# Polymorphism in Liquid Crystalline Poly[tetramethylene terephthaloylbis(4-oxybenzoate)]

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ABSTRACT: Two different crystalline forms have been observed in liquid crystalline poly[tetramethylene terephthaloylbis(4-oxybenzoate)]. Form I is produced when the sample precipitates from solution. When the sample is slowly cooled or quenched from the mesophase, form II is obtained. Form I shows an irreversible solid–solid transformation to form II upon heating, prior to the solid–mesophase transition. Once the thermal conversion of form I to form II is complete, it is not possible to recover form I without redissolving the crystals of form II. The existence of polymorphism and the transformations from the crystal to the mesophase and to the isotropic state have been studied by differential scanning calorimetry, X-ray diffraction, and thermooptical microscopy. Solid-state $^{13}C$ NMR spectroscopy has also been used in order to obtain information about the structure of these two crystalline forms. A gauche–trans–gauche conformation in the alkyl region is proposed for form I according to the chemical shifts of the methylene carbons. A more planar conformation in the flexible spacer, as well as a different orientation for the phenyl rings is suggested for form II.

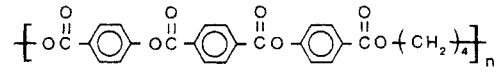
## Introduction

Liquid crystalline polymers exhibit different phases, which depend on the thermal treatment imposed on the system. In some cases, it has been possible to "freeze in" the mesophase by quenching the system from the anisotropic state.[1,2] In other polymers, it has been possible to isolate the pure crystalline phase or the pure mesomorphic state, as opposed to the coexistence of crystal and mesophase, by simply varying the preparation conditions and the thermal history of the sample.[3] Moreover, apart from the formation of anisotropic phases, polymeric liquid crystals may also show solid-state polymorphism. It has been pointed out that different solid modifications can be obtained for low molecular weight liquid crystals depending on the cooling rate and the temperature to which the sample is cooled from the anisotropic melt.[4] The existence of several crystalline polymorphs has also been reported for some liquid crystalline polymers.[5,6]

Thermotropic polyesters are one of the most commonly studied families of main-chain liquid crystalline polymers, and terephthaloylbis(oxybenzoic acid) is one of the principal mesogens used. Recently, the synthesis and characterization of this type of polymer, with linear methylene spacers ranging from 3 to 12 units, has been the subject of a number of publications.[7-11] The thermal transitions and the effect of the flexible spacer length on the type of mesophase formed have been investigated. The existence of polymorphism has only been reported in the case where the polymer contains 10 methylene units in the flexible spacer,[6] although a similar behavior was suggested for other members of the same family of polymers. However, in a dynamic-mechanical study a solid–solid transformation at low temperature (−50 °C) was suggested in samples quenched from the anisotropic melt, for members of this family with 3, 4, and 10 methylenes.[5] This was explained as the formation, at low temperature, of solids with a certain disorder that undergo a transition toward a more highly ordered phase.

High-resolution solid-state $^{13}C$ NMR spectroscopy is a very important and powerful method for the study of the structure, conformation, and dynamics of solid polymers.[12-14] The chemical shifts of carbon resonances are very sensitive to the conformation adopted by polymeric chains in the solid state. This sensitivity is manifested by significant differences in chemical shifts between different crystalline polymorphs or different phases.[15-18] Most of these differences in chemical shifts can be successfully explained by the $\gamma$-gauche effect.[19] Solid-state NMR spectroscopy has been used in the study of polymer liquid crystals,[20-23] although only a few reports discuss thermotropic polyesters.[22,23]

In this paper, we report the observation and characterization of two crystalline forms in poly[tetramethylene terephthaloylbis(4-oxybenzoate)], PTMTOB, with the structural formula



The effect of different thermal treatments on the solid–solid and solid–mesophase transition has been investigated. Solid-state $^{13}C$ NMR spectroscopy has been used in combination with X-ray diffraction in order to provide information about the structure of these two crystalline forms.

## Experimental Section

**Synthesis and Characterization.** Poly[tetramethylene terephthaloylbis(4-oxybenzoate)], PTMTOB, was synthetized in three stages using the method described by Bilibin and coworkers.[9] Firstly, terephthaloylbis(4-oxybenzoic) acid, TOBA, was prepared by condensation of terephthaloyl chloride with 4-hydroxybenzoic acid. Then, the terephthaloylbis(4-oxybenzoyl chloride), TOBC, was obtained from TOBA by reaction with thionyl chloride. Finally, the polymer was prepared by condensation of TOBC with 1,4-butanediol in a 1-chloronaphthalene solution during 12 h at 200 °C under a nitrogen gas current, with a yield of 90%. The polymer was precipitated in toluene, filtered, washed with ethanol, and vacuum-dried.

The results of the elemental analysis of the dichloride, TOBC, and the polymer, PTMTOB, are as follows. Anal. Calcd for TOBC: C, 59.59; H, 2.70; Cl, 16.03. Found: C, 59.67; H, 2.77; Cl, 15.90. Calcd for PTMTOB: C, 67.83; H, 4.35. Found: C, 68.30; H, 4.55.

$^1H$ NMR and $^{13}C$ NMR solution spectra were recorded in $DCCl_3$ for TOBC and in $DCCl_3$ + $CF_3COOH$ for PTMTOB at room temperature on a Varian XL-300 spectrometer, using TMS as an internal standard. The spectra showed the following chemical shifts for PTMTOB: $^1H$ NMR ($CDCl_3$ + $CF_3COOH$) $\delta$ (ppm from TMS) = 8.37 (4 H, terephthalate), 8.17–8.14 (4 H, d, 2,6-dicarbonylphenyl), 7.38–7.35 (4 H, d, 3,5-dicarbonylphenyl), 4.50 (4 H, methylene), 2.03 (4 H, methylene). $^{13}C$ NMR: These data are presented in the results section and summarized in Table I.

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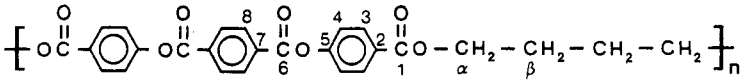
Table I
$^{13}C$ Chemical Shifts of Poly[(tetramethylene terephthaloylbis(4-oxybenzoate)] in the Solid State and in Solution



| | spacer alkyl carbons | | aromatic carbons | | | | | | CO carbons | |
|---|---|---|---|---|---|---|---|---|---|---|
| | α | β | 2 | 3 | 4 | 5 | 7 | 8 | 1 | 6 |
| solution | 66.3 | 25.2 | 127.5 | 131.9 | 122.1 | 154.7 | 133.5 | 130.8 | 165.5 | 168.5 |
| form I | 65.6 | 24.5 | | 129.2 (130.9) | 121.1 | 152.8 | 133.4 | 129.2 | 162.2 | 164.2 |
| form II | 65.6 | 24.3 26.0 | | 130.4 | 122.1 | 153.4 | 132.9 | 129.3 | 164.0 | 164.0 |

The inherent viscosity of the polymer was measured in an Ubbelohde viscometer at a concentration of 0.5 g·dL$^{-1}$ in *p*-chlorophenol at 45 °C.

**Physical Properties.** The thermal transitions were measured in a Mettler TA3000 differential scanning calorimeter with a DSC30 furnace and TA72 software. The peak maxima were taken as the transition temperature. Thermogravimetric analysis was performed on a Mettler TG50 using nitrogen as the purge gas, with a heating rate of 10 °C·min$^{-1}$.

Wide-angle X-ray diffractograms were recroded with a Philips Geiger counter X-ray diffractometer using an Anton Paar 300 temperature cell. The diffractograms were recorded in the 2θ range between 2 and 35° using Ni-filtered Cu Kα radiation at 2 dec·min$^{-1}$. Pinhole collimation and a flat plate camera were also used with a Siemens K710 generator to obtain photographic diffraction patterns with Polaroid plates.

Microscopy studies and thermooptical analysis were carried out using a Reichert Zetopan Pol polarizing microscope, equipped with a Mettler FP80 hot stage and a Nikon FX35A camera.

Raman data were recorded using a Jobin-Yvon U1000 double monochromator (Instruments SA) with photomultiplier detection and photon counting electronics. Laser excitation was provided by a Spectra Physics 2000 $Ar^+$ laser, at $\lambda_o$ = 514.5 nm, with a power of ~150 mW at the sample. Spectra were collected in a 90° geometry, between $\Delta\nu$ = 1800 and 550 cm$^{-1}$ over a 4-h period, and coadded. Prior to recording the spectra, the sample was exposed to the laser beam for an extended time period,[24] reducing the high initial fluorescent background by over 300%.

Solid-state $^{13}C$ NMR spectra were recorded at ambient temperature on a Bruker MSL 400 spectrometer, operating at a static magnetic field strength of 9.4 T ($^{13}C$ resonance of 100.6 MHz). Magic angle spinning (MAS) of the samples was achieved with a Bruker MAS-DB7 double bearing probehead. The CH signal of adamantane (29.5 ppm downfield from TMS) was used as the external reference. An optimum cross polarization contact time of 3 ms was used with a 5-s delay in all the spectra. Spectra were recorded with the usual cross polarization pulse sequence,[12] with spinning rates between 3.5 and 5 kHz, and with a TOSS pulse sequence[25] for the suppression of spinning side bands. A field strength of 50 kHz was used for dipolar decoupling (DD). Aluminum oxide rotors with poly(chlorotrifluoroethylene) end caps contained 100 mg of samples.

## Results and Discussion

The preparation of PTMTOB by the method described by Bilibin et al.[9] gives a perfectly well characterized polymer, which presents a higher molecular weight when compared with those obtained by other methods,[7,8] as is the case for other members of this family.[3] With this synthetic route it is possible to isolate and characterize the mesogenic monomer. $^1H$ and $^{13}C$ NMR data confirmed the structure of both the monomer and polymer used in this work.

IR spectra of PTMTOB presented a series of bands due to the aromatic rings and ester groups and the strong methylene $CH_2$ deformations. The Raman spectrum of the original sample of PTMTOB is shown in Figure 1. The carbonyl stretching vibrations appear at $\Delta\nu$ = 1745 and 1730 cm$^{-1}$ due to the terephthaloyl moiety and at $\Delta\nu$ =

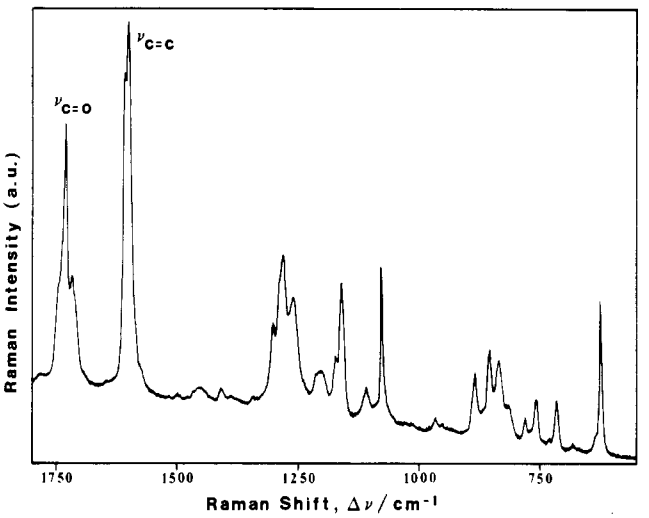



**Figure 1.** Raman spectrum of an original sample of PTMTOB.

1717 and 1710 cm$^{-1}$ due to the oxybenzoate moiety.[26] The strongest feature in the spectrum is the broad doublet at $\Delta\nu$ = 1607 and 1600 cm$^{-1}$, due to the aromatic C=C stretching vibrations. The methylene deformation modes appear very weakly between $\Delta\nu$ = 1500 and 1300 cm$^{-1}$. The region between $\Delta\nu$ = 1300 and 1200 cm$^{-1}$ is complex, with bands arising from a combination of vibrations due to the aromatic nuclei, ring—C(=O), O—C(=O), and ring—O stretching vibrations. The strong band at $\Delta\nu$ = 1161 cm$^{-1}$ is characteristic in aromatic polymers with para substitution in the chain. The spectrum obtained is highly characteristic of the poly[*n*methylene terephthaloylbis-(4-oxybenzoate)]; however spectral differences can be observed between different members of the same family with a varying number of methylene units in the spacer.[26,27] In the case where $n$ = 7, a series of bands have been demonstrated to be sensitive to the thermal history of the polymer.[26] Many of the differences observed are subtle, specially in the modes related with the methylene spacer, and a detailed vibrational spectroscopic study is currently underway[27] in order to characterize these variations.

The inherent viscosity of the polymer in *p*-chlorophenol at 45 °C is 0.33 dL·g$^{-1}$ at a concentration of 0.5 g·dL$^{-1}$. This value is higher than that reported by Lenz et al.[5]

The thermal stability of PTMTOB was studied by thermogravimetry under dynamic conditions, using a heating rate of 10 °C·min$^{-1}$ and nitrogen as the purge gas. The polymer was stable up to 350 °C and showed a loss of approximately 10% at 390 °C, as shown in Figure 2a.

The thermal behavior of the polymer was studied by DSC using several heating and cooling cycles. Figure 2b shows the heating curve for an original sample, with no thermal treatment, up to 380 °C at a heating rate of 10 °C·min$^{-1}$. A very complex endotherm centered around 280 °C, with a total enthalpy of 36.9 J·g$^{-1}$, was observed, which showed a shoulder at around 230–240 °C. This

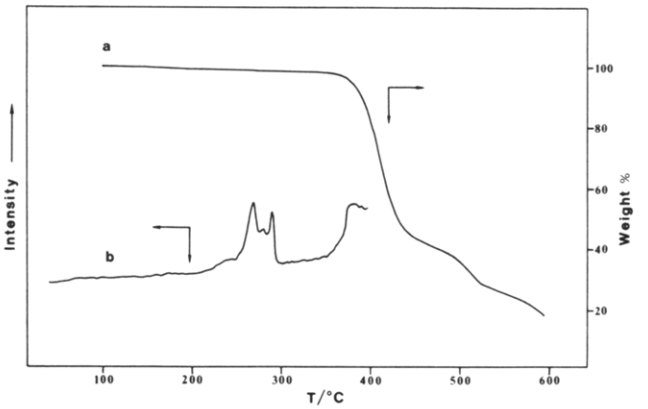



**Figure 2.** (a) Thermal stability of PTMTOB at a heating rate of 10 °C·min$^{-1}$. (b) DSC curve of an original sample of PTMTOB (heating rate 10 °C·min$^{-1}$).

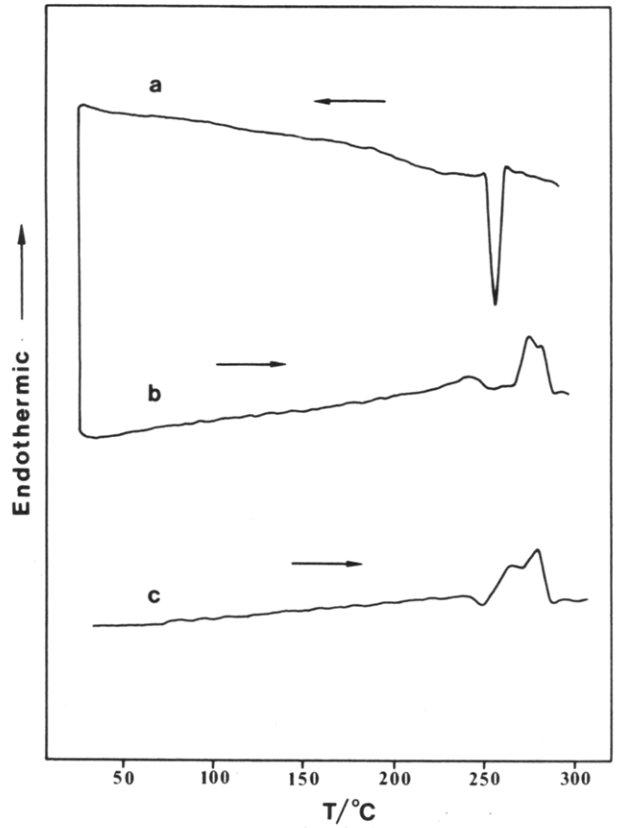



**Figure 3.** DSC curves of PTMTOB: (a) cooling from 300 °C to room temperature at 10 °C·min$^{-1}$; (b) sample "a" heated up to 300 °C; (c) sample quenched from 300 °C into liquid nitrogen and heated at 10 °C·min$^{-1}$.

endotherm has been assigned to the crystal–mesophase transition, as is later demonstrated by microscopy and X-ray studies. As observed in the thermogram in Figure 2b, the sample starts to degrade at 350 °C, and hence, it is not possible to detect the mesophase–isotropic melt transition by DSC.

Figure 3 shows the DSC runs obtained for different thermal treatments. When the sample was slowly cooled from 300 °C the thermogram showed a sharp exotherm with a maximum at 257 °C and a wide shoulder centered at 220 °C, probably due to a high concentration of low molecular weight species (Figure 3a). The subsequent heating run, without time delay between runs, showed firstly the melting of these low molecular weight species and then a sharp endotherm with a maximum at 275 °C (Figure 3b). When the sample was quenched from 300 °C into liquid nitrogen the thermogram obtained corresponded to that shown in Figure 3c, with the peak maximum of the endotherm at 280 °C. In this run, it appears that a small change of $\Delta C_p = 0.1$ J·g$^{-1}$·K$^{-1}$ takes place at 75 °C and could possibly be assigned to the glass transition temperature.

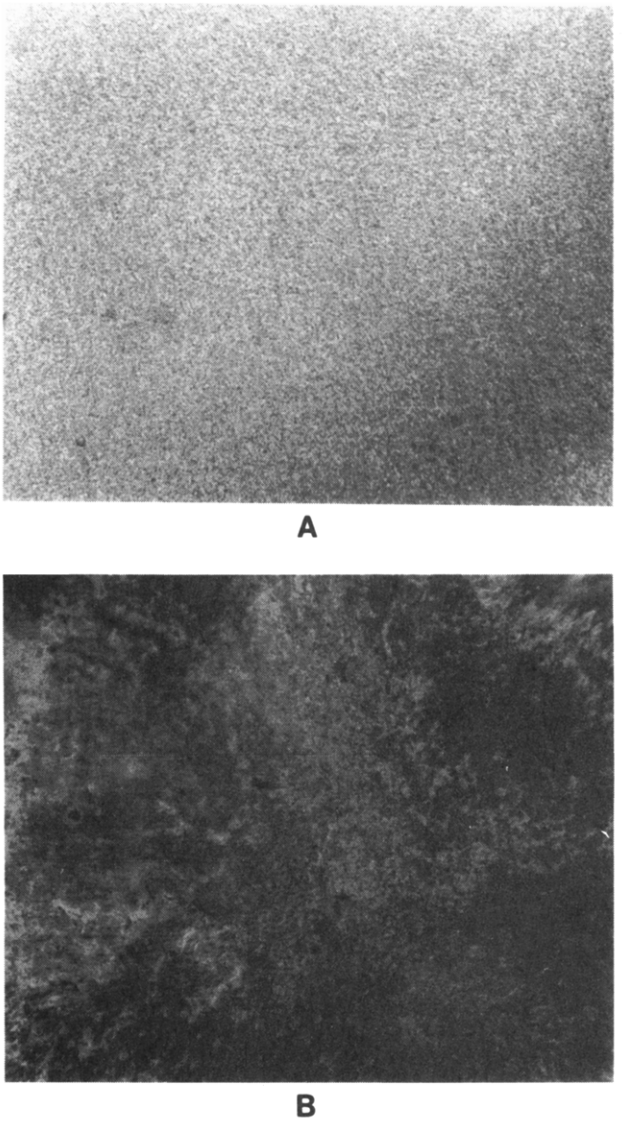



**Figure 4.** Optical microscopy photographs of PTMTOB: (A) at room temperature; (B) at 320 °C.

In order to characterize the transitions, thermooptical analysis and X-ray diffraction studies were carried out. Figure 4 shows the microphotographs of a film prepared by cooling from 310 °C to room temperature, at room temperature, and at 320 °C. On heating, a very important gain in light intensity was observed by thermooptical analysis at 280 °C, with the appearance of a marbled texture typical of a nematic mesophase. In the subsequent cooling cycle, the birefringence decreased at 240 °C, as detected by DSC. The clearing of the sample was observed at 350 °C, at the same temperature as the degradation of the polymer started, which makes it very difficult to clearly detect the transition from the mesophase to the isotropic melt.

Figure 5 shows the wide-angle X-ray diffractograms of PTMTOB for the original and thermally treated samples. The original sample, as obtained from the reaction vessel, presented several reflections at $2\theta$ = 19.4, 23.4, 27.8, and 29.5° associated with the three-dimensional order (Figure 5a). A crystallinity value of 46% was estimated from wide-

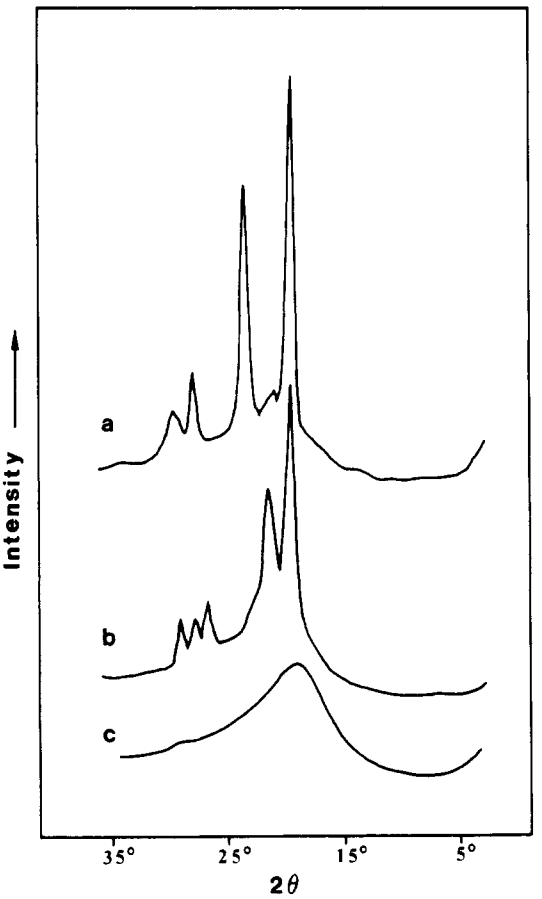



**Figure 5.** X-ray diffractograms of PTMTOB: (a) original sample; (b) sample cooled from 300 °C; (c) original sample at 290 °C.

angle X-ray spectroscopy (WAXS). Further, a series of bands in the Raman spectra of poly[*n*methylene terephthaloylbis(4-oxybenzoates)] can be related to the crystalline component of the polymer,[26,27] for example, the terephthaloyl carbonyl stretching vibration at $\Delta\nu \approx 1733$ $cm^{-1}$, and the ring-carbonyl stretching vibration at $\Delta\nu \approx 1285$ $cm^{-1}$, in the case for 7 methylene units in the spacer.[26] The corresponding bands in PTMTOB, at $\Delta\nu = 1730$ $cm^{-1}$ and 1282 $cm^{-1}$ respectively, are substantially more intense when compared to other bands in the spectrum, and other polymers in the series,[27] indicating a higher crystalline content in the material. By comparing the normalized intensity of the C=O stretch with previous results,[26] we estimated the crystallinity of the original sample of PTMTOB to be around 49%, which corresponds very well with the value obtained independently by WAXS.

When the sample was heated to 290 °C, only a broad halo centered at 19° was observed by X-ray diffraction (Figure 5c). This diffractogram, combined with the texture observed by optical microscopy can be assigned to a nematic mesophase. Finally, when the sample was cooled down from 300 °C to room temperature in air without control, the diffractogram obtained was that presented in Figure 5b. As it can be observed, this diffractogram differs markedly from that obtained for the original sample and showed several reflections at $2\theta$ = 19.4, 21.2, 26.5, 27.6, and 28.8°. The peak observed at 23.4° has disappeared. From these results, it is possible to state the existence of a second polymorph in PTMTOB, whose appearance depends on the thermal treatment imposed on the material. When the same sample was heated again and analyzed by X-ray diffraction, only the crystal–nematic mesophase transition at 290 °C was observed and no evidence for the different crystalline form was apparent.

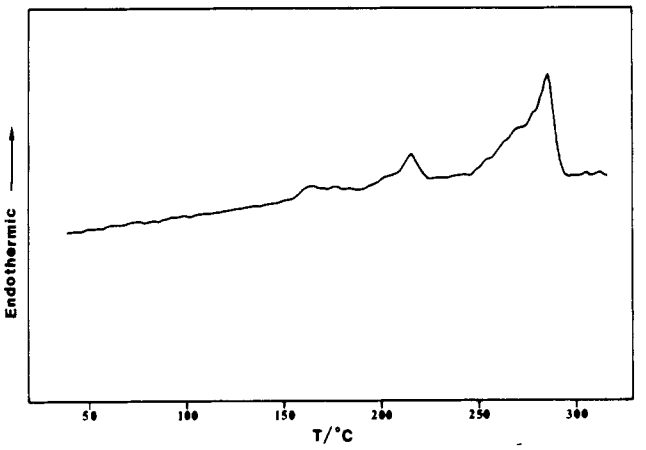



**Figure 6.** DSC curve of a PTMTOB sample prepared from solution.

When an original sample was quenched into liquid nitrogen from 300 °C, the diffractogram obtained at room temperature was identical to that shown in Figure 5b. When this sample was heated up to 300 °C again, the X-ray diffractograms obtained remained invariant up to a temperature of 290 °C, where the X-ray diagram corresponding to the nematic mesophase was observed. These observations confirm that the endotherm at 200 °C observed by DSC does not correspond to a transformation between different crystalline forms, but to different molecular weight species.

In order to obtain less heterogeneous crystals, a PTMTOB sample was prepared by evaporation from a solution in trifluoroacetic acid. Figure 6 shows the DSC curve obtained at a heating rate of 10 °C·$min^{-1}$. Besides the endotherm at 285 °C, with an ethalpic change of 24.2 J·$g^{-1}$, a second endotherm is observed at 215 °C with an enthalpy of 5.2 J·$g^{-1}$. This second endotherm is associated with a solid–solid transformation, which is demonstrated by X-ray diffraction.

The X-ray diffractogram of the sample evaporated from solution at room temperature (Figure 7a) showed the same reflections as that obtained for the original sample and presents a crystalline content of 52%. This crystalline polymorph will be designated form I. Figure 7a–f shows the X-ray diffractograms recorded at different temperatures, between room temperature and 290 °C, for the sample prepared from solution. At temperatures between 210 and 235 °C the reflection at $2\theta$ = 23.4° disappears, and a new reflection appears at $2\theta$ = 21.2°, which increases in intensity with temperature (Figure 7b–d). At 250 °C the X-ray diagram (Figure 7e) is identical to that obtained by cooling the sample from the mesophase (Figure 5b). This crystalline polymorph will be designated form II. At higher temperatures a nematic mesophase is observed (Figure 7f). These results confirm that in this case a solid–solid transformation at 220 °C takes place from one polymorph to another on heating, corresponding to the endotherm observed at 215 °C in the DSC data. However, this solid–solid transformation is irreversible, and once form I is converted to form II by heating, it is not possible to recover form I without redissolving the material. This solvent-induced crystallization has been observed in other semicrystalline polymers like syndiotactic polystyrene,[28,29] and *p*-poly(phenylene oxide).[30]

The published data on PTMTOB transitions correspond to a crystal–mesophase transition at 285 °C and a mesophase–isotropic melt transition at 360 °C,[5] which agree with our results. However, an irreversible solid–solid transformation before the formation of the mesophase has never been mentioned.

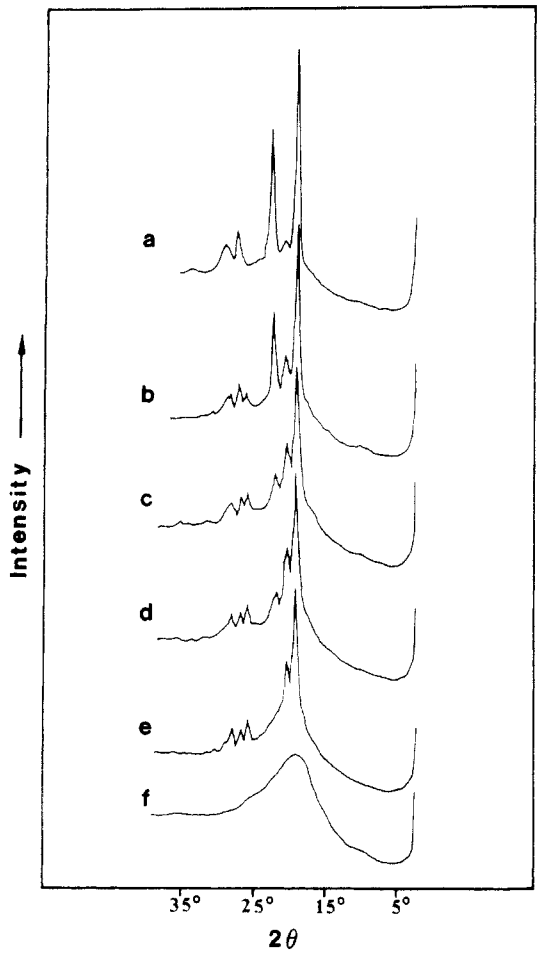



**Figure 7.** X-ray diffractograms of a PTMTOB sample prepared from solution: (a) at room temperature; (b) 210 °C; (c) 220 °C; (d) 235 °C; (e) 250 °C; (f) 290 °C.

Solid-state $^{13}C$ NMR spectroscopy was employed in order to obtain more information about the structure of the two polymorphs of PTMTOB. It has been widely demonstrated[12-19] that differences on polymer chain conformation in the solid state are manifested by significant changes in chemical shifts. Polymorphism in poly(1-butene),[17] syndiotactic polystyrene,[31] polypivalolactone,[18] and isotactic polypropylene[32,33] and in many other polymers[13,14] has been successfully analyzed by $^{13}C$ solid-state NMR spectroscopy and interpreted by considering the $\gamma$-gauche shielding effects.

The central portion of PTMTOB is identical to poly(butylene terephthalate), PBT. Several solid-state $^{13}C$ NMR studies have been carried out on PBT[34,35] and several model compounds.[36] In the study of four PBT model compounds,[36] shown in Figure 8, the structure was determined by single-crystal X-ray diffraction. Two of the model compounds displayed a trans–trans–trans conformation in the alkyl region, whilst the other two displayed a trans–trans–gauche and a gauche–trans–gauche conformation, respectively. The solid-state $^{13}C$ NMR spectra of these model compounds showed that the central methylene carbons that are gauche with respect to the ester oxygen have a chemical shift 3.0–3.7 ppm upfield from the central methylene carbons which adopt the trans arrangement.

Taking advantage of the similarities between the central part of PTMTOB and PBT and the information available for PBT and its model compounds, we have attempted to draw some conclusions about the conformation of the flexible spacer in the two polymorphs of PTMTOB.

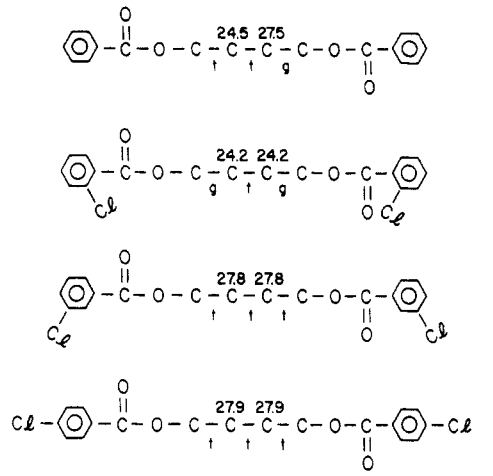



**Figure 8.** Chemical structures of four PBT model compounds.[36] The conformation of the methylene region determined by X-ray diffraction is indicated, as well as the chemical shift of the central $CH_2$ obtained from $^{13}C$ solid-state NMR spectroscopy.

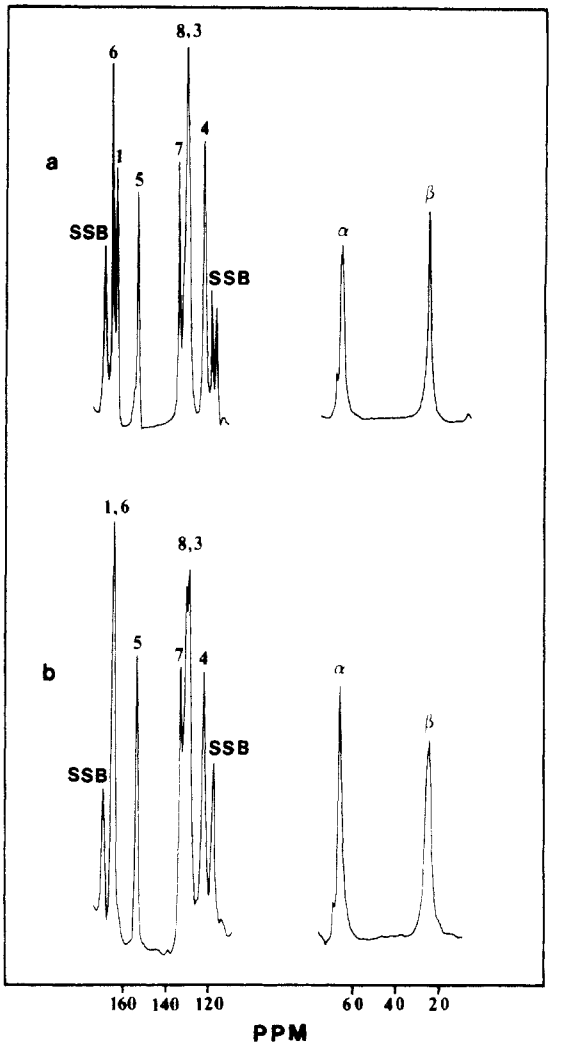



**Figure 9.** CP MASS/DD spectra of PTMTOB at room temperature: (a) form I; (b) form II.

CPMAS/DD spectra of forms I and II have been obtained at different spinning rates (4.2 and 4.7 kHz) in order to obtain the chemical shifts for all of the carbons, without overlapping of the numerous spinning side bands from the aromatic and ester carbons. A TOSS pulse sequence was also used to suppress the spinning side bands. Figure 9 shows the CPMAS/DD spectra of both polymorphs. Chemical shifts and assignments, made using

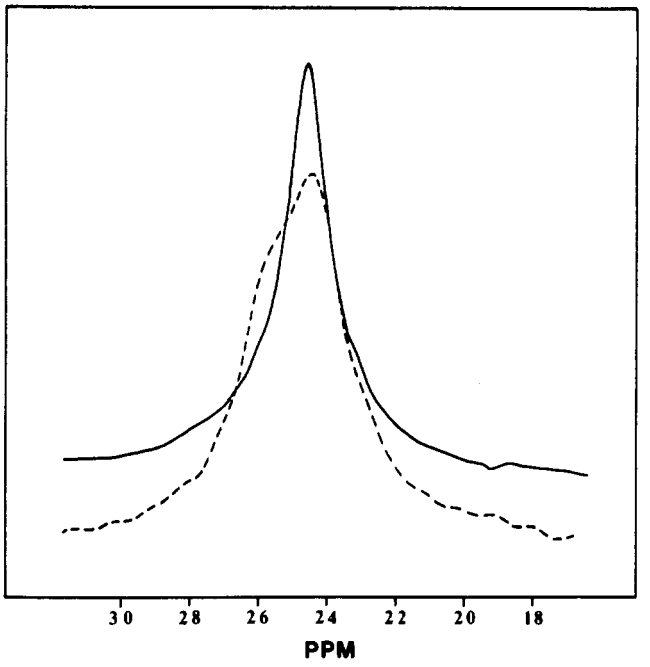



**Figure 10.** Expansion of the central methylene carbon region: (—) form I; (- - -) form II.

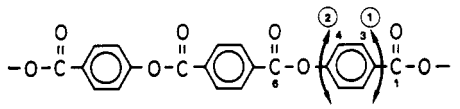


**Figure 11.** Schematic drawing of the mesogenic part of PTMTOB.

model compounds and other thermotropic polyesters[23] are given in Table I. It is clear from both Table I and Figure 9 that the main differences in both polymorphs are in the central $CH_2$, the COO, and some of the protonated carbons of the aromatic rings.

If we compare the alkyl region in both polymorphs, several conclusions can be drawn. Firstly, form I presents only a single chemical shift for the central methylene at 24.3 ppm (compared with 25.2 ppm observed in solution). The same chemical shift is observed in the PBT model compound with a gauche–trans–gauche conformation. Thus, it seems reasonable to assume a gauche–trans–gauche conformation for this polymorph. However, if we compare the chemical shift observed for the central $CH_2$ in form I with that in form II (Figure 10), we observed a shoulder at 26 ppm in form II, although a peak remains at 24.2 ppm. This suggests a more planar conformation in the alkyl region of form II, but not a completely trans arrangement which would lead to a single chemical shift at 27.8 ppm, as for β-PBT and some of the model compounds. A trans–trans–gauche conformation will give rise to two peaks at 24.2 and 27.8 ppm. Therefore, in form II one central methylene remains gauche to the ester and the other adopts a more planar conformation, but not completely trans, to the ester.

Differences in the COO carbons and in some of the protonated carbons of the aromatic rings indicate a different orientation of the terephthaloyl groups in both polymorphs. Rotations around bond 2, in Figure 11, will give rise to different chemical shifts for the ester and the protonated aromatic carbons indicated. Rotation around bond 1 will be restricted by the partial double bond nature of the bond. A more detailed solid-state $^{13}C$ NMR study including variable temperature and the dynamics of molecular motion in both polymorphs is the subject of further work.

## Conclusions

In summary, we have found two crystalline polymorphs in poly[tetramethylene terephthaloylbis(4-oxybenzoate)] which are dependent on the thermal history imposed upon the system. Form I, with a gtg conformation in the flexible spacer, is obtained when the sample is evaporated from solution. Form II, with a more planar methylene chain and with a different orientation of the rings in the mesogen, is obtained by slowly cooling or quenching from the mesophase. The polymer shows an irreversible solid–solid transition at 215 °C and a solid–mesophase transition at 285 °C. The mesophase formed in all of thermal treatments is nematic.

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**Registry No.** (TOBC)(1,4-butanediol) (copolymer), 93706-79-7; (TOBC)(1,4-butanediol) (SRU), 78666-29-2.