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Responsive Pore Size Properties of Composite NF Membranes Based on PVDF Graft Copolymers

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Abstract: Uncharged nanofiltration (NF) membranes can potentially perform size-based separations of small molecules. Thin film composite (TFC) membranes, prepared by coating a porous support membrane with a thin layer of poly(vinylidene fluoride)-*graft*-poly(oxyethylene) methacrylate (PVDF-*g*-POEM), were shown previously to have such capability, as well as exceptional fouling resistance and high pure water permeability (*Macromolecules* 2004, *37*, 7663–7668). The selectivity and permeability of these membranes arises from the microphase separation of the PVDF backbone and polyethylene oxide (PEO) side chains into bicontinuous hydrophobic and hydrophilic phases, the PVDF domains providing mechanical integrity, and the PEO domains acting as "nanochannels" whose dimensions control molecular transport through the membrane. This study explores the influence of process and solution parameters on the permeability and selectivity of PVDF-*g*-POEM TFC NF membranes. By controlling the degree of swelling of the hydrated PEO chains filling the channels, the effective pore size of the membrane is shown to be tunable. Membrane permeability to water and to organic dye molecules of approximately 1 nm diameter is found to increase when the solvent quality of the feed for the PEO chains is reduced by raising the temperature, pressure, or ionic strength, or by the addition of ethanol. This property holds promise for applications in the biochemical,

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pharmaceutical, and food industries for low-cost, high-throughput fractionation of molecules.

Keywords: Comb copolymer, graft copolymer, membrane, nanochannels, nanofiltration, responsive, self-assembly, separation, size-selective, tuning

INTRODUCTION

Nanofiltration (NF) membranes have properties between reverse osmosis (RO) and ultrafiltration (UF). They combine the advantages of relatively high flux and low operational pressures with size cut-off on the molecular scale, in the 0.5–2 nm range (1). Uncharged NF membranes can potentially operate as molecular sieves and perform separations of molecules based on size. It would be especially promising to have such molecular filters whose size cut-off can be fine-tuned according to the separation desired. This could be very useful for applications in the pharmaceutical, biochemical, and food industries (2,3) which currently lack methods for low-cost, high-throughput fractionation of molecules.

Filtration membranes whose flux and selectivity can be modulated with different process parameters have been studied extensively (4,5). Researchers have developed membranes that respond to various stimuli, including pH (6–9), temperature (10–15), ionic strength (9,10), light (16), and the presence of solvents such as ethanol (17). Most of this research focuses on membranes whose size cut-off is in the ultrafiltration (UF) or microfiltration (MF) ranges (6–10,15–17).

Studies on responsive NF membranes are much more limited. In one example, temperature-responsive, thin film composite (TFC) membranes with size cut-off in the NF range were developed by Lopez and co-workers, using a hybrid gel of poly(N-isopropylacrylamide) (PNIPAAM) and silica (13) as a mesoporous selective layer, and employing surfactants as structure forming agents during casting (18). PNIPAAM has a lower critical solution temperature (LCST) in water (nominally ~32°C): polymer chains are soluble in water below this temperature. When the temperature is raised above the LCST, the polymer becomes insoluble in water and chains collapse, resulting in a decrease in the size of polymer coils and consequently, pore enlargement. In centrifugal filtration experiments, membranes prepared with the above method were found to be essentially impermeable to water at low temperatures, whereas at 40°C, they were permeable to water, with a molecular weight cut-off (MWCO) of 7850 g/mol, based on poly(ethylene oxide) (PEO) standards. Similarly, Nykanen et al. used triblock copolymers of poly(styrene) PS-*b*-PNIPAAM-*b*-PS that form spherical and gyroid structures to make membranes whose water permeability changed drastically with temperature (11). However, the retention of solutes was not observed to change significantly in that study.

Inoue and coworkers used graft copolymers with a vinyl backbone and polypeptide side-chains to prepare membranes whose permeability to various small molecules changes according to pH (19–21): The side-chains are negatively charged at high pH, which results in a high degree of swelling and increased permeability to small molecules. At lower pH levels, the carboxyl groups on the polypeptide chains are protonated, and the membrane substantially loses its hydrophilicity, resulting in lower permeabilities. The addition of doubly-charged salts such as calcium and copper also cause a decrease in permeability due to ionic cross-linking of carboxyl groups (22). Because of the charges present, separations employing these membranes are likely to involve both size-based and charge-based (Donnan) exclusion mechanisms.

The use of amphiphilic graft copolymers as the selective layer in size-selective, uncharged nanofiltration membranes was introduced previously by Mayes and coworkers (23–25), employing poly(vinylidene fluoride)-*graft*-poly(oxyethylene) methacrylate (PVDF-*g*-POEM), a copolymer with a hydrophobic backbone of PVDF and poly(ethylene oxide) (PEO) side-chains. TFC nanofiltration membranes were prepared by coating a PVDF UF membrane support with a thin layer of PVDF-*g*-POEM solution, followed by immersion in a non-solvent. Upon precipitation, the copolymer undergoes microphase separation, forming bicontinuous hydrophilic and hydrophobic phases. The hydrophilic PEO domains act effectively as "nanochannels" for the transport of water and other small molecules. These membranes were previously shown to be promising due to their subnanometer size selectivity (23,24) and high permeability (24,25). Moreover, the strong hydrophilicity and charge neutrality of the PEO domains deliver exceptional fouling resistance to these membranes (24,25), critical for maintaining their targeted size cut-off during use.

The selectivity of PVDF-*g*-POEM TFC NF membranes is determined by the chain density within the PEO-lined nanochannels, which is in turn affected by two major factors: the length scale of the microphase separation that creates the nanochannels, and the conformation of the PEO chains. The former can be influenced by controlling manufacturing conditions such as the composition of the copolymer or the coagulation bath. This study, however, focuses on the latter, which can be changed during use by modifying the solvent quality of the feed for PEO. This property allows the selectivity of the membrane to respond to the feed conditions by systematically varying parameters such as temperature, ionic strength, and ethanol content, all of which alter the swelling of PEO chains in solution (26–41). Such capability is highly desirable, as it would allow a single membrane to be used for a range of molecular sieving operations by fine-tuning the effective pore size to the separation desired.

EXPERIMENTAL

Materials

Poly(vinylidene fluoride) (PVDF, M_n ~107 kg/mol), poly(ethylene glycol) methyl ether methacrylate (named herein poly(oxyethylene) methacrylate, POEM, $M_n = 475$ g/mol), N-methyl pyrrolidone (NMP), 4-methoxyphenol (MEHQ), N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA), Brilliant Blue R, and Reactive Red 120 were purchased from Sigma-Aldrich (St. Louis, MO). Copper (I) chloride (CuCl), basic-activated alumina, poly(ethylene glycol) (PEG, $M_n = 600$ g/mol), N,N-dimethyl formamide (DMF), hexane, ethanol, tetrahydrofuran (THF), deuterated dimethyl sulfoxide (DMSO-d_6), and sodium chloride were purchased from VWR (West Chester, PA). All chemicals and solvents were reagent grade, and were used as received. PVDF-400 ultrafiltration membranes, purchased from Sepro Membranes, Inc. (Oceanside, CA), were used as the base membrane. Deionized water was produced from a Millipore Milli-Q unit.

Synthesis of PVDF-*g*-POEM

POEM was grafted to PVDF following a slightly modified version of the atom transfer radical polymerization (ATRP) approaches previously published (42,43). PVDF (5 g) was dissolved in NMP (50 mL) in a conical flask at 50°C. The solution was cooled to room temperature and transferred to a 250 mL Schlenk flask. POEM (50 mL), CuCl (0.04 g), and PMDETA (0.26 mL) were added to the reaction vessel, which was subsequently sealed. Nitrogen gas was bubbled through the reaction mixture for 20 minutes. After a total reaction time of 45 minutes, MEHQ (2.5 g), dissolved in approximately 10 mL of THF, was added to the reaction mixture, which was then diluted with approximately 100 mL of THF. This mixture was precipitated in a 10:3 mixture of hexane and ethanol. After stirring for 2 hours, the non-solvent mixture was decanted and replaced with ethanol. This was repeated after stirring overnight. After stirring for at least 3 more hours, the polymer was vacuum filtered and dried in a vacuum oven overnight. The POEM content of the copolymer was determined by ^{1}H Nuclear Magnetic Resonance (NMR) spectroscopy in deuterated DMSO using a Bruker DPX 400 spectrometer to be 48 wt%, equivalent to 40 wt% PEO. The reaction yield was 73%.

Preparation of Coated Membranes

The polymer solution was prepared by dissolving 1 g of PVDF-*g*-POEM copolymer in 4 mL DMF at approximately 50°C. This solution was passed through a 1-µm syringe filter (Whatman) and degassed in an oven at about 90°C for approximately one hour, until no air bubbles could be seen. Membranes were coated using a control coater (Testing Machines Inc., Ronkonkoma, NY). The PVDF-400 base membrane was fixed to the coater, and the micrometer adjustable film applicator, adjusted to 30-µm gate size, was inserted. The coating solution was poured onto the base membrane to form a thin line about 0.5 cm from the blade, and the coater was used to move the blade at a constant reproducible speed (speed level 4 on the instrument). After 5 minutes, the membrane was immersed in an isopropanol bath for 10 minutes and air dried. Before filtration experiments, the membrane was cut to size and wetted in Milli-Q water for at least 15 minutes.

Filtration Experiments

Circular pieces 49 mm in diameter were cut from coated membranes and wetted in water for at least 15 minutes before performing filtration experiments. The experiments were performed using a Sepa stirred, dead-end filtration cell (Osmonics) with an effective filtration area of 16.9 cm^2 and a liquid capacity of 300 mL. The filtration cell was placed in a water bath with a temperature controller that kept the system at the desired temperature with an accuracy of ±2°C. The cell was stirred at 400 rpm using a stir plate to minimize concentration polarization.

Membrane permeability was determined by collecting the filtrate for a known period of time, weighing it and normalizing by the membrane area and pressure difference, the latter measured by an electronic pressure gauge. The permeability of the membrane P_m ($\mathrm{L/m^2 \cdot hr \cdot MPa}$) is defined as

$$P_m = \frac{Q}{A.\Delta P} \tag{1}$$

where Q is the flow rate of permeate (L/hr), A is the effective area of membrane (m^2), and ΔP is the applied pressure difference (MPa).

The effective pore size of the membrane was also probed by the permeation of rigid dye molecules. Two dyes were used in this study: Brilliant Blue R (calculated molecular diameter: 11.1 Å) was used in observing the effect of ethanol addition to the feed, and Reactive Red 120 (calculated molecular diameter: 9.8 Å) was used to observe the effects of the temperature, the pressure, and the ionic strength. The diameters were calculated using Molecular Modeling Pro software (ChemSW, Fairfield, CA) by calculating the molecular volume of the dye from its chemical structure and fitting this value to a sphere of equal volume.

The effect of ethanol content in the feed was investigated by filtering a series of solutions of Brilliant Blue R (100 mg/L) in mixtures of ethanol and water, at a pressure of 150 psi (1.03 MPa). First, the ethanol/water mixture without the dye was passed through the membrane for at least 40 minutes. Then the feed was replaced with the dye solution. After the color of the filtrate stabilized (at least 1 hour), a sample was collected. The concentration was determined by UV-visible spectroscopy at 555 nm.

The dependence of membrane permeability on temperature and pressure was investigated. Deionized (DI) water or salt solution was passed through the membrane at room temperature and 200 psi (1.38 MPa) until the flux stabilized (at least one hour). The permeate was collected for 15 minutes and weighed to determine the permeability. The pressure was then decreased to 150 psi (1.03 MPa), and the flux was allowed to stabilize for 30 minutes. Another sample was collected and weighed. This was repeated at 100 psi (0.69 MPa) and 50 psi (0.34 MPa). Then the temperature was increased, first to 50°C and then to 70°C, and after a stabilization period of one hour, the above procedure was repeated at each temperature. This procedure was subsequently repeated with a feed of 0.1 M NaCl solution.

The permeation of Reactive Red 120 at different temperatures and pressures was also tested. For these experiments, the membrane was first allowed to stabilize by passing either DI water or 0.2 M NaCl solution through at 25°C for one hour. The initial feed solution was then replaced with the dye solution and filtration was performed similar to the method described above, increasing first the pressure and then the temperature step by step, and allowing the system to stabilize before collecting each sample. At the end of this period, the cell was rinsed with DI water, and DI water at 75°C was subsequently filtered through the membrane at 200 psi for 1 hour to clean the membrane. The dye concentrations of the feed and permeate were determined by UV-visible spectroscopy at 525 nm.

RESULTS AND DISCUSSION

Membrane Permeability

The pure water permeability (PWP) of the PVDF-*g*-POEM TFC membranes used in this paper was observed to range between 3.5–20 $\mathrm{L/m^2 \cdot hr \cdot MPa}$ at room temperature. These values are substantially lower than that of the UF base membrane (PWP ~2700 L/m^2 · hr · MPa), but comparable to those of commercial NF membranes currently available (25). The membranes described in this study were prepared by a bench-scale processing technique. With improved coating methods to achieve defect-free, thinner selective layers, the permeability of these membranes might be further improved.

Effect of Ethanol Content of the Feed

The effective pore size of PVDF-*g*-POEM TFC NF membranes depends on two main factors: the length-scale of microphase separation of the backbone and side chains, and the conformation of the PEO chains that line the resulting hydrophilic nanochannels. The first is set during the manufacturing stage of the membrane. The microphase-separated morphology depends on the chemical architecture of the copolymer, specifically the length of the hydrophilic side chains and their overall volume fraction in the copolymer. The casting conditions, such as the choice of non-solvent used in the coagulant bath, will also alter the nanochannel morphology by swelling one copolymer component relative to the other during precipitation of the coating.

The responsive qualities of the membrane, however, arise from the dependence of the effective pore size on the conformation of PEO chains within the hydrophilic nanochannels. PEO chains highly swollen in a good solvent create steric hindrance to molecular transport through the channels, reducing the effective channel width. In a poor solvent, the chains collapse toward the walls of the adjacent PVDF domains, allowing relatively larger molecules through. The transition is gradual, as the radius of gyration of polymer chains varies gradually with solvent quality, giving a means to tune the selectivity within a certain range.

To demonstrate this approach, water at room temperature was employed as a good solvent for PEO (34,36,37), to which varying amounts of ethanol were added. PEO solvency is decreased by adding ethanol into water, as shown in previous calorimetric and rheological studies (28). Therefore, the permeation of a retained solute of size comparable to the channel width through a PVDF-*g*-POEM membrane is expected to increase when ethanol is added to the feed.

Figure 1 shows the percentage of Brilliant Blue R (BB) passing through the membrane versus ethanol content in the feed solution. It can be seen that when the feed is water alone, all of the BB was retained (within instrument sensitivity). Thus the effective pore diameter in water is less than the molecular diameter of BB, calculated to be 11.1 Å. As the ethanol content in the feed rose, the amount of BB passing through the

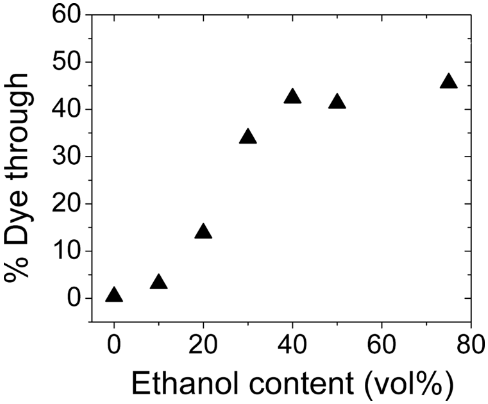


Figure 1. Percentage of Brilliant Blue R dye passing through PVDF-*g*-POEM TFC NF membrane versus ethanol content of the feed. Experiment performed at room temperature and 50 psi. Initial dye concentration: 100 mg/L. Percent dye through is defined as the ratio of the concentration of dye in the permeate to that in the feed.

membrane increased, indicating a widening of the nanochannels due to partial collapse of the PEO chains. For feed compositions beyond 40 vol. % ethanol, additional ethanol did not increase the permeation any further. The maximum percentage of dye passing through the membrane was approximately 45%. This reduction in the dye concentration in the permeate vs. the feed suggests that the diffusion of dye molecules through the membrane selective layer is hindered compared with the accompanying water molecules.

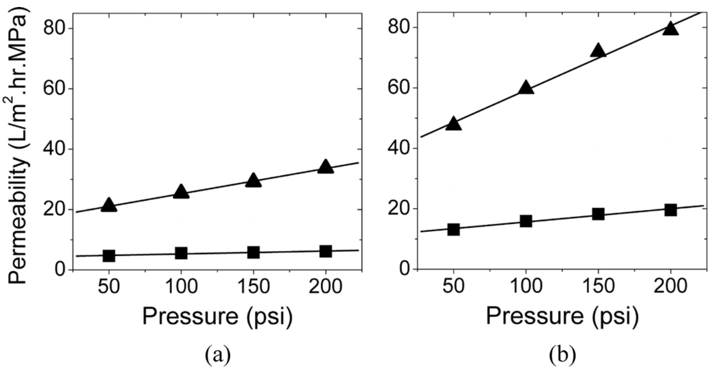
An alternative mechanism that could change the permeation of a solute through a composite membrane with feed composition is precipitation-diffusion. In this process, the change in feed concentration results in a decreased solubility for the solute. This leads to the precipitation of the solute onto the membrane surface, which increases its permeation. This mechanism, however, does not explain the effect of ethanol addition on the permeation of BB through the PVDF-*g*-POEM TFC NF membrane, because the solubility of BB is higher in ethanol than in water. In fact, BB would be expected to pass through the membrane to a lesser extent under such a mechanism.

Effect of Temperature, Pressure, and Ionic Strength

PEO-water systems have been studied extensively in the literature, both due to their applications in biotechnology and water treatment, and because of the interesting and unusual properties of PEO in water when compared with other polyethers (26–35,37,39,40). PEO-water mixtures exhibit a lower critical solution temperature (LCST), indicating that as a solution of PEO in water is heated, a temperature exists where the polymer's precipitation is thermodynamically favored. The LCST for PEO-water mixtures has been measured to be 99°C for high molecular weight PEO (1020 kg/mol). As molecular weight decreases, the LCST shifts to higher temperatures, and was measured to be 175.6°C for PEO of 2.27 kg/mol molecular weight (39). Below the LCST, the solvent quality of water for PEO increases as the temperature decreases, causing an expansion of the coils (28,29,33–35).

This property implies that the permeability of PVDF-*g*-POEM TFC NF membranes should increase with increasing feed temperature, as PEO side chains contract within the nanochannels. This can be observed in Fig. 2a, where the permeability of DI water through the membrane is shown at room temperature (triangles) and at 70°C (squares) for different pressures. At each pressure, the permeability of the membrane increased substantially when the temperature was raised to 70°C. At 50 psi pressure, the increase was almost 4.5-fold.

At higher pressures, the increase in permeability with temperature was even more dramatic—up to 5.5-fold at 200 psi. This finding is related to the fact that the LCST of PEO in water is depressed by high pressures (26–28,30). The effect of pressure on PEO solvency is relatively small at room temperature, which is quite far from the LCST. This is consistent with the data in Fig. 2a, which show that the permeability is essentially unaffected by pressure at room temperature. However, at temperatures



(a) (b)

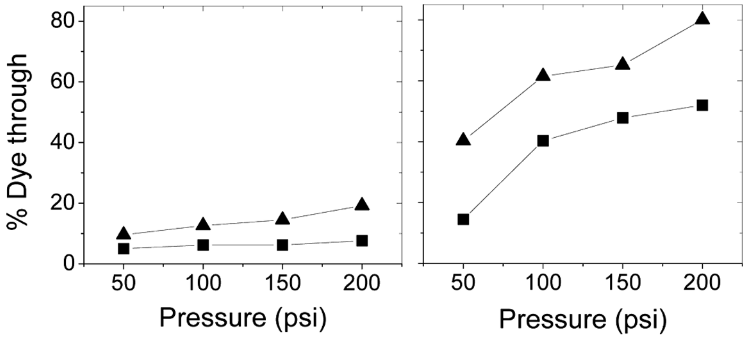
Figure 2. Permeability of PVDF-*g*-POEM TFC NF membrane with a feed of (a) DI water and (b) 0.2 M NaCl, at room temperature (■) and at 70°C (▲) at varying pressures.

closer to the LCST, the pressure effect becomes more significant. In Fig. 2a, the permeability of the membrane at 70°C increases by 60% when the pressure is increased from 50 psi to 200 psi.

Similar effects were observed when the permeation of Reactive Red 120 (RR) was investigated (Fig. 3a). At room temperature, 5% of RR permeated through the membrane at 50 psi. This increased to 7.5% when the pressure was increased to 200 psi. At 70°C, 9.6% of RR passed through the membrane at 50 psi, significantly higher than the values at room temperature. Increasing the pressure to 200 psi caused the dye permeation to double, reaching 19%.

Another important parameter in PEO-water solution behavior is the ionic strength of the solution. PEO exhibits salting-out behavior—increasing the ionic strength of a PEO-water solution causes a significant depression in its LCST and a marked decrease in solvent quality (27–29,40). The effect is especially strong when the PEO component is of low molecular weight (40). The addition of salt to a PEO-water system also results in a decrease in its lower critical solution pressure (LCSP), the pressure at which PEO falls out of solution (27–29). Therefore, high ionic strengths should increase the permeability of the PVDF-*g*-POEM TFC NF membranes and amplify the effects of high temperature and pressure on coil size.

Figure 2b shows the permeability of the PVDF-*g*-POEM TFC NF membrane at different temperatures and pressures with a feed of 0.2 M NaCl. At room temperature and 50 psi, the permeability of the membrane



(a) (b)

Figure 3. Percentage of Reactive Red 120 dye passing through PVDF-*g*-POEM TFC NF membrane with the dye dissolved in (a) DI water and (b) 0.2 M NaCl, at room temperature (■) and at 70°C (▲) at varying pressures. Initial dye concentration: 100 mg/L. Percent dye through is defined as the ratio of the concentration of dye in the permeate to that in the feed.

increased 2.8 times upon the introduction of salt to the feed. At room temperature, the change in permeability with pressure was much more pronounced compared to the DI water feed. Increasing the pressure from 50 psi to 200 psi caused a permeability increase of 50%. When the temperature was increased to 70°C at 50 psi, the permeability increased from 13 $L/m^2 \cdot hr \cdot MPa$ to 48 $L/m^2 \cdot hr \cdot MPa$. At this elevated temperature, the pressure effect was even more notable. The permeability of the membrane increased by 66%, up to 79 $L/m^2 \cdot hr \cdot MPa$, at 200 psi.

Similar trends could be observed in the filtration of Reactive Red 120 when the feed contained 0.2 M NaCl (Fig. 3b). At room temperature and 50 psi, the addition of salt caused the permeation of RR to increase to 15% from 5.0%. The effect of pressure was very evident even at room temperature, and 40% of the dye passed through the membrane when the pressure was increased to 200 psi. Increasing the pressure at 70°C caused the dye permeation to rise even further, up to 80% at 200 psi. Again, this behavior could not be explained by a precipitation-diffusion mechanism. The solubility of RR was not observed to vary significantly with salt addition. Pressure is not expected to alter solubility, whereas an increase in temperature would increase it. These results demonstrate the potential to alter the selectivity of the PVDF-*g*-POEM TFC membrane quite significantly by changing the operational temperature and pressure.

Effect of Temperature and Ionic Strength on the Swelling of PVDF-*g*-POEM

As mentioned briefly in the introduction section, there are mainly two approaches employed in the design of responsive membranes (4). The first one exploits changes in the coil size of polymer chains lining the pores to alter performance: as the coils expand, permeation is reduced due to steric effects. This is the most common strategy described for responsive UF and MF membranes (6,8,9,12,15,17). Conversely, in the second approach, polymer swelling leads to an increase in membrane permeability. In these systems, the polymer is held together by physical or chemical cross-links to regulate permeation. This is the strategy adopted for most responsive NF membranes (11,19–22).

To verify that the PVDF-*g*-POEM membranes operate under the first mechanism and not the second, the swelling of a sample of PVDF-*g*-POEM was measured at a series of temperatures, in DI water and in 0.2 M NaCl (Fig. 4). In this figure, the swelling ratio is defined as the weight of the swollen polymer to its dry weight.

The swelling of the polymer in DI water decreased gradually as temperature increased. This is consistent with the change in the solvent

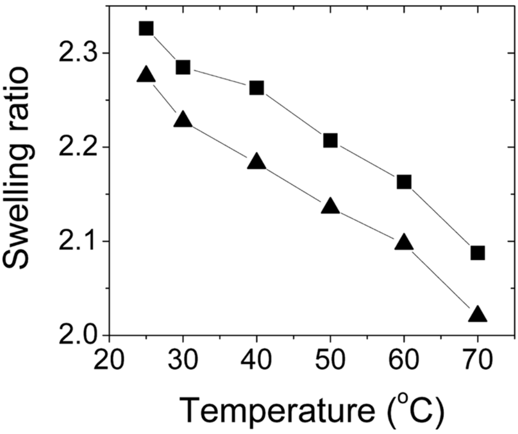


Figure 4. Change in swelling ratio of PVDF-*g*-POEM with temperature in DI water (▲) and 0.2 M NaCl (■).

quality of water for PEO with temperature. Considering the strong hydrophobicity and crystallinity of PVDF, PEO should be the only component that swells in water. A similar effect was observed when the polymer was swollen in 0.2 M NaCl solution. The degree of swelling of PVDF-*g*-POEM in salt solution was always lower than that in DI water, as expected based on the reduced solubility of PEO in salt solutions. The swelling once again decreased as the temperature was increased.

If the permeability change were caused by increased swelling of the copolymer, then the permeability of the membrane would be expected to decrease with increasing temperature and ionic strength. The fact that the permeability and effective pore size both increase with decreasing swelling is consistent with the first mechanism: the selectivity and permeability of the membrane is altered due to the change in conformation of the PEO chains lining the nanochannels.

CONCLUSION

PVDF-*g*-POEM TFC NF membranes offer a wide range of properties that are desirable for many filtration applications: easy manufacture, high pure water permeability, exceptional fouling resistance, and an ability to perform size-based fractionations of small molecules (23–25). In addition to these properties, the flux and selectivity of PVDF-*g*-POEM TFC NF membranes can be tuned by process parameters such as temperature and pressure, and can respond to solution properties such as ionic strength and ethanol content. All of these parameters affect the conformation of PEO chains lining the "nanochannels" that form upon microphase separation of PVDF-*g*-POEM. The ability to tune the molecular size cut-off using such parameters should be similarly observable with other novel NF membrane compositions incorporating PEO components that were recently described in the literature (44,45). Such capability could make viable high-throughput molecular fractionations via membrane filtration.

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