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**Block copolymer membrane self-assembly - from lab to fab: Dream or reality?**

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Molecular self-assembly of di- and triblock copolymers is a powerful method for manufacturing highly ordered structures with nano-sized patterns. Films with regular monodisperse nanopores and ultrahigh porosity are needed in applications, which vary from water purification, sensors, information storage, as templates for nanowires, scaffolds for tissue engineering and controlled drug delivery. Block copolymer self-assembly has been proposed as formation method for artificial highly selective membranes since many years. This presentation will review the recent progress in this field. Fascinating membrane structures could be manufactured, but the techniques applied were in many cases time consuming and complicated. Till today an up-scaling of the self-assembly process for membrane manufacturing was not possible. Most self-assembled block copolymer membranes described in the literature have been prepared in square mm scale and the manufacturing steps took hours or days. If we want to use standard membrane manufacturing methods like for example hollow fiber spinning, we have to shorten the membrane formation time from hours to minutes or seconds. Since this gives no time to wait for equilibrium, one is forced to take advantage of non-equilibrium structures. This is challenging but it multiplies the possibilities, since one block copolymer has only one equilibrium morphology, but many different attractive structures far from equilibrium. The trick and the challenge is to identify the structure we want and to freeze and stabilize it in a proper way.

The combination of the most common membrane formation process (non-solvent induced phase separation, NIPS) with the micro-phase separation of block copolymers was first described in 2007 /1/. This method is fast and simple, due to the fast precipitation step a transient structure can be kinetically trapped. But the mechanism was not well understood and the reproducibility with other polymers was not sufficient. We showed later that micelle formation in the membrane casting solution was the key to a successful asymmetric membrane formation /2,3,4/. The assembly of the micelles in solution is a dynamic process and small variations of the composition of the casting solution or of the manufacturing parameters can lead to different membrane morphologies. We could stabilize the micelle structure prior to membrane precipitation by the addition of transition metal ions or carbon nanotubes. Our latest result is a block copolymer membrane with a 100 nm thin self-assembled selective layer with a very high selectivity for separation of proteins of similar size.

In spite of the progress achieved, it is still a laboriously way before self assembled block copolymer membranes can be continuously manufactured with standard membrane equipment. But first trials have been made successfully and the vision "from lab to fab" will become reality.

/1/ K.-V. Peinemann et al., Asymmetric Superstructure in a Block Copolymer via Phase Separation, *Nature Materials* 2007, 6(12) 992

/2/ S. Nunes et al., Ultraporous Films with Uniform Nanochannels by Block Copolymer Micelles Assembly, *Macromolecules* 2010, 43, 8079

/3/ Nunes et al., Switchable pH-Responsive Polymeric Membranes Prepared via Block Copolymer Micelle Assembly, *ACS Nano* 2011, 5, 3516

/4/ Nunes et al., From Micelle Supramolecular Assemblies in Selective Solvents to Isoporous Membranes, *Langmuir* 2011, 27, 10184

