

**Characterization of Deformation Phenomena in Polymers
by Rapid-Scanning Fourier Transform IR (FTIR)
Spectroscopy and Mechanical Measurements
4. Uniaxial Deformation of Amorphous Poly(butylene terephthalate)**

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SUMMARY

The uniaxial deformation and recovery of primarily amorphous poly(butylene terephthalate) (PBT) has been investigated by simultaneous FTIR spectroscopy and stress-strain measurements. Contrary to annealed, crystalline samples the stress-induced transformation of the polymer chains to a conformation deviating slightly from the planar all-trans crystalline β -form has been found almost irreversible.

INTRODUCTION

The reversible change of the crystal structure of PBT with strain has been the subject of numerous publications (HALL and PASS 1976, DESBOROUGH and HALL 1977, BRERETON et al. 1978, SIESLER 1979, STAMBAUGH et al. 1980, TASHIRO et al. 1980, ALTER and BONART 1980). However, so far no spectroscopic data are available on the response of the amorphous domains to the application of stress. FTIR spectroscopy with simultaneous stress-strain monitoring has been recently shown a powerful tool for the characterization of deformation phenomena in polymers (HOLLAND-MORITZ et al. 1980, SIESLER and HOLLAND-MORITZ 1980, SIESLER 1980) and has in the present communication been applied to monitor the structural changes in primarily amorphous PBT films during uniaxial elongation and recovery.

EXPERIMENTAL

The isotropic, amorphous film samples were prepared from PBT chips characterized by an intrinsic viscosity of $[\eta] = 51 \text{ cm}^3\text{g}^{-1}$ determined on solutions in phenol/1,1,2,2-tetrachloroethane (60/40) at 298 K. The polymer was hot pressed at 24.5 MPa and rapidly quenched in ice water. The density of these samples as measured in a gradient column (carbontetrachloride/chlorobenzene) was 1.294 gcm^{-3} . Isotropic, crystalline samples with a density of 1.328 gcm^{-3} were prepared by annealing the amorphous samples for 15 h at 483 K in vacuum. Oriented, amorphous samples were obtained by drawing film strips of the isotropic specimen at room temperature to a draw ratio of $\lambda = 5$ to 6. Oriented, crystalline samples were prepared by drawing sections of the isotropic, amorphous film samples in hot water (363 K) to a draw ratio of $\lambda = 4$. The oriented samples

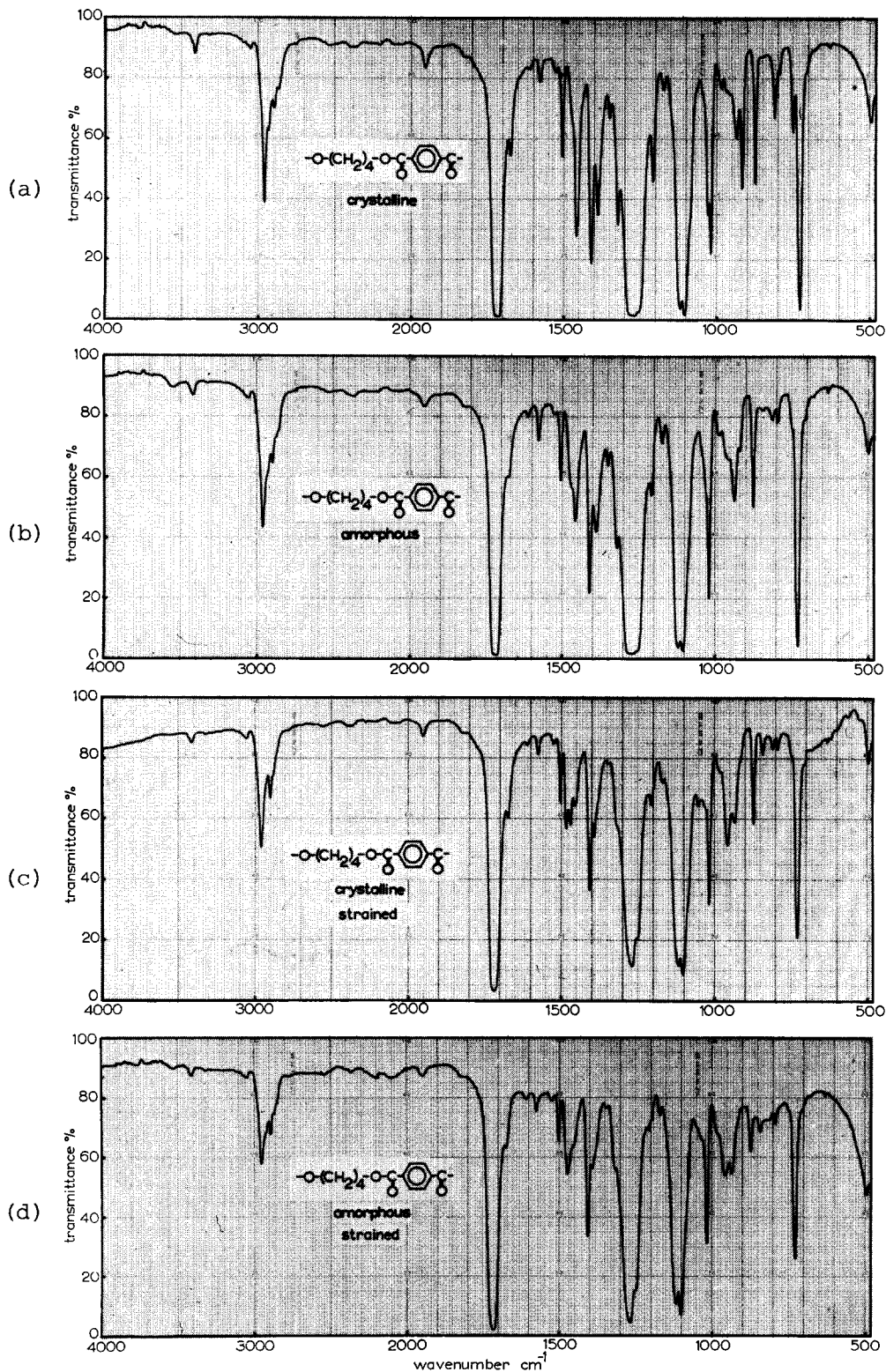


FIGURE 1 IR spectra of PBT films: (a) isotropic, crystalline, (b) isotropic, primarily amorphous, (c) oriented, strained, crystalline and (d) oriented, strained, primarily amorphous sample.

were then annealed at 483 K under vacuum for 15 h. The film strips used for the simultaneous FTIR and stress-strain measurements were cut 15 mm long and 10 mm wide from commercial PBT film (ULTRADUR B4550, BASF AG) with a thickness of 0.04 mm and a density of 1.300 g cm^{-3} . The elongation rate was 1.66% per second and 12-scan spectra were taken at 300 K in 14-second intervals on a NICOLET 7199 FTIR system with a resolution of 4 cm^{-1} . The instrumental details of the electromechanical apparatus used for these deformation experiments have been described previously (SIESLER and HOLLAND-MORITZ 1980).

RESULTS AND DISCUSSION

In Fig. 1 (a)-(d) the spectra of isotropic, crystalline and primarily amorphous PBT films are shown alongside the spectra of the corresponding uniaxially drawn samples under strain.

The change from an isotropic, crystalline to an isotropic, amorphous state is accompanied by a significant decrease of the $1460/1455 \text{ cm}^{-1}$ [$\delta(\text{CH}_2)$] and the 917 cm^{-1} [skeletal/ $\gamma(\text{CH}_2)$] absorption bands which are characteristic of a near gauche-trans-gauche conformation of the aliphatic segments in the crystalline α -phase (WARD and WILDING 1977) and an increase of relatively broad absorption bands at about 1472 cm^{-1} and 960 cm^{-1} .

The IR spectra of uniaxially oriented, crystalline and amorphous PBT films under stress are shown in Fig. 1 (c) and (d). As reported in previous investigations it can be derived from the intensity changes in the spectra of Fig. 1 (a) and (c) that under tension the near gauche-trans-gauche conformation of the crystalline α -form is transformed to the all-trans conformation of the β -modification as indicated by the appearance of the $1485/1470 \text{ cm}^{-1}$ [$\delta(\text{CH}_2)$] and the 960 cm^{-1} [skeletal/ $\gamma(\text{CH}_2)$] bands. This conformational change has been shown to be almost completely reversible with stress (BRERETON et al. 1978, SIESLER 1979, TASHIRO et al. 1980, ALTER and BONART 1980).

Upon drawing the isotropic, amorphous sample the absorption bands at $1460/1455 \text{ cm}^{-1}$ and 917 cm^{-1} decrease and bands at $1475/1470 \text{ cm}^{-1}$ (which can be resolved from the broad band at about 1472 cm^{-1} by polarization measurements) and 960 cm^{-1} increase in intensity. The spectra of the strained, crystalline and amorphous samples [see Fig. 1 (c) and (d)] are very similar with the only difference that the 1485 cm^{-1} band (elongated, crystalline β -form) is shifted to 1475 cm^{-1} in the strained, amorphous specimen. This behaviour can be qualitatively understood on the basis of the assignment of the bands associated with the CH_2 -bending vibration. By inspection of the potential energy distribution (STACH and HOLLAND-MORITZ 1980) in terms of force constants of the respective frequencies of the crumpled α and elongated β crystal modifications one can deduce that the higher frequency band in both forms (1460 cm^{-1} and 1485 cm^{-1} , respectively) is mainly caused by interaction of the methylene groups adjacent to the oxygen atoms with their neighbourhood. The lower frequency bending mode (1455 cm^{-1} and 1470 cm^{-1} , respectively) can be predominantly assigned to vibrations of the central methylene groups in trans-conformation having methylene groups as neighbours. The occurrence of the

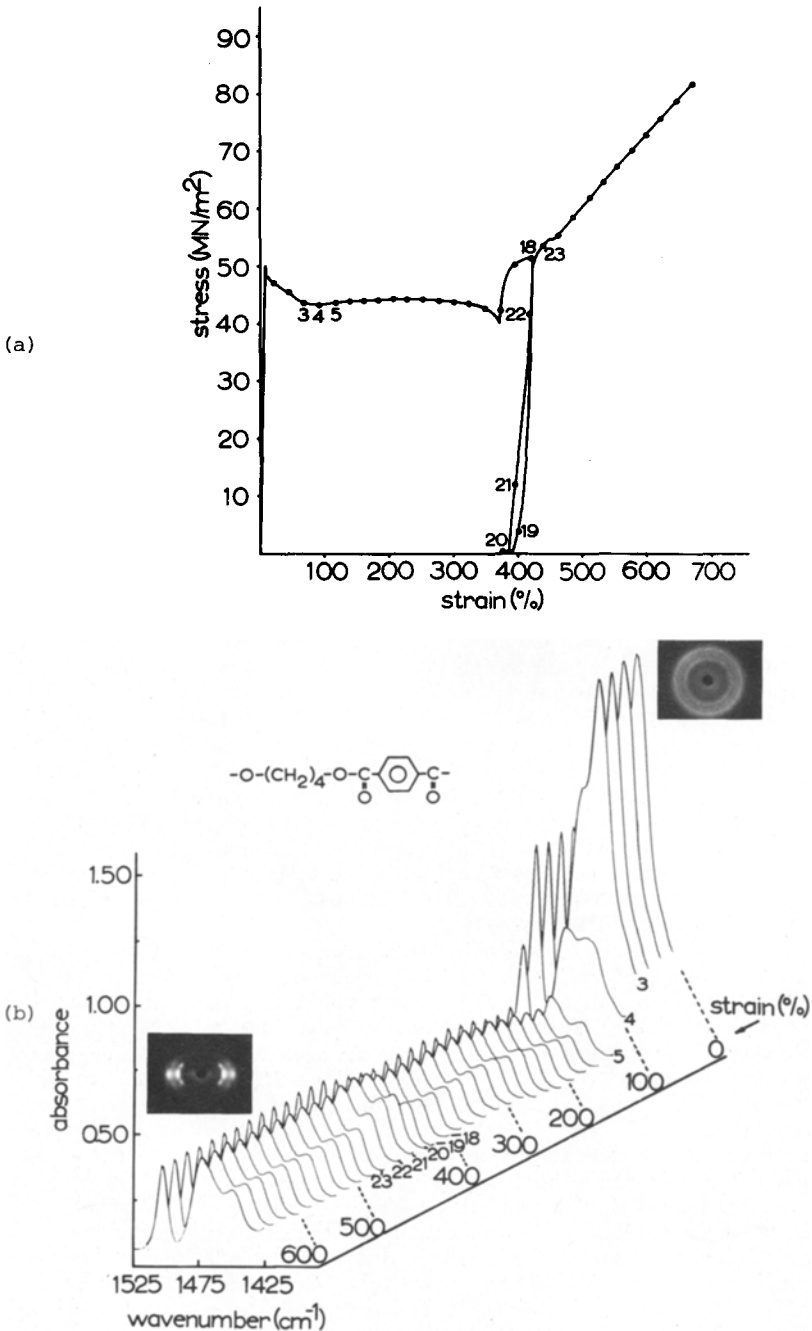


FIGURE 2 Simultaneous stress-strain and FTIR measurements during uniaxial deformation and recovery of a primarily amorphous PBT film: (a) stress-strain curve of the mechanical treatment (elongation rate: 1.66%/s), (b) FTIR spectra in the 1500-1400 cm⁻¹ $\delta(\text{CH}_2)$ region alongside the wide-angle X-ray diagrams of the original and a 600% drawn sample.

higher frequency band at 1485 cm^{-1} strongly depends on the planarity of the molecular skeleton. This effect can also be observed in the IR spectra of various polyesters measured at different temperatures (HOLLAND-MORITZ 1973). Thus, we conclude that the shift of the 1485 cm^{-1} band to 1475 cm^{-1} in the spectrum of the drawn amorphous specimen is caused by a conformation in which the CH_2 groups adjacent to the ester functionality deviate somewhat from the all-trans conformation of the almost planar β -form.

A detailed picture of the response of amorphous PBT film to the applied stress and any reversibility of the structural changes during uniaxial elongation and recovery in cyclic loading-unloading processes can be derived from simultaneous FTIR and stress-strain measurements (Fig. 2). For the representation of the spectroscopic effects the most sensitive $1500\text{-}1400\text{ cm}^{-1}$ $\delta(\text{CH}_2)$ region has been selected. As a further illustration of the orientation effects the wide-angle X-ray diagrams of the original sample and the 600% elongated sample have been included in Fig. 2 (b). The stress-strain curve of the applied mechanical treatment is shown in Fig. 2 (a). The initial steep rise of stress with strain is followed by a plateau region between 50 to about 350% strain. In this region the neck whose formation starts at a threshold value of about 50 MNm^{-2} propagates through the entire film specimen with a concomitant reduction in sample thickness from 0.04 mm to about 0.015 mm. The spectroscopic changes corresponding to this necking region are illustrated in the spectra 3 to 5 [Fig. 2 (b)] where the neck has been monitored with a laser reference system to move through the sampling area. Apart from a general intensity decrease as a consequence of the reduction in sample thickness the intensities of the $1460/1455\text{ cm}^{-1}$ bands (not resolved here) of the crystalline, crumpled α -modification drastically decrease while the intensity of the $1475/1470\text{ cm}^{-1}$ band complex exhibits a relative increase. This result can be attributed to the predominant formation of a fibrillar structure with the abovementioned imperfect all-trans conformation of the aliphatic chain segments. Once the neck has completely moved across the specimen (at about 350% strain) stress increases linearly with strain. To study the reversibility of the deformation the sample has then been subjected to an unloading-loading cycle. The spectra taken during this cycle have been labeled 18 - 23 and the small intensity changes of the $1460/1455\text{ cm}^{-1}$ bands relative to the $1475/1470\text{ cm}^{-1}$ bands and the $\nu(\text{C-C})$ aromatic ring reference band at 1505 cm^{-1} clearly reflect that there is only an extremely small portion of polymer chains reversibly recovering to the crumpled conformation upon unloading. This is also demonstrated in the wide-angle X-ray diagram of such an unloaded sample where the $(\bar{1}04)$ reflex of the elongated crystal β -modification is still observable alongside the corresponding reflex of the residual α -form. These data lead to the conclusion that under the experimental conditions (elongation rates varied between 0.26% and 3.33% per second) the reversibility of the conformational transitions occurring during elongation is strongly hampered. For the polymer chains in the amorphous domains this can be understood in terms of the lack of a driving force such as the improved molecular packing efficiency of the α -crystal form (ALTER and BONART 1980). The loss of the reversibility of the con-

formational change for the small crystalline regions distributed in the amorphous domains may be readily explained by entanglement of the polymer chains in the amorphous matrix during the elongation process.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the experimental assistance of H. Devrient and the permission of Bayer AG to publish the experimental data. K. H.-M. thanks the Deutsche Forschungsgemeinschaft for the financial support of part of this work.

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Received January 12, 1981

Accepted January 15, 1981