



	Experiment title: Studies of local reorganization in poly(trimethylene terephthalate) quasi 2D-spherulites during fast heating	Experiment number: SC-2778
Beamline: BM26B	Date of experiment: from: 02/10/2009 to: 05/10/2009	Date of report: 15.07.2010
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Report:

Segmented thermoplastic elastomers consisting of alternating hard and soft segments are melt-processable materials with elastomeric properties at service temperature [1,2]. This is due to the phase separated morphology, which is induced by the thermodynamical incompatibility of the hard and the soft segments [3]. These polymers have a phase-separated morphology depending on the molecular weight of the polyether and polyamide structural units [4,5]. The moduli of these materials range from 10 to 30 MPa, the yield strain is (in-del) between 100 and 200% and strains at break are above 1000%. Furthermore, the materials exhibit good recoverability, low permanent set and low mechanical hysteresis. On the other hand, at high polyamide ratios, the hard phase

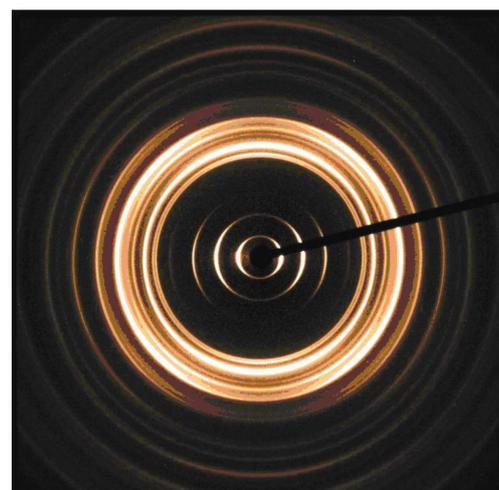


Figure 1. 2D X-ray pattern of oriented model compound MeOProp-OXA₂₆-PropOMe. The fiber axis is vertical.

becomes more and more interconnected and polymer properties change to those of typical thermoplastics [6]. A 2D diffractogram of the uniaxially-oriented MeOProp-OXA₂₆-PropOMe is presented in Figure 1. The fiber pattern was indexed to an orthorhombic unit cell with $a = 5.05 \text{ \AA}$, $b = 10.00 \text{ \AA}$ and $c = 21.98 \text{ \AA}$. With two monomers per unit cell the calculated density of the crystal amounts to 1.06 g.cm^{-3} . The 2D WAXD pattern exhibits a series of strong equatorial peaks that can be assigned to a smectic like structure, the period of which is close to the long molecular dimension (c -direction). The two other directions likely correspond to the molecular width within the hydrogen-bonded planes (a -direction) and an integer number of the hydrogen bonded sheet thickness (b -direction).

The WAXD curves of the model compound and the corresponding segmented poly(ether amide) are depicted in Figure 2. The diffraction peaks of the bisoxalamide model compound are almost absent in the scattering

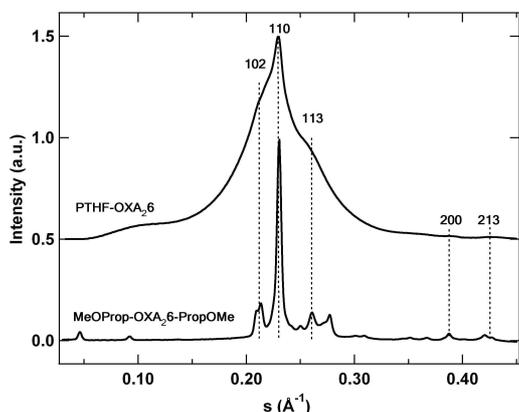


Figure 2. WAXD curves of MeOProp-OXA26-PropOMe and the corresponding segmented poly(ether amide) PTHF-OXA26.

of stacking of the phase-separated domains. Based on the fibrillar structure observed by AFM, the SAXS curves can be interpreted in terms of a 2D model, in which it is assumed that the crystalline domains are much longer in one direction than in the two others and can therefore be considered as virtually infinite fibrils. The micro-structural parameters of the samples such as the long spacing (L_B), crystal thickness (L_c) and amorphous domain thickness (L_a) can be derived from the SAXS curves in the approximation of hexagonal packing of the fibrillar crystals. The L_B corresponds to the position of the Bragg peak (Figure 3a) whereas the crystalline domain thickness (L_c) was calculated from the position of the form factor (FF) visible in the medium-angle range (Figure 3b).

The long spacing L_B and the thickness L_c increase with the number of methylene groups in the hard segment. The amorphous layer thickness L_a also increases with increasing spacer length, which is somehow unexpected since the soft segment length in all polymers is identical. A possible explanation can be that the segment tilt influences the local density of the PTHF at the crystal-amorphous interface, which results in a change of the total amorphous layer thickness.

of the corresponding copolymer and only a broad amorphous halo originating from the PTHF phase is visible. This can be explained by the small crystal size along the c -direction. The maximum on top of the amorphous halo at 4.36 \AA corresponds to the 110 peak whereas the small maximum at 2.57 \AA is the 200 peak. Since the reciprocal space vectors corresponding to these diffraction peaks are oriented perpendicular to the c -direction, the crystal size along these directions can be larger.

Room-temperature SAXS curves are presented in Figure 3a. The SAXS curves show one interference maximum indicative

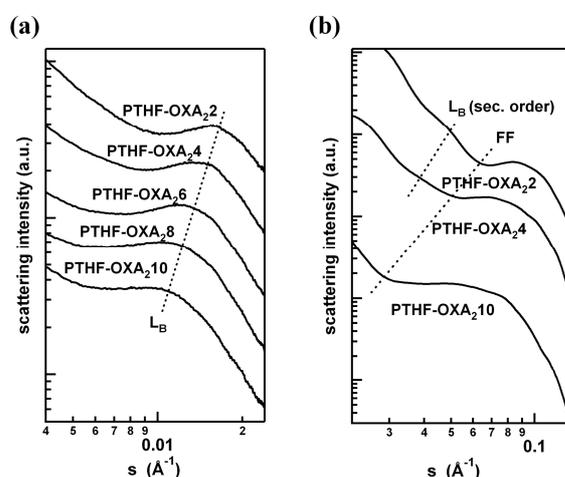


Figure 3. (a) SAXS intensities corresponding to bisoxalamide-based segmented poly(ether amide)s. (b) Medium-angle scattering intensities for bisoxalamide based segmented poly(ether amide)s extracted from WAXD curves.

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