Polymer Bulletin 1, 551–556 (1979)

Polymer Bulletin

Highly Oriented Block Copoly(ether ester) by Solid State Extrusion

Michael Dröscher and Walter Regel

Institut für Makromolekulare Chemie der Albert-Ludwigs-Universität, Hermann-Staudinger-Haus, Stefan-Meier-Straße 31, 7800 Freiburg i. Br., Federal Republic of Germany

SUMMARY

A segmented block copoly(ether ester) based on poly(butylene terephthalate) as "hard" segments and on poly(oxytetramethylene) as "soft" segments was highly oriented by cold flow extrusion. Upon further stretching of the high modulus material, the crystallites are tilted by 34° with respect to the stretching direction and a four point small angle X-ray pattern is obtained.

INTRODUCTION

The properties of highly oriented, high modulus polymers have attracted a significant interest. The investigations carried out are mainly focused on homopolymers like polyethylene (ODELL et al. 1978, MEAD and PORTER 1978, GIBSON et al. 1978) or poly(oxymethylene) (BREW and WARD 1978).

Recently, a new class of material, the segmented block copoly(ether esters) consisting of crystallizing sequences of poly(tetramethylene terephthalate) (PBT) as the "hard" segments and sequences containing the noncrystallizing "soft" segments of poly(oxytetramethylene) (POTM), have become of comercial and scientific interest (HOESCHELE and WITSIEPE 1973, HOESCHELE 1974, CELLA 1973, SEYMOUR et al. 1975). The morphology of these copolymers is strongly dependent on the mechanical and thermal history and on the chemical structure of the sample (WEGNER et al. 1978).

Now, we have employed the method of extrusion below the melting temperature of the polyester segments for the orientation of the PBT-POTM-copolymer.

EXPERIMENTAL SECTION

The polymer sample was kindly supplied by Toyobo Co., Ltd., Otsu City, Japan. It has been described and characterized in detail by WEGNER et al. (1978) where

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it is called B-1-n-14. The average molecular weight of the POTM and PBT sequences is 1000 and 2700, respectively. The mole fraction of PBT is 0.92, the specific viscosity was determined as 1.50 dl/g.

For the cold flow extrusion experiment a homogeneous rod was prepared by melt extrusion through a Göttfert Rheograph 2000 capillary rheometer at 230°C. After machining the rod to the appropriate size, the material was pressed at a rate of 0.01 mm/sec through a rectangular slit with trumpet-like inlet, 1 to 10 mm in cross-section and 50 mm long. At the extrusion temperature of 195°C a pressure of nearly 200 MPa was necessary. The extruded material was transparent and isotropic in the direction perpendicular to the extrusion direction.

By use of a microtom 100 microns thick slices of the cold extruded material were cut for the stress-strain experiments which were conducted with an Instron 1122 apparatus at ambient temperature, stretching the sample 1 mm/min. X-ray investigations were performed on 0.5 mm thick samples with Cu-Kα radiation using a Kiessig camera for the small angle scattering. All defraction patterns were recorded on flat film.

D.s.c. measurements were run with a DSC-2 (Perkin-Elmer Co.)

RESULTS and DISCUSSION

The properties of the cold extruded PBT-POTM-copolymer sample A are listed in TABLE 1, together with the subsequently stretched sample B and the isotropic melt crystallized and well annealed sample C.

TABLE 1

Influence of the sample history on the properties for a segmented PBT-POTM-copolymer

Sample	History	T_m a)/°C	Δh_m b)/Jg^{-1}	w_c c)
A	cold extruded at 195°C	215	44.1	0.42
B	A stretched to 230 %, recovered at constant strain, residue strain 166%	214	49.5	0.48
C	melt crystallized, 24 hours at 205°C annealed	216	55.5	0.54

a) melting temperature (melt endotherm maximum)
b) heat of melting
c) weight fraction of crystallized hard segments

The melting temperature is only to a small amount influenced by the thermal and mechanical treatment. The heat of melting and, thus, the degree of crystallization increases upon stretching, the crystallinity of the oriented samples A and B being lower than that of the well annealed sample C.

The wide angle (WAXS) and the small angle X-ray (SAXS) diagrams of sample A are presented in FIGURE 1. Both patterns reveal the high orientation of the sample. The WAXS pattern is consistent with the so-called α-structure of PBT (DESBOROUGH and HALL 1977). The corresponding scattering diagrams for sample B are shown in FIGURE 2.

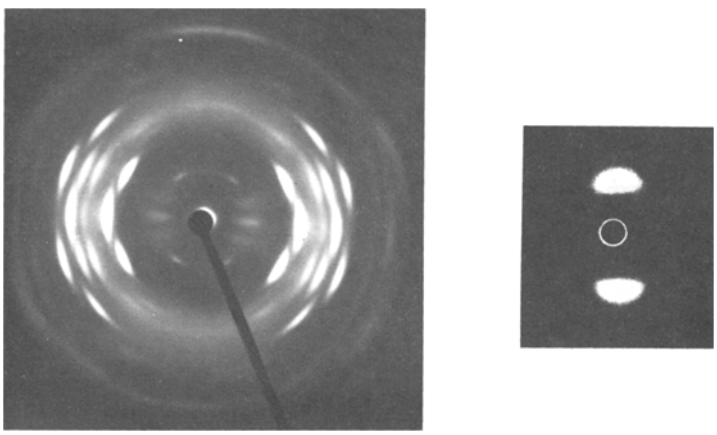

FIGURE 1 WAXS and SAXS patterns for sample A

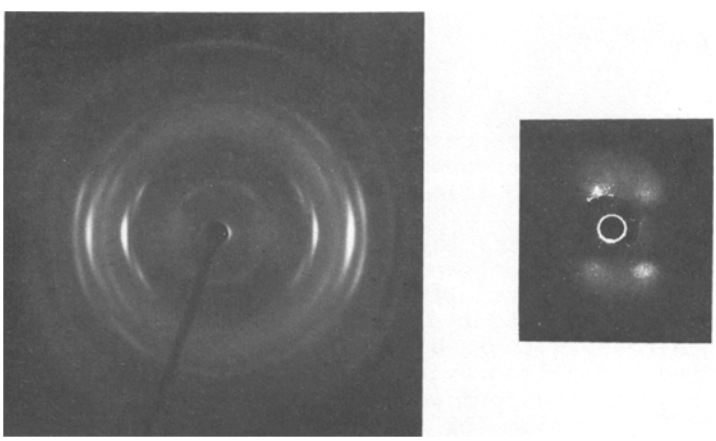

FIGURE 2 WAXS and SAXS patterns for sample B

Obviously, the arcing observed in the WAXS pattern of sample B is more significant than in the case of sample A. Thus, upon stretching the orientation of the crystallites in c-direction is decreased.

The most important structure change during the stretching process is documented by the transformation of the two point SAXS pattern into a four point pattern. In FIGURE 3 a very schematic graph is presented for explanation.

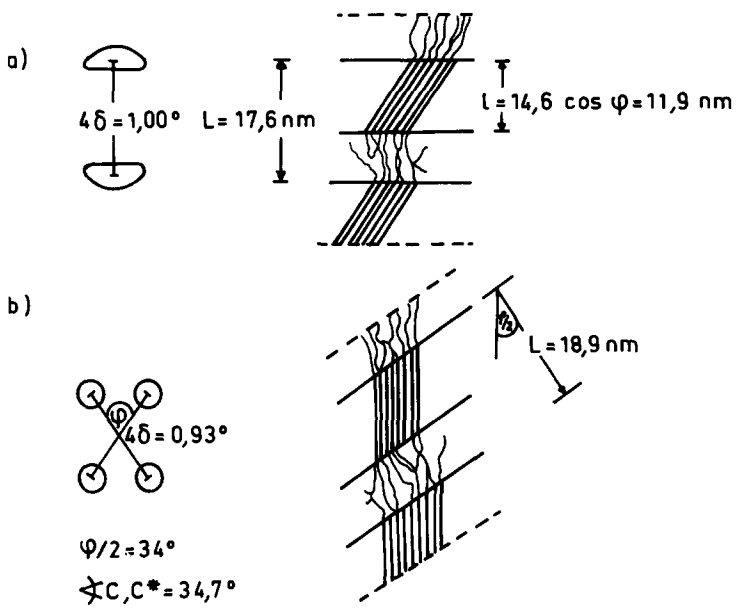

FIGURE 3 Schematic representation of the SAXS pattern and the corresponding structure for samples A (a) and B (b), L = long spacing

In sample A (FIGURE 3a) the crystallites are stacked with their ab-plane perpendicular to the extrusion direction c. In the triclinic lattice of PBT the chains are inclined to the extrusion direction. Applying stress in the c-direction, the crystals are sheared and tilted by about 34°, the angle being determined from the four point pattern in FIGURE 3b. The theoretical value for the angle between the c and the c^*-direction is 34.7°, in good agreement with the experimental result.

Similar four point patterns were observed in several other cases, e.g. for well oriented polyethylene (KAJI et al. 1978), where the tilt angle of the lamellae is 35°, too.

Upon stretching the long period L increases from 17.6 to 18.9 nm. The value for the unstretched sample is in good accordance with the data reported by WEGNER et al. (1978) for a sample crystallized at a supercooling of 20°C. The supercooling normally is defined as temperature difference between the melting temperature and the crystallization temperature; in our case, the latter has to be defined as extrusion temperature.

The paracrystalline structure or the lateral dimensions of the crystallites are not discussed in this paper.

A typical stress-strain plot for sample A, where the stretching direction is parallel to the extrusion direction is shown in FIGURE 4.

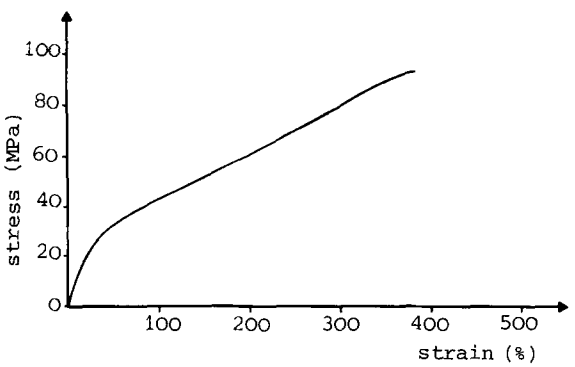

FIGURE 4 Stress vs. strain plot for a PBT-POTM-copolymer extruded below the melting temperature of the polyester blocks. Strain rate 1 mm/min, ambient temperature

Up to an elongation of 10 to 15% the deformation is reversible, the Young's modulus being about 220 MPa. At higher strain the sample starts to flow and the break occurs at a strain of about 400%. The ultimate stress is of the order of 90 to 100 MPa. As shown in the previous chapter, the flow is partially due to the tilting of the crystallites.

CONCLUSION

Employing the cold flow extrusion process on a PBT-POTM-copolymer high modulus material is obtained, where the ab-planes of the crystallites are oriented perpendicular to the extrusion direction. Upon stretching of the sample in the extrusion direction the chains in the crystallites are tilted towards the stretching direction and the crystallites are sheared by 34°, the angle between the c and the c*-direction.

ACKNOLEDGEMENT

The authors acknoledge financial support by the Deutsche Forschungsgemeinschaft.

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Received May 1o, 1979