Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Engineering 44 (2012) 194 – 197

Procedia Engineering

www.elsevier.com/locate/procedia

Euromembrane Conference 2012

[OB05]
Self-assembled integral asymmetric block copolymer membranes: Structure formation and properties

V. Abetz*, V. Filiz, S. Rangou, C. Abetz, A. Jung, K. Buhr et al
[1]*Helmholtz-Zentrum Geesthacht, Germany,* [2]*Technion-Israel Institute of Technology, Israel,*
[3]*University of Bayreuth, Germany,* [4]*Pall Europe Limited, UK,* [5]*Pall Corporation, USA*

Introduction:

Isoporous membranes have received increasing attention during the last couple of years, after it had been shown possible to cast membranes from block copolymers forming cylindrical or cocontinuous (double-gryoid) morphologies.(1-7) The advantage of these materials is to give access to membranes with a very high number density of pores with controlled diameters, thus leading to ultrafiltration membranes with a very high permeability, and simultaneously also with a very high selectivity in terms of size exclusion. Different approaches have been reported. Yang et al. managed to cast a regular membrane from a polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) diblock copolymer mixed with a short poly(methyl methacrylate) homopolymer, which formed standing cylindrical PMMA domains in a PS matrix.(3) After transferring the thin film onto a porous support, the PMMA homopolymer was removed and open channels generated, which could separate proteins from viruses. Similar strategies involving chemical edging or rinsing steps have also been applied by other groups.(4) In such composite membranes composed of a thin separating layer on top of a porous support the thin top layer may be rather sensitive towards mechanical stresses at the interface between top and support layer. Therefore an alternative strategy is to form integral asymmetric membranes, where the thin top layer is continuously changing into a spongy support layer, thus avoiding the build-up of mechanical stresses.(5-7) This happens by subjecting the cast polymer solution film into a precipitant, inducing the so-called phase inversion by exchange of solvent with the non-solvent. Here it is important to have a system where solvent and nonsolvent are fully miscible with each other. This strategy also enables the direct formation of open pores without a subsequent edging step, if the solvents and nonsolvents are appropriately chosen. Such membranes can be cast on larger scales.

Experimental:

The block copolymers of the membranes have been prepared by living sequential anionic polymerization. The solvents and non-solvents for membrane casting were of p.a. or technical grade, and used without further purifications. Membranes were either hand or machine cast.

The morphological properties in bulk are compared with the structures in solution, during casting and the final morphological properties of the cast membranes by applying (cryo) transmission electron microscopy, (cryo) scanning electron microscopy, scanning force microscopy, small-angle neutron scattering (SANS), and synchrotron small-angle x-ray scattering (SAXS).

pH-dependent water flux and retention measurements were carried out using a testing device at transmembrane pressures up to 2 bars.

Results:

1877-7058 © 2012 Published by Elsevier Ltd.
doi:10.1016/j.proeng.2012.08.355

Different types of amphiphilic diblock and triblock copolymers based on styrene, 2- or 4-vinyl pyridine, and ethylene oxide with various compositions and molecular weights will be discussed. These block copolymers were dissolved at different concentrations in various solvent mixtures, and then machine or hand cast on a non-woven support, which was either pretreated with a liquid, or not. The pretreatment was mainly carried out to prevent the block copolymer solution from rinsing through the porous support during casting, which would lead to an irregular shaped membrane and blocked pores. This problem occurs for solutions with too low viscosities, i.e., in the case of solutions of block copolymers with lower molecular weights, or solutions with a low concentration of block copolymer. It is already known that the choice of the liquid used for filling the pores of the support has a great influence on the morphological behaviour of the block copolymer layer. (8) Varying the time before the cast solution was subjected to phase inversion, as well as choosing the temperature of the precipitation bath, are further parameters having strong influence on the obtained membrane film structure. The membranes show huge water flux values at the early stages of flux measurements (> 1000 L/(m^2 h bar)), however the flux decreases with time, but still remains at relatively large values (several hundreds L/(m^2 h bar)). Membranes with pore forming blocks showing pH-sensitive or temperature swelling behaviour can be reversibly switched from an open state to a closed state. The size of the pores can be controlled by both molecular weight and composition of the block copolymers (Figure 1).

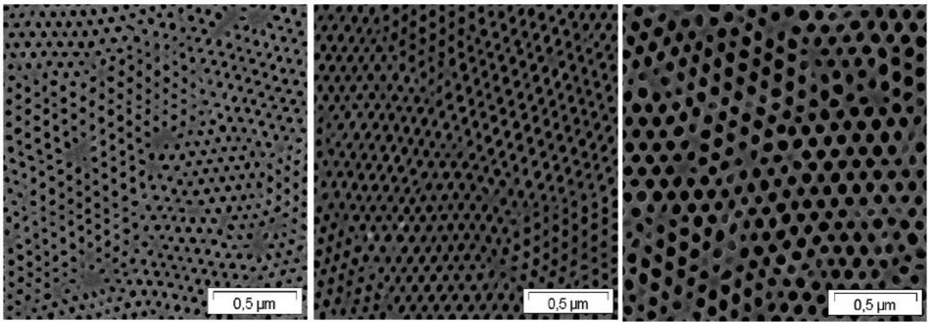

Figure 1: Influence of composition and molecular weight on pore diameters. From left to right: polystyrene-*block*-poly(4-vinylpyridine)s with increasing molecular weight and increasing amount of poly(4-vinylpyridine)

Besides the size of the pore, also the functionality of the pores is important when the selectivity for biomacromolecules is considered. This is demonstrated by filtration experiments using integral asymmetric membranes composed of polystyrene-*block*-poly(2-vinylpyridine) or polystyrene-*block*-poly(4-vinylpyridine). Here the type of vinyl pyridine influences strongly the selectivity as demonstrated by retention tests.

On the example of polystyrene-*block*-poly(4-vinylpyridine) also the solution properties as a function of solvent quality were studied by SANS and cryo transmission and scanning electron microscopy. The micellization behaviour was observed even at a low block copolymer concentration, while larger scale structure formation was observed immediately after the addition of very small amounts of non-solvent.

Using a typical block copolymer casting solution of a similar diblock copolymer, the casting process on a support, including the influence of contacting the highly swollen block copolymer film with a non-solvent, could be monitored by SAXS and a rather dramatic shift of the length scale of the forming membrane structure was observed (Figure 2). These results will be discussed in view of the possible formation of micelles and inverse micelles, respectively.