

Study of the Cold Drawing of Arnitel by *In Situ* Simultaneous Small- and Wide-Angle X-Ray Scattering Techniques.

A. Nogales, T. Ezquerro, I. Sics, and F. Baltá-Calleja (*I. Estructura de la Materia, CSIC, Spain*)

Abstract No. noga2054

Beamline(s): X3A2, X27C

Introduction: Block copolymers of poly(butylene terephthalate) (PBT) and poly (tetramethylene oxide) PTMO are poly (ether esters). They consist on hard segments formed by the PBT blocks and soft segments consisting of PTMO. In these copolymers, the hard segments tend to form rigid domains, where crystallization can take place, embedded in an amorphous matrix. The behaviour of these materials during mechanical deformation is highly dependent on the microphase separation. The behaviour of these systems under mechanical stress is of extraordinary technological interest. It is known that, PBT suffers a solid-state phase transition on its crystalline phase when stretched above a given strain. The beamtime was used to investigate, in-situ, the drawing behavior of PBT-PTMO block copolymers and compare to that of PBT.

Methods and Materials: Arnitel samples, (ARNITEL EM 550, DSM), spun at 50 mpm were used in this study. The system is based on PBT (hard segments) and PTMO (polytetramethylene oxide) - soft segments. The content of hard blocks based on PBT - 50%. The average molecular weight of both hard and soft blocks is approx. 1500. The overall molecular weight is approx. 25.000. The melting temperature of this Arnitel is 185°C. It can be extruded at 220°C. Two-dimensional SAXS and WAXS patterns were recorded on Fuji HR-VTM image plates (200 x 250 mm) with sample to detector distances of 130 and 21.5 cm respectively. The WAXS image plate contains a central hole with a diameter of 2cm, allowing the passage of the SAXS signal. A FUJI BAS2000 IPTM image plate scanning station digitized the image recorded on the plates. The patterns were digitized at a resolution of 100 μm /pixel.

Results: (WAXS) Before drawing, the WAXS patterns consist on circular reflections corresponding to the Bragg reflections of the α modification of PBT. During the cold drawing on the elastic region area, the Bragg reflections apparently are not deformed, indicating that there is not apparent orientation on the crystals. However, as soon as the elastic deformation region is finished, an arcing of the Bragg reflections is produced, which finally leads to a two spot diagram. For strains between 20% and 50%, the two spot pattern coexists with the ring pattern. However, for strains higher than 50%, only the two-spot diagram is observed. If one analyzes the WAXS pattern into more detail, it is possible to observe that, the two spots are not located exactly in the same q -position than that of the previous rings, but there exist a small displacement. Previous works on the deformation behaviour of PBT have shown that, there exist a reversible solid-state transition between the α and the β forms of PBT induced by extension and relaxation of the extension. This transformation occurs when the α form is stretched about 12%. (SAXS) From the inspection of SAXS patterns, a broad circular maximum is observed, demonstrating that the Arnitel sample, before drawing is unoriented. Upon an increase in strain, the broad ring starts deforming, even in the region of elastic deformation. When the elastic region is finished the SAXS patterns, the broad maximum disappears and a two-lobe pattern develops, showing different features in the meridian and in the equator. Lying on the equator, there is a pair of broad reflections moving outward from the beam stop as the strain is increased. On the meridian, one may find a narrow streak that is becoming sharper as the strain increases.

Conclusions: Similarly to what happened in PBT, the stretching of block copolymers (Arnitel) induces a solid-state phase transition in the crystalline phase of PBT. However, due to the presence of soft segments, the percentage of stretching necessary to provoke this transition is higher, since some of the applied deformation force is absorbed by the soft segments.

Acknowledgments: Financial support from the Fullbright foundation for cooperation between Spain and The United States is gratefully acknowledged.

References:

- A. Lilaonitkul, A., J.C. West and S.L. Cooper. *J. Macromol. Sci.*, **B12**, 563, 1976.
- G. Wegner, T. Fuji, W. Meyer and G. Lieser. *Angew Makromol Chem.*, **74**, 295, 1978.
- K. Tashiro, Y. Nakai, M. Kobayashi and H. Tadokoro *Macromolecules* **13**, 137, 1980.

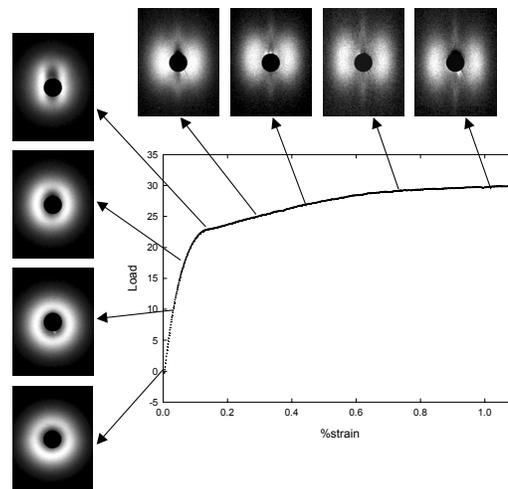


Figure 1. Two-dimensional SAXS patterns for Arnitel, at various stress levels, as indicated.