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Polymer Brush Membranes for Pervaporation of Organic Solvents from Water

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ABSTRACT: Atom transfer radical polymerization (ATRP) of 2-hydroxyethyl methacrylate from initiators immobilized on porous supports yields high-flux pervaporation membranes that can be readily modified to control their properties. Derivatization of poly(2-hydroxyethyl methacrylate) (PHEMA) coatings with octyl (C8-PHEMA), hexadecyl (C16-PHEMA), or pentadecafluorooctyl (fluorinated PHEMA) side chains provides films that are sufficiently hydrophobic to allow selective pervaporation of volatile organic compounds (VOCs) from water. For all of these derivatized PHEMA membranes, VOC/water selectivities generally increase with decreasing solubility of the VOC in water, and trichloroethylene/water selectivities are about 500. Sorption data suggest that fluorinated PHEMA has the highest free volume and that C16-PHEMA has the lowest, and consistent with this inference, fluxes decrease in the order fluorinated PHEMA > C8-PHEMA > C16-PHEMA. The ATRP and derivatization reactions readily yield defect-free films with thicknesses <200 nm, and this minimal thickness results in fluxes of ~1.4 kg/(m^2 h) (0.05 wt % VOCs at 22 °C) through fluorinated films. These fluxes are generally an order of magnitude greater than those through high-performance poly(dimethylsiloxane) pervaporation membranes. The use of different monomers or derivatization reagents may further enhance the flux and selectivity of pervaporation membranes prepared by ATRP.

Introduction

Pervaporation is a promising membrane-based technique that has been used for dehydration of organic solvents[1−4] as well as removal of organic molecules from aqueous solutions.[5−8] In the pervaporation process, a liquid mixture contacts the surface of a membrane, and selective transport of one component through the membrane to a vapor phase affords separation. Although selective removal of organics from water may be useful in chemical analysis and purification of waste streams,[9,10] the majority of pervaporation applications have thus far focused on dehydration of organic solvents,[1,4,11] in part because water is small and diffuses more quickly through membranes than organic molecules. The solution/diffusion mechanism suggests that pervaporation of organic compounds from water will require a material with a high sorption selectivity for the organic molecule and a minimal diffusion selectivity for water.[12−14] Hydrophobic polymers with high free volumes, e.g., poly(dimethylsiloxane) (PDMS) and poly(trimethylsilylpropyne), provide these characteristics, and there are a number of reports of selective pervaporation of volatile organic compounds through such materials.[5,15−18]

In addition to selectivity, both analytical and preparative pervaporation applications require high fluxes that necessitate the use of membranes that are as thin as possible.[19,20] However, because of the mechanical weakness of ultrathin polymer films, high-flux membranes generally consist of a thin, selective skin layer on a nonselective, highly porous support.[6,7,21] Such membrane structures are prepared by either a phase-inversion process that results in a dense surface layer on a porous bulk or deposition of a thin, selective layer on a preformed, microporous support. The latter method, which yields composite membranes, is advantageous in that very little of the potentially expensive selective layer is needed.[22] However, using simple techniques for forming PDMS membranes, it can be difficult to achieve defect-free skin layers that are less than 500 nm thick.[23]

In this article, we report preparation of composite pervaporation membranes via atom transfer radical polymerization (ATRP)[24−27] of 2-hydroxyethyl methacrylate (HEMA)[28−30] from the surface of a porous substrate (Scheme 1). Although this work employs porous alumina as a support, formation of brush membranes should be possible from a wide range of porous materials such as cellulose,[31] PDMS,[32] polystyrene,[33] and polyelectrolytes adsorbed on various surfaces.[34] To make poly(2-hydroxyethyl methacrylate) (PHEMA) membranes sufficiently hydrophobic for pervaporation of organic analytes from water, we derivatize them with hydrophobic acid chlorides, i.e., octanoyl chloride, palmitoyl chloride, and pentadecafluorooctanoyl chloride. Jennings previously showed that derivatization of PHEMA can yield hydrophobic films,[35,36] and we reported that fluorinated PHEMA membranes show modest selectivities in gas separations.[34] However, derivatized PHEMA films are much more attractive for pervaporation than gas separations, as they allow unusually high pervaporation fluxes (>1 kg/(m^2 h)). The ability to derivatize PHEMA with a variety of hydrophobic molecules permits comparison of different membrane materials without the need to develop new polymerization processes, and this article compares the pervaporation properties of three different elaborations of PHEMA. Sorption studies help elucidate the factors behind the selectivities of different films.

Experimental Section

Materials. Octanoyl chloride (99%), palmitoyl chloride (98%), pentadecafluorooctanoyl chloride (97%), dimethylformamide (DMF, anhydrous, 99.8%), tetrahydrofuran (THF, anhydrous, inhibitor free, 99.8%), 11-mercaptoundecanol (97%),

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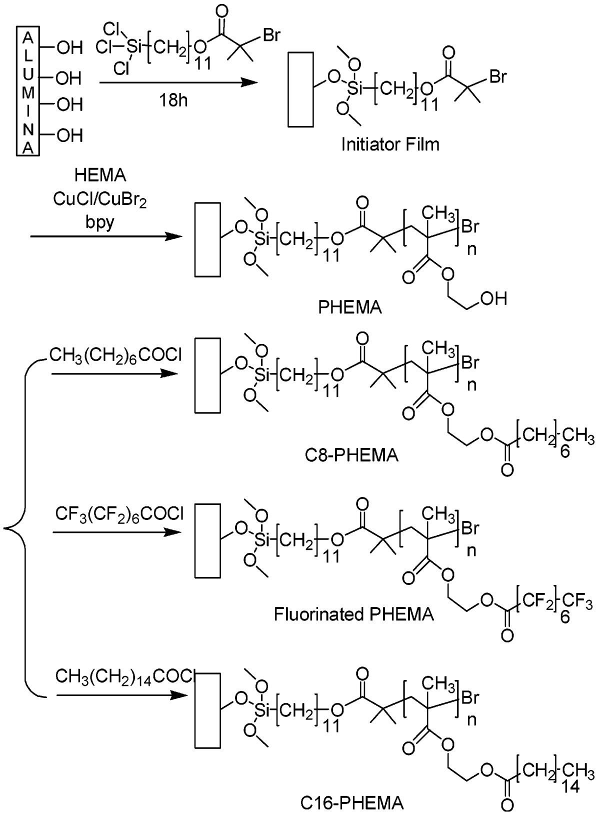
Scheme 1. Attachment of a Trichlorosilane Initiator to a Porous Alumina Support, ATRP from the Immobilized Initiators, and Derivatization of PHEMA with Acid Chlorides



2-bromopropionyl bromide (97%), ethyl 2-bromoisobutyrate (98%), CuCl (99.999%), $CuBr_2$ (99%), and 2,2′-bipyridine (bpy, 99%) were used as received from Aldrich. 2-Hydroxyethyl methacrylate (HEMA, Aldrich, 97%, inhibited with 300 ppm hydroquinone monomethyl ether) was purified by passing it through a column of activated basic alumina (Spectrum), and the trichlorosilane initiator (11-(2-bromo-2-methyl)propionyloxy)undecyltrichlorosilane) was synthesized according to a literature procedure.[37] Sorption and pervaporation tests employed deionized water (Milli-Q, 18.2 MΩ cm) and one of the following solvents: ethyl alcohol (EtOH, 100%, Pharmco), ethyl acetate (EtOAc), dichloromethane (CH_2Cl_2), trichloroethylene (TCE), or benzene. Other than ethanol, solvents were analytical grade and purchased from Aldrich. Anodisc porous alumina membranes (Fisher) with 0.02 μm diameter surface pores were used as supports for membrane formation, while gold-coated wafers (200 nm of sputtered Au on 20 nm Cr on a Si (100) wafer) were used as substrates for ellipsometry, contact angle, and reflectance Fourier transform infrared (FTIR) spectroscopy.

Polymerization of HEMA and Subsequent Derivatization. The alumina substrates were first cleaned in a UV/ozone cleaner (Boekel model 135500) for 15 min, inserted into a glovebox, and immersed in a 2 μM solution of trichlorosilane initiator in anhydrous THF for ~12 h. After removal from the glovebox, samples were rinsed with acetone, sonicated in DMF for 5 min, rinsed with water and acetone, and finally dried with a flow of nitrogen. Deposition of initiators on Au-coated wafers occurred through formation of a mercaptoundecanol monolayer and subsequent derivatization of this layer with 2-bromopropionyl bromide.[30]

Polymerization of HEMA occurred by immersion of the initiator-coated substrate in an aqueous HEMA solution containing a Cu catalyst system (Scheme 1).[28] To prepare this polymerization solution, 15 mL of purified monomer was added to 15 mL of deionized water, and this solution was degassed via three freeze−pump−thaw cycles. Next, 82.5 mg (0.825 mmol) of CuCl, 54 mg (0.24 mmol) of $CuBr_2$, and 320 mg (2.04 mmol) of bpy were quickly added to the mixture, which was then subjected to another freeze−pump−thaw cycle and stirred until a homogeneous, dark brown solution formed. Initiator-coated substrates and the sealed flask containing the polymerization solution were then transferred to a glovebag that was purged with nitrogen for about 1 h. The polymerization solution was finally transferred to the container holding the substrates, and polymerization was carried out for 2 h. After polymerization, substrates were removed from the container, sonicated in DMF for 10 min, rinsed with water followed by acetone, and dried with a flow of nitrogen. Subsequent derivatizations of PHEMA were carried out by immersing the PHEMA-coated substrates in DMF solutions containing 0.2 M octanoyl chloride, pentadecafluorooctanoyl chloride, or palmitoyl chloride and 0.1 M pyridine. After a 2 h immersion in the solution of acid chloride, substrates were rinsed with DMF followed by ethanol and dried with a flow of nitrogen.

Characterization of Membranes. Film growth on alumina supports was verified by field-emission scanning electron microscopy (FESEM, Hitachi S-4700II, acceleration voltage of 10 kV). Membranes were freeze-fractured under liquid N_2 and sputter-coated (Pelco model SC-7) on both sides with 5 nm of gold prior to FESEM. Ellipsometric thickness determinations were performed using a rotating analyzer ellipsometer (model M-44, J.A. Woollam). We assumed a film refractive index of 1.5, except in the case of the fluorinated film, where both refractive index and thickness were fit to ellipsometric data. These ellipsometric studies were carried out with films grown from gold-coated wafers. For each polymer film, thicknesses were measured at three different spots and averaged. Reflectance FTIR spectroscopy of films on gold-coated wafers was performed with a Nicolet Magna-IR 560 instrument using a Pike grazing angle (80°) accessory. Static water contact angle measurements (Firsttenangstroms contact angle analyzer) on alumina membranes were also performed before and after derivatization.

Pervaporation Experiments. Our home-built pervaporation apparatus was described previously.[38] Briefly, the solution was pumped across the surface of a membrane (effective area of 3.1 cm^2) that was supported by a stainless steel frit. The membrane cell was connected to a coiled stainless steel feed tube, and both the membrane cell and coiled tube were immersed into a thermostated water bath to control the temperature of the feed solution. On the permeate side of the membrane, a vacuum pressure of 0.06 mbar was applied, and the permeate was collected in one of two liquid nitrogen-cooled traps. Feed solution was usually pumped across the membrane at a flow rate of 5 mL/min, but in a few experiments, we did vary flow rate to determine whether there were large boundary layer effects on transport. In pervaporation of 0.05 wt % EtOAc, CH_2Cl_2, or TCE through C8-PHEMA at 65 °C, variation of feed flow rates from 1.4 to 11 mL/min yielded minimal changes in flux ($<$5% variation) and selectivity ($<$10% variation). Pervaporation of 0.05 wt % CH_2Cl_2 through fluorinated PHEMA membranes at 22 °C also showed little dependence on flow rate, suggesting that boundary layer effects are negligible. Tubing on the permeate side was warmed with heating tape to avoid condensation. Prior to sample collection, pervaporation was performed for at least 1 h to achieve stable, steady-state fluxes, and then the samples were collected in a second trap. The masses of the collected samples were measured using an electronic balance, and the composition of the permeate was determined by gas chromatography (Shimadzu GC-17A equipped with a Restek RTx-BAC1 column), using methanol as an internal standard. In cases where the permeate separated into organic and aqueous phases, the sample was diluted sufficiently with water to achieve a homogeneous mixture.

The separation effectiveness of pervaporation is quantified by two parameters, flux and selectivity. Flux (J) can be calculated using eq 1

$$J = \frac{Q}{At} \tag{1}$$

where Q is the mass of the permeate collected in time t, and A is the effective surface area of the membrane. In the case of a binary feed of components A and B, selectivity or separation factor, $\alpha_{\mathrm{B}}^{\mathrm{A}}$, can be expressed by eq 2

$$\alpha_{\mathrm{B}}^{\mathrm{A}} = \frac{y_{\mathrm{A}}/y_{\mathrm{B}}}{x_{\mathrm{A}}/x_{\mathrm{B}}} \tag{2}$$

where x and y represent mass fractions in the feed and permeate, respectively. Reported selectivities and fluxes are averages of results from three different membranes.

Sorption Measurements. Sorption experiments were performed with bulk polymers because of the inherent difficulties in measuring sorption in ultrathin films. Derivatized HEMA monomers were first synthesized by allowing acid chlorides to react with HEMA, and then the monomer was polymerized in solution. Specifically, HEMA (10 mL, 0.08 mol) was placed in a 250 mL round-bottom flask and dissolved in 100 mL of anhydrous dichloromethane. The flask was sealed with a septum, and pyridine (8 mL, 0.1 mol) was added to this solution followed by 0.09 mol of the desired acid chloride. The solution was purged with nitrogen for 1 h and stirred overnight at room temperature. The mixture was extracted with 1 M aqueous HCl and dried over Na_2SO_4, and the solvent was removed by rotary evaporation. The product was purified by column chromatography (20% EtOAc in hexanes, basic alumina as stationary phase) and dried under vacuum to obtain monomers as colorless oils. C8-HEMA (18 g, 90% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.17−6.04 (1H, d), 5.65−5.49 (1H, d), 4.47−4.19 (4H, m), 2.45−2.19 (2H, m), 2.06−1.84 (3H, s), 1.76−1.49 (2H, m), 1.42−1.23 (8H, m), 1.01−0.75 (3H, m). C16-HEMA (25 g, 85% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.19−6.03 (1H, d), 5.65−5.48 (1H, d), 4.44−4.22 (4H, m), 2.47−2.19 (2H, m), 2.03−1.85 (3H, s), 1.72−1.47 (2H, m), 1.44−1.10 (24H, m), 0.98−0.76 (3H, m). Fluorinated HEMA (30 g, 70% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.23−6.02 (1H, d), 5.70−5.49 (1H, d), 4.39−4.16 (2H, m), 3.94−3.67 (2H, m), 2.07−1.83 (3H, s).

For polymerization, 0.05 mol of monomer was added to a 100 mL Schlenk flask and degassed by three freeze−pump−thaw cycles. The flask was then inserted into a glovebox, and 40 mL of anhydrous dichloromethane was added to the monomer. Next $CuBr_2$, CuCl, and bpy (0.82, 0.24, and 2.0 mmol, respectively) were added to the solution followed by the initiator, 0.50 mmol of ethyl 2-bromoisobutyrate. After 10 h, the flask was taken out of the glovebox, and the brown solution was extracted with aqueous 1 M HCl to remove the copper complex. Evaporation of the solvent yielded colorless, viscous polymers. Those polymers were then dissolved in acetone (3 g/10 mL), and 2 mL of this polymer solution was cast on a 2 × 1 cm gold-coated Si wafer. After letting the acetone evaporate for 4 h at room temperature, the cast films were dried overnight in an oven at 60 °C and finally removed from the substrate.

To measure sorption selectivities and polymer swelling by solvents, the derivatized bulk PHEMA films were immersed for 24 h in room temperature aqueous solutions containing 0.05 wt % of a volatile organic compound (VOC). After that, the membranes were taken out of the vessel, wiped quickly with filter paper, and weighed. Degree of sorption of the VOC solution into the membranes was determined using eq 3, where m_0 and m_1 denote the weights of the dried membrane and the swollen membrane, respectively.

$$\text{degree of sorption} = (m_1 - m_0)/m_0 \times 100 \tag{3}$$

In determining sorption selectivity, we employed a literature procedure.[39] Briefly, solvent-swollen membranes were dried with filter paper and placed in a trap that was quickly cooled with liquid nitrogen and subsequently evacuated. The sample was then heated with a blow drier, and the vapor was collected in a second, cooled flask that was connected to the first by a valve. The mass of the bulk polymer was then measured again to make sure that we had removed essentially all of the water and solvent. The concentration of the VOC in the collected solution was determined by gas chromatography, and the sorption separation factor was calculated using eq 2 with y representing the composition of the adsorbed liquid that was eventually collected.

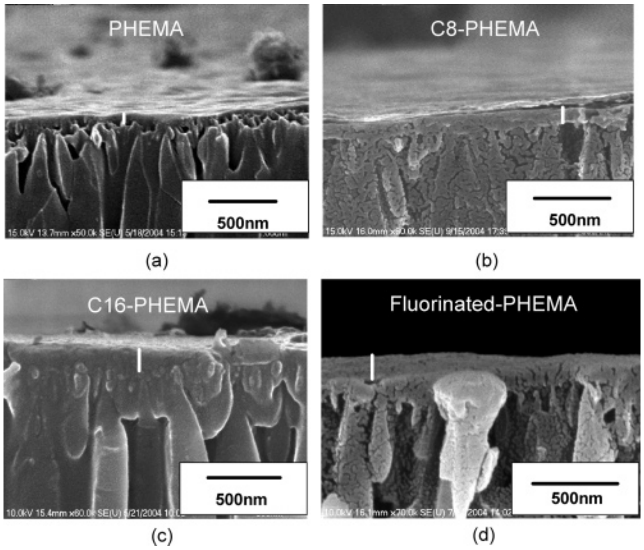


Figure 1. Cross-sectional FESEM images of alumina supports coated with (a) PHEMA, (b) C8-PHEMA, (c) C16-PHEMA, and (d) fluorinated PHEMA.

Results and Discussion

FTIR and SEM Characterization of Derivatized PHEMA Membranes. PHEMA is relatively hydrophilic and, hence, would not be expected to allow selective pervaporation of VOCs from water. However, each repeat unit of PHEMA has a hydroxyl group that can be easily esterified with a variety of acid chlorides. We let PHEMA films react with octanoyl chloride, palmitoyl chloride, and pentadecafluorooctanoyl chloride in the presence of a base to obtain polymers with hydrophobic side chains (Scheme 1). The static water contact angle on native PHEMA films is 50°, but contact angles increase to 75°, 95°, and 98° for films derivatized with octanoyl chloride (C8-PHEMA), palmitoyl chloride (C16-PHEMA), and pentadecafluorooctanoyl chloride (fluorinated PHEMA), respectively. These values fall between the advancing and receding contact angles reported by Jennings and co-workers.[36,40] To verify derivatization of PHEMA using reflectance FTIR spectroscopy, we grew films on gold-coated wafers as described previously.[28,36] Figure 1 of the Supporting Information shows the reflectance FTIR spectra of PHEMA films before and after esterification. Nearly complete disappearance of the OH stretch at 3500 cm^{-1} and a doubling of the carbonyl (CO) stretch at 1700 cm^{-1} suggest >90% conversion of the hydroxyl groups to esters.[28]

Figure 1 shows cross-sectional FESEM images of PHEMA, C8-PHEMA, C16-PHEMA, and fluorinated PHEMA films grown from porous alumina supports. Before derivatization, the thickness of PHEMA films is about 50 nm, as shown in Figure 1a, and the film fully covers substrate pores. Ellipsometric measurements of PHEMA films grown on gold-coated wafers under the same conditions also give a film thickness of 50 nm. After derivatization with octanoyl chloride, the molec-

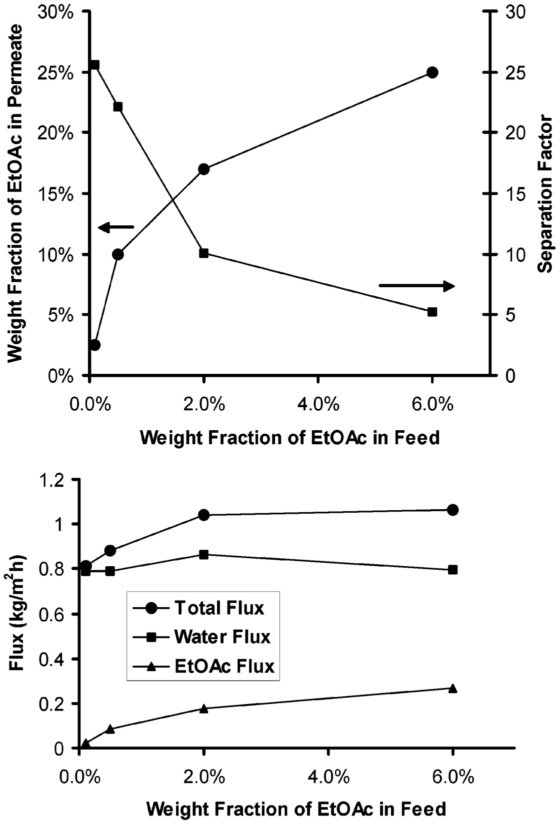


Figure 2. Permeate concentration (top), separation factor (top), and flux (bottom) in pervaporation of several ethyl acetate/water mixtures through C8-PHEMA membranes at 50 °C. The standard deviations of flux values and ethyl acetate weight fractions in the permeate were less than 15%.

ular weight of the polymer repeat unit should approximately double, so we would expect that the thickness of C8-PHEMA films would be about twice that for PHEMA, assuming a similar density for both films.[28] Both ellipsometry results and SEM images such as that in Figure 1b indicate that film thickness does indeed double upon reaction with octanoyl chloride.

For C16-PHEMA, we would expect to see a 180% increase in film thickness based solely on the molecular weight of the new repeat unit. Ellipsometric measurements show a thickness increase of 125%. The SEM image in Figure 1c suggests a ~200% increase in thickness, but it is difficult to determine exactly where the film begins in this image. In the case of fluorinated films, the polymer density should be higher than that of hydrogenated aliphatic polymers,[41,42] so it is not difficult to understand why we saw only a 170% increase in film thickness in ellipsometry despite a 300% increase in the molecular weight of the monomer unit. The FESEM image suggests a 240% increase in thickness. We should note that the high density of fluorinated PHEMA reflects the high atomic mass of fluorine relative to H and does not imply a low free volume for the fluorinated film. Most importantly, the PHEMA membranes and their derivatives are an order of magnitude or more thinner than typical PDMS membranes and other types of hydrophobic membranes currently used in pervaporation.[43-45] Moreover, the ATRP process (Scheme 1) should allow effective control over the thickness of the membranes by changing the polymerization time.

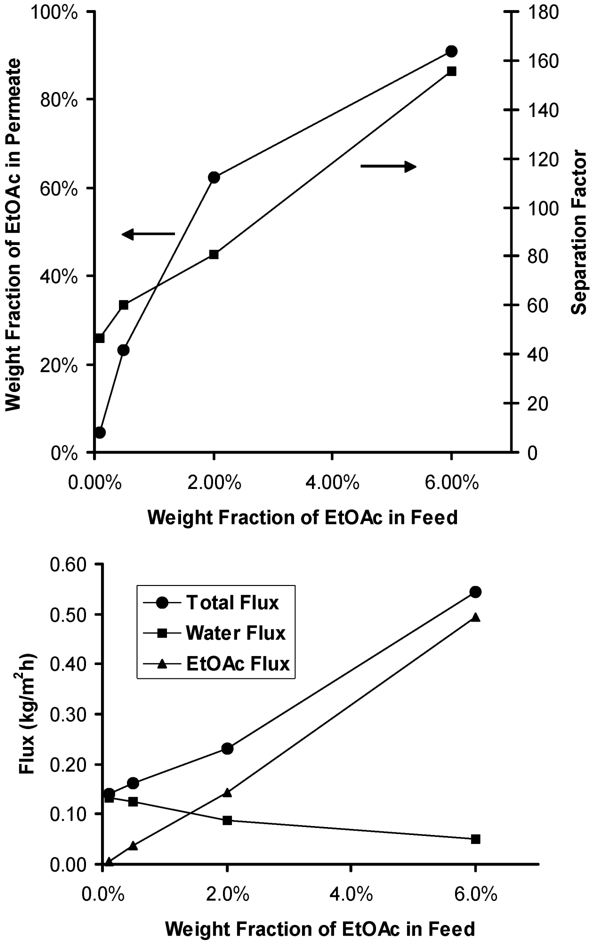


Figure 3. Permeate concentration (top), separation factor (top), and flux (bottom) in pervaporation of several ethyl acetate/water mixtures through C16-PHEMA membranes at 50 °C. The standard deviations of flux values and ethyl acetate weight fractions in the permeate were less than 15%.

Pervaporation of Ethyl Acetate−Water Mixtures Using Derivatized PHEMA. *Effect of Feed Concentration.* We initially employed EtOAc/water mixtures to probe the pervaporation properties of derivatized PHEMA membranes as a function of feed concentration and temperature. Figures 2−4 show that trends in flux and selectivity related to feed composition vary dramatically among the different membranes. For C8-PHEMA membranes (Figure 2), the total flux increases modestly from 0.8 to 1.1 kg/(m^2 h) as the EtOAc concentration in the feed goes from 0.1% to 6%. In contrast, total flux increases 4-fold on going from 0.1 to 6% EtOAc with C16-PHEMA membranes (Figure 3), although even with 6% EtOAc, fluxes through C16-PHEMA are half of those through C8-PHEMA. Fluorinated PHEMA membranes allow the highest fluxes (3−6-fold higher than with C8-PHEMA), with a doubling in flux as EtOAc concentration goes from 0.1 to 6% (Figure 4).

The trends in flux values are likely a reflection of differences in side chain packing in the different membrane systems. Hexadecyl side chains should pack in a more crystalline arrangement than shorter octyl side chains, so one would expect lower fluxes through C16-PHEMA membranes. (C16-PHEMA films are also 50% thicker than C8-PHEMA membranes, but this should result in only a ~33% lower flux for these membranes.) The more hydrophobic C16-PHEMA should also be more

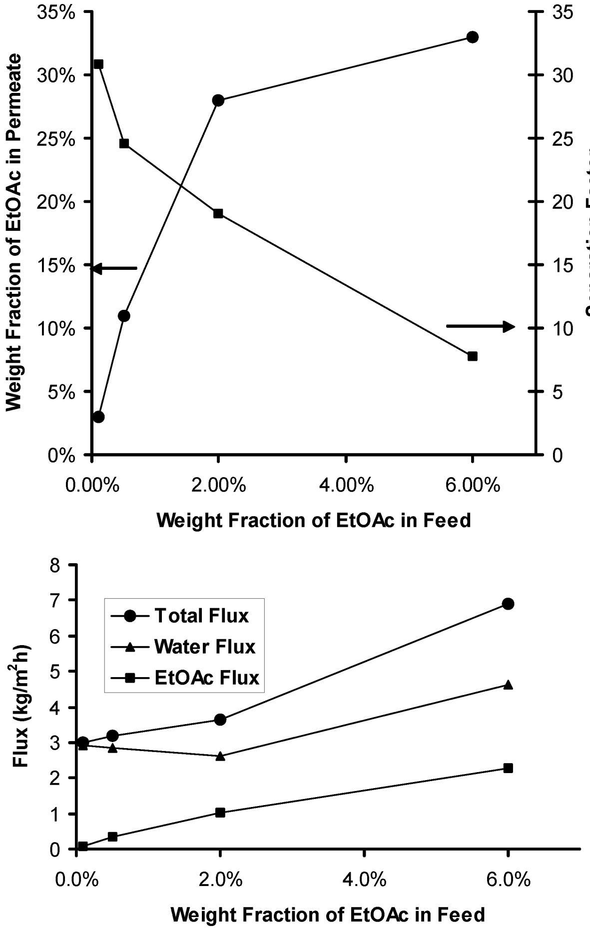


Figure 4. Permeate concentration (top), separation factor (top), and flux (bottom) in pervaporation of several ethyl acetate/water mixtures through fluorinated PHEMA membranes at 50 °C. The standard deviations of flux values and ethyl acetate weight fractions in the permeate were less than 15%.

susceptible to plasticization than C8-PHEMA, which is consistent with the large increase in flux through C16-PHEMA on going from 2% to 6% EtOAc. In the case of fluorinated PHEMA, the perfluorooctyl chain is bulkier than typical octyl chains, and this likely leads to higher free volume and, hence, higher permeability for the fluorinated PHEMA relative to C8-PHEMA.[46,47] Although the fluorinated films have a slightly higher water contact angle than C16-PHEMA, the fluorinated system appears to be less prone to plasticization, as suggested from a smaller relative increase in flux on going from 0.1 to 6% EtOAc. This may reflect the fact that typical hydrocarbons are less soluble in fluorinated than hydrogenated aliphatic chains.[48]

Separation factors also seem to depend on polymer packing. At low EtOAc concentrations (0.1%), separation factors are similar for all three membranes (25, 45, and 30 for C8-PHEMA, C16-PHEMA, and fluorinated PHEMA, respectively). However, separation factors for C8-PHEMA and fluorinated PHEMA decrease with increasing EtOAc concentration, while selectivities of C16-PHEMA membranes show a 4-fold increase on going from 0.1 to 6% EtOAc (Figures 2−4). Perhaps due to the tight packing in C16-PHEMA films, absorbed EtOAc molecules block the transport of water. Such an effect was seen previously in the separation of TCE from water using a fluoroalkyl methacrylate-grafted PDMS membrane.[49]

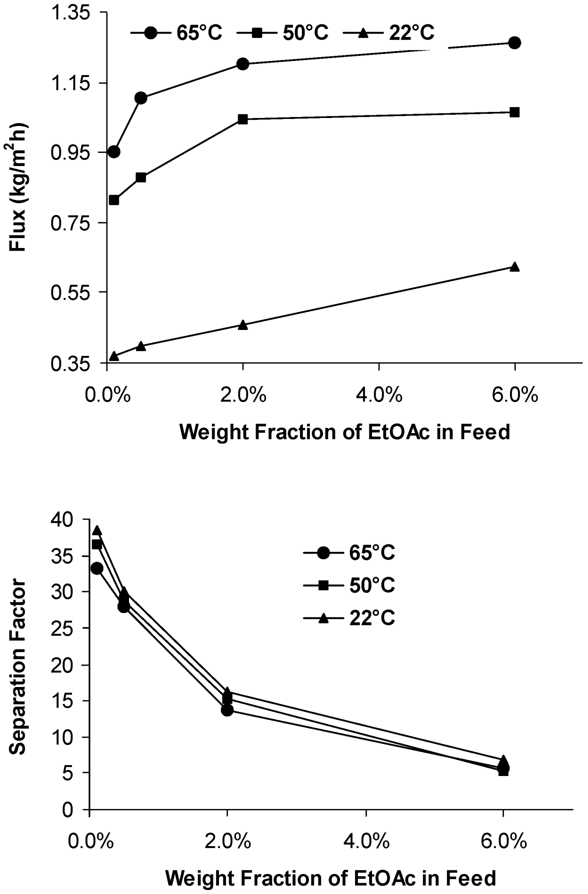


Figure 5. Flux (top) and separation factor (bottom) for pervaporation of water/ethyl acetate mixtures through C8-PHEMA membranes at several temperatures. The standard deviations of flux values and separation factors were less than 15%.

Effect of Feed Temperature. Figure 5 shows the fluxes and selectivities for pervaporation of EtOAc solutions through C8-PHEMA membranes at several temperatures. In agreement with other studies,[5,50,51] flux increases with increasing feed temperature, while selectivity remains essentially constant. Generally, as temperature increases, the thermal motion of polymer chains and permeate molecules intensifies, leading to more rapid diffusion of analytes through the membrane and, hence, higher fluxes. In contrast, temperature changes do not greatly alter separation factors because solubility (sorption) selectivity among permeating molecules is not a strong function of temperature.[5]

High pervaporation temperatures could also affect membrane performance by inducing polymer degradation. To test the stability of C8-PHEMA membranes, we performed pervaporation of 0.05 wt % EtOAc at 65 °C before and after storage of the membrane in the hot pervaporation solution for 1 week. The week-long exposure to 65 °C water had no significant effect on pervaporation. Additionally, we examined the stability of C16-PHEMA and fluorinated PHEMA films on gold wafers using FTIR spectroscopy. Storage of these films in 65 °C water for 1 week yielded no change in their IR spectra other than a uniform ∼10% decrease in intensity, which is probably due to desorption of a small quantity of polymer from the gold surface. The desorption could result from a small amount of physisorbed polymer or the instability of the Au−thiol linkage at high temperatures.[52]

Table 1. Molecular Properties[47] of Several VOCs and Separation Factors (VOC/Water) for Pervaporation (22 °C) of 0.05% Solutions through C8-PHEMA, C16-PHEMA, and Fluorinated PHEMA Membranes

compound	molar volume (mL/mol)	bp (°C)	solubility in water (wt %)	separation factor		
				C8	C16	fluorinated
water	18.0	100				
EtOH	58.5	78	miscible	2.0 ± 0.5	3.0 ± 0.3	1.0 ± 0.5
EtOAc	98.5	77	8.24	48 ± 3	56 ± 5	49 ± 1
CH_2Cl_2	63.9	40	2.00	330 ± 30	430 ± 60	430 ± 60
benzene	89.0	80	0.18	190 ± 30	250 ± 20	240 ± 20
TCE	90.2	87	0.11	430 ± 50	540 ± 50	510 ± 90

Table 2. Degrees of Sorption and Sorption Selectivities for Five VOCs (0.05% Aqueous Solutions) in C8-PHEMA, C16-PHEMA, and Fluorinated PHEMA Films

compound	solubility in water (wt %)	degree of sorption			sorption separation factor		
		C8	C16	fluorinated	C8	C16	fluorinated
EtOH	miscible	4.2 ± 0.7	3.7 ± 0.4	6.4 ± 0.7	8.1 ± 1.2	12.3 ± 0.5	3.5 ± 1.2
EtOAc	8.24	48 ± 5	10 ± 1	59 ± 7	203 ± 30	369 ± 5	120 ± 17
CH_2Cl_2	2.00	50 ± 8	20 ± 2	68 ± 7	520 ± 5	645 ± 6	450 ± 23
benzene	0.18	55 ± 12	27 ± 1	88 ± 9	580 ± 56	1600 ± 20	310 ± 30
TCE	0.11	68 ± 9	32 ± 2	99 ± 15	1540 ± 90	3700 ± 50	570 ± 80

Table 3. Separation Factors (22 °C) for Pervaporation (α_{PV}), Sorption (α_S), and Diffusion (α_D) of VOCs (0.05% Aqueous Solutions) in C8-PHEMA, C16-PHEMA, and Fluorinated PHEMA Membranes

compound	molar volume (mL/mol)	C8-PHEMA			C16-PHEMA			fluorinated PHEMA		
		α_{PV}	α_S	α_D	α_{PV}	α_S	α_D	α_{PV}	α_S	α_D
EtOH	58.5	2.0	8.1	0.25	3.0	12.3	0.24	1.0	3.5	0.26
EtOAc	98.5	48	203	0.24	56	369	0.15	49	120	0.41
CH_2Cl_2	63.9	330	520	0.63	430	645	0.67	430	460	0.93
benzene	89.0	190	580	0.33	250	1600	0.16	240	310	0.77
TCE	90.2	430	1540	0.28	540	3700	0.14	510	570	0.89

Pervaporation of Different Organic Compounds through Derivatized PHEMA Membranes. To further compare the properties of the derivatized PHEMA membranes, we examined pervaporation of a series of VOCs in water. We utilized a relatively low VOC concentration (0.05%) in these experiments to avoid plasticization and ensure that the VOCs remained soluble. For all VOCs, flux decreased in the order fluorinated PHEMA (1.2−1.5 kg/(m^2 h)) > C8-PHEMA (0.3−0.5 kg/(m^2 h)) > C16-PHEMA (0.1−0.2 kg/(m^2 h)). However, VOC/water separation factors did not vary greatly among the three types of membranes (Table 1). Selectivity did increase with the hydrophobicity of the VOC (decreasing water solubility) from EtOH to TCE, with the exception of CH_2Cl_2. The higher than expected CH_2Cl_2/water selectivity may occur in part because the small molar volume of CH_2Cl_2 relative to EtOAc, benzene, and TCE results in more rapid diffusion of CH_2Cl_2.[53] The low boiling point of CH_2Cl_2 may also increase its pervaporative transport.

Sorption Behavior and the Solution-Diffusion Model. In the solution-diffusion model, transport through membranes includes both sorption and diffusion. To decouple the effects of diffusion and sorption on selectivity, we measured sorption directly for all three PHEMA derivatives. To attain sufficient sensitivity for these measurements, we employed bulk polymers rather than thin polymer brushes grown from a surface, but sorption properties of bulk polymers and thin films should be similar. Table 2 shows that both the degrees of sorption and VOC/water sorption selectivities for the three derivatized PHEMA membranes generally increase with decreasing water solubility of the VOCs, as would be expected. The fluorinated membrane provides the only exception to this trend with the sorption selectivity of benzene being 30% lower than that of CH_2Cl_2.

Among the three membranes, C16-PHEMA exhibits both the highest sorption selectivity and the lowest degree of sorption. This is consistent with the high hydrophobicity of this polymer and a low free volume. The fluorinated polymer has the highest degree of sorption of the three derivatives, suggesting again that this material has a high free volume. However, with the exception of CH_2Cl_2, sorption selectivities for C8-PHEMA are 70−170% greater than those for fluorinated PHEMA. Although the fluorinated membrane has a higher water contact angle than C8-PHEMA, the low solubility of organics in fluorous phases likely reduces VOC/water sorption selectivity.[49]

The pervaporation separation factor, α_{PV}, in the solution-diffusion model is simply the product of the sorption selectivity, α_S, and the diffusion selectivity, α_D. Table 3 contains values of α_{PV} and α_S along with calculated values of α_D for all three membranes. Because of the small molar volume of water (18 mL/mol), α_D is less than 1 for all of the membranes. The higher diffusion selectivity for the fluorinated membranes (lower water/VOC selectivity) is probably another reflection of a high free volume. Among the VOCs, CH_2Cl_2 shows the largest α_D, which would be expected for this relatively small molecule. However, ethanol has an even lower molar volume than CH_2Cl_2, but its α_D is around 0.25 for all of the membranes. Perhaps ethanol is diffusing through the membrane in a hydrated state.[54] Trends in α_D for EtOAc, benzene, CH_2Cl_2, and TCE correlate reasonably well with molar volume, with the exception of TCE in the fluorinated membrane.

Comparison with Related Membrane Systems. Table 4 compares the pervaporation performance of fluorinated PHEMA membranes with several PDMS membranes. Blume and co-workers coated microporous polymer supports with PDMS to achieve 3.5 μm thick

Table 4. Comparison of the Pervaporation Performance of Fluorinated PHEMA and Several PDMS Membranes

membrane	VOC	feed concn (wt %)	T (°C)	membrane thickness (μm)	total flux ($\mathrm{kg/(m^2\,h)}$)	separation factor
PDMS[23]	TCE	0.05	30	3.5	0.2	440
fluorinated PHEMA	TCE	0.05	22	0.17	1.5	510
DMS (PERVAP 1060)[43]	EtOAc	1	30	8	0.4[a]	300
PDMS (PERVAP 1070)[43]	EtOAc	1	30	10	0.1[a]	450
fluorinated PHEMA	EtOAc	1	22	0.17	1[a]	25
PDMSDMMA[16]	benzene	0.05	40	270	0.0514	1853
fluorinated PHEMA	benzene	0.05	22	0.17	1.5	240

[a] EtOAc flux only.

PDMS skins (row 1, Table 4). These membranes show TCE/water pervaporation selectivities that are similar to those of fluorinated PHEMA, but the fluorinated PHEMA allows a 7-fold higher flux because it is 20 times thinner. When normalized to film thickness, the PDMS membranes are more permeable than fluorinated PHEMA, but Blume and co-workers reported that their coating method could not produce defect-free films with thicknesses less than 0.5 μm.

In the case of commercial PERVAP 1060 and 1070 membranes, EtOAc/water selectivity is 10–20-fold higher for the commercial membranes than for fluorinated PHEMA. However, EtOAc flux is 2.5–10-fold higher for fluorinated PHEMA, again because of the minimal thickness of the polymer brushes (Table 4). (Both PERVAP 1060 and PERVAP 1070 are composite membranes with a PDMS skin, but PERVAP 1070 is filled with zeolites.) In a recent paper, Uragami and coworkers polymerized PDMS dimethyl methacrylate macromonomers to prepare extremely selective membranes for pervaporation of benzene from water.[16] These membranes have 8-fold higher benzene/water selectivities than fluorinated PHEMA, but again the polymer brush membranes allow much higher fluxes. All of these comparisons neglect the fact that the transport through PHEMA membranes was measured at lower temperatures than those used with the comparison membranes. Higher pervaporation temperatures could result in as much as a doubling of flux, so transport through fluorinated PHEMA is often an order of magnitude or more greater than that reported for high-performance membranes. Additionally, decreasing the thickness of fluorinated PHEMA films may also allow further increases in flux. Although these comparisons demonstrate the high fluxes that can be achieved by using ultrathin polymer brushes as the skin layers in composite membranes, they also show that it may be possible to achieve even higher fluxes and selectivities if polymer brushes with different compositions can be prepared. Our future work will focus on this area.

Conclusions

Reflectance FTIR spectroscopy and FESEM measurements confirm that ATRP of HEMA followed by derivatization with acid chlorides yields derivatized PHEMA membranes that fully cover porous alumina substrates. VOC/water pervaporation selectivities of derivatized PHEMA reach values as high as 500, and the minimal thickness of the PHEMA films allows fluxes that are about an order of magnitude higher than those of currently used pervaporation membranes. Flux through fluorinated PHEMA is higher than through C8- or C16-PHEMA, presumably because the bulky fluorinated side chains pack less tightly than alkyl chains. C16-PHEMA exhibits the highest sorption selectivities, but the tight packing of these materials gives significant water/organic diffusion selectivity, so the overall selectivities of fluorinated PHEMA, C8-PHEMA, and C16-PHEMA are similar. Given the similar selectivities, the fluorinated system appears to be most promising because of its high flux.

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Supporting Information Available: Reflectance FTIR spectra of PHEMA films on gold before and after derivatization with octanoyl chloride, pentadecafluorooctanoyl chloride, and palmitoyl chloride. This material is available free of charge via the Internet at http://pubs.acs.org.

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