



# High performance organic solvent nanofiltration membranes: Development and thorough testing of thin film composite membranes made of polymers of intrinsic microporosity (PIMs)

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## ABSTRACT

High free volume polymers are characterized by much higher permeability and diffusivity for gases and vapors than commodity polymers. Polymers of intrinsic microporosity (PIMs), an important member of this class of polymers, are only soluble in a few solvents. This gives reason to expect stability in many solvents and an application in organic solvent nanofiltration (OSN) may be feasible. Thin film composite membranes of PIM-1 and PIM copolymers were developed on a polyacrylonitrile (PAN) porous support. For control of swelling, a simple, technically realizable method of cross-linking was produced by blending the PIM with polyethyleneimine, coating to give thin film composites (TFCs) and thermally or chemically cross-linking the separation layer on the supporting membrane. The TFCs were tested in OSN with the solvents n-heptane, toluene, chloroform, tetrahydrofuran, and alcohols, and compared to similarly cross-linked poly(trimethylsilyl propyne) TFCs and state of the art industrial Starmem™ 240 membranes. Better retention, a steeper retention curve and much higher fluxes were detected for the newly developed PIM TFC membranes.

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## 1. Introduction

Nanofiltration is the pressure driven membrane separation of solutes from liquids in the molecular weight range from 200 to 1000 g/mol. Nanofiltration involving organic solvents is still a niche market of membrane separation, however, it is expected to have high potential for strongly increasing applications in petrochemicals, fine chemicals and some large scale processes [1,2]. Either inorganic [3,4] or organic (polymeric) [5–13] membranes in porous or non-porous form are considered for this application or are in operation. In principle, inorganic membranes may be expected to give more precise results and to be more durable, because of their inertness to organic solvents. The porous structure will not swell under the action of various solvents and the retention will be independent of the solvent, in contrast to porous polymeric membranes. Nevertheless, porous polymeric membranes [14,15] made from polyimides available previously under the trade name STARMEM™, rank among the best nanofiltration membranes on the market. This type of membrane is nowadays further developed and merchandized under the trade names DuraMem® and

PuraMem® by Evonik Industries. Obviously, the swelling of polymers by organic solvents that influences flux as well as retention is no disqualifier for application in organic solvent nanofiltration (OSN). In the case of polymer membranes, in addition to these porous membranes also non-porous or homogenous (dense) membranes can be applied. Previously developed polydimethylsiloxane (PDMS) thin film composite membranes (TFC) [16,17] can be modified to control flux and selectivity by thickness and, more effectively, by increasing the cross-linking density of the selective separation layer [18,19]. The flux through a dense polymer layer, as well as depending on thickness, depends for the most part on a high diffusion coefficient of the solvent. The solvent diffusion coefficient is strongly dependent on the solvent properties, i.e., its polarity or, more precisely, solubility parameters (see, e.g. [20]) and temperature. Next to PDMS, high free volume polymers such as polyacetylenes and polymers of intrinsic microporosity (PIMs) display even higher diffusion coefficients, and so are expected to give high flux and eventually high retention nanofiltration membranes. To date, little work has been done to test this approach. The polyacetylene poly(1-(trimethylsilyl)-1-propyne) (PTMSP) was previously considered for OSN [21–23], though only polar solvents such as alcohols and acetone were applied as solvents and dyes were used as markers for retention. Dyes, with their hydrophobic main part and usually at least one charge, may interact with the separation layer and adsorb to some extent, thus

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resulting in a detected “negative” retention [21,24] making physically no sense as no uphill transport is assumed. PIM polymers are soluble only in a very few solvents, with solubility parameters centering around those of tetrahydrofuran (THF) and chloroform. In other solvents, either in polar (alcohols, ketones), aromatic (benzene, toluene), non-polar (alkanes) or aprotic polar (DMF, NMP, DMSO), more or less swelling is observed, thus demonstrating solvent stability of the virgin membrane to most organic solvents. Within the first published reports on PIMs, the organophilic behavior of PIM-1 was demonstrated using the example of pervaporative separation of phenol from water [25]. Compared to pervaporation with the required phase change liquid–gaseous–liquid, the solely pressure driven nanofiltration process is considerably less costly. Immediately after the advent of PIMs [25–27] we suggested the application of PIM-1 for OSN [28], however, the tested solvents acetone and toluene did swell the membrane to high extent resulting in a very high flux and low retention to the tested polyethylene glycol (PEG). For further examination we synthesized PIM-1 and PIM1 copolymers, prepared solvent resistant thin film composite membranes and analyzed flux and retention with various solvents and retention markers. In addition, a simple cross-linking method was developed to allow application for a large range of solvents and to keep the selective separation layer highly selective and stable even to the best solvents for PIMs. Furthermore, this method of cross-linking was easily transferred to membrane preparation on an industrial scale.

## 2. Experimental

### 2.1. Chemicals

Solvents were analytical grade (p.a.) from Merck or Aldrich. The retention marker hexaphenylbenzene (HPB) was derived from ABCR. The silica Nanopol XP21 from Nano Resins AG, Geesthacht, Germany was applied.

### 2.2. Polymers and oligomers

PIM-1 was prepared as described by Kricheldorf et al. [29], PIM1-CO1-50 and PIM1-CO6-50 were similarly prepared [30] using a modified fast synthesis method originally developed by Guiver's group [31]. The PIM polymers had intrinsic viscosity in  $\text{CHCl}_3$  of 30–40  $\text{cm}^3/\text{g}$  (at 30 °C), thus formed excellent films. Other applied polymers were from commercial source as listed below.

PTMSP (poly(1-trimethylsilyl-1-propyne), ABCR #AB109219), PEG 600 (polyethylene glycol, Mw ~ 600 g/mol, Merck # 807486), PEI (branched polyethyleneimine, Mn ~ 10,000 g/mol, Aldrich #408727), PEGDEG (cross-linker; poly(ethylene glycol) diglycidyl ether, Mn ~ 526 g/mol, Aldrich #475696).

### 2.3. Membranes

A GKSS in-house fabricated polyacrylonitrile (PAN) support membrane was applied showing an air flow of 100–150  $\text{m}^3/(\text{m}^2 \text{ h bar})$  and a pore diameter between 15 and 20 nm as detected by capillary flow porometry. Thin film composite membranes were prepared by dip-coating on the PAN support applying either a home made lab dip-coater (band type, 10–20 cm × 100 cm) or a technical coating machine (60–100 cm, endless). Typically, a 1% solution of the polymer having an intrinsic viscosity of above 30  $\text{cm}^3/\text{g}$  measured in  $\text{CHCl}_3$  at 30 °C was applied. Cross-linked thin film composites were prepared similarly by adding the cross-linker to the coating solution and finishing cross-linking by a heating step, either during the coating with the coating machine (set to 100 °C about 10 min residence time in the oven) or afterwards treating the sample in an oven at 120 °C for

some hours. The PEGDEG cross-linker was applied after membrane fabrication from 3 to 5 wt.% methanol solution, reacting over night and washed thoroughly by methanol. In some cases PAN support with an intermediate gutter layer was applied; the gutter layer was either Teflon® AF or polydimethylsiloxane (PDMS).

### 2.4. Flux and retention measurement

#### 2.4.1. Stirred cell

First tests were made using a solvent-resistant stirred cell from Millipore (stainless steel, 76 mm filter diameter, glass and solvent stable O-ring). Prior to measurement the membrane stamp was soaked in the utilized solvent overnight to start with an already swollen membrane. The cell fitted with the membrane was charged with ca. 100–200 ml solution containing the marker HPB (Mw 535 g/mol, 8 mg/l). A constant pressure of 3–6 bar  $\text{N}_2$  by the gas inlet was applied depending on the membrane flux. After permeation of 50 ml the next 10 ml of permeate were used for the flux and retention measurement. Permeance was calculated and is given in  $\text{l}/(\text{m}^2 \text{ h bar})$ . Concentration of HPB in feed, retentate and permeate were analyzed by gel permeation chromatography (GPC) fitted with a RI- and UV-detector in THF. GPC-software from PSS was applied yielding directly retention ( $R_i$ ) of HPB applying Eq. (1). In all cases the feed concentration was detected to be lower than the retentate concentration. The retentate concentration was in all cases below the solubility limit of HPB in the applied solvent. The retentate concentration was corrected by taking the arithmetic mean of feed and measured retentate concentration at the end of the experiment.

$$R_i = \left(1 - \frac{C_{Pi}}{C_{Ri}}\right) \times 100\% \quad (1)$$

$C_{Pi}$  is the permeate concentration and  $C_{Ri}$  is the retentate concentration.

#### 2.4.2. Cross-flow

For the cross-flow tests two setups were used. Prior to this work, with both set-ups comparative tests in toluene of commercially available membranes were made in toluene. The measured deviations between membrane sheets were in the usual range of variation. The first filtration setup was operated with n-heptane and the second setup with toluene. Both filtration setups include three flat sheet membrane cells. One filtration cell has 20 cm × 4 cm of active membrane surface and a feed channel height of 1 mm. The first filtration setup has membrane cells connected in parallel, where in the second setup membrane cells are connected in series. Otherwise the two setups are built and operated in the same manner. The setups contain a closed jacket 2 l feed tank. A high pressure pump delivers 3 kg/h, respectively 5 kg/h, of fresh feed out of the feed tank into the recirculation loop. The recirculation flow is approximately 200 l/h for each cell, associated with a Reynolds number of ~4500. With this set-up also concentration polarization is practically avoided. At the cross-flow velocity of 1.4 m/s a maximum contribution of the concentration polarization from 0.12 to 0.22% with increasing molecular weight of the polystyrene is calculated.

Retentate and permeate are redirected into the feed tank, hence a filtration experiment can be run continuously at constant feed. During the operation permeate was collected and weighted in specific time intervals. Permeance was calculated and given in  $\text{kg}/(\text{m}^2 \text{ h bar})$ . In order to determine membrane performance in steady state, all membranes were first operated with pure solvent for a minimum of 3 days. Subsequently, pure solvent was replaced by solvent with styrene oligomers [32]. The samples of permeate and feed were taken after a minimum of 24 h after introducing oligostyrene or changing the transmembrane pressure. The conditioning and sampling procedures were the same for all

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