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# Small-angle synchrotron study of liquid crystalline poly[oxybis(trimethylene) *p,p'*-bibenzoate]

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**Summary**

Small-angle synchrotron experiments have been performed in two samples of poly[oxybis(trimethylene) *p,p'*-bibenzoate], PDTMB. Owing to the very slow transformation of the mesophase of this polymer into the crystal, only the liquid crystalline phase is present in a PDTMB sample quenched from the melt, while about 30% crystallinity is found in the annealed specimen. The results indicate that the layer spacing peak for the mesophase is very close to a crystal diffraction. This seems to be a general fact in thermotropic polybibenzoates. Moreover, no long spacing has been detected in the quenched sample. On the contrary, the annealed specimen exhibits a long spacing centered at about 16 nm, corresponding to a rather small crystal thickness.

## Introduction

The industrial and academic interest on mesophase structures found in liquid crystalline polymers has grown considerably in recent years. However, owing to the necessity of rigid mesogenic groups, most of the main-chain liquid crystalline polymers exhibit very high transition temperatures. Moreover, the mesophases in these systems usually undergo a rapid transformation into a three-dimensional crystal, leading to narrow temperature intervals of mesophase stability.

The introduction of flexible aliphatic spacers is one of the usual methods for lowering the transition temperatures in thermotropic polymers (1,2), and the stability of the mesophase can be improved by the use of spacers including ether groups (3-5). This is the case of poly[oxybis(trimethylene) *p,p'*-bibenzoate], PDTMB, where the presence of the central oxygen atom in the spacer results on a great inhibition of the mesophase-crystal transformation, although the thermodynamic properties of the liquid crystalline phase of PDTMB are very similar to those of poly(heptamethylene *p,p'*-bibenzoate), P7MB, the analogue polyester with an all-methylene spacer (3-5).

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Thus, the mesophase of PDTMB is stable (at least for several days) at any temperature below its isotropization point, and the properties of this phase can be easily studied at room temperature. However, at very long annealing times at the appropriate temperatures the mesophase of PDTMB is able to undergo the transformation to the crystal (4,6).

The purpose of this work is to study two samples of PDTMB with different phase content by small-angle X-ray scattering (SAXS), using synchrotron radiation, in order to get more insight into the phase structure of this polymer.

**Experimental**

PDTMB was synthesized by melt transesterification of the diethyl ester of *p,p'*-bibenzoic acid (4,4'-biphenyldicarboxylic acid) and 3,3'-oxybis(propanol), the dimer of trimethylene glycol, using isopropyl titanate as catalyst. The details of the preparation and characterization of the dimer and the polymer have been given elsewhere (3,4,7).

A polymer film was prepared by compression moulding at 200°C. Part of this film was subsequently annealed at 70°C during 24 days in a thermostatic bath (sample PDTMB-A). Another part was molten again at 200°C in the synchrotron site and quenched to room temperature (sample PDTMB-Q).

Wide-angle X-ray diffractograms of these two PDTMB samples have been previously reported (6) as well as the DSC melting patterns (4).

Small-angle experiments at room temperature were carried out at Daresbury Laboratory, U.K. (station 8.2) using synchrotron radiation. A sample-detector distance of 1.6 m was employed (spacings range from about 1.5 to 35 nm). Rat-tail collagen (L=67.0 nm) was used for calibration.

**Results and discussion**

The wide-angle X-ray diffractograms of PDTMB reveal that even after 24 days of annealing at 70°C a rather small amount of crystallinity is developed. Thus, from the top diagram in figure 1 and from solid-state NMR experiments a crystallinity of about 30% has been deduced for sample PDTMB-A (6). The lower diffractogram in figure 1, corresponding to sample PDTMB-Q, is characteristic of a smectic mesophase, showing a broad peak (very similar (4) in shape to that of the isotropic melt) and the narrow diffractions corresponding to the smectic layer spacing, with a first order appearing at $2\theta$=5.2±0.2 degrees (d=1.70±0.07 nm). This peak seems to be maintained in the annealed sample, and the question arises whether it represents a crystalline diffraction or it comes from the remaining mesophase. The resolution of the diffractograms in figure 1 is not enough to

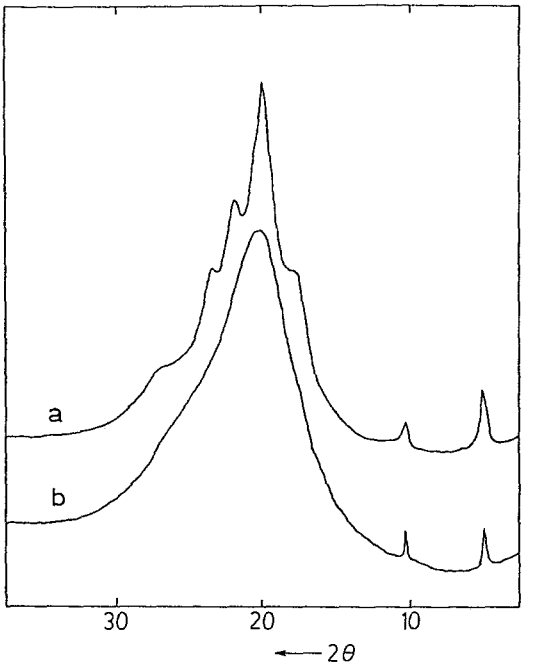


Fig. 1. Wide-angle X-ray diffractograms (6) of annealed (curve a) and quenched (curve b) PDTMB samples.

establish possible differences in peak position.

The synchrotron experiments, with a superior instrumental resolution, show a clear difference between the two samples in the diffraction appearing at intermediate angles, as it is observed in figure 2. Thus, sample PDTMB-Q exhibits a very narrow peak, corresponding to a spacing of 1.618±0.004 nm. On the other hand, the diffraction of the annealed sample is much broader and centered at a spacing of 1.631±0.004 nm. The broadness of this diffraction can be partially attributed to the fact that the transformation of the mesophase into the crystal is likely incomplete (the crystallinity exhibited by a similar sample (6) of P7MB, where the transformation is much faster, is considerably higher). The conclusion is that the crystal gives rise to a repeat distance very close but distinct from the smectic layer spacing.

The similarity between these two spacings has been also found in other thermotropic polybibenzoates (8). Namely, we have recently performed variable-temperature synchrotron experiments monitoring the transformation, under real-time conditions, from

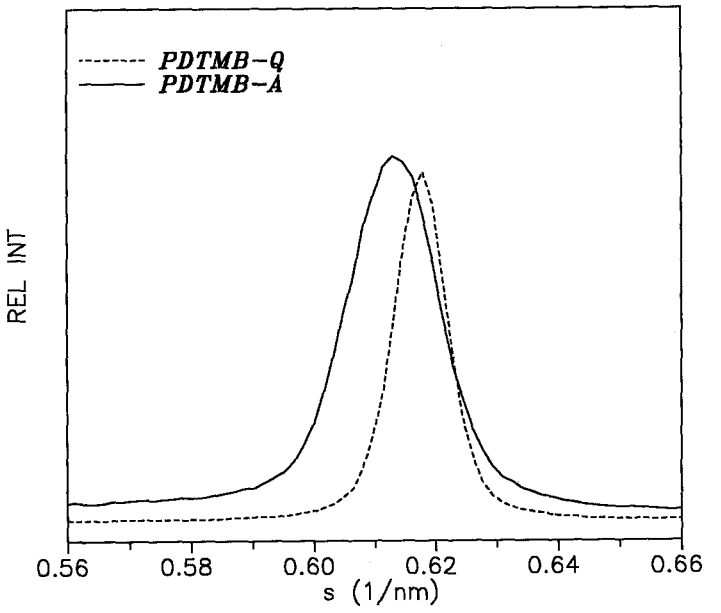


Fig. 2. Intermediate-angle synchrotron profiles as a function of the scattering vector, s, for the two samples of PDTMB.

the mesophase to the crystal in a sample of P7MB. The results indicate that the mesophase peak is also very close to a crystal diffraction (1.709±0.004 and 1.672±0.004 nm, respectively), but now the crystal exhibits a smaller spacing than that of the mesophase and both peaks are of comparable width when the transformation to the crystal is complete (this similarity may be just incidental, as the width of the peaks is determined both by the reproducibility of each layer spacing and by the number of layers (9), and it is expected that these two parameters follow opposite trends for the two phases). In the case of PDTMB, the annealed sample does not represent the crystal totally transformed, and thus the pure shape of the diffraction for this phase is expected to be narrower and probably shifted to a slightly higher spacing than the actual one found for the specimen PDTMB-A.

Regarding the region of real low angles, figure 3 shows the SAXS profiles for the two PDTMB samples. It can be observed that the quenched sample does not exhibit a defined long spacing (this quenched sample was also analyzed with a longer sample-detector distance, and no long spacing was found up to the experimental

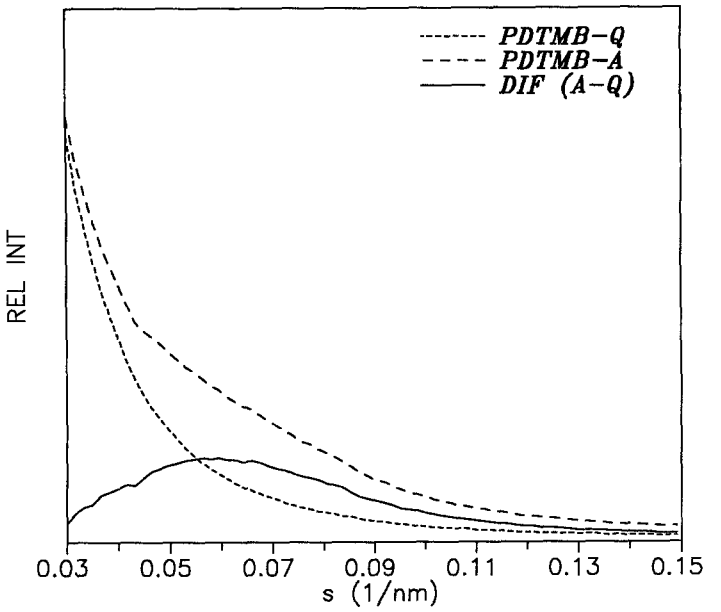


Fig. 3. Small-angle synchrotron profiles as a function of the scattering vector, s, for the two samples of PDTMB. The difference DIF (A-Q) is also shown.

limit of 60 nm). On the other hand, the annealed specimen shows a long spacing not very well defined, which can be explained, at least in part, considering the small crystallinity of the sample. A better definition is obtained in the curve representing the difference between the profiles of the two samples (see figure 3), that clearly shows a long spacing centered at about 16 nm. Having into account the crystallinity of the sample and assuming a simple phase model, the estimated crystal thickness in sample PDTMB-A gives a rather small value which represents only about three monomeric units included in the crystallites.

In conclusion, the synchrotron experiments for the two samples of PDTMB with different phase content indicate that the layer spacing peak for the mesophase is very close to a crystal diffraction. This seems to be a general fact in thermotropic polybibenzoates. Moreover, no long spacing has been detected in the quenched sample. On the contrary, the annealed specimen exhibits a long spacing centered at about 16 nm, corresponding to a rather small crystal thickness.

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**References**

1. Ober CK, Jin J, Fhou Q, Lenz RW (1984) Adv Polym Sci 59: 103
2. Varsney SK (1986) J Macromol Sci Rev C26: 551
3. Bello A, Pérez E, Marugán MM, Pereña JM (1990) Macromolecules 23: 905
4. Bello A, Riande E, Pérez E, Marugán MM, Pereña JM (1993) Macromolecules 26: 1072
5. Pérez E, Riande E, Bello A, Benavente R, Pereña JM (1992) Macromolecules 25: 605
6. Pérez E, Marugán MM, VanderHart DL (1993) Macromolecules 26: 0000
7. González CC, Bello A, Pereña JM (1989) Makromol Chem 190: 1217
8. Unpublished results
9. Strobl GR, Schneider M (1980) J Polym Sci Polym Phys Ed 18: 1343

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