

Investigation of phase transition in main chain liquid crystals: poly[tris(oxymethylene) oxycarbonyl-1,4-phenyleneoxy-terephthaloyloxy-1,4-phenylenecarbonyl]*

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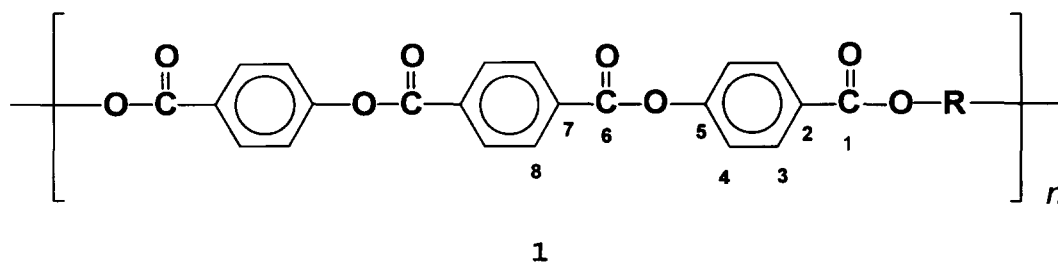
Thermal transitions in a new main chain liquid crystal polymer, poly[tris(oxymethylene) oxycarbonyl-1,4-phenyleneoxy-terephthaloyloxy-1,4-phenylenecarbonyl], PTOPTO, have been studied by differential scanning calorimetry, optical microscopy and wide-angle X-ray diffraction, employing synchrotron radiation. The thermal behaviour of this polymer is very complex and includes four main transitions at 36, 70, 141 and 176°C, associated with the glass transition, a smectic S_C to S_A transition, a change from smectic S_A to the nematic phase and the isotropization temperature, respectively. Changes in the structure from fan-shaped to focal conic structures confirm the transition from S_C to S_A and the appearance of Williams domains confirm the transition from S_A to nematic. These observations coincide with the data obtained by X-ray diffraction, in which a shift in the peak at $2\theta = 3.35^\circ$ is detected. Reflections associated with three-dimensional order were not observed, due to the asymmetry of the spacer. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Thermotropic polyesters with mesogenic units in the main chain are one of the most interesting groups of liquid crystalline polymers^{1–3}. The synthesis and characterization of polyesters based on 4,4'-(terephthaloyldioxy)dibenzoic acid with a mesogenic triad unit with three aromatic rings has been described^{4–7} and analysed previously in our laboratory^{8–13}. These polyesters have the general structure:

Recently, polyesters based on this aromatic triad and oxyalkylene spacers have been analysed^{14–22}. Most of these studies have been carried out by using propylene glycol and their optically active isomers. However, a detailed analysis of their behaviour and the influence of the spacer on the thermal transitions, morphology and crystallinity, if any, has been carried out in only a few cases.

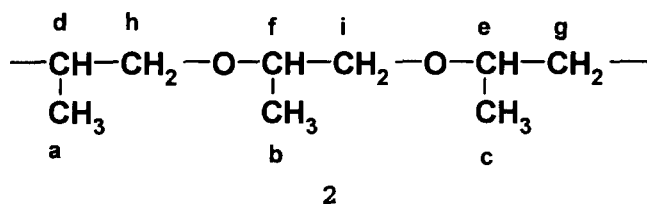


where R are linear and branched spacers.

* In memoriam to Prof. H. G. Zachmann, an outstanding scientist and good friend

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The present study was undertaken in order to determine the influence of the different propylene glycol units on the properties of these liquid crystals. The polyester analysed has R:



as the flexible spacer.

In this paper, we report the synthesis, the characterization and the thermal and structural behaviour of this system, by using differential scanning calorimetry (d.s.c.), thermo-optical analysis, t.o.a., and, as a powerful tool, wide angle X-ray scattering (WAXS) employing synchrotron radiation.

EXPERIMENTAL

Synthesis and characterization

Poly[tris(oxymethylethylene) oxycarbonyl-1,4-phenyleneoxy-terephthaloyloxy-1,4-phenylenecarbonyl] (PTOPTO) was prepared by the method described by Bilibin and coworkers⁵⁻⁷ in three stages. In brief, the 4,4'-terephthaloyldioxydibenzoic acid (TOBA) was prepared by condensation of terephthaloyl chloride with 4-hydroxybenzoic acid. The 4,4'-terephthaloyldioxydibenzoyl chloride (TOBC) was obtained by reaction of TOBA with thionyl chloride. The polymer was prepared by polycondensation of TOBC and tripropylene glycol in a diphenyl oxide solution, at 200°C, in flowing nitrogen gas.

The polymer was precipitated in toluene, filtered and washed with ethanol and finally dried under vacuum.

The results of the elemental analysis of the polymer, PTOPTO, are as follows. C₃₁H₃₀O₁₀ (562.57): Calc., C 66.19, H 5.37; Found, C 65.94, H 5.90.

¹H nuclear magnetic resonance (n.m.r.) and ¹³C n.m.r. spectra of PTOPTO were determined on a 200 MHz Bruker spectrometer and on a Varian 300 MHz spectrometer, respectively, at room temperature. The following chemical shifts were observed (the δ subscripts are those of the corresponding carbon and hydrogen atom numbers according to the previously defined structures 1 and 2).

¹H n.m.r. (CDCl₃) (δ in ppm from tetramethylsilane): δ₈ = 8.34(4H); δ₃ = 8.17–8.13 (4H); δ₄ = 7.35–7.28 (4H); δ_d = 5.36–5.30 (1H); δ_g = 4.32–4.27 (2H); δ_e = 3.98–3.92 (1H); δ_{h,f,i} = 3.75–3.45 (5H); δ_c = 1.25 (3H); δ_b = 1.17 (3H); δ_a = 1.37–1.33 (3H).

¹³C n.m.r. (CDCl₃) (δ in ppm from tetramethylsilane): δ₁ = 165.2 (2C); δ₆ = 163.7 (2C); δ₅ = 154.3 (2C); δ₇ = 133.7 (2C); δ₃ = 131.5 (4C); δ₈ = 130.4 (4C); δ₂ = 128.6 (2C); δ₄ = 121.7 (4C); δ_d = 76.9 (1C); δ_g = 75.5 (1C); δ_e = 73.9 (1C); δ_{h,f,i} = 70.2–70.8 (3C); δ_a = 17.1 (1C); δ_c = 16.8 (1C); δ_b = 16.7 (1C).

The inherent viscosity of the polymer solution was measured in an Ubbelohde viscosimeter at a concentration of 0.5 g dl⁻¹, in chloroform at 30°C.

Molecular weight averages and molecular weight distribution were determined by gel permeation chromatography (g.p.c.), using a Laboratory Data Control Constametric 2G/PE601 system. The diluent was tetrahydrofuran (THF).

Thermal properties

Thermogravimetric analysis (t.g.a.) was performed using a Mettler TG-50 thermobalance with a nitrogen purge, at a heating rate of 10°C min⁻¹.

The thermal transitions were determined using a d.s.c. Mettler TA-4000 apparatus with DSC-30 oven, coupled to a PC with TA-72 thermal analysis software. The heating and cooling rates were 10°C min⁻¹, taking the peak maximum as the transition temperature and the mid-point in the case of the glass transition temperature (*T*_g).

Morphological and structural analysis

Thermo-optical studies were carried out by using a Reichert Zetopan transmitted polarized light microscope with a Mettler FP-80HT hot stage and a Nikon FX35A camera.

Wide angle X-ray diffractograms were obtained using synchrotron radiation at the polymer beam line at HASYLAB (DESY, Hamburg). The beam is monochromatized (1.5 Å) by Bragg reflection at a germanium single crystal which is bent in order to focus the beam in a horizontal direction. For focusing in the vertical direction a mirror was used. The scattering was detected by means of a linear Gabriel detector. Further details concerning the instrument can be found elsewhere²³.

RESULTS

Preparation of PTOPTO by the method described in the Experimental section gave rise to a very clean and uniform polymer with a perfectly defined chemical structure, as confirmed by the results of the elemental analysis and by ¹H n.m.r. and ¹³C n.m.r. spectroscopy.

The inherent viscosity is 0.27 dl g⁻¹ and the weight- and number-molecular weight averages, determined by g.p.c. are 18 000 and 10 000, respectively.

Previous to the determination of the thermal transitions, t.g.a. was carried out under dynamic conditions in order to determine the thermal stability. PTOPTO is shown to be stable up to 330°C, and only a 10% weight loss is observed at 370°C.

The thermal transitions were studied by d.s.c. using several heating and cooling cycles for the same sample at a heating and cooling rate of 10°C min⁻¹.

Figure 1 (run a) shows the d.s.c. scan for a PTOPTO sample, as prepared. Four transitions were observed at 36, 70, 141 and 176°C. These endothermic changes can be associated with the glass transition (I), the smectic S_C–S_A transition (II), the smectic S_A to nematic phase (III), and the isotropization temperature (IV), respectively. These assignments are confirmed below by the t.o.a. and X-ray diffraction data.

Figure 1 (run b) shows the cooling process from 230 to 0°C, with transitions approximately at the same temperatures. The only difference is that the glass transition appears without a relaxation enthalpy and the S_A–S_C transition cannot be observed, probably as a consequence of the low enthalpy and its occurrence over a wide temperature range. The following heating cycle, Figure 1 (run c) shows once again the occurrence of the transitions I, III and IV.

No differences in the d.s.c. curves were observed when quenching was performed from different temperatures corresponding to the isotropic state or different mesophases, respectively. This behaviour is different to that observed in other thermotropic polyesters, as will be discussed later. Table 1 lists the calorimetric data of the transitions corresponding to the runs shown in Figure 1.

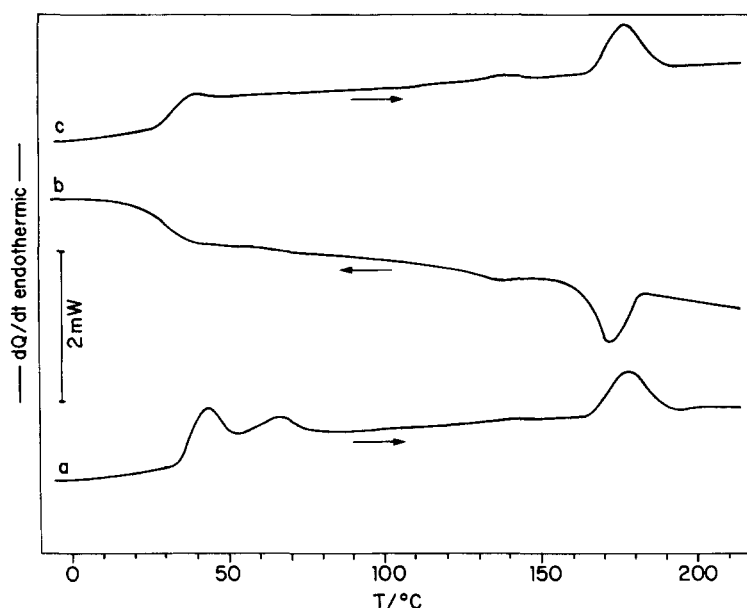


Figure 1 D.s.c. curves for PTOPTO. (a) Heating curve of an original sample. (b) Cooling from 230 to 0°C. (c) Sample 'b' heated up to 230°C. (dQ/dt: amount of heat applied per unit time)

Thermo-optical analysis of films prepared by cooling from both the mesophases and the isotropic state was undertaken. *Figure 2* shows the changes in light intensity vs temperature for a sample prepared from the isotropic melt, corresponding to the third d.s.c. run (run c, *Table 1*), together with micrographs taken at several temperatures. In the range from room temperature to 100°C a typical marble texture is observed, *Figure 2a*. At higher temperatures, in the range from 110 to 120°C, there is a small change in intensity and polygonal batonnets were observed, *Figure 2b*, with focal-conic textures observed in the range 130–140°C, *Figure 2c*. A greater variation in intensity at 145–150°C is related with characteristic structures known as Williams domains, found in other polyesters^{24–26}, *Figure 2d*. Finally, a very dramatic loss of intensity above 160°C is associated with the clearing point.

The wide angle X-ray diffractograms in *Figure 3* show the changes in a heating cycle from 50 to 220°C. A strong sharp peak can be observed at about $2\theta = 3.35^\circ$ which indicates the existence of a smectic structure. Also a shift from 3.35 to 3.10 in the region between 80 and 130°C is observed, which we interpret as a transition from S_C to S_A in agreement with the change in morphology observed in t.o.a. As it can be observed in *Figure 4*, the low angle peak changes drastically between 80 and 130°C, and this cannot be interpreted only in terms of the effect of temperature. At temperatures above 150°C, this peak practically disappears.

Further, the diffractograms obtained in the cooling process from the isotropic state demonstrate that the changes in intensity and diffraction angle of the smectic peak are reversible.

DISCUSSION

The thermal behaviour of PTOPTO is very complex and includes mesomorphism, whilst, on the contrary, the existence of a three-dimensionally ordered crystalline phase has not been detected. The absence of the crystallization process is quite a common phenomenon in side chain liquid crystals polymers^{27,28}, although it is not typical in main chain systems^{9,29–33}. Either depending on the thermal treatment⁹ or through the introduction of alkyl groups in the flexible spacer, it is possible to generate a strong steric impediment in the molecular packing^{26,34,35}. This fact eliminates the presence of crystallinity and, therefore, leads to an isolated meso-phasic state.

PTOPTO has a T_g of 36°C, slightly lower than the value of 87°C which is found with its homologous polyester with oxypropylenic spacers¹⁴. This is a consequence of the increase in flexibility due to the increment of oxypropylenic units in the flexible spacer. Moreover it is slightly higher than the reported value¹⁴ of 20–30°C for the polyester with trioxyethylenic spacers, as a consequence of the increase in the stiffness originated by the lateral substitution of the spacer.

The existence of a transition from a disordered smectic mesophase of the type S_C to another disordered smectic S_A , was detected by t.o.a. where the changes of fan-shaped and batonnets to focal-conic structures was observed. This observation coincides with the shift of the reflection at low angles, detected by X-ray diffraction, indicating an increase of the monolayer smectic spacing from 26.4 Å to 28.5 Å, *Figure 4*. This result suggests the existence of a tilt angle of 22° in the smectic

Table 1 Phase transitions and their thermodynamic parameters for PTOPTO

Sample	T_g (°C)	$\Delta C_p(T_g)$ ($J g^{-1} °C^{-1}$)	$T_{S_C-S_A}$ (°C)	T_{S_A-N} (°C)	ΔH_{S_A-N} ($J g^{-1}$)	T_{N-I} (°C)	ΔH_{N-I} ($J g^{-1}$)
a	36	0.29	70	141	0.5	176	5.7
b	28	0.36	85–108 ^a	148	1.4	173	4.2
c	32	0.25	80–110 ^a	140	0.5	175	5.3

^a By t.o.a.

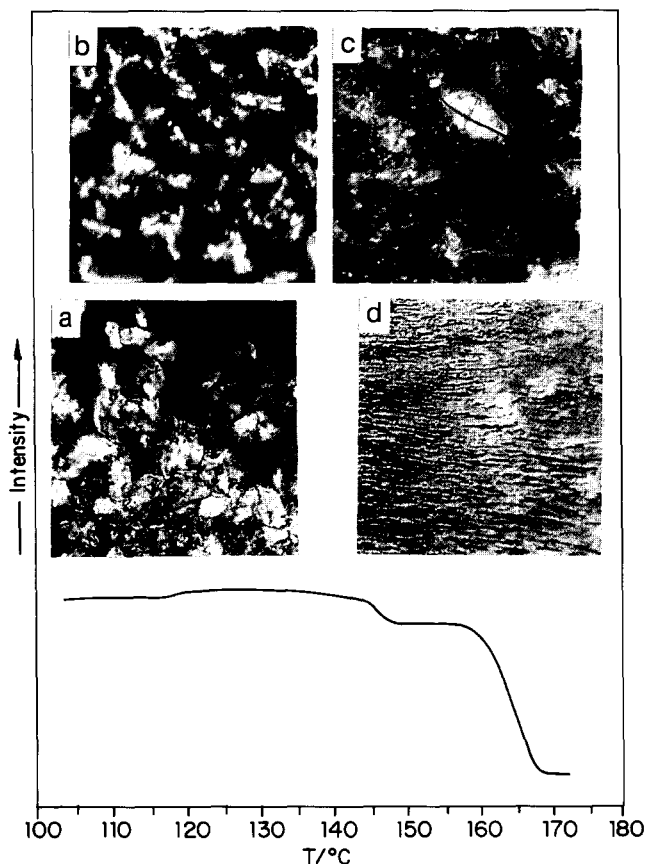


Figure 2 Thermo-optical analysis for PTOPTO corresponding to the third heating d.s.c. experiment (run C, Table 1), and polarizing light microscopy photographs taken at the temperature range indicated in the text

S_C phase, that becomes zero for the orthogonal arrangement in the smectic S_A mesophase, admitting the existence of *gauche* conformations in the flexible spacer. It has not been possible to obtain fibre patterns of oriented samples in order to corroborate the mesophase type. However, a study by high resolution electron microscopy is in progress.

As we can see in Figure 5, the half width of the halo at wide angles increases with temperature in the range in

which the transition from smectic S_A to nematic occurs. By increasing the temperature, a second step takes place between 160 and 180°C, corresponding to the nematic–isotropic transformation. Similar situation has been reported for the case of thermotropic copolyesters derived from PET³⁶.

Evolution of the textures observed by t.o.a. seems to support the existence of a S_C – S_A transition, rather than the possible transformation of some *gauche* to *trans* conformations, that would justify the increase of the spacing in the smectic monolayer, in this temperature range. At higher temperatures, in the range from 140 to 150°C, the loss of the reflection at low angles, together with the appearance of the Williams domains (phenomena coincident with the appearance of a very low enthalpy endotherm in the d.s.c. curve), confirm the transformation into a nematic mesophase. Finally, at 176°C the transition from the nematic phase to the isotropic state occurs. A biphasic behaviour in the transition³⁷, as found in the aforementioned thermal conditions, is not observed.

Such mesomorphic transitions have been frequently found in thermotropic polyesters based on the mesogen derived from the 4,4'-terephthaloyldioxydibenzoic acid and different types of flexible spacer^{17,21,38–41}. This behaviour has been associated with the long mesogenic unit^{39,40}. The structure of the mesophases and their stability is determined by the specific structure and length of the flexible spacer. Smectic mesophases have been reported recently^{42–45}.

The flexible spacer of the PTOPTO is a structural isomeric mixture of tripropyleneglycol, that is to say, a racemic structure. According to our knowledge, there are no previous studies of this thermotropic polyester in the literature. However there is information on liquid crystal polymers with the same mesogenic unit as that in PTOPTO, but in which the flexible spacer is based on 1,2-propanediol with and without optical activity^{14,17}, or on its dimers and trimers with optical activity^{21,40}.

When we compare the general properties and thermal transitions of the PTOPTO with those corresponding with the homologous polyester with optically active trioxypropylenic spacer, (head-to-tail trimer)¹⁷, important differences are observed. In the first place, the

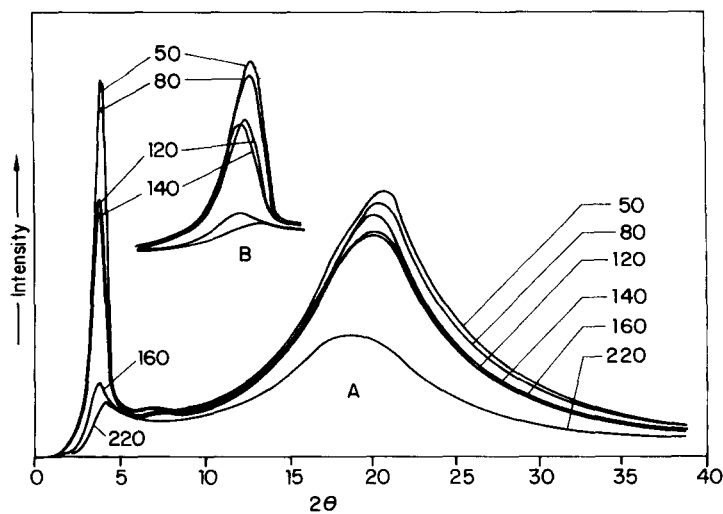


Figure 3 X-ray diffractograms of PTOPTO original sample. (a) Heating cycle from 50 to 220°C, at indicated temperatures. (b) Zoom from the low angle region

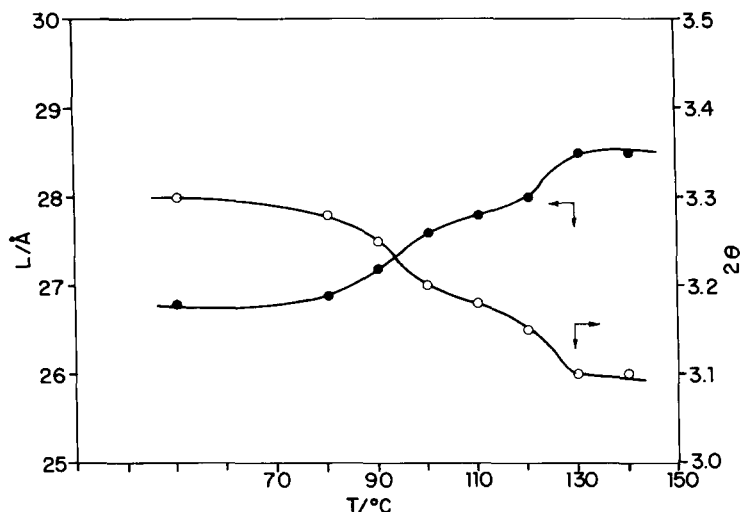


Figure 4 Variation with temperature of both monolayer smectic spacing and low angle reflection position of PTOPTO

optically active polyester is practically insoluble in all solvents, except H_2SO_4 and hot $\text{CF}_3\text{-COOH}$ ¹⁷, whilst PTOPTO is soluble in CHCl_3 and related solvents. On the other hand, it is very important to indicate that the WAXS diffractogram of the original PTOPTO at 50°C , Figure 3, does not present any reflection that could correspond to three-dimensional order of the polymer. This is a clear indication of the absence of crystallinity in this material. Moreover, the X-ray diffractogram registered at 60°C , after cooling from the isotropic state, Figure 4, does not show reflections associated with three-dimensional order. The same behaviour is observed when the cooling is accomplished from any of the mesomorphic states previously described. On the contrary, the other polyester with optical activity shows a crystal-liquid crystal transition at 275°C with an enthalpy change of 6.3 J g^{-1} ¹⁷. This indicates that the existence of configurational regularity in the chiral flexible spacer favours the existence of crystalline order. This cannot be achieved in PTOPTO, due to the difficulty of the packing polyester chain with asymmetric spacers. On the other hand, PTOPTO presents a S_C - S_A transition that is absent in the polyester with optical activity, and a transition to nematic order at 175°C , lower than 305°C , that corresponds to the transition from ordered smectic state to a 'twisted smectic'

mesophase that takes place in the chiral polyester¹⁷. These differences cannot be attributed to differences in the molecular weight of both polyesters, but, on the contrary, to the existence of the chirality.

The increase in one oxypropylenic unit in the spacer length also manifests itself when the properties of PTOPTO are compared with those of the homologous polyester with the racemic dioxypropylenic spacer⁴⁰. Although both polyesters present mesomorphism, differences exist in the type of mesophase as well as in the temperature range in which they appear. In the first place, the polyester with dioxypropylenic spacer forms a crystalline phase at high supercooling from the mesophase. In PTOPTO, the smectic mesophase S_C is obtained by quenching from the different existing mesophases in the polymer as well as from the isotropic state, independently of the thermal treatment. On the other hand, the polyester with racemic dioxypropylenic spacer presents a highly ordered smectic mesophase of the type S_H between 110 and 160°C ⁴⁰, that has not been detected in PTOPTO. In the same temperature range, this polymer presents the S_C - S_A - N transitions. This behaviour, which can originate from the increase in the spacer length, which confers a great flexibility in the case of PTOPTO, can also arise from the difference in molecular weight between both polyesters. PTOPTO

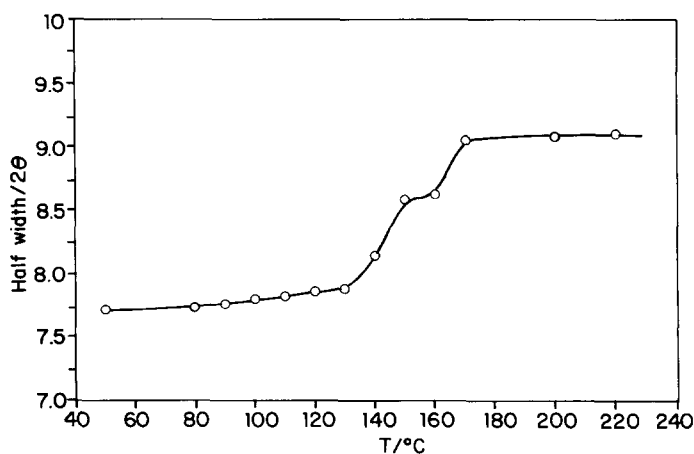


Figure 5 Variation with temperature of the half width of the halo at wide angles of PTOPTO

presents an inherent viscosity in CHCl_3 of 0.27 dl g^{-1} and a M_n of 10 000, while the derivative dioxypropylenic presents an inherent viscosity of 0.14 dl g^{-1} in a mixture of 1/1 by weight of *p*-chlorophenol and 1,2-dichloroethane, its M_n corresponding to a value between 4000 and 5000^{5,17,20,41}.

In summary, we can conclude that thermotropic polyester PTOPTO presents the phase transitions S_C-S_A-N-I . The mesomorphic behaviour of this polymer is a general fact in thermotropic polyesters with mesogenic unit derived from 4,4'-terephthaloyldioxydibenzoic acid. The stability as well as the nature of the mesophases is determined by the structure and length of the flexible spacer.

Three-dimensional crystalline order was not detected, independent of thermal treatments, as consequence of the hindered packing polyester chain due to the asymmetry of the flexible spacer.

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