variation of the successive melting profiles as a function of various parameters (temperature, time, treatment conditions in the nematic state). A differential scanning calorimeter has been used to identify the transition temperatures and enthalpies; the nature of the transitions has been checked by means of a polarizing microscope equipped with a hot stage.

EXPERIMENTAL

Materials

The polymers used in this investigation are segmented nematic polyesters obtained by joining together 4,4′-(dodecanedioyldioxy)dibenzoyl dichloride or 4,4′-(sebacoyldioxy)dibenzoyl dichloride with hydroquinone or 2-methylhydroquinone, respectively.

The monomeric intermediates and the polyesters have been obtained following the same procedure as that reported in detail in refs 12, 13 and 14. Sample OHO10 has intrinsic viscosity of 1.32 dl g^{-1} in phenol/1,1,2,2-tetrachloroethane (TCE) 60/40 (v/v) at 25°C and sample OMO8 has a value of 1.84 dl g^{-1} in TCE at 25°C.

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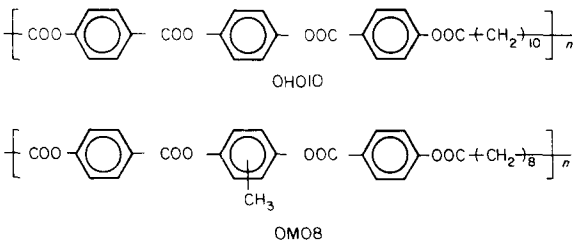

Thermogravimetric analysis, carried out under a nitrogen atmosphere with a Perkin–Elmer TGS2 analyser, indicates that they are stable up to 400°C.

Thermal analysis

The analysis was performed with a computer-interfaced Mettler TA 3000 system (measuring cell DSC 30). The melting enthalpies were evaluated by using the software Graphware TA72; the partly superimposed peaks were resolved into their component curves using a deconvolution method[15]. D.s.c. pans were always filled with the same quantity of polymer (10 ± 1 mg). Before each treatment the samples were heated to the nematic state and kept at constant temperature for a certain time.

The isothermal crystallization samples, after the above treatment, were cooled within the calorimeter to the predetermined crystallization temperature T_c as quickly as possible and kept there for different time periods t_c. The non-isothermal crystallization samples were cooled from the nematic state to 20°C at 20°C min^{-1}; in a few experiments a very quick heating to the isotropic state preceded the treatment of the samples in the nematic phase. The samples were then heated again to nematic melts and the d.s.c. heating traces were recorded. T_{m1} and T_{m2} correspond to the positions of the first and the second endothermic peaks of the final heating cycle; ΔH_{m1} and ΔH_{m2} are the associated heats of transition.

D.s.c. transition temperatures were compared with optical observations carried out with a Polyvar Pol Reichert polarizing microscope equipped with a Mettler FP82 hot stage (control unit FP 80) or a Linkam THMS 600/TMS 91 system.

RESULTS

Polymer OHO10 exhibits a nematic phase between 285.8 and 342.9°C (*Figure 1*, curve a); the associated melting and isotropization enthalpies are 21.2 and 5.5 kJ mol^{-1}, respectively. On cooling from the nematic state (*Figure 1*, curve b), after a treatment of 5 min at 310°C, a fast crystallization occurs (at 255°C, associated enthalpy 10.9 kJ mol^{-1}); the second heating run exhibits a double melting peak ($T_{m1} = 267.9$ and $T_{m2} = 273.4$°C, total enthalpy 17.3 kJ mol^{-1}) and the isotropization endotherm (*Figure 1*, curve c). Both the cooling and the heating profiles are substantially modified after a very quick heating to the isotropic state (370°C), followed by non-isothermal crystallization (*Figure 2*, curve a) and reheating (*Figure 2*, curve b); crystallization occurs at 192.5°C (5.9 kJ mol^{-1}) and the polymer melts with a single endotherm at 211.3°C (7.1 kJ mol^{-1}).

The melting behaviour of OHO10 samples, treated at 310°C for 5 min and isothermally crystallized at different temperature T_c keeping the crystallization time t_c constant, is shown in *Figure 3*. Samples crystallized at lower temperature melt with a double peak T_{m1}, T_{m2};

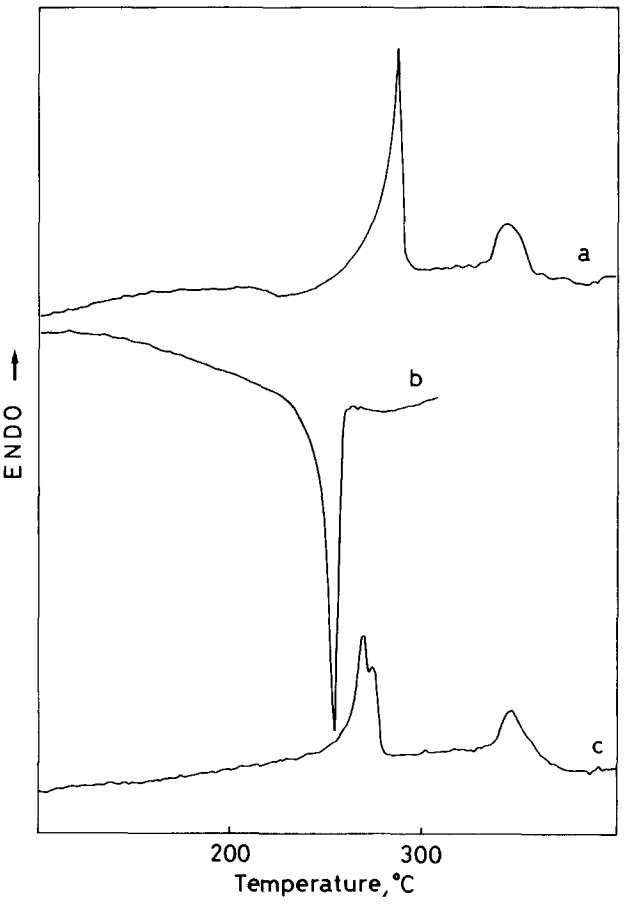

Figure 1 D.s.c. curves of polymer OHO10: (a) first heating profile at 10°C min^{-1}, (b) cooling trace from 310°C at 20°C min^{-1}, (c) second heating profile at 10°C min^{-1}

samples crystallized at elevated temperature exhibit a single endotherm in the reheating cycle. T_{m2} is practically independent of the crystallization temperature, whereas T_{m1} increases with T_c.

Variations of the crystallization time at constant T_c show a similar trend; T_{m1} exhibits a weak dependence on t_c, from 267.4°C ($t_c = 0.5$ min) to 272.8°C ($t_c = 20$ min) whereas T_{m2} is almost constant (275 ± 1°C). The enthalpies of the low- and high-temperature endotherms (ΔH_{m1}, ΔH_{m2}) are reported in *Figure 4* as a function of the crystallization time; ΔH_{m2} reaches instantaneously a plateau value, ΔH_{m1} increases continuously with the logarithm of t_c.

In order to investigate the effect of the thermal treatment before crystallization, samples crystallized at 250°C for 10 min have been previously maintained in the nematic range for 5 min at 310 or 320°C or quickly heated to isotropic state at 360°C, before being kept at 310°C for 5 min. The results are reported in *Figure 5*; stronger conditions act in shifting the melting peaks towards lower temperatures, cancel the higher-temperature endotherm and reduce the tendency of OHO10 to crystallize. A similar role is played by the permanence time in the nematic state at constant temperature. A certain influence of the temperature reached in the isotropic state has also been noted. The thermodynamic parameters related to curve c of *Figure 5* are 261.2°C and 2.0 kJ mol^{-1}; they become 264.0°C and 4.4 kJ mol^{-1} and 261.0°C and 0.8 kJ mol^{-1} going to 350 and 370°C, respectively. No variation has been observed on increasing the treatment temperature in the isotropic state up to 375°C.

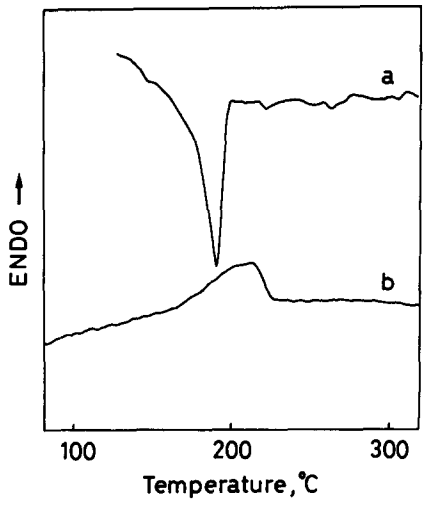

Figure 2 D.s.c. cooling trace of OHO10 from 370°C at 20°C min^{-1} (curve a) and second melting profile at 10°C min^{-1} (curve b)

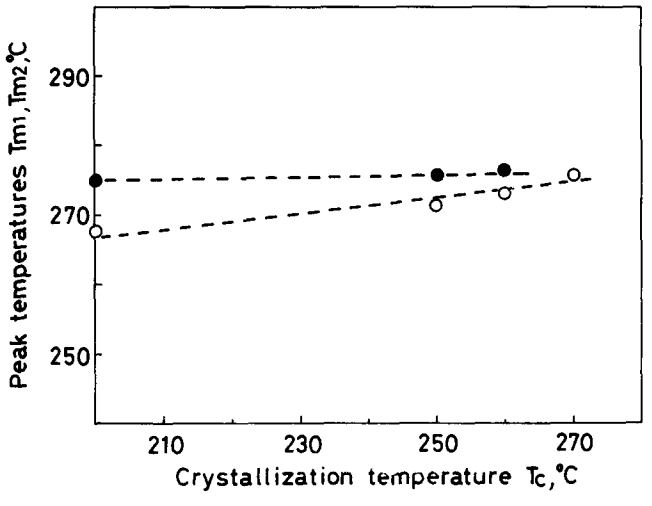

Figure 3 Variation of the melting temperatures T_{m1} (○) and T_{m2} (●) of OHO10 with the crystallization temperature T_c (crystallization time 10 min)

The two possible history effects in the mesophase region, i.e. melting of the crystalline phase or cooling of the isotropic melt, have also been investigated by non-isothermal experiments. In *Figure 6* the melting temperature of samples non-isothermally crystallized from 310°C is reported as a function of the annealing time in the nematic state; curve a refers to samples cooled from the isotropic phase, curve b to samples melted from the crystalline state.

331.7°C; the heats of the transitions are 10 and 3.2 kJ mol^{-1}, respectively. A sample kept in the nematic state at 260°C for 10 min crystallizes on cooling at 178.6°C (3.9 kJ mol^{-1}) and melts in a second cycle with a double endotherm partly superimposed at 198°C (5.2 kJ mol^{-1}).

Isothermally crystallized samples at different temperatures T_c for the same time t_c or at constant T_c for different times t_c show a double melting profile; the endotherm at T_{m2} is almost constant, whereas that at T_{m1} varies with the crystallization conditions until it is superimposed on T_{m2} (*Figures 7* and *8*). The transition enthalpies ΔH_{m1} and ΔH_{m2} are shown in *Figure 9* as a function of the

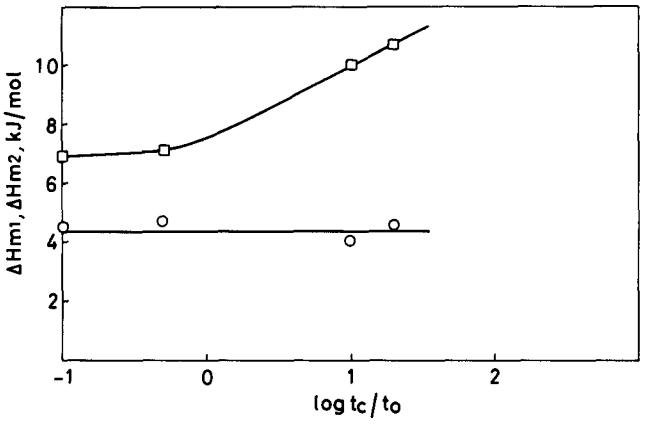

Figure 4 Variation of the melting enthalpies ΔH_{m1} (□) and ΔH_{m2} (○) with the crystallization time t_c ($t_0 = 1$ min) for OHO10 at 250°C

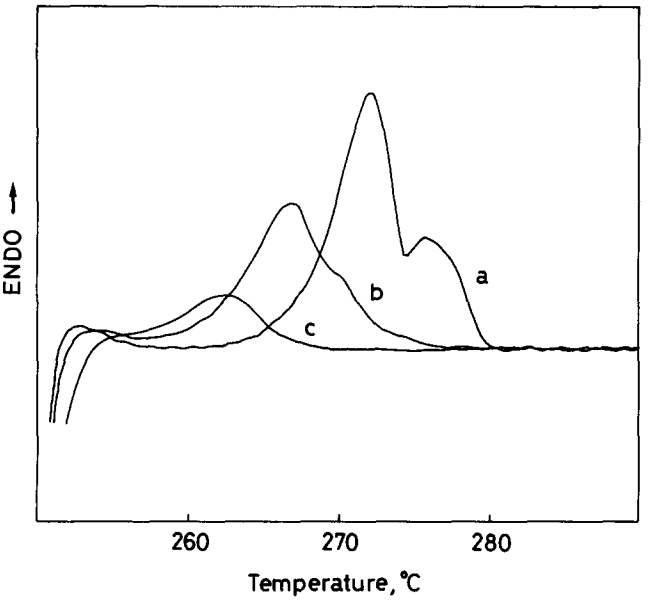

Figure 5 Melting profiles at 10°C min^{-1} of OHO10 samples crystallized at 250°C for 10 min after different thermal treatments: (a) 5 min at 310°C, (b) 5 min at 320°C, (c) 5 min at 310°C preceded by a quick heating to 360°C

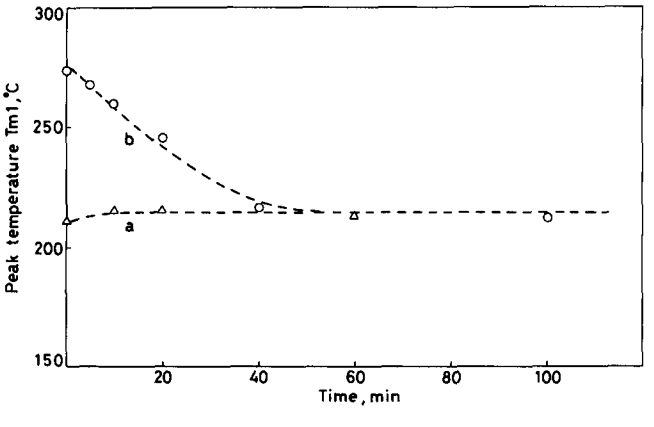

Figure 6 Variation of the melting temperature T_{m1} with the annealing time at 310°C of OHO10 samples non-isothermally crystallized at 20°C min^{-1} from 310°C: (a) samples quenched from the isotropic melt (370°C); (b) samples heated from the crystalline state

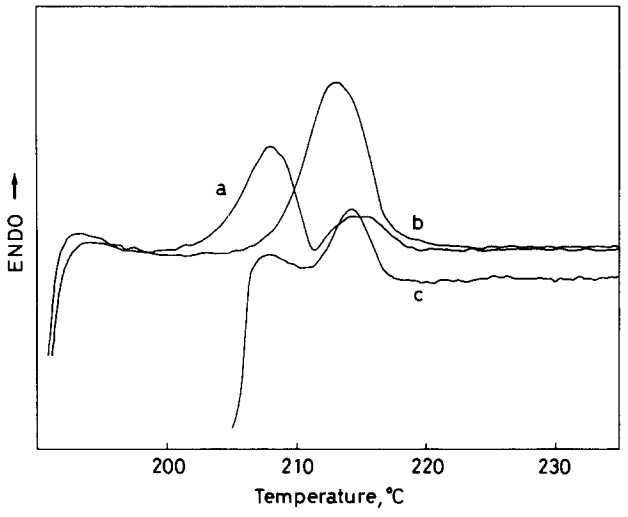

Figure 7 Melting profiles at 10°C min^{-1} of OMO8 samples crystallized under different conditions after being maintained at 260°C for 10 min: (a) 15 min at 190°C, (b) 1050 min at 190°C, (c) 15 min at 205°C

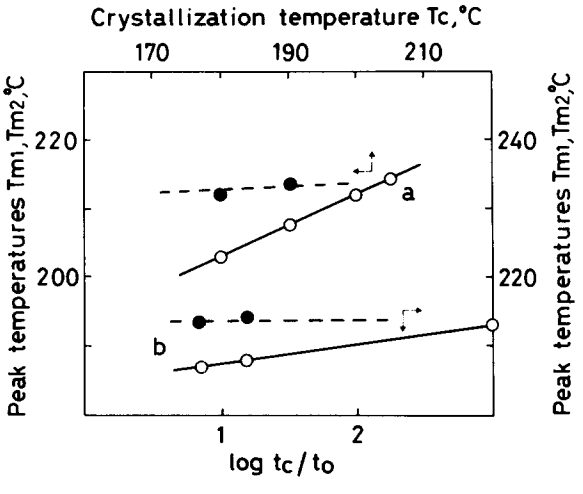

Figure 8 Dependence of T_{m1} (○) and T_{m2} (●) on crystallization temperature (curve a, $t_c = 15$ min) and time (curve b, $T_c = 190$°C, $t_0 = 1$ min) for polymer OMO8

crystallization time at 190°C; ΔH_{m1} increases continuously, ΔH_{m2} is independent of t_c.

The effect of the annealing conditions in the nematic phase on OMO8 samples crystallized at 190°C for 15 min is shown in *Figure 10*. The general trend is completely similar to the one shown by polymer OHO10.

DISCUSSION

The appearance of a double melting peak at T_{m1}, T_{m2} in the heating profiles of samples crystallized from the nematic phase and the contrasting effect on T_{m1} and T_{m2} of the crystallization conditions seem to be features common to the majority of thermotropic polymers. In the case of wholly aromatic copolyesters this behaviour has been seen by several authors[1,3,6] and assigned to the melting of crystals of different size, arising from a mechanism of crystallization that occurs with different rates at different places within the sample[1]. The high-melting peak, corresponding to crystals formed by fast solidification on cooling, is independent of the crystallization conditions; the low-melting peak, on the contrary, is strongly affected by crystallization temperature and time.

More recently, qualitatively similar experimental results have been obtained on a segmented polyester; the double melting peak has been attributed to the presence of different components of the morphology, arising from a crystallization that occurs in two stages and leads to crystals of different size[10].

The dependence of T_{m1}, T_{m2} on the crystallization conditions, shown by the investigated polyesters OHO10 and OMO8, follows the expected trend (see *Figures 3*, *7* and *8*), as well as the variation of ΔH_{m1}, ΔH_{m2} with the crystallization time at constant T_c (see *Figures 4* and *9*). Therefore the existence of a double melting peak must be related, also for these systems, to a size effect. The constant value of ΔH_{m2} as a function of the logarithm of t_c, as already discussed[10], actually indicates that we are not dealing with a crystal reorganization process[16–20]; moreover, X-ray experiments demonstrate that no structural transition takes place by heating up to melting samples cooled down from the nematic state[14]. Several factors can cause the different crystallization rates of the

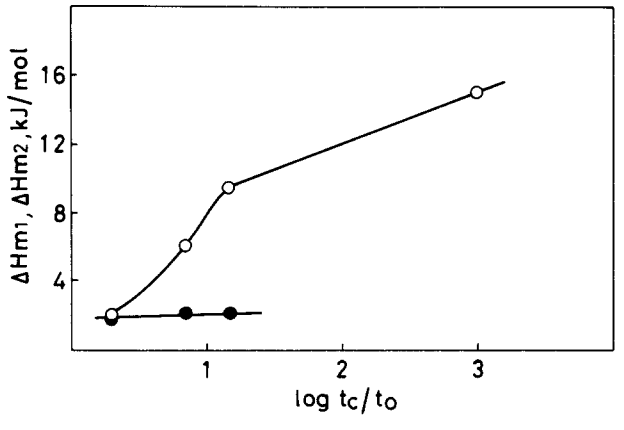

Figure 9 Variation of the melting enthalpies ΔH_{m1} (○) and ΔH_{m2} (●) with the crystallization time t_c ($t_0 = 1$ min) for OMO8 at 190°C

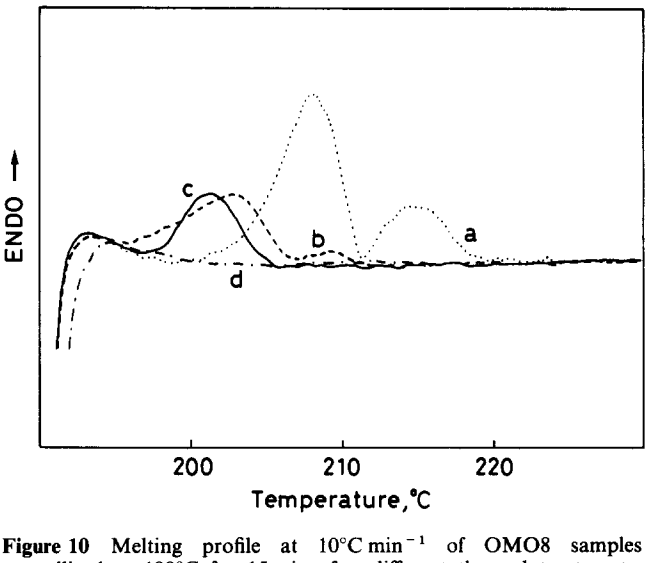

Figure 10 Melting profile at 10°C min^{-1} of OMO8 samples crystallized at 190°C for 15 min after different thermal treatments: (a) 10 min at 260°C, (b) 20 min at 260°C, (c) 10 min at 280°C, (d) 40 min at 260°C or 10 min at 300°C

two polymers, evidenced in *Figures 4* and *9*: the chemical nature of the repeat unit, the degree of undercooling, the preliminary thermal history (see below).

A new aspect, introduced in our previous paper[10], was that the melting behaviour of thermotropic polymers depends strongly on the preliminary thermal history of the sample. In particular, on increasing the temperature or the time of the annealing treatment in the nematic state, the melting peaks shift towards lower temperatures, the higher-temperature endotherm can be cancelled and the tendency of the polymer to crystallize is decreased. This behaviour has been justified on the basis of a new scheme[10], which accounts for the slow evolution of the nematic melt towards its thermodynamic equilibrium. Above the crystal–nematic transition a certain registry of neighbouring chains persists in the melt, which becomes poorer and poorer upon increasing temperature and time and eventually disappears when equilibrium is attained. The non-equilibrium effects are particularly pronounced at high molecular weight and are affected by the flexibility of the polymeric chain[11,21,22].

To support the above-mentioned model, polymers OHO10 and OMO8 have been investigated in the present paper mainly as far as the role of the preliminary treatment on the crystallization behaviour is concerned. In order to exclude the occurrence of chemical processes during annealing at high temperature, which as known[6,23–25] could affect the thermal profiles of treated polymers, tests of thermal stability have been carried out by keeping OHO10 and OMO8 samples for a few minutes at 330 and 300°C, respectively, and dissolving them to clear their thermal history. The d.s.c. heating curves of these samples, after precipitation, drying and isothermal crystallization under the standard conditions adopted in the present paper (10 min at 250°C after 5 min at 310°C, and 15 min at 190°C after 10 min at 260°C, for OHO10 and OMO8, respectively), are quite identical to curves a of *Figures 5* and *10*, meaning that chemical processes have little influence on the thermal behaviour of these systems.

The effect of a 10°C increase of the annealing temperature in the nematic state of OHO10 appears from the comparison of traces a and b of *Figure 5*; both T_{m1} and T_{m2} decrease and the total melting enthalpy is considerably reduced. *Figure 5* shows furthermore a relevant difference between profiles a and c; this result can be justified by taking into account that, even if curves a and c refer to samples submitted to the same treatment in the nematic state, the nematic phase is obtained differently in the two cases: by melting the crystalline phase (curve a) or by cooling the isotropic melt (curve c). The improved chain mobility in the isotropic state allows the persistent registry to be more easily cancelled and the thermodynamic equilibrium of the nematic phase to be approached more rapidly. The same interpretation can be given to the observed time effect in the nematic phase; by increasing the permanence time at constant temperature, the ability of OHO10 to crystallize under the adopted conditions practically vanishes. Non-isothermal experiments of curve b of *Figure 6* evidence the same effect.

Polymer OMO8 behaves similarly: on increasing the annealing time at 260°C (curves a, b and d of *Figure 10*) or the temperature, keeping the time constant (curves a, c and d), the fraction able to crystallize during 15 min at 190°C continuously decreases and is finally suppressed.

The results obtained, on the whole, agree with the existence of non-equilibrium states of liquid crystallinity, arising from a memory of crystal organization, when the mesophase is accessed by melting the crystal form. As shown in *Figure 6*, curve b, the melting temperature T_{m1} of non-isothermally crystallized samples decreases continuously with annealing time at 310°C, tending to a plateau value for treatments long enough to cancel the memory effect. The attempt to reach equilibrium conditions more quickly by running into the isotropic phase and then cooling into the mesophase before crystallization (*Figure 6*, curve a) indicates that shorter times are needed for the ordering process of the nematic melt of OHO10. These findings raise some fundamental questions on the ability of thermotropic polymers to crystallize from the nematic melt. This phenomenon is expected to occur rapidly, compared to that from the isotropic state; however, a careful adjustment of the process parameters, in terms of temperature and time, must be achieved to obtain reproducible results and to control the final properties of the material.

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