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Solvent nanofiltration through high permeability glassy polymers: Effect of polymer and solute nature

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ABSTRACT

The effect of solute nature on the retention performance of membrane materials based on PTMSP, PMP and PIM-1 has been investigated in ethanol media. Using the examples of PMP and PIM-1, it was shown that membrane swelling could enhance the solvent transport across the membrane, regardless of the initial gas permeability. All polymers show the same level and order of retention for low molecular weight dyes (350 Da) regardless of the difference in polymer nature; in particular, negative retention of the neutral dye Solvent Blue 35 was observed for PTMSP, PMP and PIM-1: −17%, −11% and −4%, respectively. This retention behavior was explained by a "blocking effect" due to high dye-membrane interaction and comparable size of the solute ($V_{calc}=685$ Å^3) and available free volume elements within the polymer (5–12 Å). An increase of dye retention is attributed to a decrease of solute-membrane interaction; for example, PIM-1: Solvent Blue 35 ($K=1107$; $|\delta_{PIM-1}-\delta_{solute}|=4.2$) < Safranine O ($K=47.0$; $|\delta_{PIM-1}-\delta_{solute}|=6.1$) < Orange II ($K=3.3$; $|\delta_{PIM-1}-\delta_{solute}|=9.7$). The retention of higher molecular weight solutes is expected to be limited mainly by free volume size. Thus, it is possible to control nanofiltration parameters by proper selection of the polymer and the variety in the chemical nature of high permeability glassy polymers provides additional flexibility in solvent resistance and further modifications (e.g. cross-linking). A new possible application of PIM-1 as a polymeric sorbent with selectivity towards dissolved neutral compounds is proposed.

1. Introduction

Organic solvent nanofiltration (OSN) is a promising area of membrane separation that has been developing during the last decade. Many advantages of this technology have already been underlined in the literature [1–3]. Meanwhile, one of the major drawbacks preventing implementation of this technology in industry is the limited number of membrane materials that offer high filtration performance (solvent permeability/retention) and at the same time show high chemical and mechanical stability. Previously it was shown that glassy polymers with high fraction of free volume (FFV), such as PTMSP [4,5], are prospective membrane materials for this application. Due to the rigid nature of their macromolecular chains, a porous structure with free volume elements of about 1 nm size is naturally formed during casting of the polymeric solution and no subsequent treatment (e.g. immersion precipitation) is required. It was already shown that such an intrinsic microporous structure of PTMSP provides much higher ethanol permeability over high permeability rubbery polymers like poly[dimethylsiloxane] (PDMS) [4]. Due to good mechanical properties, PTMSP and PIM-1 have already been applied as a thin film selective layer (thickness less than 1 μm) to fabricate high performance OSN membranes [5,6]. These tailor-made composite membranes show superior nanofiltration performance over commercially available OSN membranes (e.g. MPF-50 or Starmem^{TM}).

Besides this, there is a lack of information in the literature regarding the membrane-solute interaction for this type of polymer and its influence on retention performance. For example, Fritsch et al. in the recent publication [6] used markers that possess little interaction with the separation layer based on PIM-1 to measure the retention curve. However, it was already shown that membrane-solute interaction could play a significant role in the separation process for aqueous and non-aqueous systems [7,8]. Therefore, the main goal of this work was to study the effect of the solute nature (mainly, charge and size) on the filtration performance of membrane materials based on different types of high permeability glassy polymer, mainly poly[1-(trimethylsilyl)-1-propyne]

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(PTMSP), poly[4–methyl–2–pentyne] (PMP) and polymer PIM-1 (polycondensation product of 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane and tetrafluoroterephthalonitrile).

2. Experimental part

2.1. Polymer synthesis

PTMSP was synthesized in toluene solution using $TaCl_5$ with cocatalyst triisobutylaluminum (TIBA) as the catalyst [9]. Polymerizations were carried out under the following conditions: [Monomer]/[Catalyst] = 50, [Cocatalyst]/[Catalyst] = 0.3, $[\text{Monomer}]_0 = 1$ mol/l, $T = 25$°C ($M_w = 1{,}600{,}000$, $M_w/M_n = 2.9$, $[\eta]^{25}_{\text{toluene}} = 6.9$ dl/g). PMP was synthesized in cyclohexane solution with the catalytic system $NbCl_5$/Et_3SiH [10]. Polymerization was carried out at the following conditions: [Monomer]/[Catalyst] = 50, [Cocatalyst]/[Catalyst] = 1, $[\text{Monomer}]_0 = 1$ mol/l, $T = 25$ °C ($M_w = 140000$, $M_w/M_n = 10.0$, $[\eta]^{25}_{\text{toluene}} = 0.48$ dl/g). PIM-1 was synthesized by reaction of 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane with tetrafluoroterephthalonitrile as described previously [11], and purified by washing with 1,4-dioxane ($M_w = 137000$ g mol^{-1}, $M_w/M_n = 10$, $[\eta] = 0.47$ dl/g from multi-detector gel permeation chromatography in chloroform at room temperature). Fig. 1 illustrates the structures of selected high permeability glassy polymers.

2.2. Membrane preparation

The dense membranes were cast from solution with polymer concentration of 0.5–1.0 wt% (solvent: cyclohexane or chloroform) onto commercial cellophane. The cast film was then covered with a Petri dish and left for slow evaporation for several days, followed by drying in the oven at 40 °C to a constant sample weight. This allows dense membranes with a thickness of 20–30 μm (for filtration) and up to 100 μm (for sorption/swelling) to be obtained. Further treatment of all membranes was according to standard protocol of membrane preparation [12], which includes soaking of membrane samples in *n*-butanol (1 day) and ethanol aqueous solutions with stepwise decreasing of alcohol concentration from 96% to 0% (2 day) followed by drying at ambient conditions (1 day).

2.3. Filtration study

The filtration experiments were carried out at room temperature and pressure of 0–30 bar in dead-end filtration cells (effective membrane surface area of 33.2 cm^2) equipped with magnetic stirring bar (5 mm above the membrane) to minimize the concentration polarization effect. Technical grade ethanol was used as a solvent. Helium was used to pressurize the liquid above the membrane due to insignificant difference in solubility of the gas in ethanol. The membrane samples were soaked in ethanol overnight, and then placed into the filtration cell in a swollen state. The chamber above the membrane was filled with liquid (ethanol or dye solution) with volume of about 500 ml in order to maintain solute concentration on the same level during the experiment. The permeate collector was arranged so as to minimize solvent evaporation; the volume of each collected liquid sample was 2.5 ± 0.5 ml. All reported results are an average obtained using at least two different membrane samples, therefore, all flux and permeability data reported in this work were normalized by dry membrane thickness.

For retention experiments, four different dyes with a concentration in ethanol of 10 mg/l were used—Solvent Blue 35, Safranine O, Orange II and Remazol Brilliant Blue R (see Table 1). The dye concentration in the feed and permeate was determined using UV–vis spectroscopy at the $\lambda_{\max}$ experimentally obtained for each dye. The feed was also periodically sampled (after every 5–10 single filtration tests) without depressurizing the chamber above the membrane (via inlet system) for control of dye content. To estimate actual feed concentration for each single experiment, changes of dye content in the feed during filtration were calculated based on mass balance. After collecting about 75–100 ml of liquid, the filtration cells were depressurized, and after analysis all collected samples of permeate and feed were returned to the relevant cell in order to restore initial feed composition. The dye retention values were calculated using the following equation:

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) 100\%$$

where C_p and C_f are the dye concentration in the permeate and the feed, respectively. All filtration tests with a selected dye were repeated for each membrane sample until steady-state data were reached—deviation in retention less than 2% (3–10 day). All reported results are steady-state data, and an average obtained using at least two different membrane samples.

2.4. Sorption and swelling experiments

Dense membranes with thickness of up to 100 μm were soaked in ethanol for 2 day to reach equilibrium. After removal of the excess of the solvent from the surface, the membrane size and weight were measured, and polymer swelling degree (*SD*) in ethanol was calculated for PTMSP, PMP and PIM-1. In addition, dense membranes were also placed into 10 mg/l ethanol-dye solutions. Total sorption value was estimated from the difference in weight between the swollen and dry sample. The dye concentration in the membrane was determined by measuring the solution concentration before and after sorption. The distribution coefficient *K* of the dye between solution (C_S) and membrane (C_M) was expressed as:

$$K = \frac{C_M}{C_S} = \frac{(m_{\text{dye}}/m_{\text{ethanol}} + m_{\text{dye}} + m_{\text{membrane}})}{(m_{\text{dye}}/m_{\text{ethanol}} + m_{\text{dye}})}$$

where m_{ethanol}, m_{dye}, m_{membrane} are the weight of ethanol, dye and membrane respectively, C_M is the equilibrium dye concentration in the membrane, C_S is the equilibrium dye concentration in the solution in contact with membrane. For all experiments the mass balance indicated that solvent evaporation was negligible.

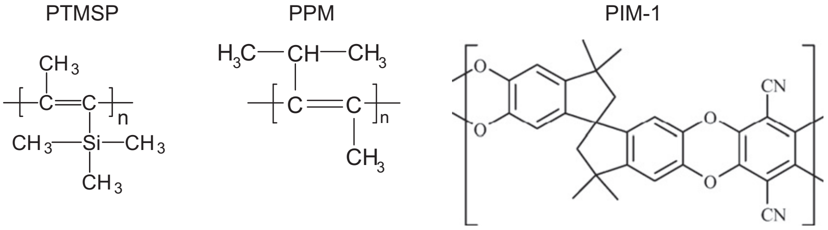

Fig. 1. Structure of high permeability glassy polymers: PTMSP, PMP and PIM-1.