Thermal and structural study of the phase transitions in liquid crystalline poly(heptamethylene terephthaloyl-bis-4-oxybenzoate)

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The structure and thermal transitions of liquid crystalline poly(heptamethylene terephthaloyl-bis-4-oxybenzoate) have been studied by differential scanning calorimetry, X-ray diffraction and optical microscopy. A very important influence of different thermal treatments in the formation of crystal and mesophase has been found. The sample originating from the synthesis has a crystalline and a liquid crystalline phase at room temperature. However, by evaporation of trifluoroacetic acid solution, it is possible to obtain only the crystalline phase. By quenching the sample from the liquid crystal state into liquid nitrogen, the smectic mesophase can be 'frozen in'.

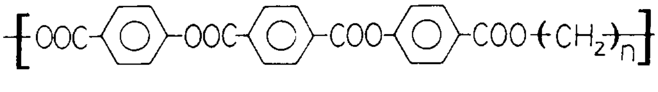
(**Keywords: thermotropic polyester; thermal transitions; smectic mesophases; liquid crystalline behaviour**)

INTRODUCTION

Recent interest in thermotropic polyesters with mesogenic units in the main chain has resulted in the synthesis and characterization of a variety of new polymers[1–3]. Structurally these polyesters consist of stiff mesogenic units containing two to three aromatic moieties connected by suitable linkages, generally ester and ether groups. These units are separated by flexible segments in order to modify the properties, particularly the thermal properties.

Different types of polyesters with terephthaloyl and oxybenzoyl mesogenic units and methylene spacers have been studied and reported in the literature[3,4]. The arrangements of these units within the polymeric chain are very variable, producing different structures, and consequently changing the properties of the polymers dramatically.

Polyesters, based on an alternating sequence containing a mesogenic triad unit with three aromatic rings and polymethylene flexible spacers, have been described[4–8], with the general structure:



However, the molecular weights of these polymers, from their intrinsic viscosity values, were relatively low when the method of synthesis described by Lenz and co-workers[4,5] was used.

More recently, Bilibin *et al.*[6] have proposed a scheme for the synthesis of high molecular weight alkylene aromatic polyesters containing mesogenic triads. The mesogenic dichloride, terephthaloyl bis-(4-oxybenzoyl chloride), was separated and characterized, and polycondensation with diols results in polymers with higher molecular weights. This is an important feature to enable analysis of the thermal properties, transitions, morphologies and crystallization of these systems. Although a large series of thermotropic polymers have been synthesized, a detailed analysis of their behaviour has only been carried out in a few cases.

The present study, undertaken to determine the relationship between structure and mesomorphic parameters with properties, forms part of a general project on liquid crystals based on different mesogenic units and several linear and branched, symmetrically and asymmetrically substituted polyglycols, with between three and 10 methylene units.

The initial aim has been the study of the thermal behaviour of these alkylene aromatic polyesters when heptamethylene glycol is used as the flexible segment. Special emphasis has been placed on analysing the influence of thermal history on the transitions of these polymers. To our knowledge, the only values reported in the literature for poly(heptamethylene terephthaloyl-bis-4-oxybenzoate) (PHTOB) are the transition temperatures[5], with no studies of the thermal and structural behaviour under different conditions.

EXPERIMENTAL

Materials

PHTOB was prepared by the method described by Bilibin *et al.*[6] in three stages. In brief, the terephthaloyl-

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bis-(4-oxybenzoic) acid (TOBA) was prepared by condensation of terephthaloyl chloride with 4-hydroxybenzoic acid. The dichloride, terephthaloyl-bis-(4-oxybenzoyl chloride) (TOBC) was obtained by reaction of TOBA with thionyl chloride. Preparation of the polymer was carried out by polycondensation of TOBC and 1-7-heptamethylenediol in a diphenyl oxide solution for 8 h at 200°C, maintaining a nitrogen gas current. On completion of the reaction, the polymer was precipitated in toluene, filtered, washed several times with ethanol, and finally dried under vacuum.

The results of the elemental analysis of the dichloride (TOBC) and of the polymer (PHTOB) are as follows.

TOBC. Found, C 59.67%; H 2.77%; Cl 15.90%. Calculated, C 59.60%; H 2.73%; Cl 16.00%.

PHTOB. Found, C 69.90%; H 5.40%. Calculated, C 69.32%; H 5.20%.

^{1}H n.m.r. spectra were determined on a 200 MHz Bruker spectrometer in $CDCl_3$ solution at room temperature for TOBC and in trifluoroacetic acid (CF_3COOH) solution for PHTOB, using tetramethylsilane as internal reference. The spectra showed the following chemical shifts.

TOBC. ^{1}H n.m.r. ($CDCl_3$): δ (ppm from TMS) = 8.34 (4H, terephthalate); 8.09–8.06 (4H(d),2,6-carbonylphenyl); 7.49–7.45 (4H(d), 3,5-carbonylphenyl).

PHTOB. ^{1}H n.m.r. (CF_3COOH): δ (ppm from TMS) = 8.50 (4H, terephthalate); 8.31–8.27 (4H(d), 2,6-carbonylphenyl); 7.47–7.42 (4H(d), 3,5-carbonylphenyl); 4.56 (4H(t), methylene); 1.98 (4H(m), methylene); 1.64 (6H(m), methylene).

Procedures

The inherent viscosity of the polymer solution was measured in an Ubbelohde viscosimeter, at a concentration of 0.5 dl g^{-1} in *p*-chlorophenol at 45°C.

A d.s.c. Mettler TA 3000 apparatus, with a DSC-30 furnace and TA72 software, was used for obtaining the transition temperatures. Microscopy studies and thermo-optical analysis were carried out using a Reichert Zetopan Pol polarizing microscope equipped with a Mettler FP80 hot stage and a Nikon FX35A camera.

Thermogravimetric analysis was performed on a Perkin-Elmer 7/7700, using nitrogen as the purge gas. The samples were heated at 10°C min^{-1} from 30 to 500°C or maintained isothermally at a certain temperature during 90 min.

X-ray diffractograms were obtained in a Phillips Geiger counter X-ray diffractometer with an Anton Paar 300 temperature camera. The diffractograms were recorded in the 2θ range between 2° and 30° using Ni filtered CuKα radiation at 2° min^{-1}.

RESULTS AND DISCUSSION

Preparation of PHTOB by the method described by Bilibin *et al.*[6] gave rise to a very clean and uniform polymer, since during the synthesis the mesogenic monomer, TOBC, can be isolated and purified. This was demonstrated in the case of polydecamethylene terephthaloyl-bis-(4-oxybenzoate) (PDTOB)[6]; however, only the properties of the polymers with n = 3, 4, 5, 6 and 10 were described by these authors.

Earlier reports[5] on this type of polyester describe the synthesis of a series with odd and even numbers of CH_2 groups from 2 to 10. In this case, the dichloride was not separated from the reaction system and the dichloride formed *in situ* was used for the polycondensation, resulting in polymers with extremely low intrinsic viscosities. For the case of heptamethyleneglycol, the inherent viscosity was reported to be 0.196 dl g^{-1}.

However, the tentative use of this method produced, in our case, very heterogeneous and contaminated polymers, probably due to the very influential role of the purity of the dichloride and the existence of degraded materials.

It has been pointed out[6] that these differences in the synthesis could explain the discrepancies found between the viscosities and, consequently, the phase transition temperatures.

In our case, the viscosity of PHTOB in *p*-chlorophenol at 45°C is 0.67 dl g^{-1}; this is more than three times higher than that reported by Ober *et al.*[5], which to our knowledge is the only reported data on this polymer. Other differences will be commented on below. It is important to remark that the results obtained from the elemental analysis and the ^{1}H n.m.r. spectra confirm the structures of TOBC and PHTOB and their purity.

Thermal transitions

Before analysing the transitions, the thermal stability of PHTOB was studied by thermogravimetry and the weight loss curve was obtained under dynamic conditions using a heating rate of 10° min^{-1}. The polymer was stable up to 350°C, and showed a 10% loss at approximately 385°C. On the other hand, under isothermal conditions at 280°C there was no indication of degradation after 90 min. Consequently, from these data, the heating cycles used for studying thermal transitions never exceeded 340°C.

Liquid crystalline behaviour was studied by d.s.c. using several heating and cooling cycles, which are shown in *Figure 1*. The original sample was prepared by precipitation from the final reaction mixture. *Figure 1a* shows the curve obtained from this original sample up to 340°C at a heating rate of 10°C min^{-1}. It displays four different transitions at 60–70°C, 115–150°C, 173°C and 295°C.

The transition at 60–70°C has a significant change in the specific heat C_p which seems to be related to the corresponding glass transition of the amorphous polymer. The transition between 115 and 150°C is an exothermic process with a very low enthalpy, 2.6 J g^{-1}, corresponding to crystallization of the sample. The endothermic peak observed at 173°C, with an enthalpy of 10.3 J g^{-1}, corresponds to the crystal–liquid crystal transition, T_l, and that observed with a maximum at 295°C corresponds to the isotropization of the anisotropic liquid, T_i, with an enthalpy of 13.3 J g^{-1}. It is important to point out that for the crystal–liquid crystal transition the notation T_m has been used by some authors[4–8]. However, this transition does not correspond to a real melting process; for this reason we consider that it is better to use the notation T_l for this transition.

The differences in enthalpies between the crystallization process and the T_l transition must be due to a certain degree of crystallinity present in the original sample, which increases slightly at a temperature above the glass transition temperature. Experimental evidence illustrating this point will be shown below in the analysis of the X-ray diffractograms.

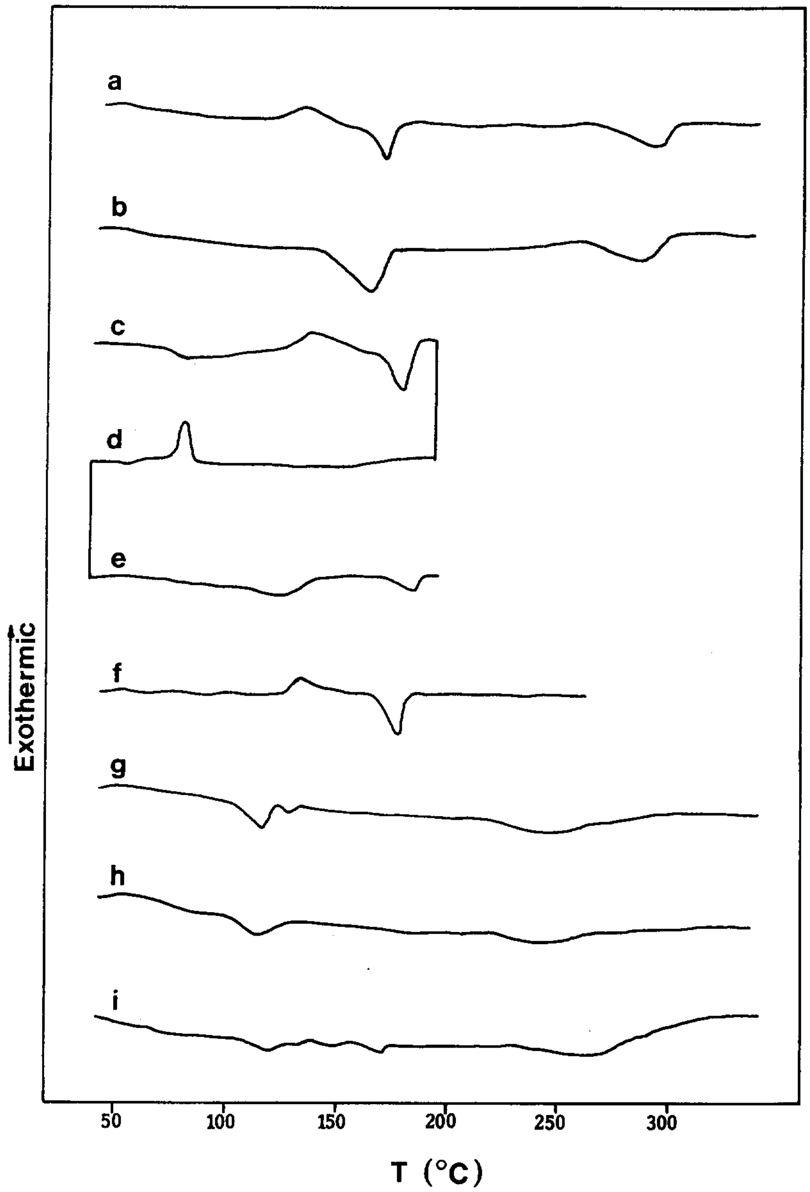

Figure 1 D.s.c. curves of PHTOB: a, original sample; b, sample precipitated from solution; c, original sample heated up to 200°C; d, sample c cooled down to room temperature; e, sample d heated to 200°C; f, sample previously quenched from 200°C into liquid nitrogen and heated up to 250°C; g,h,i, sample previously cooled from the molten state at 40°C min^{-1}(g), 10°C min^{-1}(h) and quenched into liquid nitrogen (i) and heated up to 340°C. All the d.s.c. curves were obtained at a heating rate of 10°C min^{-1}

When the PHTOB sample was prepared from a solution in CF_3COOH which was subsequently evaporated, the d.s.c. curve showed the crystal–liquid crystal transition at the same temperature with an enthalpy of 17.5 J g^{-1} (*Figure 1b*). Since the crystallinity is dramatically enhanced in this sample, no crystallization was observed during the heating cycle.

We have paid special attention to the effect of thermal treatments on PHTOB. The original sample was heated to 200°C (*Figure 1c*) and cooled down to room temperature at 10°C min^{-1} (*Figure 1d*). In the cooling traces, the existence of an exothermic peak, which started at 90°C and presented a maximum at 80°C, showed the crystallization of the sample at a relatively high undercooling.

When the sample was treated in a subsequent heating cycle (*Figure 1e*), two endothermic peaks at 130°C and 180°C appeared. It is important to mention that the sum of the enthalpies of the two melting processes produce the same values as the non-isothermal crystallization heat (*Table 1*). A study of the isothermal crystallization of this polymer will be published elsewhere[9].

As is generally known, multiple melting or endothermic peaks have been found in semicrystalline polymers and several origins for these peaks have been widely discussed[10–16]. They have been mainly attributed to different crystalline forms[10,11], differences in crystal sizes[12,13], differences in morphology[16] and melting–recrystallization processes[14,15]. In order to discharge the possible existence of polymorphism in this system, X-ray analysis was carried out and only the reflections corresponding to one crystalline form were obtained, using the same thermal treatments as reported above.

Other thermal treatments from the mesophase have also been considered. When PHTOB was quenched from the mesophase (200°C) into liquid nitrogen, the

Table 1 Thermal transitions and thermodynamic parameters of PHTOB

Sample	T_c[a] (°C)	ΔH_c (J g^{-1})	T_l[a] (°C)	ΔH_l (J g^{-1})	T_i[a] (°C)	ΔH_i (J g^{-1})	ΔT[b] (°C)	$1-\lambda$[c]	$1-\lambda$[d]
1a	132	2.6	173	10.3	295	13.0	122	0.23	0.30
1b	–	–	170	17.8	290	12.4	120	0.52	0.52
1d	80	9.7	–	–	–	–	–	–	0.29
1e	–	–	130–180	9.4	–	–	–	0.29	0.29
1f	130	10.3	175	11.0	–	–	–	0.02	0.32
1h	–	–	115–130	5.9	250	15.0	–[e]	–[e]	–[e]
1i	–	–	110–170	–[e]	250	–[e]	–[e]	–[e]	–[e]

[a] Maximum of the transitions

[b] $\Delta T = T_i - T_l$

[c] Initial crystallinity of the sample

[d] Maximum crystallinity of the sample in this cycle

[e] Could not be evaluated

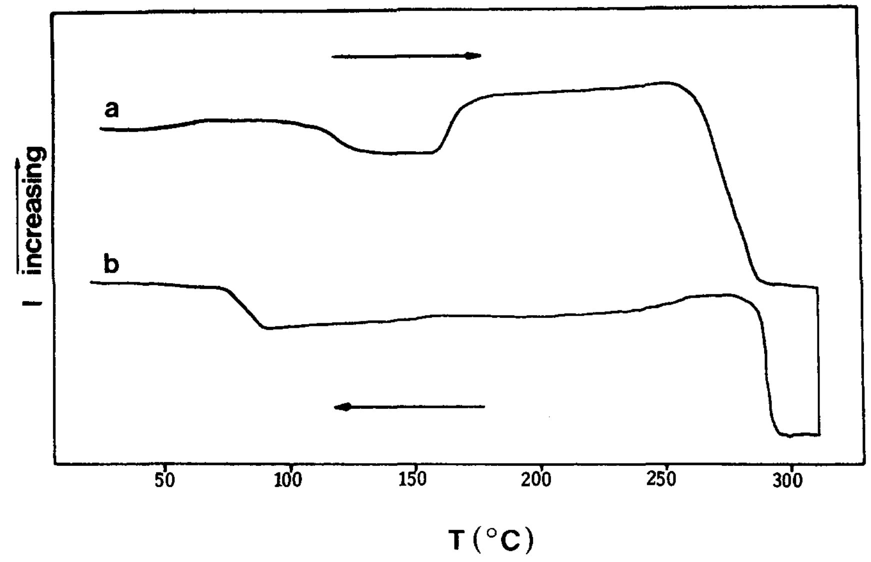

Figure 2 Thermooptical analysis of PHTOB: a, heating cycle; b, cooling cycle. In both cases the heating rate was 10°C min^{-1}

subsequent heating cycle showed an exothermic crystallization in the range from 100 to 150°C, with a maximum at 130°C, and an endothermic peak at 175°C (*Figure 1f*), corresponding to the crystal–liquid crystal transition. The enthalpy associated with the crystallization peak is 10.3 J g^{-1} and that corresponding to the T_l transition peak is 11.0 J g^{-1}. The approximately equal values indicate that only the crystalline fraction is formed during the heating cycle. In other words, in the quenching process, crystallization does not take place; consequently there is no three-dimensional order and the PHTOB presents a glassy mesophase.

The crystalline array which is formed under the heating conditions is rather homogeneous, as shown by the d.s.c. curve with a single sharp peak.

Different thermal histories from the isotropic state were also considered. For this purpose the samples were cooled from the molten state ($T = 340$°C), at three different rates: 40°C min^{-1}; 10°C min^{-1}; and very rapidly by quenching into liquid nitrogen. *Figures 1g–i* show the subsequent curves obtained at a heating rate of 10°C min^{-1}. In each case, multiple peaks are observed in the lower temperature range, and two wide endothermic peaks are present, which correspond to the crystal–liquid crystal and liquid crystal–isotropic transitions. The fact that the temperature of the isotropic melt (340°C) is in the range in which degradation of the material is initiated, may be the explanation for these wide peaks.

Finally, the thermooptical analysis of a film prepared by cooling from 200°C to room temperature shows the existence of three transitions detected by d.s.c. experiments, with important changes in light intensity. One intensity loss is located at 100–120°C, which corresponds to the melting of small or imperfect crystallites, similar to the curve depicted in *Figure 1e*. A light gain in the range 165–185°C corresponds to the crystal–liquid crystal transition. Finally, a complete loss of intensity at 310°C is due to the liquid crystal–isotropic transition (*Figure 2a*). In the cooling cycle (*Figure 2b*) these transitions are confirmed. The microphotographs obtained at 30 and 190°C show the existence of a smectic mesophase.

In order to discuss all these results, the d.s.c. data are summarized in *Table 1*. It should be noticed that the published data[5] on PHTOB transitions correspond to $T_l = 176$°C and $T_i = 253$°C. The first value, reported as T_m in the original work, is in agreement with that found in this work. However, T_i is significantly lower.

The differences in the reported values in the thermotropic polyester could be explained in several ways. Firstly, the molecular weight and the molecular weight distribution play an important role in the nature of the transitions and the crystallization behaviour, although there are few publications in which these parameters have been considered[17]. Secondly, the location of the transitions depends on the thermal history and, before comparing results from different authors, either the thermal treatment or state of the sample (powder, as obtained by casting from the melt or from solution) should be specified. Lastly, but by no means least, are the experimental conditions in which the transitions are analysed and, more specifically, the heating or cooling rate at which the d.s.c. curves are obtained. As is well known, this is a very crucial point in the determination of T_g and T_m in amorphous and semicrystalline polymers.

The analysis of the transitions in PHTOB carried out in this work corresponds to samples with an inherent viscosity of 0.67 dl g^{-1}, much higher than the previously reported[5] value of 0.196 dl g^{-1}. Therefore, higher values of T_l and T_i should be expected for our sample. However, the heating rate used in this work is 10°C min^{-1}, lower than that used by Ober *et al.*[5]. This fact may represent a compensation for the effect of molecular weight, because higher heating rates very often lead to superheating of the sample and, consequently, to higher experimental transition temperatures. Thus, T_l is approximately the same as the values reported in this work.

Nevertheless, the T_i values show a significant difference of more than 40°C. It was previously reported[5] that the value at 253°C was very imprecise, and its significance was questioned since during the optical determination of the value some discoloration in the sample was observed. It is quite possible that in this temperature range, due to the low molecular weight of the sample, some degradation could occur. Therefore, our value of 296°C for the liquid crystal–isotropic transition is more plausible. Moreover, the significance of the difference between the two values is not trivial. The consequence is that the temperature range in which the mesophase exists spans 122°C, that is to say, the mesophase is very stable over a wide temperature range. As far as we know, it is the widest range which has been found in these thermotropic polyesters, the only exception being the polymer with five methylene groups as the spacer[6].

The values of ΔH_l and ΔS_l for the original sample are 1.6 kcal mol^{-1} and 2.8 cal mol^{-1} K^{-1}, respectively; values for the sample prepared from solution are slightly lower, being 1.5 kcal mol^{-1} and 2.7 cal mol^{-1} K^{-1}, respectively. The values found for ΔH_l agree with those reported in the literature[5] and ΔS_l values are slightly lower, which corresponds with the differences in T_l discussed previously.

It is important to note that a ΔS_l value of 2.7 cal mol^{-1} K^{-1} has been reported for polyester with five and nine methylene groups[6]. The coincidence with the value obtained in this work is apparent and thus similar structures are expected for the mesophases, which are smectic in all of these cases.

X-ray diffraction patterns

As previously mentioned, the physical properties of PHTOB depend mainly on the method of preparation of the sample and on its thermal history. In order to confirm the conclusions obtained from d.s.c. experiments, wide angle X-ray diffraction measurements were performed at room temperature on samples with different treatments.

The original sample of PHTOB, obtained as a powder by precipitation from the reaction vessel, shows an X-ray pattern with three strong reflections at $2\theta = 3.8$, 19.7 and 23.4° and an amorphous halo centred around $2\theta = 28$ (*Figure 3a*). The reflections at $2\theta = 19.7$ and 23.4° are related to the crystalline array, while the reflection at $2\theta = 3.8°$ may correspond to the molecular order related to the smectic mesophase.

When the original sample is heated up to 200°C and cooled down from this temperature to room temperature, the X-ray pattern shows the same reflections but with considerably less crystallinity (*Figure 3b*). The smectic mesophase is more apparent and the reflection at $2\theta = 3.8°$ is stronger and more defined. This reflection corresponds to a spacing of $d = 23.3$ Å.

When the sample is quenched into liquid nitrogen from 200°C, the X-ray diffractogram obtained at room temperature shows that the reflections corresponding to the crystalline order disappear and only the reflection

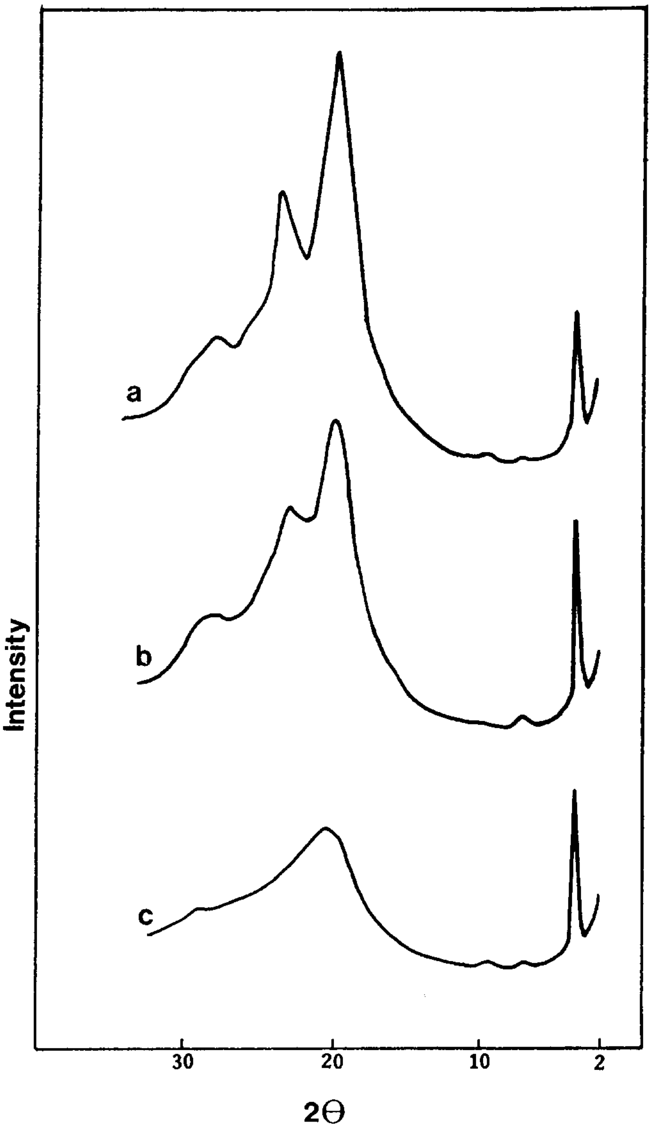

Figure 3 X-ray diffractograms of PHTOB at room temperature: a, original sample; b, sample cooled down from 200°C to room temperature; c, sample quenched into liquid nitrogen from 200°C

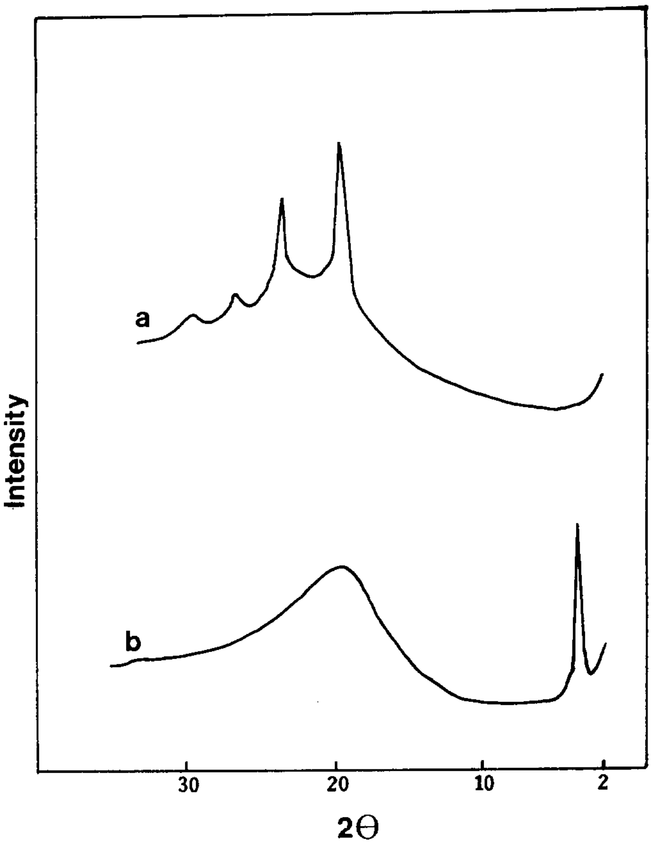

Figure 4 X-ray diffractograms of PHTOB sample prepared from CF_3COOH solution: a, at room temperature; b, at 200°C

due to the smectic mesophase is present (*Figure 3c*). This is a very important result because it confirms the absence of three-dimensional order as observed by d.s.c. Moreover, the crystallinity is not generated from the mesophase when these quenching conditions are applied and only a very low level of crystallinity, if any, is obtained. Put in another way, a solid with intermolecular order is present which can undergo, by heating, a transition towards a more ordered phase. This transition corresponds to the crystallization observed in *Figure 1f*.

When the sample was prepared from solution in CF_3COOH with further evaporation of the solvent, the X-ray pattern showed only the reflections corresponding to the crystalline order (*Figure 4a*). Only when this sample was heated up to 200°C was the crystal–liquid crystal transition observed, with the appearance of the reflection at $2\theta = 3.8°$ and the disappearance of the reflections at $2\theta = 19.7$ and $23.4°$. This effect is shown in *Figure 4b*.

From the results described above it is concluded that the method of preparing the sample and the thermal history affect the physical structure of PHTOB. The three-dimensional order and the intermolecular order related with a smectic mesophase coexist. Only when the sample is obtained from solution is the crystalline three-dimensional order isolated. Finally, it is possible to 'freeze in' the mesophase by quenching from the liquid crystal state into liquid nitrogen. The possibility of obtaining the mesophase and the crystalline structure separately for the same sample is not very common in main chain liquid crystals where, in general, crystallization partially prevents quenching of the mesophase. This is a very important feature of PHTOB, which enables the study of different phases at room temperature.

Two regions can be distinguished in the X-ray patterns. The reflections in the low angle region are associated with the distance between the smectic planes in the smectic structures or with the thickness of the lamellae in the crystal. The reflections in the wide angle region correspond to the lateral organization of the polymer chain in the lamellae or in the smectic layers of the smectic phases[18]. The X-ray patterns obtained in this work are characteristic of the existence of a smectic orthogonal phase (S_A) or a smectic tilted phase (S_C). These disordered smectic phases exhibit a sharp signal in the low angle region and a diffuse band in the wide angle region.

In order to discriminate between the orthogonal and the tilted phase, the distance between the smectic layers deduced from the low angle X-ray reflections and the length of the repeating unit can be compared. This last parameter, in its fully extended all *trans* conformation, corresponds to 28.3 Å, calculated from known bond distances and angles[19,20]. However, the Bragg spacing, corresponding to the reflection at $2\theta = 3.8°$, is 23.3 Å. This means that the polymer chains are tilted by an angle of 34.6° to the normal of the layers, maintaining all the C–C bonds of the methylenic spacer in the *trans* conformation. In this case the smectic mesophase is S_C.

Another possibility is the existence of *gauche* conformations in some C–C bonds which allows the polymer chains to be orthogonal to the plane of the layers, in an S_A phase. Solid state n.m.r. studies are now in progress to study the possible existence in the mesophase of *gauche* bonds in the alkyl region[21]. However, the theoretical calculations[22] and i.r. studies[23] have suggested that in the case of thermotropic polyesters with ester linkages (or bridges) the transition is accompanied by an increase of *gauche* conformations in the alkyl region[23], in contrast to those with ether bridges where no essential conformational changes were observed during the transition to the mesophase.

Particular attention has been paid to the analysis of the structural behaviour at different temperatures by X-ray measurements. *Figure 5* shows the patterns at several temperatures between room temperature and 190°C for an original sample. Changes in the intensity of the reflections were not observed between room temperature and 120°C, and the crystallinity was calculated to be 23%. From 120 to 150°C a slight increase in crystallinity was observed (30%) with the appearance of two small reflections at $2\theta = 26.4$ and $29.6°$. At 190°C, the reflections corresponding to the three-dimensional order disappeared and only the sharp reflection in the low angle region assigned to the smectic mesophase persisted up to the isotropic melt. *Figure 6* shows the X-ray patterns at different temperatures of a sample of PHTOB quenched from 200°C into liquid nitrogen. At room temperature the X-ray diagram of the smectic mesophase was observed. At temperatures between 100 and 150°C the growth of the crystalline peaks was observed; this crystallization process was also detected by d.s.c. (*Figure 1f*). At temperatures higher than 180°C (the crystal–liquid crystal transition) only the X-ray diagram of the mesophase was obtained. Other crystalline forms were not observed by X-ray diffraction in any of the thermal treatments used in this work.

From the values of crystallinity obtained from X-ray

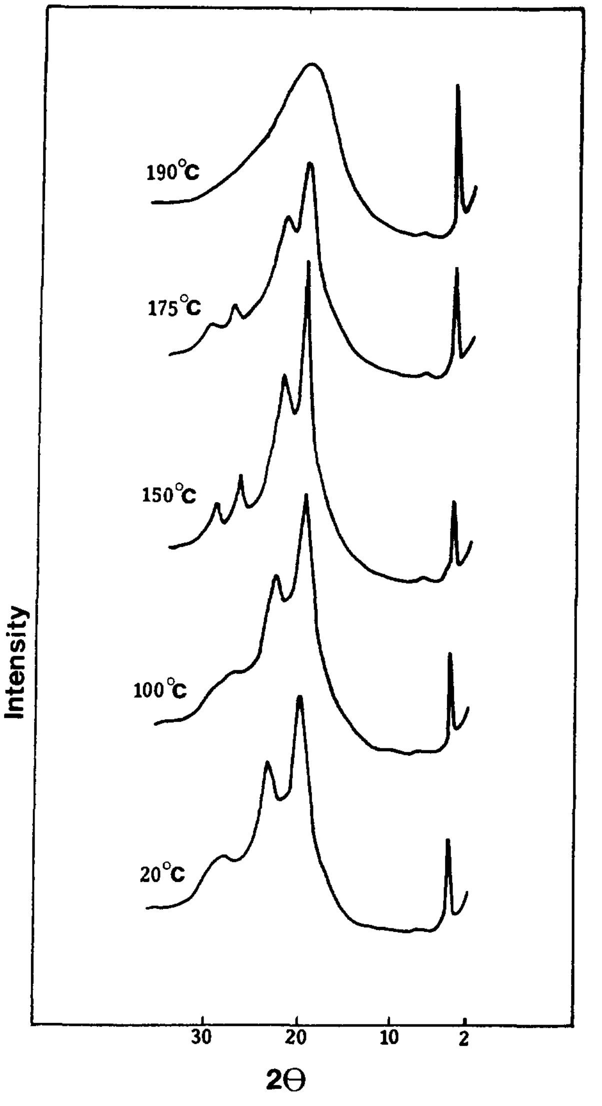

Figure 5 X-ray diffractograms of PHTOB original sample as a function of temperature

patterns of the samples crystallized from solution and quenched from liquid nitrogen, and the corresponding values of the enthalpies obtained from d.s.c. experiments on samples crystallized in the same conditions, it is possible to obtain the enthalpy corresponding to the melting of 100% crystalline PHTOB. This value is 34 J g^{-1} and it is a very important parameter in the analysis of the melting and crystallization processes of this polymer[9].

In summary, we have studied the thermal behaviour and the structure of liquid crystalline poly(heptamethylene terephthaloyl-bis-4-oxybenzoate). As a result of d.s.c., X-ray and microscopy measurements, the influence of different thermal treatments on the crystal and mesophase formation was found to be very important. The sample originating from the synthesis demonstrated a coexistence of crystalline and liquid crystalline phases. However, by evaporation of CF_3COOH solution, it was possible to isolate the crystalline phase. Finally, the smectic mesophase could be 'frozen in' by quenching the sample into liquid nitrogen.

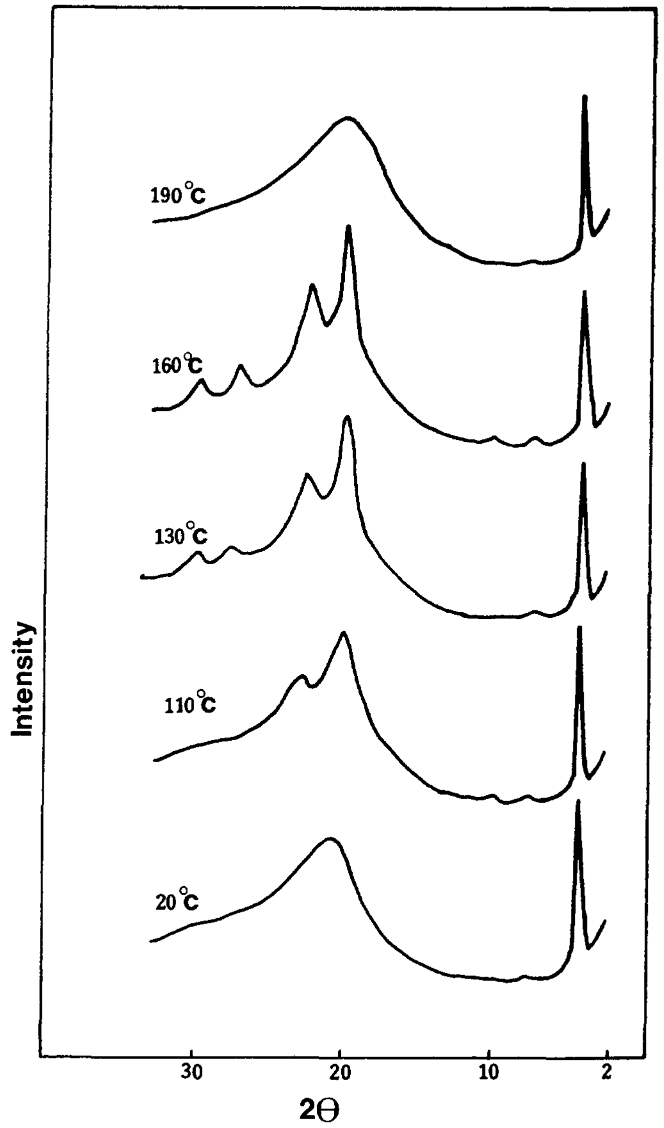

Figure 6 X-ray diffractograms of PHTOB sample quenched from 200°C into liquid nitrogen as a function of temperature

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