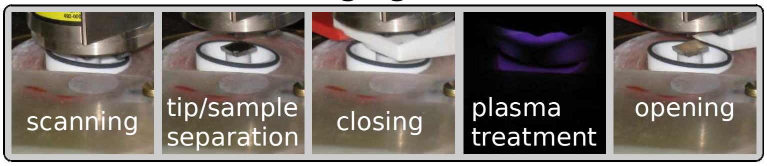
Quasi in-situ SFM nanotomography as a powerful tool for understanding complex morphologies in thin polymer films

Markus Hund[1], Alexandra Sperschneider[2], Clemens Liedel[3], Axel H.E. Müller[2], Larisa Tsarkova[1], Andreas Fery[1,5] and Alexander Böker[3,4]

[1]Physikalische Chemie II, [2]Makromolekulare Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany
[3]Makromolekulare Materialien and Oberflächen and [4]DWI an der RWTH e.V., RWTH Aachen University, D-52056 Aachen, Germany
[5]Bayreuther Zentrum für Kolloide und Grenzflächen, D-95440 Bayreuth, Germany

Quasi in-situ SFM imaging



- Low pressure plasma technology as superior ablation method to remove even sensitive material step-by-step
- Straightforward calibration and nanotomographic examination inside the SFM (no time-consuming re-location protocols)
- Mechanical property mapping by SFM TappingMode™ imaging (or other SFM-modes like HarmoniX®) without significant stress to the sample (other methods are normally restricted to intensity-only mapping)
- Compatibility with commercial SFMs; here a retrofitted NanoScope® IV system (Veeco Instruments Inc.)
- Data acquisition time roughly determined by the time needed to scan a image series
- QIS-technique has full automation capabilities
- Flexible patented technology (DE 102004043191 B4 and U.S. patent application 20080229812 A1)

Post-processing

- Registration and combination of topography data $z_n(x,y)$ and phase data $\varphi_n(x,y)$ (material property) to a 3D image Φ_n by self-developed C++ software package and bash scripting
- General voxelization algorithm works also for non-linear etch behavior: In contrast to the algorithm found in literature where Φ_n is sampled at the points [x,y,z_n(x,y)-n<d>] spanning a regular mesh within the specimen (Magerle, R., Phys. Rev. Lett. 85, 2749, 2000), here a optimized algorithm takes into account possible non-linear etch behavior. The assumed constant thickness of a removed layer <d> is replaced by a etch-time dependent ablation function a(t)
- The material-specific ablation function a(t) is based on high-quality QIS-SFM calibration data sets and can be derived from film thickness differences (D_n-D_0) vs. etch time plots (not shown here)
- The displayed isosurfaces enclose all parts of a volume that are brighter than a specific threshold value. This can be interpreted as specific materials in the volume.
- Visualization of the 3D raw data and further processing with commercial 3D software, AMIRA, Visage Imaging Inc., USA
- Inherent high depth-resolution (<1 nm) because the z-coordinate is calculated from SFM-data and high-resolution depth profiling using low pressure plasma

$$\Phi_n[x, y, \overbrace{z_n(x,y)+a(t_n)}^{z}] \quad with \quad a(t_n)\le 0$$

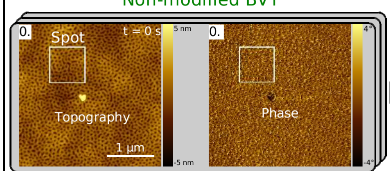
References: Hund et al., Rev. Sci. Instrum., **78**, 063703 (2007), Olszowka et al., Soft Matter, **2**, 1089 (2006) and Olszowka et al., ACS Nano, **3**, 1091 (2009).

Microphase separation in terblock copolymer[(a)]

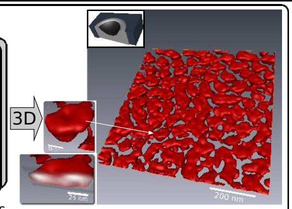
- Non-modified BVT: Asymetric three component perforated lamella
- Hydroborated BVT: Column-like structure and channel-like microphase separated structure suitable for membrane technology
- Imaging techniques like electron tomography do not work because the electron beam destroys the sensitive material

[(a)]BVT: 14 wt% polybutadiene (PB), 18 wt% poly(2-vinyl pyridine) (P2VP) and 68 wt% poly(*tert*-butyl methacrylate) (PtBMA), M_W = 165 kg/mol

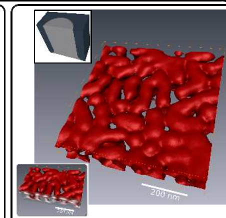
Non-modified BVT



- The sample surface prior to the plasma treatment reveals coexisting morphologies of dark stripes and dots embedded in a bright matrix
- Phase image: PB (dark), P2VP and PtBMA (bright)



3D reconstruction of non-modified BVT: The displayed isosurface encloses volume parts consisting of P2VP supplemented by the soft polybutadiene. The matrix material PtBMA (see schematic inset) is not colored, 250 x 250 x 15 voxels, 9 process steps.



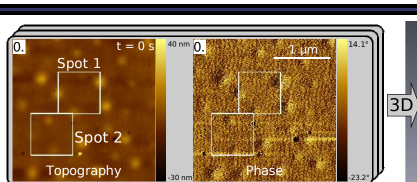
3D reconstruction of hydroborated BVT: The isosurface encloses volume parts consisting of P2VP and HO-PB. The matrix material PtBMA (see inset) is not colored, 200 x 200 x 65 voxels, 14 process steps.

Reference: Sperschneider et al., submitted.

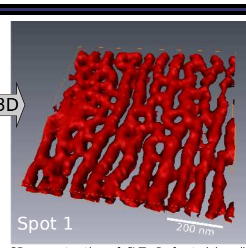
Alignment of a cylindrical terpolymer[(b)]

- Microphase separated pattern of SVT has been aligned by simultaneously treatment by solvent vapor under a high electric field (time-resolved QIS-SFM study)
- Experimental evidence for coexistence of perforated lamellar and cylindrical phase in aligned SVT polymer
- SVT is difficult to study with techniques like SEM or electron tomography because of the destructive effect of the electron beam

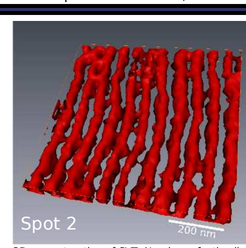
[(b)]SVT: 16 wt% polystyrene (PS), 21 wt% poly(2-vinyl pyridine) (P2VP) and 63 wt% poly(*tert*-butyl methacrylate) (PtBMA), M_W = 140 kg/mol



- Only limited information of the unetched sample because of a covering PtBMA layer
- Consecutive etching uncovers the underlaying structures by 22 process steps



3D reconstruction of SVT: Perforated lamella and cylinders. The core shell structures consists of PVP and PS (core PS; shell PVP). The matrix material PtBMA is not colored, 300 x 300 x 32 voxels.



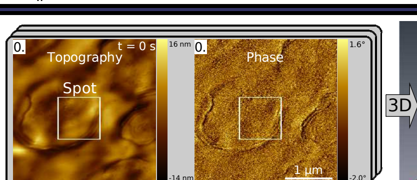
3D reconstruction of SVT: Nearly perfectly aligned core shell cylinders, 300 x 300 x 31 voxels.

Reference: Liedel et al., in preparation.

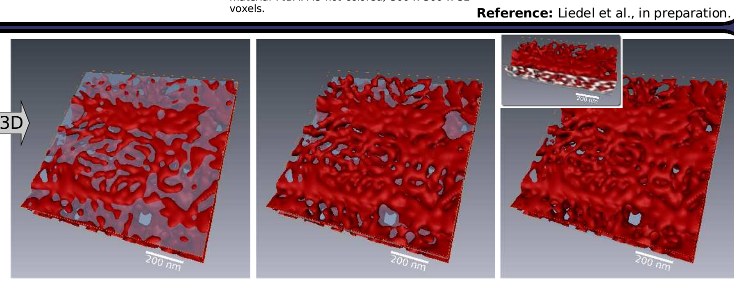
Lamella diblock copolymer film[(c)]

- Complex combination of lying and up-standing lamella is discovered[1]
- Dissipative Brownian dynamic simulations confirm the gained structures[2]

[(c)]SV: Polystyrene-*block*-poly(2-vinyl pyridine) diblock copolymer with a volume fraction of polystyrene (PS) of 0.56, M_W = 99 kg/mol



- Only limited information of the unetched sample
- Consecutive etching uncovers the underlaying structures by 21 process steps



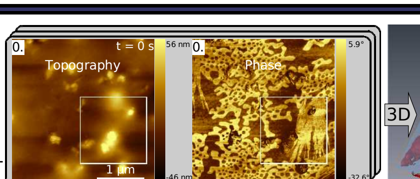
3D reconstruction of SV: A rather complex structure is observed. The displayed 3D object was flipped by 180°, 300 x 300 x 63 voxels.

References: [1]Gensel et al., Soft Matter, 2009 (online), [2]V. Neratova, P. Khalatur and A. R. Khokhlov, unpublished.

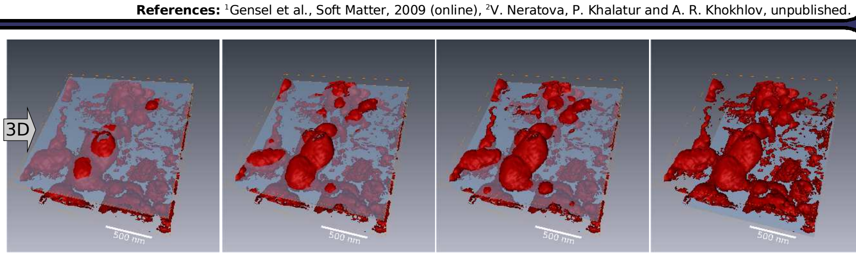
Latex dispersion[(d)]

- Classical x-ray diffraction makes problems by semicrystalline and non-ordered samples

[(d)]Commercial polymer latex dispersion utilized for high-gloss water paint



- Only limited information of the unetched sample
- Consecutive etching uncovers the underlaying structure by 22 process steps



3D reconstruction of a commercial polymer latex dispersion: Clusters of nanoparticles of different sizes are found, 480 x 480 x 201 voxels (1.4 x 1.4 x 0.58 µm³).

Conclusions

- The unique QIS-SFM technology makes the world of 3D-imaging accessable for the scanning probe microscopist
- Excellent reliability, high sample throughput and reasonable acquisition times
- Outstanding depth resolution due to unique combination of the SFM instrumentation with plasma technology

This work was supported by the Sonderforschungsbereich 481 funded by the Deutsche Forschungsgemeinschaft.