



A correlation between structural features of an amphiphilic diblock copolymer in solution and the structure of the porous surface in an integral asymmetric membrane



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ABSTRACT

A correlation between the pore size of isoporous block copolymer membranes produced *via* the combination of self-assembly with non-solvent induced phase separation (SNIPS) on one side and the macromolecular dimensions of the block copolymer in the casting solution on the other side is presented. Dilute solutions of a polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) diblock copolymer and corresponding polystyrene (PS) and poly(4-vinylpyridine) (P4VP) homopolymers similar to the respective blocks of the diblock copolymer are investigated separately by static and dynamic light scattering (SLS, DLS) in solvent mixtures of tetrahydrofuran/*N,N*-dimethylformamide (THF/DMF). These measurements provide information about the size of the individual polymers in solution. Solutions of the diblock copolymer at higher concentrations are studied furthermore by small-angle X-ray scattering (SAXS) and cryo-scanning electron microscopy (cryo-SEM) in order to estimate the size of self-assembled structures in concentrated solution, as well as by scanning electron microscopy (SEM) in the final membrane. The pore radius of the selective layer in the resulting membrane obtained by SNIPS is shown to be similar to the hydrodynamic diameter of the pore forming block, as determined in dilute solution.

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1. Introduction

Block copolymers have gained an immense interest over the last decades. Their ability to self-assemble and microphase separate leads to several structures such as spheres, cylinders, double gyroids, lamellae or more complex structures with regard to the number of blocks, the architecture or the use of additives [1–15]. A large amount of information has been revealed after many studies on their behavior in bulk [16–18] or in solution in an appropriate solvent or solvent mixture [19–33]. Additionally, block copolymers received interest as bulk materials, but also as compatibilizers, blends or templates for nanopatterning [34–38]. Lately, they are also used for developing different types of membranes, such as dense membranes for gas separation from multiblock copolymers [39,40] or porous membranes mostly from diblock copolymers for

ultrafiltration [41–50].

In this work, we study solutions of polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) used for fabrication of isoporous integral asymmetric block copolymer membranes *via* self-assembly and non-solvent induced phase separation (SNIPS) and compare structural features of the block copolymer in solution with the finally formed membrane [42]. The isoporous membranes are formed by casting a solution using a doctor blade, where the block copolymer is dissolved in a proper solvent or solvent mixture, onto a flat substrate. Then a part of the solvent evaporates what induces the build-up of a gradient of the solvent concentration from the upper surface towards the bottom, initiating microphase separation and directing it along the gradient before the following immersion into a non-solvent precipitation bath traps the formed structure. This procedure was first developed for casting flat sheet membranes by doctor blading but has also been successfully transferred to the fabrication of hollow fiber membranes [51–54] or spraying membranes [55]. There are several parameters affecting the structure occurring in solution and in the final membrane, with

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the most important ones being the incompatibility between the different polymer blocks, the block copolymer composition, and the solvent selectivity. The solvent quality for each block affects the critical micelle concentration and may lead to different structures [30,56,57]. Several additives which selectively interact with the pore forming block have been used in order to enhance the formation of an isoporous surface layer, and it was shown that different additives might result in different pore sizes [58–60].

Different methods have been used to investigate the structure formation in membrane casting solutions. Small-angle X-ray scattering (SAXS) can give information on the structure in solution [61,62]. Structure evolution during evaporation of solvent has also been followed by the *in situ* SAXS [32]. The influence of the addition of small amounts of non-solvent to a block copolymer solution was investigated by small angle neutron scattering (SANS) [30]. Another powerful method to investigate structures in solutions at high concentrations is cryo-scanning electron microscopy (cryo-SEM). Oss-Ronen et al. [30] studied the micellar and structural evolution in solutions in this way while later Marques et al. [31] studied the block copolymer membrane formation through time-resolved GISAXS and cryo-microscopy characterization.

The objective of the present work is to find a relationship between the structural features of a diblock copolymer in solution and the surface structure of the final membrane obtained by the SNIPS process. The system under investigation consists of polystyrene (PS), poly(4-vinylpyridine) (P4VP) homopolymers and PS-*b*-P4VP diblock copolymer in tetrahydrofuran/*N,N*-dimethylformamide (THF/DMF) solvent mixtures with, the first solvent being selective for the PS block and the second being slightly selective for the P4VP block. In order to have a better understanding of the behavior of the diblock copolymer in the dilute region, the hydrodynamic radius, R_h , of PS-*b*-P4VP is investigated in different solvents and solvent mixtures. Since a combination of THF and DMF has been widely used for the preparation of isoporous integral asymmetric membranes from this type of diblock copolymer [42,63], we focus our work accordingly, with the aim to observe the structure and pore formation process. The basic criterion for the selection of this system is that the solvent mixture can dissolve both blocks, giving the opportunity to observe better each step. This includes the observation of the starting random coil, the micelle formation as well as the structure formed in the final membrane with increasing concentration in a changing solvent composition due to the selective evaporation of THF.

2. Experimental part

2.1. Materials

The PS and P4VP homopolymers, as well as the PS-*b*-P4VP diblock copolymer, were synthesized *via* anionic polymerization [63]. For the synthesis of PS homopolymer and PS-*b*-P4VP diblock copolymer THF was used as a solvent. It was purified by successive distillation from molecular sieves and *sec*-butyllithium. Styrene was cleaned *via* aluminum oxide column and distillation over dibutylmagnesium. 4-Vinyl pyridine was purified *via* distillation from calcium hydride and ethylaluminum dichloride. The polymerization was carried out at -78 °C. The polymerization of styrene was initiated with *sec*-butyllithium. In the case of the synthesis of the homopolymer at that point, the polymerization was terminated with a mixture of degassed methanol/acetic acid. In the case of the diblock copolymer after a small aliquot extraction for characterization, the 4-vinyl pyridine monomer was added in the solution and left to polymerize overnight at -78 °C. The polymerization was terminated with a mixture of degassed methanol/acetic acid. The polymers were precipitated in water and dried under

vacuum. The composition of the diblock copolymer was determined by $^1\text{H-NMR}$ spectroscopy. For the polymerization of P4VP the solvent was anhydrous pyridine, and the initiation was done with the use of *sec*-butyllithium at -20 °C. The solution was left overnight under stirring at -20 °C and the termination was done with degassed methanol/acetic acid mixture. Ethyl acetate was used as precipitant. The sample was thoroughly dried under vacuum. Molecular weights and polydispersity indexes of the PS precursor and PS-*b*-P4VP diblock copolymer, as well as P4VP homopolymer, were determined by gel permeation chromatography (GPC), at 50 °C, with dimethylacetamide as a solvent. The GPC was calibrated with polystyrene standards.

For the structural investigations of the polymer solutions THF and DMF (99.8%, Merck, Germany) were used without any further purification. For the polymers the following nomenclature is used: in PS^c, P4VP^c and PS_a-*b*-P4VP_b^c, a and b are the PS and P4VP weight fractions in the diblock copolymer, while c is the total weight average molecular weight (M_w) of the homopolymers and the diblock copolymer in kg/mol. All concentrations and solvent ratios are given in wt% unless specified otherwise.

2.2. Membrane formation

The membrane was prepared *via* the SNIPS process as described elsewhere [42]. A PS_{80.2}-*b*-P4VP_{19.8}¹⁴⁶ diblock copolymer solution of a 26.5 wt% concentration in a solvent mixture of THF/DMF: 35/65 was prepared and stirred for 48 h. After stirring, it was cast onto a glass substrate to form the flat sheet membrane and to easily detach it for further SEM investigations. The casting procedure was done manually using a doctor blade at a height of 200 μm and the cast film was left for 2 s under room atmosphere before immersion in Millipore water (0.055 $\mu\text{S/cm}$) where it was left overnight for completion of the solvent-non-solvent exchange. Before the investigation, it was dried at 60 °C for 48 h under vacuum.

2.3. Characterization methods

2.3.1. Dynamic light scattering

Dynamic light scattering (DLS) measurements were conducted on an ALV/CGS-3 Compact Goniometer using an ALV/LSE-5003 Multiple Tau Digital Correlator equipped with a Nd:YAG Laser emitting at a wavelength of $\lambda = 532$ nm. The measurements were done at different scattering angles (40–140°) and the temperature was kept constant at 25 °C. Solutions with a concentration of 0.1 g/L were prepared for the PS and PS-*b*-P4VP polymers and of 0.5 g/L for P4VP homopolymer in different solvents and solvent mixtures.

2.3.2. Static light scattering

Static light scattering (SLS) measurements were conducted on an ALV/CGS-3 Compact Goniometer equipped with a He/Ne Laser using an ALV/LSE-5003 Multiple Tau Digital Correlator emitting at a wavelength of $\lambda = 632.8$ nm. The temperature was kept constant at 25 °C. Several solutions with concentrations varying from 0.1 to 1.5 g/L were prepared. The solvent mixture used in these measurements was THF/DMF in a ratio of 40/60 and 10/90.

All solutions used for static and dynamic light scattering experiments were left to dissolve in the solvent mixture for 24 h and filtered through 0.45 μm polytetrafluoroethylene (PTFE) filters prior to use.

2.3.3. Small-angle X-Ray scattering

Small-angle X-ray (SAXS) scattering experiments were performed at the Beamline P12 of Petra III synchrotron storage ring at DESY in Hamburg, Germany. A Pilatus 2 M detector was used at a distance of 3.0 m. The exposure time was 0.05 s and the exposure

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