Crystallization and melting behaviour of segmented thermotropic polymers:
2. A poly(ether ester) of low isotropization temperature

E. Marsano*, U. Salati and B. Valenti
Istituto di Chimica Industriale, Università di Genova, Corso Europa 30, I-16132, Genoa, Italy
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Differential scanning calorimetry has been used to investigate the crystallization and melting behaviour after different thermal treatments, both in the nematic and in the isotropic state, of a poly(ether ester) of low isotropization temperature obtained by reacting 4,4'-dichloroformyl-α,ω-diphenoxydodecane and 2-methyl-hydroquinone. Isothermal crystallizations have been studied in terms of variation of the successive melting profiles as a function of various parameters; the appearance of multiple endotherms has been attributed to crystal reorganization processes. In non-isothermal experiments from the nematic or isotropic state, crystallization generally occurs partially on cooling and partially on heating, the overall enthalpy being almost constant; the effect of various parameters has been investigated and interpreted in terms of a slow rate of ordering and disordering of the nematic phase, which leads to non-equilibrium effects. The influence of the molecular weight and of the chain rigidity is briefly discussed.

(Keywords: crystallization; thermotropic polymer; melting behaviour)

INTRODUCTION

Polymers with alternating rigid mesogenic units and flexible spacers in the main chain have been studied extensively in the last 10 years for the correlation between chemical structure and liquid crystalline properties[1–5]. However, very few investigations on the crystallization behaviour of these systems have been reported in the literature[6–10].

Several authors[11–16] have focused their attention on the mechanism of crystallization of the nematic melt of rigid chain polymers upon cooling. Nevertheless, little or no information is available on the crystallization process of liquid crystalline polymers from the isotropic melt, since many polymers of this class have high isotropization temperature and are chemically unstable at this temperature.

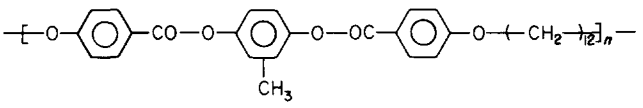
The polymer used in this study, having ether linkages between the rigid moiety and the flexible polymethylene spacer of 12 units, has low isotropization temperature and is chemically stable. Therefore it appears to be a suitable system for studying the crystallization process of samples previously submitted to different thermal treatments, both in the nematic and in the isotropic state.

Differential scanning calorimetry and optical microscopy have been used to investigate the crystallization behaviour, which qualitatively agrees with a new scheme, recently proposed[7], to explain the unusual thermodynamic and kinetic properties observed at the nematic–solid transition. However, some aspects appear to be peculiar to the polymer under investigation.

EXPERIMENTAL

Materials

The polymer considered in this paper is a segmented thermotropic poly(ether ester) obtained by reacting 4,4'-dichloroformyl-α,ω-diphenoxydodecane with 2-methyl-hydroquinone



The monomeric intermediate and the polymer have been synthesized as described elsewhere[17–19]. Samples characterized by intrinsic viscosities in 1,1,2,2-tetrachloroethane at 25°C ranging between 0.2 and 0.4 dl g^{-1} have been obtained by using polymerization temperatures of 0°C or 50°C, reaction times of 24 or 48 h, and molar ratios of dichloride/diphenol and pyridine/diphenol ranging between 1 and 1.08, and 5 and 11, respectively. All the samples were dissolved in chloroform and reprecipitated with acetone, before being dried and used.

This polymer is nematic over a 70°C range (from about 170 to 240°C) and thermogravimetric analysis[19] demonstrates that it is stable up to 380°C.

Thermal analysis

The analysis was performed with a computer-interfaced Mettler TA 3000 system (measuring cell DSC 30). The transition enthalpies were evaluated by using the software Graphware TA72. All the experiments were performed under dry nitrogen atmosphere; high purity melting

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* To whom correspondence should be addressed

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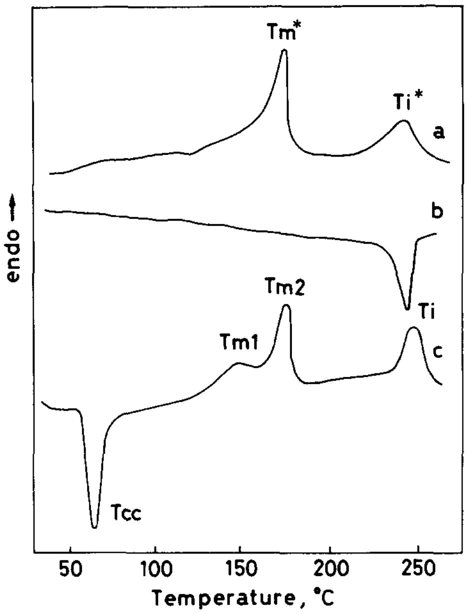

Figure 1 D.s.c. traces of an as-polymerized sample of $[\eta]=0.4\,\mathrm{dl\,g^{-1}}$: a, first heating cycle at $20\,\mathrm{K\,min^{-1}}$; b, cooling profile at $10\,\mathrm{K\,min^{-1}}$; c, second heating at $20\,\mathrm{K\,min^{-1}}$

standards were used for calibration of temperature and heat of transition. Aluminium pans were always filled with the same quantity of polymer (10 ± 1 mg) in the form of small grains.

Isothermal and non-isothermal crystallizations were carried out on samples previously treated according to the following procedures:

(a) heated to the nematic state at T_n and kept at this temperature for 10 min;
(b) heated to the isotropic state at 270°C and maintained at this temperature for 5 min, before being kept at T_n for 10 min;
(c) similar to (b), but the annealing step at T_n was omitted.

The isothermally crystallized samples, after the above treatments, were cooled within the calorimeter to the predetermined crystallization temperature (ranging between 110 and 160°C) as quickly as possible and kept there for different times (up to 1000 min). The non-isothermally crystallized samples were cooled to 20°C at different cooling rates, ranging between 1 and $20\,\mathrm{K\,min^{-1}}$. The samples were then heated again and the d.s.c. heating traces were recorded. Peak temperatures for both heating and cooling traces were used.

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).

RESULTS AND DISCUSSION

Figure 1 shows the d.s.c. thermal characteristics of an as-polymerized sample of $[\eta]=0.4\,\mathrm{dl\,g^{-1}}$; the first heating cycle (curve a) shows melting and isotropization peaks (T_m^* at 168.3°C, $\Delta H_m^* = 17.3\,\mathrm{kJ\,mol^{-1}}$, T_i^* at 238.8°C, $\Delta H_i^* = 7.9\,\mathrm{kJ\,mol^{-1}}$). On cooling at $10\,\mathrm{K\,min^{-1}}$ from the isotropic state (curve b) only the isotropic–nematic transition appears (245.4°C, $7.9\,\mathrm{kJ\,mol^{-1}}$) and the polymer is frozen in a nematic glassy state. The d.s.c. trace of the second heating run (curve c) indicates a cold crystallization at 63.8°C ($9.1\,\mathrm{kJ\,mol^{-1}}$), a double melting endotherm at $T_{m1}=147.8$°C, $T_{m2}=174.4$°C (total enthalpy $10.5\,\mathrm{kJ\,mol^{-1}}$) and isotropization at $T_i=246.7$°C ($\Delta H_i = 8.1\,\mathrm{kJ\,mol^{-1}}$).

The essential characteristics of the phase behaviour are common to all the samples investigated. Quickly cooled samples demonstrate a cold crystallization on heating above T_g (which is close to 20°C). Going from the first to the second heating cycle the melting peak changes from a single (T_m^*) to a double endotherm (T_{m1}, T_{m2}), with T_{m1} always lower and T_{m2} higher than T_m^*; the isotropization transition shifts towards higher temperatures (*Figure 2*). However, d.s.c. runs following the second heating are reproducible. Every thermal treatment (see procedures (a)–(c) in the Experimental section) performed on the as-polymerized samples leads to the same result in terms of shape of final heating profile and peak temperatures T_{m2} and T_i; only the low temperature melting peak at T_{m1} is affected by the treatment conditions.

In order to assign the d.s.c. peaks of this polymer, its chemical stability against thermal treatments have been checked by keeping two samples at 180°C for 10 and 360 min, respectively, and dissolving them in chloroform to remove their thermal history. The d.s.c. curves of these samples, after precipitation and drying, are identical to the second heating of the original polymers and subsequent scans are reproducible; this suggests that the above effect arises from post-polymerization processes, already evidenced in liquid crystal polymers maintained in the nematic state or annealed at high temperature[16,20,21].

Isothermal crystallization studies have been carried out on the $0.4\,\mathrm{dl\,g^{-1}}$ polymer at temperatures ranging between 110 and 160°C for crystallization times up to 1000 min, using samples treated with procedures (a) and (b) ($T_n = 190$°C), described in the Experimental section. The d.s.c. profiles on subsequent heating are quite complex, due to the presence of multiple endotherms arising from crystal reorganization processes[22–26]. A few examples are shown in *Figure 3*; the general trend of the melting behaviour of samples crystallized at different

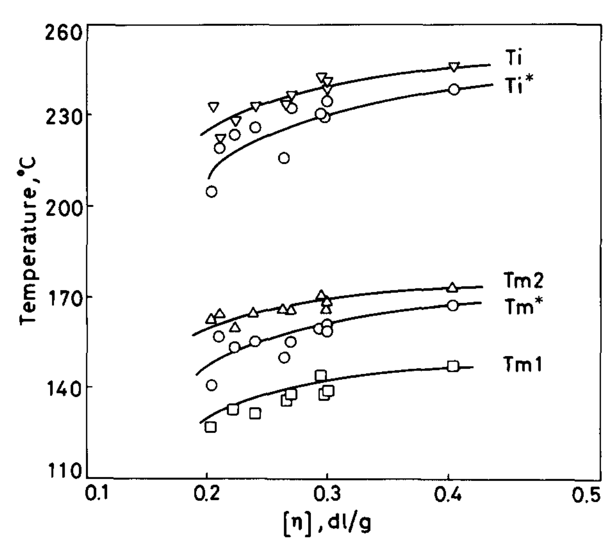

Figure 2 Variations of the transition temperatures from the first to the second heating cycle for samples of different $[\eta]$ (scan rate $20\,\mathrm{K\,min^{-1}}$)

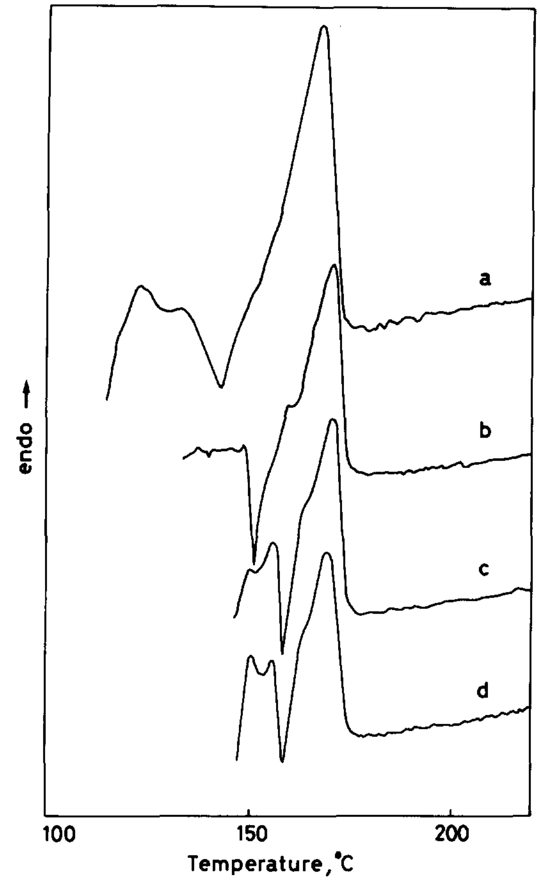

Figure 3 Melting profiles of samples isothermally crystallized after different thermal treatments; T_n of 190°C is used for all samples: a, 2 h at 110°C after treatment (a); b, 16 h at 130°C after treatment (b); c, 16 h at 145°C after treatment (a); d, 16 h at 145°C after treatment (b) (scan rate 10 K min^{-1})

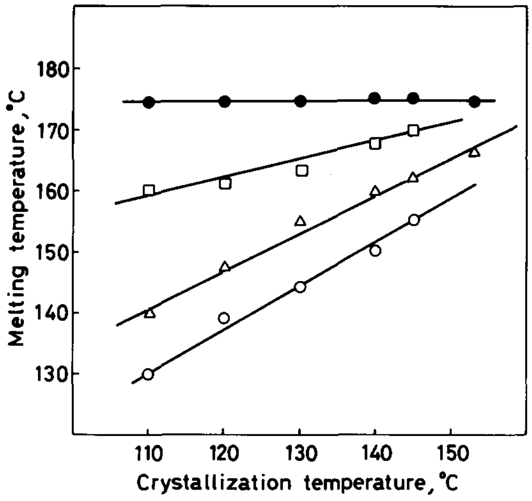

Figure 4 Variation of the melting temperatures with the crystallization temperature for times of about 1000 min: ●, T_{m2}; □, △, ○, lower temperature peaks. Samples submitted to preliminary treatment (a) with $T_n = 190$°C

temperatures for long enough times (in the order of 1000 min) is reported in *Figure 4*.

The melting peak at T_{m2} (at about 175°C) occurs in samples previously submitted to both the (a) and (b) thermal treatments; the only difference between the two series of samples is that the ones heated to the isotropic state exhibit a lower tendency to crystallize. Indeed, whereas after treatment (b) crystallization does not occur at 155°C even for a crystallization time of 1000 min, treatment (a) allows a sample to crystallize completely under the same conditions and partially after being maintained for the same time at 160°C.

Non-isothermal crystallization of the 0.4 dl g^{-1} sample, treated according to procedure (a) have been studied as a function of T_n (180–210°C) and of the cooling rate V_c (3–10 K min^{-1}). Using fairly slow cooling rates crystallization occurs partially on cooling at T_c with associated enthalpy ΔH_c, and partially during the following heating run at T_{cc} with associated enthalpy ΔH_{cc}, the overall enthalpy $\Delta H_c + \Delta H_{cc}$ being almost constant. *Figure 5* shows this effect for a sample cooled at 5 K min^{-1}. The results obtained as a function of T_n and V_c are summarized in *Tables 1* and *2*. T_n values ranging between 180 and 210°C allow crystallization to occur both on cooling and on heating with variable ratios; cooling rates as low as 3 K min^{-1} or as high as 20 K min^{-1} permit the separation of the two phenomena. It must be noted that T_{m2} of all these samples is almost

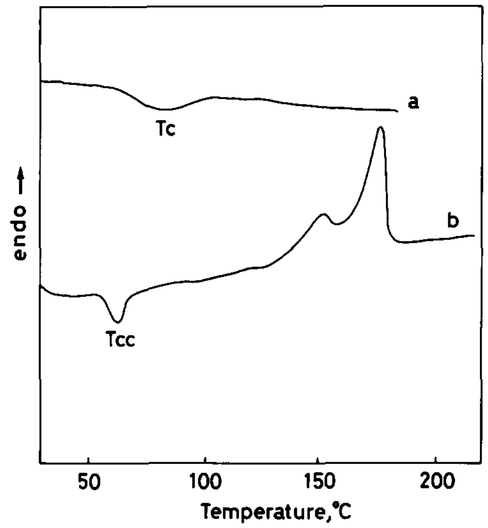

Figure 5 Cooling (curve a) and second heating profile (curve b) of a sample treated according to procedure (a) with a T_n of 190°C ($V_c = 5$ K min^{-1}, heating rate 20 K min^{-1})

Table 1 Effect of T_n on the non-isothermal crystallization behaviour of samples treated according to procedure (a) (d.s.c. cooling traces at a constant V_c of 5 K min^{-1}; heating rate 20 K min^{-1})

T_n (°C)	T_c (°C)	ΔH_c (kJ mol^{-1})	T_{cc} (°C)	ΔH_{cc} (kJ mol^{-1})
180	80.2	7.5	61.7	1.4
190	82.2	7.3	61.6	1.8
200	81.8	6.2	62.5	2.2
210	81.8	4.9	62.7	3.4

Table 2 Effect of cooling rate on the non-isothermal crystallization behaviour of samples treated according to procedure (a) (samples cooled from a constant T_n value of 190°C; heating rate 20 K min^{-1})

V_c (K min^{-1})	T_c (°C)	ΔH_c (kJ mol^{-1})	T_{cc} (°C)	ΔH_{cc} (kJ mol^{-1})
3	92.1	10.2	–	–
5	82.2	7.3	61.6	1.8
10	73.7	1.4	62.9	8.1
20	–	–	63.5	9.3

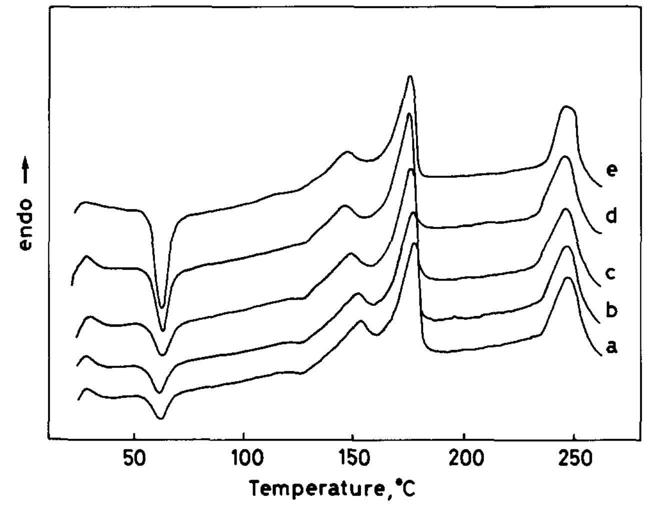

Figure 6 Melting profiles of samples non-isothermally crystallized at 5 K min^{-1} after different thermal treatments. Treatment (a) with various T_n values: a, 180°C; b, 190°C; c, 200°C; d, 210°C; treatment (b): e, $T_n = 190$°C

Table 3 Effect of the preliminary thermal treatment (see Experimental section) on samples non-isothermally crystallized at 5 K min^{-1} and reheated at 20 K min^{-1} ($T_n = 190$°C)

Preliminary treatment	T_c (°C)	ΔH_c (kJ mol^{-1})	T_{cc} (°C)	ΔH_{cc} (kJ mol^{-1})
(a)	82.2	7.3	61.6	1.8
(b)	82.6	5.4	63.9	4.1
(c)	76.5	3.6	62.9	5.9

the same (about 175°C); T_{m1} depends slightly on T_n (traces a–d of *Figure 6*). Samples treated with procedure (b) exhibit a similar behaviour, the only difference being greater difficulty in crystallizing during the cooling cycle (trace e of *Figure 6*). The effect of the preliminary thermal treatment on samples non-isothermally crystallized at $V_c = 5$ K min^{-1} and reheated at 20 K min^{-1} is shown in *Table 3*. The general trend is confirmed by the effect of V_c on samples treated according to procedure (c), reported in *Table 4*.

Polymeric samples with lower values of $[\eta]$ show greater difficulty in crystallizing, even if, qualitatively, they show a general behaviour very similar to that of the sample with $[\eta] = 0.4$ dl g^{-1}. In fact, using a 0.22 dl g^{-1} sample and T_n value of 180°C, cooling rates as low as 1 K min^{-1} are required to get complete crystallization on cooling ($\Delta H_{cc} \simeq 0$) and 5 K min^{-1} to freeze the sample in the glassy state ($\Delta H_c \simeq 0$).

The reported results, on the whole, seem to indicate that the polymer under investigation behaves differently from the segmented polyesters we have recently considered[7,8]. For the above systems the higher transition at T_{m2}, due to the persistence of a certain registry of neighbouring chains in the nematic melt, appeared to be a function of the treatment conditions in the nematic phase. Appropriate conditions of treatment, in terms of temperature or time, led to the disappearance of the transition at T_{m2} and to a strong reduction of the polymer crystallizability. These effects were justified taking into account a slow evolution of the nematic melt towards its thermodynamic equilibrium[7,8], already proposed by Feijoo *et al.*[9] to justify the dependence of isotropization temperature on annealing conditions in the rematic phase. For the poly(ether ester) studied here, preliminary thermal histories in the nematic or isotropic state are unable to eliminate the peak at T_{m2} or to shift significantly the melting transitions towards lower temperatures (see *Figure 6*). Actually, for this system, the multiple melting peaks must be attributed to crystal reorganization processes during heating[22–26], clearly evidenced in *Figures 3* and *4* by samples isothermally crystallized from the melt and, to a lesser extent, in *Figure 6* where non-isothermally crystallized samples exhibit two major peaks, both probably arising from the reorganization process of an initial population of imperfect small crystals. As a consequence, T_{m1} and T_{m2} values, as well as their dependence on the various parameters, have little significance in interpreting the crystallization process of this polymer; we must consider its behaviour on cooling.

Table 4 Effect of cooling rate on the non-isothermal crystallization behaviour of samples treated according to procedure (c) (5 min at 270°C, heating rate 20 K min^{-1})

V_c (K min^{-1})	T_c (°C)	ΔH_c (kJ mol^{-1})	T_{cc} (°C)	ΔH_{cc} (kJ mol^{-1})
1	100.0	11.5	–	–
5	76.5	3.6	62.9	5.9
10	–	–	63.8	9.1

The role played by the cooling rate V_c on non-isothermal experiments from a constant T_n, reported in *Table 2* in terms of ΔH_c and ΔH_{cc}, shows that we are not dealing with a fast solidification process, as reported in the literature[7,11] for thermotropic polymers. The comparison of data in *Tables 2* and *4* shows that the crystallization tendency on cooling of samples treated with procedure (c) is lower than that of samples cooled from the nematic melt (procedure (a)), since in the former case a slower V_c is needed to get the same crystallization on cooling, measured by ΔH_c. Non-equilibrium effects in the nematic melt can justify this behaviour; the slow rate of disordering from the crystalline phase and of ordering from the isotropic liquid leads to V_c and T_n effects on the crystallization process. Further evidence is given by comparison of the results in *Table 3* dealing with procedures (b) and (c): on cooling from the isotropic state a permanence of 10 min at 190°C (procedure (b)) increases ΔH_c from 3.6 to 5.4 kJ mol^{-1}. Data in *Table 1* show that an increase of T_n acts in disordering the nematic melt which, on cooling at constant V_c, exhibits a reduced tendency to crystallize. By using a higher cooling rate (20 K min^{-1}) crystallization does not occur if $T_n = 190$°C ($\Delta H_c = 0$), whereas it partially occurs on cooling from $T_n = 180$°C ($\Delta H_c = 1.4$ kJ mol^{-1}).

However, non-equilibrium effects in this poly(ether ester) appear to be less pronounced than in the case of the segmented polyesters we have investigated in other papers[7,8]; this difference may be due to the combined effect of a low molecular weight and a reduced chain rigidity, the latter arising from the length of the polymethylene spacer, which accounts for about 45% of the length of the repeating unit. Moreover ether linkages between the rigid and the flexible units, compared to the ester linkage of one of the polyesters investigated elsewhere bearing the same mesogenic moiety[8], favour a less effective molecular packing and alignment between the polymer molecules in the nematic phase, which in turn destabilizes the mesophase[27].

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