



# Capillary pore membranes with grafted diblock copolymers showing reversibly changing ultrafiltration properties with independent response to ions and temperature



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## ABSTRACT

Track-etched polyethylene terephthalate membranes with a pore size of 110 nm have been modified by a grafted diblock copolymer structure in order to obtain dual-responsive ultrafiltration membranes. The temperature-responsive poly-N-isopropylacrylamide (PNIPAAm) and the ion-responsive poly-N,N-dimethyl-N-methacryloyloxyethyl-N-(3-sulfopropyl) ammonium betaine (PSPE) were grafted from the pore walls by sequential surface-initiated atom transfer radical polymerization. To achieve a well controlled pore functionalization, the polymerization rate had been adjusted to a very slow chain growth. A successful grafting of PSPE as first block and of PNIPAAm as second block could be demonstrated. To study the temperature and ion responsivity, hydraulic permeability and dextran diffusion experiments at 25 °C and 40 °C with different salt solutions had been carried out. It could be shown that such membranes can change their barrier pore size from a more open to a more closed state in dependency of temperature as well as kind of ions and their concentration in the feed. The grafted layer thickness showed a particularly strong increase in the presence of KClO<sub>4</sub>. Like expected for a well defined polymer brush, an expanded or collapsed state for each of the individual blocks could be obtained. In presence of KClO<sub>4</sub> at 25 °C both blocks are expanded and the pores are in a more closed state. If one of these stimuli is changed, for example when temperature is increased to 40 °C or ions are removed, the block copolymer brushes collapse partially what leads to more open pores. However, if both stimuli are applied together, i.e. if temperature is 40 °C and no ions are in solution, diblock copolymers collapse fully what leads to fully opened pores. It had also been demonstrated that this dual responsivity and the magnitude of the effects depend very strongly on the absolute degree of grafting and the ratio between the two different responsive polymer blocks. Furthermore, the ability of changing effective membrane barrier pore size by ions and temperature has been investigated in more detail by dextran diffusion experiments, and very pronounced and reversible changes of molecular sieving curve and molecular weight cut-off could be obtained.

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## 1. Introduction

Stimuli responsive materials, in particular polymers, had gained a lot of interest in recent years due to their unique ability of a large, rapid and reversible change of their properties in response to a small variation of the environmental conditions [1]. This concept had also been applied to obtain stimuli-responsive membranes [2], and already reported materials can be sensitive towards, for example, temperature [3], pH [4], ionic strength [5],

specific ions [6], even larger molecules such as proteins [7], as well as light irradiation [8] or magnetic fields [9]. A commonly used mechanism to obtain responsive barrier properties is based on a reversible swelling/deswelling transition of polymeric hydrogels confined on the membrane surface or in membrane pores. However, many of these membranes comprise not well controllable functional polymer structures because conventional radical polymerization had been used for synthesis or fabrication. Therefore, the full potential of advanced functional polymeric architectures cannot be utilized.

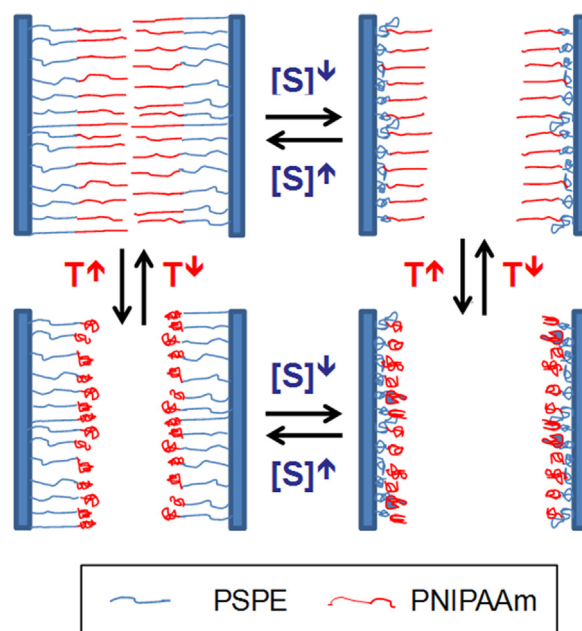
For this work, atom transfer radical polymerization (ATRP) had been chosen what allows the easy control of polymer chain length and functionality, and synthesis parameters can be readily adjusted

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so that it can be optimized to many different polymers and specific demands [10]. Moreover, this technique makes it possible to achieve well-defined macromolecular architectures like diblock- [11,12] or multiblock structures [13,14], with controlled molecular weight and low polydispersity of each block. In the recent decades, this technique had also been used for surface functionalization of materials [10]. Several groups have already reported about the modification of different membrane materials by surface initiated (SI) ATRP for various applications. For instance, Fu et al. have grafted polystyrene derivatives on polyphosphazene membranes leading to novel ion exchange membranes for fuel cell technologies [15]. Singh et al. have prepared high-capacity macroporous membrane adsorbers by grafting of the weak polyelectrolyte poly(acrylic acid) (PAA) on the surface of regenerated cellulose membranes [16]. Other reports had been about improved antifouling properties by grafting of poly(ethylene glycol) (PEG)-containing or polyzwitterionic brushes on membrane surfaces [17,18]. Furthermore, Singh et al. and Wandera et al. reported about modifications of ultrafiltration membranes for simultaneous changing of sieving and improving antifouling properties; the key to success had been using SI-ATRP conditions enabling very slow chain growth [19,20].

Due to their “smart”, tunable permeability and separation properties many groups focused on stimuli-responsive membranes prepared by SI-ATRP. The stimuli-responsive polymers can be introduced into the membranes as blend with the bulk material or grafted on the surface and on the pore walls what leads to a pore size tunable by external conditions [21]. Friebe and Ulbricht had obtained temperature-responsive membranes by grafting poly(*N*-isopropylacrylamide) (PNIPAAm) layers with a thickness of up to 80 nm on the walls of capillary pores in track-etched polyethylene terephthalate (PET) membranes with pore diameters of about 700 nm, what lead to reversible swelling and deswelling of the layer within the pore, at temperatures below and above the lower critical solution temperature (LCST) of this polymer (32 °C) [22]. Yang and Ulbricht published about analogous PET-based capillary pore membranes, but with grafted poly(*N,N*-dimethyl-*N*-methacryloxyethyl-*N*-(3-sulfopropyl) ammonium betain) (PSPE) which were able to change the permeate flux in dependency of the ion type and concentration [23]. Li et al. had used PAA for the grafting on nylon membranes what led to pH-responsive membranes [24]. However, mostly membranes with barrier pores larger than 400 nm had been modified. For modification of pores which are smaller than 100 nm, very well controlled polymerization conditions leading to very slow chain growth are required because otherwise the polymer distribution will be uneven and this may even lead to clogged pores. That had been demonstrated by Alem et al. when modifying a track-etched membrane with 80 nm pores with PNIPAAm in an aqueous system. They observed a flux decrease after raising the temperature what might be due to the long polymer chains on the outer surface which build a dense layer onto of the pores when collapsing [25]. Frost and Ulbricht have proven the importance of a very well controlled polymerization by modifying PET track-etched membranes with a pore diameter of 110 nm with PNIPAAm and obtaining well-defined ultrafiltration membranes which reversibly open or close their pores at high or low temperature, respectively [26]. There have been also several reports about grafting of diblock copolymers on microfiltration membrane surface what leads to dual- or even multi-responsive materials with novel properties and possible applications. For example, temperature- and pH-responsive microfiltration membranes had been obtained by grafting of PNIPAAm as a first block and PAA as the second block [27] or by using the reverse sequence [28]. There are also reports about pH- and temperature-responsive membranes by grafting of blocks of poly(diethylene glycol)methyl ether methacrylate) or PNIPAAm, in combination with either poly(methacrylic acid) or poly(*N,N*-dimethylaminoethyl methacrylate)



**Fig. 1.** Schematic depiction of grafted diblock copolymer brushes with PSPE as first block and PNIPAAm as second block in a cylindrical pore. The block structure leads to four different pore diameters due to four different chain expansion states in dependency of the stimuli salt type and concentration ([S]) and temperature ([T]).

[29,30]. Kumar et al. reported about a membrane for release of dye in response to temperature, pH or exposure to UV light [31]. However, for the preparation of ultrafiltration membranes with grafted diblock structures within the pores a very well controlled polymerization is required, and this had not yet been reported. Besides a multi-step adjustable molecular weight cut-off in the ultrafiltration range or advanced control of macromolecular drug release through a membrane, such materials could also be developed toward logic gates [32].

Here we report about dual-responsive ultrafiltration membranes with a tailored functional polymer structure and architecture and tunable pore size. A track-etched PET membrane has been functionalized by grafting of a diblock copolymer made of PSPE and PNIPAAm, leading to materials where pore size can be reversibly manipulated by ion concentration or kind of ions and temperature like it is shown in Fig. 1. First, SI-ATRP conditions had been adjusted to a very slow polymer chain growth what leads to well controlled polymer brush length and only few termination reactions. This had then been utilized to prepare membranes with well defined grafted diblock copolymer brushes on the pore walls at different overall degree of grafting and block ratios. The responsiveness of the membranes towards ions and temperature has finally been carefully evaluated by hydraulic permeability and dextran diffusion experiments at varied solution conditions and temperature.

## 2. Experimental section

### 2.1. Materials and chemicals

Polyethylene terephthalate (PET) track-etched (TE) membranes with a nominal pore diameter of 80 nm, a porosity of 10% and a thickness of 8 μm were purchased from Oxyphen AG (Switzerland). Potassium permanganate (> 99%), 2-aminoethanol (> 99%), 4-(dimethylamino) pyridine (> 98%), triethylamine (> 99.5%), potassium perchlorate (KClO<sub>4</sub>; > 98.5%), and aluminum chloride (AlCl<sub>3</sub>; > 99%) were purchased from Fluka. Sulfuric acid (> 95%), methanol (99.99%), acetonitrile (99.99%), acetone (99.99%), and diethyl ether (99.99%) were from Fisher Scientific. Hydrochloric acid (37%) aqueous solution and *N,N*-dimethylformamide (DMF; > 99.8%) were from Bernd Kraft (Germany). *N,N*-Diisopropylcarbodiimide (> 97%) and copper(II) bromide

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