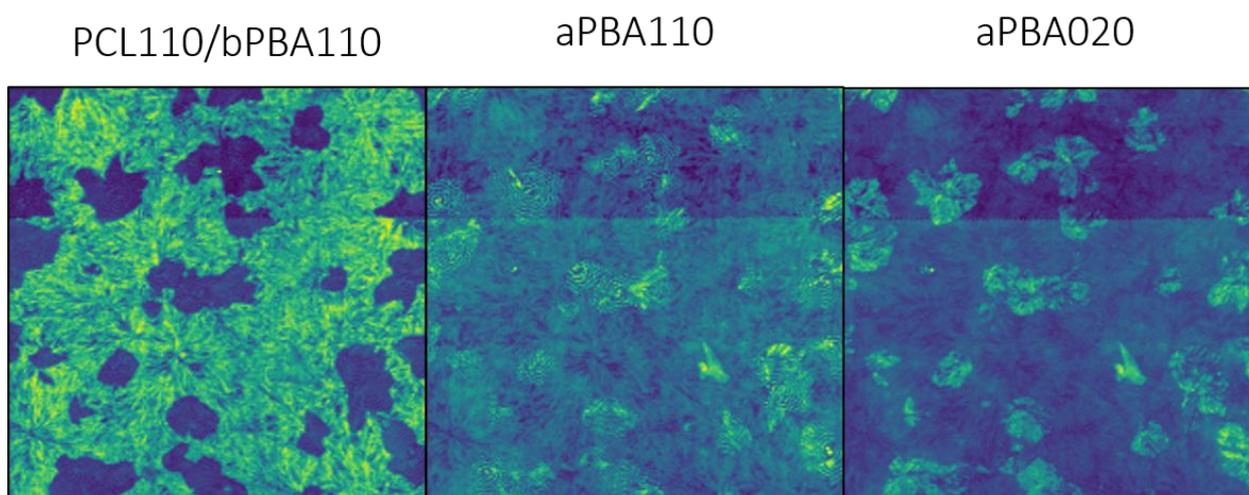


In the course of the experiment, samples of bottlebrush elastomers with crystallizable side chains made of polycaprolactone (PCL with degree of polymerization 13) were studied. TPUs are linear block copolymers consisting of polycaprolactone and poly(1,4 – butylene adipate) (PBA) with different ratios. The hard block are diol-urethane fragments synthesized from aromatic diisocyanates (2,4-toluene diisocyanate) and aliphatic (1,6 – hexamethylenediisocyanate).

For microfocused X-ray diffraction analysis, free-standing films of both TPUs and PCL bottlebrush elastomers were needed. After solvent evaporation at various ambient temperatures (14, 23, 32°C), the semi-crystalline films with spherulitic morphology were detached from glass substrates by floating them off onto hydrofluoric acid solutions (2 wt%) and were lifted with foil frames. Microfocus X-ray experiments were implemented at the microdiffraction facility of the ID13 beamline using a wavelength λ of 0.95 Å. The monochromatic X-ray beam size at the focus point was 500 nm along both axes. The distance between sample and detector was 280m that allows us to detect SAXS and WAXS simultaneously. The 2D diffractograms were recorded with a Eiger4M CCD detector (active area: 155.2 mm x 162.5 mm; pixel size=75 μ m). The scattering vector norm was calibrated with an aluminum oxide standard. The samples were scanned in two dimensions with 100-200 in each direction. Calibration, radial and azimuthal integrations and map constructing were performed using home-built programs based on pyFAI package (Python). 2D intensity maps represent the average intensity distribution of 2D diffractograms in the selected radial and angular range. Orientation maps determine the angle with the highest intensity in the selected radial range and put a line segment in this direction.



It has been shown that TPU with PBA/PCL ratio of 20/80 forms ring-banded and non-banded spherulites in the same film. Ring-banded consists of beta-PBA crystals with (100) growth direction, while non-banded spherulites are alpha-PBA with (020) growth direction.

