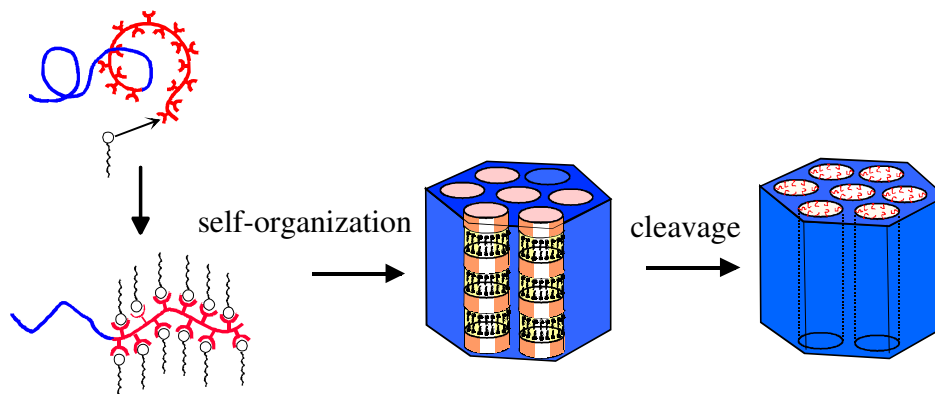


Application for beam time at ESRF – Experimental Method

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Aims of the experiment and scientific background

Introduction (identical to previous application 26-02-245; measurements to be performed On 17-20/12 2004) During recent years we showed, in close cooperation with the group of Prof. Ikkala at the Helsinki University of Technology, that the combination of supramolecular chemistry and block copolymer self-assembly is a most promising route to create nanostructured materials with potentially externally controllable functionalities. If suitable diblock copolymers are used, the relatively short length scale connected with these “side chains” imply that hierarchically ordered materials appear in a most natural way. The possibility of removing the “side chains” after the self-assembly process is ideal when aiming for nano objects and porous materials and this concept forms the basis for our most recent investigations [1-2]. Our most recent efforts concern comb-shaped supramolecules obtained by hydrogen bonding of octylgallate (OG) to a polyisoprene-block-poly(2-vinylpyridine) (PI-b-P2VP) diblock copolymer. Here one of the objectives is to prepare elastic membranes consisting of a cross-linked polyisoprene matrix with partly empty hexagonally ordered channels (see Scheme below). These channels are the remainders of the hexagonally ordered cylinders consisting of the comb-shaped P2VP(OG) blocks after removal of OG. In this way membranes with channels of a tunable diameter (biaxial stretching of the elastic membrane) can be constructed that can be used as e.g. templates for the polymerisation of thin electronically conducting fibers.



Since self-assembly in block copolymer systems invariably leads to a defect-rich multi-domain structure, large amplitude oscillatory shear is routinely used in our group to macroscopically align the ordered structures. To follow this ordering process in detail an existing Bohlin rheometer has been modified in such a way that it allows in-situ SAXS measurements both in tangential and radial direction [3]. During our latest ESRF-BM26B SAXS measurements on PI-b-P2VP(OG) under large amplitude oscillatory shear as a function of temperature, we obtained very puzzling results. For both PI-b-P2VP(OG)_{0.75} and PI-b-P2VP(OG)_{1.0} (here the subscript indicates the number of OG molecules per pyridine unit) an initially lamellar structure at room temperature turns into a hexagonally ordered cylindrical structure at elevated

temperature. However, at intermediate temperatures several complex structures and transitions between different ordered structures (e.g. from one hexagonal to another manifested as an abrupt change in cylinder diameter) were observed that did not occur under quiescent conditions. Apparently, the trajectory followed from low temperature (“room temperature”) lamellar to high temperature (ca 200C) cylindrical under shear is completely different from that followed when no shear is present. One possible reason could be the hydrogen bonds between P2VP and OG. The fraction of hydrogen bonded pyridine groups obviously decreases on increasing temperature, as witnessed by e.g. FTIR, but it is not unlikely that shear has an additional reducing effect.

The still to be performed 26-02 245 experiments concern a systematic investigation of the role of large amplitude oscillatory shear on the temperature sequence of ordered structures observed in PI-b-P2VP(OG). The strain amplitude and frequency will be the essential parameters to be varied.

New continuation proposal. Recent efforts demonstrated that diblock copolymers are not the best choice for preparing elastic membranes. Isoprene blocks coming from different cylinders of the hexagonally ordered cylindrical structure hardly overlap making crosslinking very ineffective. This problem can be overcome if instead of PI-b-P2VP diblock copolymers, PI-b-P2VP-b-PI triblock copolymers are used. For suitable block lengths the PI-b-P2VP(OG)-b-PI supramolecules will again form a hexagonally ordered cylindrical structure with the P2VP(OG) blocks forming the cylinders. In this case, however, some of the PI-blocks will connect neighboring cylinders and thus creating an elastic membrane by itself. After removing the OG from the cylinders the partly empty cylinders will be connected by PI chains. At room temperature the P2VP chains inside the cylinders might be in a glassy state and a kind of nanoporous “thermoplastic elastomer” has been obtained. In addition, the PI matrix can now be effectively crosslinked leading to a genuine network structure. With the present proposal we seek to study in detail the influence of large amplitude oscillatory shear on the alignment and ordering of PI-b-P2VP-b-PI triblock copolymer based PI-b-P2VP(OG)-b-PI supramolecules systems.

Experimental method

The rheometer will be placed in the BM26B beamline and SAXS will be recorded during large amplitude oscillatory shear of PI-b-P2VP(OG)-b-PI as a function of temperature. Whenever necessary, both tangential and radial scattering patterns will be taken.

Results expected

We hope to get a clear picture of the alignment of hexagonally ordered cylindrical structures of PI-b-P2VP(OG)-b-PI systems as a function of shear parameters (amplitude, frequency). Additionally, inspired by the effect observed in the diblock-based PI-b-P2VP(OG) systems, we will investigate the sequence of ordered structures appearing during heating from room temperature, comparing quiescent conditions with large amplitude oscillatory shear conditions.

References

1. "Functional Materials Based on Self-Assembly of Polymeric Supramolecules", Olli Ikkala and Gerrit ten Brinke *Science* **2002**, 295, 2407-2409
2. “Smart materials based on self-assembled hydrogen-bonded comb-shaped supramolecules” G. ten Brinke and O. Ikkala *Chem. Rec.* **2004**, 4, 219-230.
3. "In-situ *Radial* Small Angle Synchrotron X-Ray Scattering Study of Shear-Induced Macroscopic Orientation of Hierarchically Structured Comb-Shaped Supramolecules" Evgeny Polushkin, Gert Alberda van Ekenstein, Igor Dolbnya, Wim Bras, Olli Ikkala and Gerrit ten Brinke, *Macromolecules* **2003**, 36, 1421-14

