



Weak polyelectrolyte multilayers as tunable membranes for solvent resistant nanofiltration



Shazia Ilyas^{a,b}, Nithya Joseph^b, Anthony Szymczyk^c, Alexander Volodin^d, Kitty Nijmeijer^a, Wiebe M. de Vos^{a,*}, Ivo F.J. Vankelecom^b

^a Membrane Science and Technology, MESA+ Institute for Nanotechnology, University of Twente, Faculty of Science and Technology, P.O. Box 217, 7500 AE Enschede, The Netherlands

^b Centre for Surface Chemistry and Catalysis, Faculty of Bioengineering Sciences, Katholieke Universiteit Leuven, Celestijnenlaan 200F - Box 2461, 3001 Leuven, Belgium

^c Institut des Sciences Chimiques de Rennes, CNRS, UMR 6226, Université de Rennes 1, 35042 Rennes, France

^d Laboratory of Solid-State Physics and Magnetism, Katholieke Universiteit Leuven, Celestijnenlaan 200 D, 3001 Leuven, Belgium

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ABSTRACT

This manuscript encompasses the investigation into the solvent resistant nanofiltration (SRNF) performance of multilayer membranes prepared from weak polyelectrolytes. These weak polyelectrolytes are unique in that the charge density is not fixed and depends on the coating pH, adding an extra variable as tuning parameter for SRNF performance. The weak polyelectrolyte based multilayers (PEMs) were prepared on a hydrolyzed PAN support membrane from poly(allylamine hydrochloride) (PAH) as polycation and poly(acrylic acid) (PAA) as polyanion. Detailed investigations on the role of the pH of the coating solution on the performance of the prepared SRNF-membranes were carried out with organic dyes of different size (~300–1000 Da) and charge. Variation in pH of the coating solutions was found to lead to a large degree of control over the separation performance of the prepared SRNF-membranes for the different dyes. The solvent permeabilities and the dye retentions were measured and correlated to variations in the PEM membrane structures, with more dye adsorption being found for membranes with more free acid and amine groups. The membranes were also found to be stable for long term-filtrations in solvents such as isopropyl alcohol (IPA), acetonitrile (ACN), tetrahydrofuran (THF) and in the challenging polar aprotic solvent, N,N-dimethylformamide (DMF). Results of this study clearly demonstrate the potential of using pH as tuning parameter for weak PEMs to prepare SRNF-membranes optimized for specific applications.

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1. Introduction

Nanofiltration (NF) is among the pressure-driven membrane processes which have gained a lot of attention recently, with separation characteristics falling in the range between RO and UF membranes. This makes the technology especially promising for separations on a molecular level. One of the key current challenges for NF is to broaden the range of applications from aqueous to organic feeds in the form of solvent-resistant nanofiltration (SRNF) membranes [1]. As SRNF separation does not involve an energy demanding phase transition, it has drawn considerable attention as an alternative separation technique to alleviate the energy costs and related environmental problems caused by conventional separation methods such as distillation [2,3]. SRNF has potential

applications in strategic fields, such as the petrochemical industry, pharmaceutical industry and food industry to separate desired molecules from solvents and/or to recover solvents and solutes from waste streams [4–8]. However, there is lack of membranes that are thermally and chemically stable, that have a high permeability and that provide effective separation of molecules in the range of 200–1000 g mol⁻¹ in various organic solvents over long time-scales [1,3,9–11]. Polymers are an interesting material for SRNF related applications but very few polymeric membranes are stable: swelling and/or dissolution of the polymeric matrix often results in a loss of membrane selectivity.

In membrane technology, layer by layer (LbL) based self-assembly of charged polyelectrolytes (PEs) on an oppositely charged porous support has recently emerged as one of the simplest, most versatile, and most environmentally benign techniques to fabricate membranes with selective top-layers [12]. Fig. 1 shows schematically the LbL process to create membranes with a polyelectrolyte multilayer (PEM) top layer. A key strength of the PEM membranes

* Corresponding author.

E-mail address: w.m.devos@utwente.nl (W.M. de Vos).

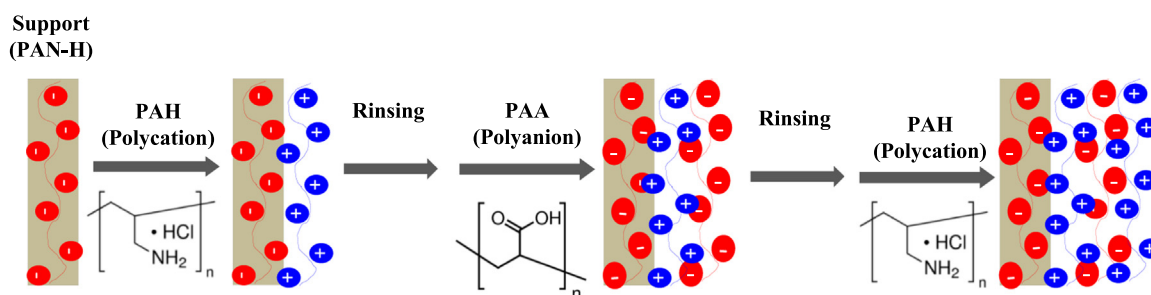


Fig. 1. Overview of the LbL assembly of PEMs of PAH/PAA on a charged membrane support.

is their versatility as the layer properties, and thus the separation properties, can be controlled via the types of PEs used, the number of deposited layers and the pH and ionic strength during coating [13]. PEMs have already been used to make different kinds of membranes such as reverse osmosis [14,15], ion selective [13,16–19], nanofiltration [14,20–26] and SRNF membranes [27–32].

Tetrahydrofuran (THF), N,N-dimethylformamide (DMF), acetonitrile (ACN), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP) and dichloromethane (DCM) are some of the important industrial solvents that are still problematic for most of the currently available SRNF membranes [1]. These aprotic solvents demand an extremely high chemical stability from any membrane they come into contact with. Recently, PEM-based SRNF-membranes were reported to have promising and stable performance for some of these solvents [27–31]. Furthermore, PEM-based membranes typically possess a highly charged top layer allowing the possibility for Donnan based exclusion of similarly charged molecules [33]. However, all previous studies utilized at least one strong PE, making their systems relatively insensitive to the pH at which the layers are formed. With such a combination of PEs, salt addition to the PE dipping solutions best controls the thickness and morphology of the adsorbed layer. With the addition of salt the polymer chains become more coiled due to the screening of the charges along the polyelectrolyte chain. Furthermore, the ionic strength can determine the structure of the formed polyelectrolyte complex. To describe this, Schlenoff et al., [34] defined two types of charge compensations in polyelectrolyte complexation, intrinsic and extrinsic. In the former, a polymeric charge is balanced by an opposite charge of the other polyelectrolyte, while in the later most the polymeric charge is balanced by a counter ion. Increasing the ionic strength shifts the equilibrium from intrinsic to extrinsic charge compensation which leads to thicker, more mobile and more swollen layers [34]. Thicker layers on a membrane lead to lower membrane permeabilities, whereas more open layers can increase the permeability [35]. However, the effectiveness of this parameter is often limited to a small range of salt concentrations because of either solubility problems or decomposition of the multilayer films when increasing the ionic strength [36,37].

The use of two weak PEs (both the polycation and the polyanion) can provide the opportunity to use the pH during coating to allow a large degree of control over membrane performance [38]. Unlike strong PEs, which remains charged over the entire pH range, the degree of ionization of weak PEs depends greatly on the deposition solution pH. So the resulting charge density of PEs and the thickness of deposited PEMs can be affected by both the pH and the salt concentration of the PE solutions [39–42]. SRNF-membranes fabricated by the LbL deposition of weak PEs thus have an obvious advantage: the molecular structure inside of the PEM and the charge on the outside of the PEM can be controlled by an additional parameter, the pH. An added advantage of using weak PEs based membranes is that after fouling their cleaning can be made very easy using a sacrificial layer approach [43,44].

In this work, the first example of a PEM-based SRNF-membrane is presented prepared from weak PEs, a system where variation in pH can be used to tailor the membrane performance for specific solutes. More specifically, poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH) based PEMs were used, as this system has already shown itself promising in traditional NF-applications [38,43]. The pH of the coating solution was used as a parameter to control the layer thickness and the molecular organization of the multilayers, which in turn leads to different separation behavior for different solutes. PEMs were prepared under three pH combinations (PAH/PAA: 7.5/7.5, 7.5/3.5 and 3.5/3.5) and were characterized on model surfaces in order to understand the effect of coating pH on their resulting multilayer composition. The PEMs were then prepared on a hydrolyzed PAN support membrane under the same coating conditions and were characterized in terms of surface roughness, contact angle and IPA permeance. The performance of these multilayered membranes was characterized in terms of their ability to retain different organic solutes of varying size and charge from IPA in order to understand the effect of coating pH on membrane performance. Finally, the multilayered membranes were tested for their stability towards aprotic solvents such as acetonitrile (ACN), dimethylformamide (DMF) and tetrahydrofuran (THF) for long periods of time (> 50 h).

2. Experimental

2.1. Chemicals

Polyacrylonitrile (PAN, MW = 150,000 Da) was purchased from Scientific Polymer Products Inc., Ontario, New York. Isopropyl alcohol (IPA), acetonitrile (ACN), tetrahydrofuran (THF), N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were obtained from VWR, Leuven, Belgium, and were used as solvents. Rose bengal (RB), acid fuchsin (AF), bromothymol blue (BTB), methylene blue (MB) and methyl orange (MO) were purchased from Sigma–Aldrich and used as solutes (see Table 1 for more details). The PEs used in this study were poly(allylamine) hydrochloride (PAH; $M_w = 15,000 \text{ g mol}^{-1}$) and poly(acrylic acid) (PAA; $M_w = 15,000 \text{ g mol}^{-1}$). Sodium nitrate (NaNO_3) was used to adjust the ionic strength in all solutions. Sodium hydroxide

Table 1
Properties of solutes used in this study.

Solute	Mol. weight (Dalton)	Charge	Molar volume ($\text{cm}^3 \text{ mol}^{-1}$)
Rose Bengal (RB)	1017	–2	273
Methyl Orange (MO)	327	–1	160
Bromothymol Blue (BTB)	624	0	281
Methylene Blue (MB)	320	+1	242
Acid Fuchsin (AF)	585	–2	247

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