



Formation of high thermally stable isoporous integral asymmetric block copolymer membranes

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ABSTRACT

Tailor-made poly(α -methylstyrene)- and poly(4-methylstyrene)-*block*-poly(4-vinylpyridine) diblock copolymers with poly(4-vinylpyridine) as the minority component were synthesised via living anionic polymerisation. In bulk they show spherical or cylindrical microphases. From these block copolymers highly-ordered isoporous block copolymer membranes were prepared by combining block copolymer selfassembly and the nonsolvent induced phase separation process (SNIPS). The membrane properties were analysed by water flux and retention measurements. Due to the high glass transition temperatures of the major blocks these block copolymer membranes show a thermal stability up to 150 °C.

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1. Introduction

The high growth of world population in combination with the shortage of resources and the environmental pollution has entailed an ever-increasing demand for energy-efficient and sustainable technologies. Among those, ultrafiltration (UF) membranes have attracted increasing attention e.g. in waste water treatment, dairy, and food industry in recent years.

An essential goal in the development of new ultrafiltration (UF) membranes is to combine high selectivity with high flux at the same time. Therefore, an ideal membrane should have a thin selective top layer with a narrow pore size distribution and a highly porous supporting layer as a mechanical support for the selective layer.

Microphase separating block copolymers offer a large potential for many applications due to their ability to self-assemble into various highly-ordered periodic structures on the length scale of about 10–100 nm [1]. For UF membranes block copolymers are of interest, which self-assemble into spherical, cylindrical, or gyroid morphologies. The combination of the self-assembly of amphiphilic block copolymers and the non-solvent induced phase separation (SNIPS) process can lead to isoporous membranes with an integral asymmetric structure. High surface pore regularity and open pores can be obtained directly in a fast and effective one-step process [2,3].

Contrary to the conventional film casting of block copolymers which can be combined with porogenic additives like, i.e. water soluble homopolymers [4], the SNIPS process avoids elaborate transfer, selective swelling [5–7] or etching steps. More

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recently, a remarkable progress has been made in the development and understanding of the structure formation process of isoporous integral asymmetric block copolymer membranes [3,8–10].

Based on the initial development of a polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) membrane in 2007 [11], later works demonstrated possibilities to control the pore size of these membranes by blending [12,13] and by changing the block copolymers' molecular weight or its P4VP content [14]. The membranes can be generated in flat and in hollow fibre [15–19] geometry. Various types of diblock copolymers [20–23] or even triblock terpolymers [24,25] have been used for membrane fabrication. Structure formation can be supported by additives in the casting solution [10,12,26].

The potential and the performance of a membrane material depend on its properties like mechanical strength, chemical and thermal stability. The latter property can be optimised by using block copolymers with a matrix-forming block having a high glass-transition temperature (T_g). The well investigated PS-*b*-P4VP shows a T_g of 100 °C for the matrix forming PS block and a T_g of 145 °C [27] for the pore forming P4VP block. Consequently, the thermal stability is limited to approximately 100 °C which is too low for applications where membrane cleaning is required e.g. via steam sterilisation [28]. As described by Hahn et al. [21] integral asymmetric membranes casted from poly(4-trimethylsilylstyrene)-*block*-poly(4-vinylpyridine) (PTMSS-*b*-P4VP) and poly(*tert*-butylstyrene)-*block*-poly(4-vinylpyridine) (PtBS-*b*-P4VP) show an increased thermal stability. According to the T_g of the matrix forming block the poly(4-trimethylsilylstyrene) and the poly(*tert*-butylstyrene) containing membranes are stable up to 110 °C and 125 °C, respectively.

In this study, we report on the development and characterisation of integral asymmetric membranes with a narrow pore size distribution using poly(4-methylstyrene)-*block*-poly(4-vinylpyridine) (P4MS-*b*-P4VP) and poly(α -methylstyrene)-*block*-poly(4-vinylpyridine) (P α MS-*b*-P4VP) diblock copolymers, respectively. The glass transition temperatures of P4MS (111 °C) [29,30] and P α MS (171 °C) [31] lead to membranes with higher thermal stability as all previously reported membranes with a similar structure.

2. Experimental

2.1. Materials and their purification

Tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) were ordered from Th. Geyer. 1,4-Dioxane (DOX), 4-methylstyrene (4MS), α -methylstyrene (α MS), 4-vinylpyridine (4VP), ethylaluminum dichloride (EtAlCl₂, 1 M in hexane), di-*n*-butylmagnesium (MgBu₂), calciumhydride (CaH₂) and *sec*-butyllithium (*sec*-BuLi) were purchased from Sigma-Aldrich. THF was purified by successive distillation from potassium under argon atmosphere. α -methylstyrene was purified by filtration over Al₂O₃, treated with MgBu₂ and freshly distilled prior to use. 4-methylstyrene was purified by filtration over Al₂O₃, treated with MgBu₂ and freshly distilled prior to use. 4VP was distilled under reduced pressure, stored over CaH₂ and distilled again after treating twice with ethylaluminum dichloride.

2.2. Synthesis of poly(α methylstyrene)-*block*-poly(4-vinylpyridine) (P α MS-*b*-P4VP) and poly(4-methylstyrene)-*block*-poly(4-vinylpyridine) (P4MS-*b*-P4VP)

P α MS-*b*-P4VP and P4MS-*b*-P4VP were synthesised via sequential anionic polymerisation in THF at –70 °C using *sec*-BuLi as initiator in the presence of LiCl.

The polymerisation of α MS or 4MS was initiated by *sec*-BuLi. After 5 or 6 h 4VP was added via a syringe and the solution was stirred overnight. The polymerisation was quenched with degassed methanol/HCl. After partial removal of THF under reduced pressure the polymer was precipitated into water. The precipitated polymer was filtered and dried in vacuum until constant weight.

2.3. Characterisation of block copolymers

The compositions of P α MS-*b*-P4VP and P4MS-*b*-P4VP block copolymers were determined by proton nuclear magnetic resonance spectroscopy (¹H NMR). ¹H NMR measurements were performed on a Bruker Advance 300 NMR spectrometer (300 MHz) using CDCl₃ as solvent (Supporting Informations, Figs. S1 and S2).

Molecular weights of the precursors and polydispersities were determined by gel permeation chromatography (GPC). The measurements were performed at 50 °C in *N,N*-dimethylacetamide with addition of lithium chloride (DMAc + LiCl) using PSS GRAM columns [GRAM precolumn (dimension 8 · 50 mm), GRAM column (porosity 3000 Å, dimension 8 · 300 mm, particle size 10 μm) and GRAM column (porosity 1000 Å, dimension 8 · 300 mm, particle size 10 μm)], at a flow rate of 1.0 mL min⁻¹ (VWR-Hitachi 2130 pump). A Shodex RI-101 refractive index detector with a polystyrene calibration was used. Therefore, only apparent molecular weights could be determined.

In order to study the glass transition temperatures (T_g) of the different block copolymers a DSC 1 (Star system) from Mettler Toledo was used in the temperature range of 30–200 °C using nitrogen as a purge gas stream. All DSC runs were performed at a scan rate of 10 K min⁻¹ and the T_g values were determined from the second heating trace.

The morphology of the bulk samples was characterised by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS). The samples were prepared from a solution of the respective block copolymer in chloroform by slowly

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