

High-performance PDMS membranes for pervaporative removal of VOCs from water: The role of alkyl grafting

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ABSTRACT: To improve the pervaporation performance of PDMS membrane, alkyl groups with different chain length were grafted into PDMS matrix. The prepared membranes were characterized by ATR-IR, DSC, TGA, PALS, and tensile testing. The effects of alkyl grafting on pervaporation performance of PDMS membrane were investigated in separation of ethyl acetate/water mixture. Experimental results show that the separation factor of PDMS membrane is largely improved by alkyl grafting because of the enhanced preferential sorption of ethyl acetate, and this improvement depends on alkyl grafting ratio and alkyl chain length. The total flux of PDMS membrane reduces after alkyl grafting owing to the decreased free volume. When grafting ratio is above 6.9%, membrane grafted with shorter alkyl groups is preferred for pervaporation. The best pervaporation performance is achieved by 9% octyl grafted PDMS membranes with a separation factor of 592 and a total flux of $188 \text{ gm}^{-2} \text{ h}^{-1}$ in separation of 1% ethyl acetate/water mixture at 40°C . Moreover, this octyl grafted PDMS membrane also exhibits excellent separation performance in removal of butyl acetate, methyl-tert-butyl ether, and n-butanol from water. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43700.

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INTRODUCTION

Volatile organic compounds (VOCs) are widely used in manufacture of various products, such as paints, pharmaceuticals, plasticizers, varnishes, and adhesive agents,^{1–3} and VOCs emissions have become a serious environmental problem nowadays. Wastewaters containing VOCs from chemical factories are harmful to human health and can produce secondary air pollution if not treated promptly. Meanwhile, the presence of VOCs in wastewaters signifies an inefficient usage of raw materials and an increase of cost. Thus, it is of great importance to eliminate or recover VOCs from wastewaters. Many methods including air stripping, adsorption, distillation, advance oxidation, biological treatment, and membrane technology have been proposed to remove VOCs from water, and the pros and cons of these methods have been discussed previously.⁴ Pervaporation was regarded as an attractive separation technique for this application with obvious advantages of high efficiency, energy-saving, and eco-friendly.⁵

Recently, great efforts have been devoted to the development of suitable pervaporation membranes for removal of VOCs from water. Inorganic membranes, such as Ge-ZSM-5 and phenyl functionalized silica membranes, showed excellent separation perform-

ance for organics/water mixtures.^{6–8} However, their applications have been somewhat limited by the difficulty in fabrication of continuous inorganic membrane structures on technologically scalable, low-cost platforms.⁹ On the contrary, polymer-based membranes are more suitable for commercial applications, due to their versatile and tunable properties, as well as easy processibility in large-scale fabrication processes. Various polymer membranes have been attempted to remove VOCs from water, such as polyurethaneurea (PU),^{10,11} poly(vinylidene fluoride-co-hexafluoropropene) P(VDF-co-HFP),^{12,13} poly(ethylene-co-vinyl acetate) (PEVA),¹⁴ ethylene propylene diene monomer (EPDM),¹⁵ poly(dimethylsiloxane) (PDMS),¹⁶ poly(octylmethylsiloxane) (POMS),¹⁷ and polyether-block-polyamides (PEBA).¹⁸ These polymer-based membranes exhibited good separation performance and their selectivities were comparable to or even higher than that of inorganic membranes in removal of some organics from water. Among them, PDMS membrane provides an outstanding performance in terms of flux, selectivity, thermal stability, and processing ability.

In order to further improve the performance of PDMS membrane, physical blending with inorganic particles into PDMS matrix has been extensively explored.^{19–21} The pervaporation performance of PDMS membrane was largely enhanced by incorporation of zeolite

for certain organics/water separation.^{22,23} Another method to improve the performance of PDMS membrane is chemical modification with functional groups. Bennett *et al.*^{24,25} reported that PDMS membrane functionalized with basic groups like amino, pyridyl, and cyano showed enhanced selectivity toward weakly acidic phenol and p-cresol. Jadav *et al.*²⁶ claimed that PDMS membranes cross-linked by n-octadecyltrichlorosilane and trichloro(1H, 1H,2H,2H-perfluorooctyl)silane exhibited high efficiency in removal of benzene and dichloromethane from wastewaters. Ohshima *et al.*²⁷ investigated the effects of various divinyl compounds containing functional groups on the pervaporation performance of PDMS membrane. They found that membranes cross-linked by divinylbenzene and divinylperfluorohexane displayed improved selectivity toward chloroform and benzene. Given that the majority of VOCs (i.e., esters, ethers, ketones, and hydrocarbons) are weakly polar, the introduction of long alkyl chains into PDMS matrix might be effective in improving the separation of VOCs from water. Therefore, we systematically investigated the effects of alkyl grafting ratio and alkyl chain length on the physicochemical properties and pervaporation performance of PDMS membrane in removal of VOCs from aqueous solution, and clarified the mechanisms behind various phenomena induced by alkyl groups.

The alkyl grafted PDMS membranes with different alkyl chain length were prepared by two steps. First, a known quantity of alkyl groups were introduced into a linear poly(hydromethylsiloxane) (PHMS). Then, alkyl grafted PDMS membranes were obtained by cross-linking alkyl modified PHMS with vinyl terminated poly(dimethylsiloxane). The physicochemical properties of the prepared membranes were evaluated by DSC, TGA, PALS, and tensile testing. The effects of alkyl grafting ratio and alkyl chain length on the pervaporation performance were investigated in separation of ethyl acetate (EA) from water. The octyl grafted PDMS membranes were further employed in removal of butyl acetate (BA), methyl-tert-butyl ether (MTBE), and n-butanol (BuOH) from water, and the corresponding composite membranes were also prepared and compared with membranes reported in the literature.

EXPERIMENTAL

Materials

Vinyl terminated poly(dimethylsiloxane) was supplied by GE Toshiba silicones Co., Ltd., Tokyo Japan. PHMS ($M_n = 2242$, determined by matrix-assisted laser desorption ionization time-of-flight mass spectrometry) and 1-alkenes (1-octylene, 1-dodecene, and 1-cetene) were purchased from J&K scientific Co., Ltd., Beijing China. Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyl-disiloxane complex solution was purchased from Sigma-Aldrich Co., Shanghai, China. n-heptane, EA, BA, MTBE, and BuOH of analytical grade were obtained from Beijing Chemical Plant, Beijing, China. Polyacrylonitrile (PAN) ultrafiltration membranes used as substrates were purchased from Sepro Membranes Inc., Oceanside, CA, USA.

Modification of PHMS

PHMS and 1-alkene were charged into a round-bottom flask with n-heptane as the reaction solution. Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyl-disiloxane complex solution was added as catalyst. The mixed solution was stirred at room temperature for 5 h. Then, the solvent was removed by using rotary evaporator and the product was obtained by further removing the traces

Table I. Details for Modification of PHMS

Modified PHMS	Dosage (g)			
	PHMS	1-alkene	Pt catalyst ^a	n-heptane
C8-PHMS	2.93	4.07	0.02	13.00
C12-PHMS	2.27	4.73	0.02	13.00
C16-PHMS	1.86	5.14	0.04	13.00

^aPt catalyst represents platinum (0)-1,3-divinyl-1,1,3,3-tetramethyl-disiloxane complex solution.

volatiles under high vacuum.²⁴ More information for modification of PHMS was shown in Table I. PHMS modified by octyl, dodecyl, and cetyl were denoted as C8-PHMS, C12-PHMS, and C16-PHMS, separately. All modified PHMS were stored in a freezer for further characterization and use. It was found that the PHMS modified by octyl and dodecyl (C8-PHMS and C12-PHMS) were highly viscous liquids, while PHMS modified by cetyl (C16-PHMS) was paste.

Membrane Preparation

The preparation of polymer solution was carried out at room temperature by mixing the modified PHMS and vinyl-terminated poly(dimethylsiloxane) in n-heptane. The polymer concentration of the mixed solution was 30 wt %. The mass ratios of vinyl-terminated poly(dimethylsiloxane) to modified PHMS for different membranes were shown in Table II. Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyl-disiloxane complex solution was added as catalyst with a concentration of 0.9 wt %. The mixed solution was agitated vigorously until the viscosity increased noticeably. Then the mixed solution was cast on stainless steel plates. After keeping in an oven at 90 °C for 24 h, homogeneous membranes were obtained by peeling from stainless steel plates. Membranes prepared by pristine PHMS, C8-PHMS, C12-PHMS, and C16-PHMS were named as PDMS, C8-PDMS, C12-PDMS, and C16-PDMS, respectively. The alkyl grafting ratio was defined as the mole percentage of modified siloxane units containing long alkyl groups (octyl, dodecyl, or cetyl) within the membrane. The thickness of homogeneous membranes was measured on 10 different places by a Screw Micrometer (Hua Lun Co., China) and calculated as an average value. Composite octyl grafted PDMS membranes were also prepared and the fabricating method was similar to homogeneous membranes except membrane solution was casted on PAN substrates.

Table II. Mass Ratio of Vinyl-Terminated Poly(Dimethylsiloxane) to Modified PHMS in Preparation of Membranes with Different Grafting Ratios

Mass ratio	Membrane	Grafting ratio (%)				
		4.7	5.6	6.9	9.0	12.9
	C8-PDMS	7.73	6.45	5.16	3.87	2.58
	C12-PDMS	6.00	5.00	4.00	3.00	2.00
	C16-PDMS	4.90	4.08	3.27	2.45	1.63

Characterization

The chemical structure of modified PHMS was determined by ¹H NMR with an AVANCE III 600 NMR spectrometer (Bruker Corp., Germany) using CDCl₃ as solvent. ATR-IR spectra of alkyl grafted PDMS membranes were recorded with a Nicolet iS50 FT-IR spectrometer (Thermo Fisher Scientific Corp.) at a scanning range of 400–4000 cm⁻¹.

The thermodynamic properties of alkyl grafted PDMS membranes were measured by a Dupont 1090B Thermal Analyzer (Dupont Corp.) over the temperature range of -140 to 40 °C at a constant heating rate of 5 °C/min. The thermal stability of alkyl grafted PDMS membranes were examined with a STA 449C Simultaneous Thermal Analyzer (Netzsch Corp., Germany) in the temperature range from 30 to 800 °C at a heating rate of 5 °C/min with a nitrogen flow of 40 mL/min.

The mechanical properties of alkyl grafted PDMS membranes were measured by an Instron 3365 Tensile Testing Machine (Instron Corp.). The width of measured samples was 10 mm and the length between the jaws was 40 mm. The mechanical measurement for each sample was repeated for 5 times. All the measurements were conducted at a crosshead speed of 10 mm/min and room temperature.

The free volume of alkyl grafted PDMS membranes was assessed by positron annihilation lifetime spectroscopy (PALS). The membranes were cut into 10 mm × 10 mm pieces and assembled into 0.5 mm thick stacks. A radioactive source of ²²Na was inserted between two stacks of the tested sample and the positron annihilation lifetimes were recorded using a fast-coincidence timing system. The time resolution of this system was 208 ps. All the PALS spectra were deconvoluted using LT 9.0 software and resolved into four lifetime components. The lifetimes (τ₃ and τ₄) belonging to *ortho*-positronium (o-Ps) annihilation were used to determine the mean sizes of free-volume holes in polymers and the corresponding intensities (I₃ and I₄) were considered as a rough measurement of the holes densities.^{28,29} The mean free volume radius (r_j, in Å) was calculated by a semi-empirical equation based on a spherical infinite potential well model, as described below³⁰:

$$\tau_j^{-1} = 2 \left[1 - \frac{r_j}{r_j + \Delta r} + \frac{1}{2\pi} \sin \left(\frac{2\pi r_j}{r_j + \Delta r} \right) \right], \quad (1)$$

where $j = 3$ or 4 and Δr is an empirical parameter (1.656 Å) determined by fitting well-known cavities. The apparent fraction free volume (f_v) was estimated by eq. (2)^{31–33}:

$$f_v = I_3 V_3 + I_4 V_4, \quad (2)$$

where V_3 and V_4 are the mean free volumes of spheres with radiuses r_3 and r_4 , respectively, according to eq. (3):

$$V_j = \frac{4\pi r_j^3}{3}. \quad (3)$$

Pervaporation

Pervaporation experiments were carried out with a home-made apparatus as described previously.³⁴ A flat membrane with an effective membrane area of 72.34 cm² was fixed into a pervaporation test cell. A peristaltic pump was used to circulate feed from feed tank to the pervaporation cell. The feed flow rate

through the pervaporation cell was kept at 2.2 L/min monitored by a rotameter. The downstream pressure was maintained around 400 Pa by a vacuum pump. The feed was maintained at 40 °C in water bath. The pervaporation experiment was initially conducted for 1 h to reach a steady state. After that, permeate was condensed in a cold trap, which was cooled with liquid nitrogen. Samples of both retentate and permeate were collected for analysis. The pervaporation performance of the membrane was evaluated in terms of the permeate flux and separation factor. The permeate flux was obtained by weighing the permeate collected in the cold trap for a given time. The separation factor was calculated by analyzing the compositions of retentate and permeate, which were determined by an Agilent 7890 Gas Chromatography (Agilent Corp.).

To eliminate the effect of membrane thickness on flux, the normalized flux (J , normalized to 100 μm) was used, as calculated by following equation:

$$J = \frac{Wd}{100At}, \quad (4)$$

where W (g) is the weight of liquid collected in the traps during an experiment time interval t (h). A (m²) and d (μm) are the effective area and thickness of the homogeneous membrane, respectively.

The separation factor α was calculated as:

$$\alpha_{o/w} = \frac{Y_o/Y_w}{X_o/X_w}, \quad (5)$$

where X and Y are the weight fractions of substances in the feed and permeate, respectively. Subscript o and w denotes organics and water, respectively.

Because normally there is a trade-off between permeability and selectivity for membranes, the pervaporation separation index (PSI) was used to evaluate the overall performance of membranes, and defined as³⁵:

$$PSI = J(\alpha - 1). \quad (6)$$

RESULTS AND DISCUSSION

Characterization

Characterization of Membrane Materials. Alkyl modified PHMS were obtained by hydrosilylation of linear PHMS with *n*-alkenes. The chemical structures and substitution rate of alkyl modified PHMS were confirmed by the ¹H NMR spectra. As can be seen from Figure 1, the resonance peak intensity of Si-H-proton at 4.7 ppm decreased after hydrosilylation reaction and three new resonance peaks at 1.29, 0.91, and 0.54 ppm were observed for alkyl modified PHMS. The three new peaks belong to the resonance peaks of -CH₂-proton, -CH₃-proton of alkyl groups, and Si-CH₂-proton, respectively. The presence of resonance peak of Si-CH₂-proton, together with the decreased peak intensity of Si-H-proton, suggests that alkyl groups were introduced into the side chain of PHMS. The degree of substitution by alkyl groups (Ds, %) for modified PHMS was calculated from the peak areas of Si-CH₂- and Si-H, according to the following equation:

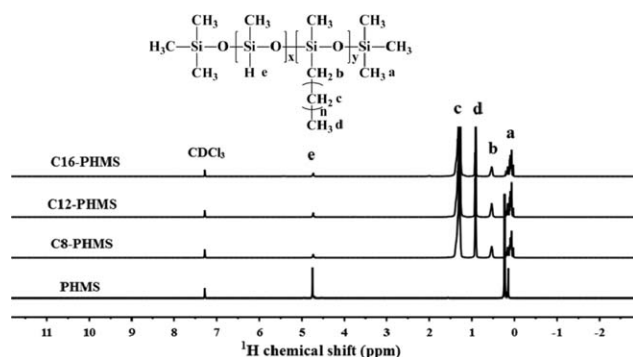


Figure 1. ^1H NMR spectra for pristine PHMS and modified PHMS (C16-PHMS, C12-PHMS and C8-PHMS).

$$Ds(\%) = 100 \times \frac{0.5 \times A_{\text{Si-CH}_2}}{0.5 \times A_{\text{Si-CH}_2} + A_{\text{Si-H}}} \quad (7)$$

Table III lists the peak areas integrals of the two relevant groups and the analysis results of ^1H NMR spectra (Figure 1), showing that the D_s was about 80% for each kind of modified PHMS. As the repeat unit number for pristine PHMS molecule was 34 determined by the average molecular weight, these ^1H NMR results indicate that about 27 siloxane units were functionalized by alkyl groups, and the residual 7 siloxane units containing Si-H groups were used as the cross-linking sites for membrane preparation.

Characterization of Homogeneous Membranes. The ATR-IR spectra for alkyl grafted PDMS membranes are shown in Figure 2. The adsorption band of Si-H group (at 2160 cm^{-1}) was barely detected for all alkyl grafted PDMS membranes, indicating that the residual Si-H groups in modified PHMS were completely cross-linked with vinyl terminated poly(dimethylsiloxane). Compared with PDMS membrane, alkyl grafted PDMS membranes exhibited two new peaks at 2854 and 2923 cm^{-1} . The two peaks were the symmetric and asymmetric stretching vibration of methylene derived from alkyl groups. For membranes with the same alkyl grafting ratio, intensities of the two peaks increased with the increase of alkyl chain length. Those results indicate that alkyl groups were successfully grafted into PDMS membranes.

To investigate the effect of alkyl groups on the thermodynamic properties of PDMS membrane, DSC was carried out and the results are presented in Figure 3. All alkyl grafted PDMS membranes showed a single T_g , similar to that of PDMS. This implies that no phase separation existed in these membranes. However, cetyl and dodecyl grafted membranes (C16-PDMS and C12-PDMS) displayed two melting tempera-

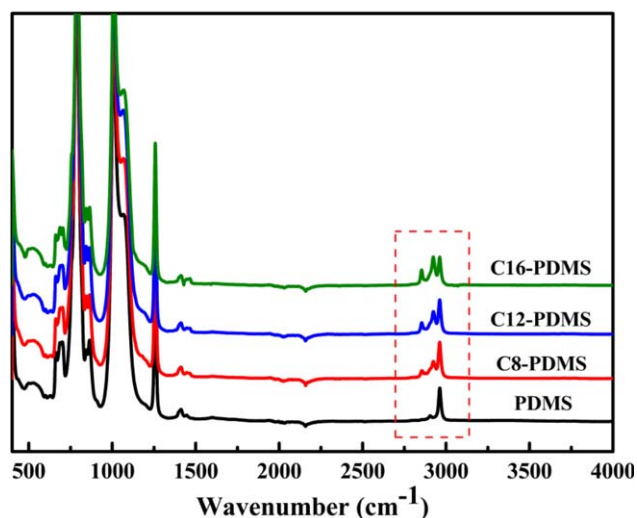


Figure 2. ATR-IR spectra for PDMS membrane and alkyl grafted PDMS membranes with 6.9% grafting ratio (C16-PDMS, C12-PDMS, and C8-PDMS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tures (T_m) compared with PDMS membrane. The first T_m (about -46°C) was close to the T_m value of PDMS membrane, corresponding to the crystallization of dimethylsiloxane units. The second T_m was attributed to the side-chain crystallization of dodecyl or cetyl groups. Because of the inherent low side-chain crystalline ability of octyl group and the “dilution effect” of dimethylsiloxane units,³⁶ the second T_m cannot be found for octyl grafted membranes (C8-PDMS). Lee *et al.*³⁷ synthesized alkyl-substituted hydroxypropylcellulose (HPC) and found that HPC substituted by octadecyl and dodecyl exhibited a side-chain crystallization, while octyl- and hexyl-substituted HPC did not. This side-chain crystallization might influence the packing of the semiflexible backbone and thus affected the properties of C16-PDMS and C12-PDMS membranes.³⁷

The thermal stability of alkyl grafted PDMS and PDMS membranes are illustrated by TGA curves in Figure 4. All the membranes exhibited an onset of degradation above 325°C and a one-step weight loss profile in the nitrogen atmosphere. This suggests that alkyl groups did not change the thermal stability of PDMS membrane.

The mechanical property is an important factor influencing the membrane durability in practical pervaporation process. Figure 5 shows the tensile properties of three kinds of alkyl grafted PDMS membranes and the pristine PDMS membranes. For

Table III. ^1H NMR Analysis Results of Modified PHMS

Modified PHMS	Peak area integral		Repeat unit number		Degree of substitution (%)
	$A_{\text{Si-H}}$	$A_{\text{Si-CH}_2}$	x	y	
C8-PHMS	1	7.61	7	27	79.2
C12-PHMS	1	8.23	7	27	80.4
C16-PHMS	1	7.87	7	27	79.7

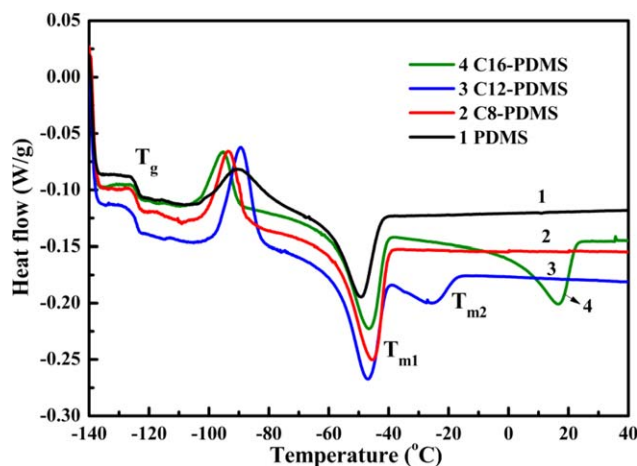


Figure 3. DSC thermograms of PDMS membrane and alkyl grafted PDMS membranes with 6.9% grafting ratio (C16-PDMS, C12-PDMS, and C8-PDMS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

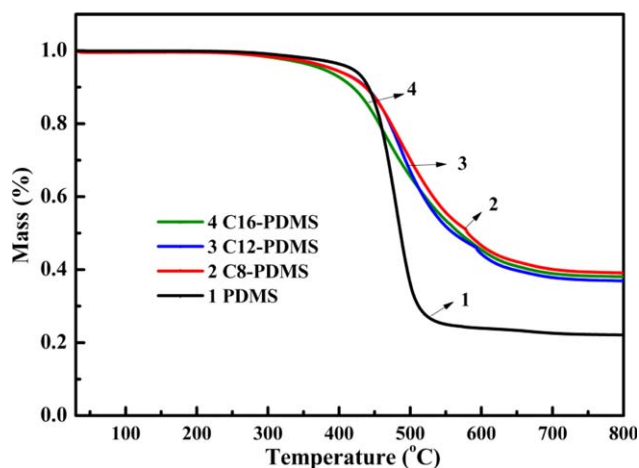


Figure 4. TGA thermograms of PDMS membrane and alkyl grafted PDMS membranes with 6.9% grafting ratio (C16-PDMS, C12-PDMS, and C8-PDMS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

alkyl grafted PDMS membranes, increasing the ratio of modified PHMS to vinyl-terminated poly(dimethylsiloxane) would result in an increased content of cross-linking sites (i.e., Si-H content). While for the pristine PDMS membrane, the Si-H content was adjusted by changing the addition of unmodified PHMS amount.^{38,39} Therefore, in Figure 5, the grafting ratio and Si-H content on X-coordinate were correlative except for the pristine PDMS membrane. As can be seen from Figure 5(A), the alkyl grafted PDMS membranes exhibited higher tensile strength than PDMS membranes at low Si-H content, due to the physical entanglement of alkyl groups. While such positive effect became negligible with increase of Si-H content (i.e., cross-linking degree), and when the grafting ratio was higher than 9%, a large amount of alkyl chains produced a negative effect on the chemical cross-linking reaction, thus decreasing the tensile strength of PDMS membrane, especially for the longer alkyl chains. Moreover, at the same grafting ratio, the tensile strength decreased

with the increase of alkyl chain length, which might be due to the side-chain crystallization of C12-PDMS and C16-PDMS membranes, as shown in Figure 3. The elongation at break of membranes is shown in Figure 5(B). Except for membranes with quite low grafting ratio, alkyl grafted PDMS membranes displayed smaller elongation at break than PDMS membrane at the same Si-H content. The difference in elongation at break between alkyl grafted PDMS and PDMS membranes became more pronounced with the increase of alkyl grafting ratio, but hardly affected by the alkyl chain length. It means that the toughness of PDMS membrane was reduced by introduction of alkyl groups, and such reduction was more obvious at higher grafting ratio.

Free volume is considered as a convenient and direct parameter to evaluate the membrane structure and has the potential to connect the microscopic membrane morphology with its macroscopic separation performance.³² In this study, PALS was adopted to determine the free volume of alkyl grafted PDMS

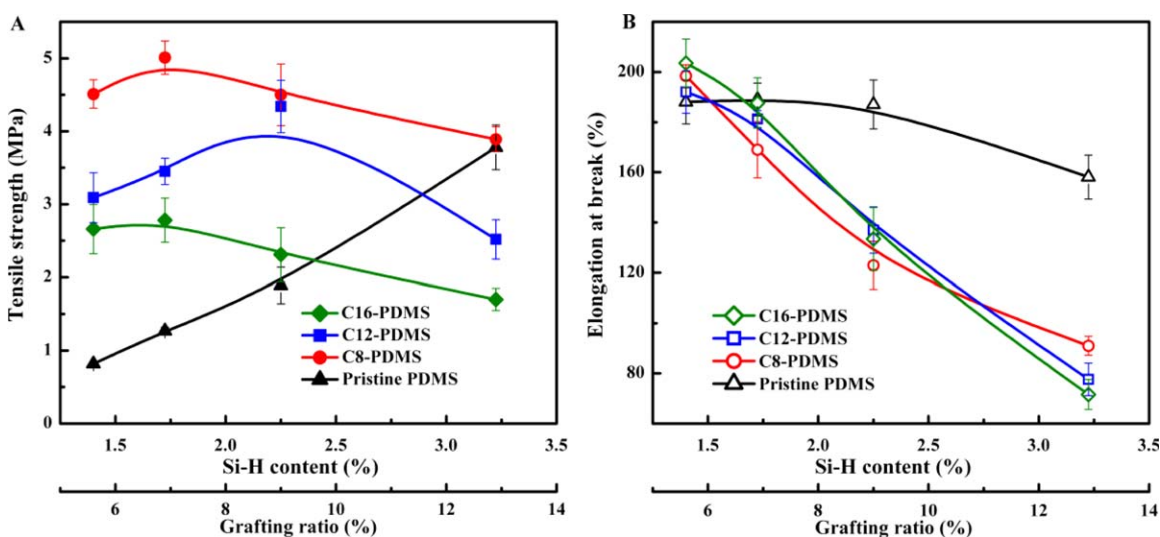


Figure 5. Tensile strength (A) and elongation at break (B) for pristine PDMS membrane and alkyl grafted PDMS membranes with different grafting ratios (C16-PDMS, C12-PDMS, and C8-PDMS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Free Volume Parameters of PDMS Membrane and Alkyl Grafted PDMS Membranes

Samples	τ_3 (ns)	τ_4 (ns)	I_3 (%)	I_4 (%)	r_3 (Å)	r_4 (Å)	f_{v3}	f_{v4}	f_v
PDMS	1.065	3.587	12.780	38.750	1.76	4.00	0.0029	0.1038	0.1067
C8-6.9% ^a	1.148	3.598	11.800	37.450	1.89	4.01	0.0033	0.1009	0.1042
C12-6.9%	1.112	3.548	12.080	36.800	1.83	3.98	0.0031	0.0972	0.1003
C16-6.9%	1.045	3.499	11.992	32.489	1.73	3.95	0.0026	0.0839	0.0865
C8-12.9%	1.110	3.543	12.473	33.434	1.83	3.97	0.0032	0.0878	0.0910
C12-12.9%	1.131	3.461	11.640	33.200	1.86	3.92	0.0031	0.0840	0.0872
C16-12.9%	1.091	3.390	11.752	27.798	1.80	3.88	0.0029	0.0680	0.0709

^aC8-6.9% represents octyl grafted PDMS membrane with 6.9% grafting ratio.

membranes, and the results are summarized in Table IV. The PDMS membrane exhibited a shorter lifetime τ_3 at 1.065 ns and a longer lifetime τ_4 at 3.587 ns, which corresponded to the small network holes of 1.76 Å and large aggregate holes at 4.00 Å, respectively.⁴⁰ With the increase of alkyl grafting ratio and alkyl chain length, the longer lifetime τ_4 and its intensity I_4 of membranes decreased, while the shorter lifetime τ_3 and its intensity I_3 did not significantly change. Similar phenomenon was reported by Lue *et al.*⁴¹ for polyurethane/poly(dimethylsiloxane) blended membranes. Those results indicated that alkyl grafting caused the decrease in aggregate hole size (reflected by τ_4) and hole density (reflected by I_4) for PDMS membrane. As the long alkyl groups grafted on the side chain of polysiloxane, the effect of polymer entanglement increased and the voids between the polymers aggregates were filled with the polymer segments.^{42,43} More and longer alkyl groups on the side chain further aggravated the polymer entanglement, and thus decreased the aggregate hole size and hole density. The total apparent free volume (f_v) calculated by Eq. (2) are presented in last columns of Table IV. Compared with PDMS membrane, the f_v showed a decrease trend for alkyl grafted PDMS membranes and this trend was more notable for membranes with higher grafting ratio. The effect of alkyl chain length on f_v exhibited the same tendency as that of grafting ratio. Those results imply that the alkyl grafting ratio and alkyl chain length made a large contribution to the free volume. So it could be deduced that proper alkyl grafting ratio and alkyl chain length would lead to a better separation performance.

Pervaporation Performance of Homogeneous Membranes

The pervaporation performance of homogeneous alkyl grafted PDMS membranes were investigated in the separation of EA/water mixture. Figure 6 shows the effects of alkyl grafting ratio and alkyl chain length on the separation factor. With the increase of alkyl grafting ratio, the separation factor increased rapidly and then decreased slightly. The alkyl chain length also affected separation factor. Based on solution-diffusion model,⁵ those variations in separation factor could be explained by solubility and diffusivity of EA and water in membranes. Table V shows the space distance of solubility parameters between membranes and EA ($\Delta\delta_E$) or water ($\Delta\delta_w$).⁴⁴⁻⁴⁶ A small $\Delta\delta_E$ means that the membrane had a strong affinity to EA and the ratio $\Delta\delta_E/\Delta\delta_w$ was considered as a measure of preferential sorption for EA in the membrane.^{35,47,48} Compared with PDMS membrane, alkyl grafted

PDMS membranes exhibited a lower $\Delta\delta_E/\Delta\delta_w$ and this value decreased with the increase of alkyl grafting ratio and alkyl chain length (Table V). This implies that the sorption selectivity toward EA increased with the increase of alkyl grafting ratio and alkyl chain length.⁴⁹ However, the diffusion selectivity toward EA varied in the opposite way. As discussed, the total free volume decreased with the increase of alkyl grafting ratio and alkyl chain length, especially for the aggregate holes (diameter around 3.9×2 Å). Due to the big kinetic diameter of 5.2 Å (Table V), the EA molecules can only transport through the aggregate holes. The diffusion of EA was more susceptible to the decrease of free volume than that of water and hence the diffusion selectivity toward EA decreased. Therefore, the variation of separation factor was caused by the tradeoff between free volume and preferential sorption. At low grafting ratio (<6.9%), the increase of sorption selectivity dominated the separation process. As a result, the separation factor increased with the increase of grafting ratio, and octyl grafted PDMS membranes showed the lowest separation factor due to its lowest sorption selectivity among the three kinds of alkyl grafted PDMS membranes at low grafting ratio. But at high grafting ratio (>6.9%), the reduction of diffusion selectivity caused by the decrease of free volume became more significant. Thus the octyl grafted PDMS membranes showed the highest

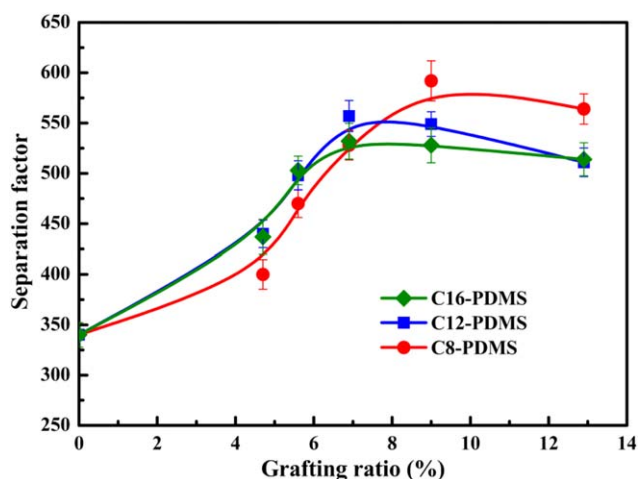


Figure 6. Effect of grafting ratio on separation factor for alkyl grafted PDMS membranes (C16-PDMS, 12-PDMS, and C8-PDMS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Kinetic Diameters, Solubility Parameters of Permeants and Membranes

	Kinetic diameter (Å) ⁴⁴	Solubility parameter δ (MPa ^{0.5})	$\Delta\delta_i = \delta_{\text{membrane}} - \delta_i $		$\frac{\Delta\delta_E}{\Delta\delta_W}$
			$\Delta\delta_E$	$\Delta\delta_W$	
Water	3.2	47.8 ^a			
EA	5.2	18.1 ^a			
PDMS		15.11 ^b	2.99	32.69	0.091
C8-6.9% ^c		15.36 ^b	2.74	32.44	0.084
C12-6.9%		15.48 ^b	2.62	32.32	0.081
C16-6.9%		15.59 ^b	2.51	32.21	0.078
C8-12.9%		15.54 ^b	2.56	32.26	0.079
C12-12.9%		15.72 ^b	2.38	32.08	0.074
C16-12.9%		15.88 ^b	2.22	31.92	0.070

^a Solubility parameters from literature.⁴⁵

^b Solubility parameters calculated by the group contribution method.⁴⁶

^c C8-6.9% represents octyl grafted PDMS membrane with 6.9% grafting ratio.

separation factor due to its highest free volume among the three kinds of membranes at high grafting ratio.

Figure 7 shows the total flux and partial fluxes of EA and water for alkyl grafted PDMS membranes. It can be seen that both the total flux and EA flux decreased with the increase of alkyl grafting ratio and alkyl chain length [Figure 7(A,B)]. Such decrease was attributed to the reduced free volume

(Table IV). A sharp decrease was also observed for water flux with the increase of alkyl grafting ratio, but this variation greatly slowed down when grafting ratio was above 6.9% [Figure 7(C)]. Compared to PDMS membrane, the water flux reduced by 17.4–48.1%, 23.3–50.5%, and 27.7–53.7% for octyl, dodecyl, and cetyl grafted PDMS membranes (grafting ratios were from 4.7 to 12.9%), respectively, while the corresponding EA flux only declined by 2.0–15.0%, 3.9–17.6%, and

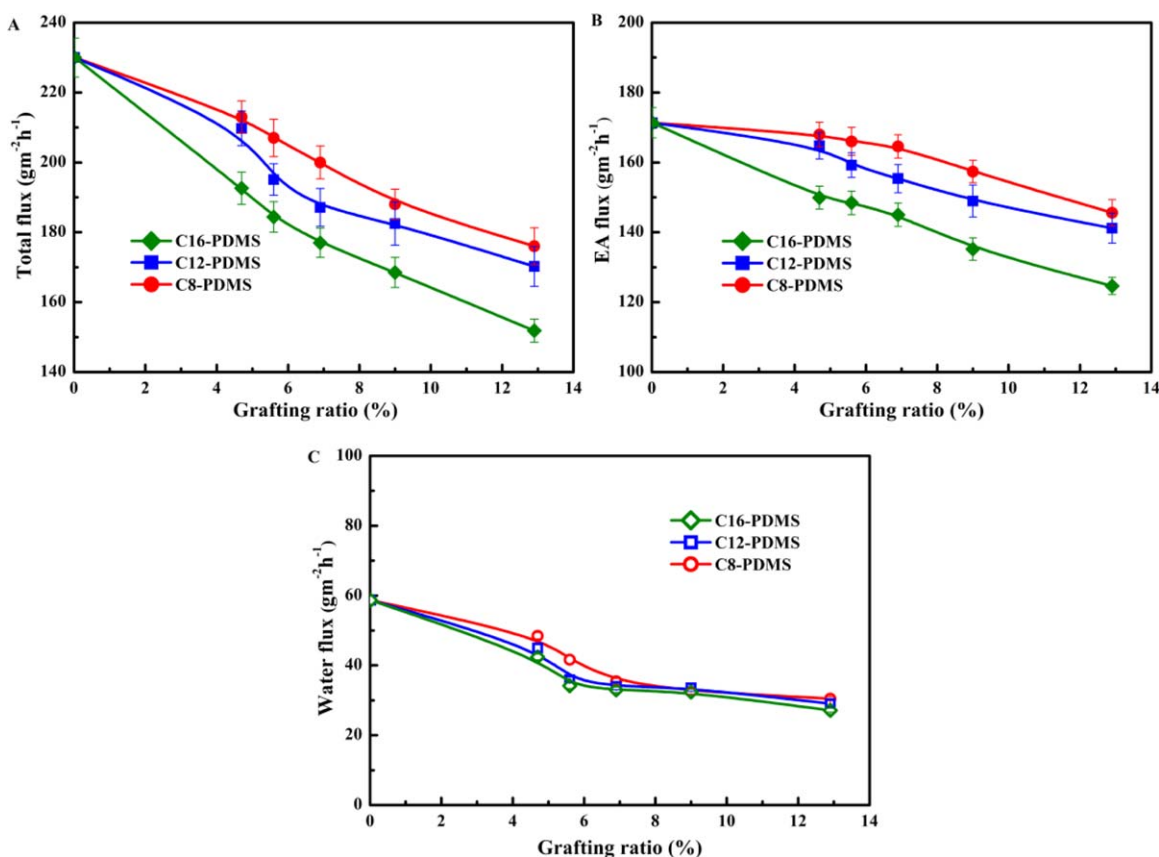


Figure 7. Effect of grafting ratio on total flux (A), EA flux (B) and water flux (C) for alkyl grafted PDMS membranes (C16-PDMS, C12-PDMS, and C8-PDMS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

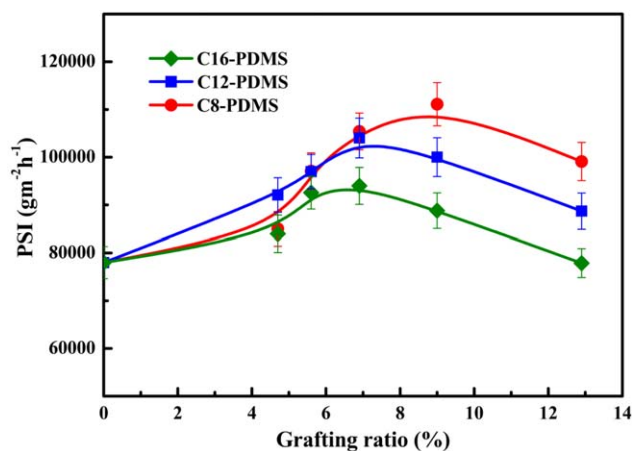


Figure 8. Effect of grafting ratio on PSI for alkyl grafted PDMS membranes (C16-PDMS, C12-PDMS, and C8-PDMS). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

12.5–27.3%, respectively. Accordingly, water flux showed a much greater reduction than EA with increase of grafting ratio. It implies that the water transport was not only inhibited by the decreased free volume but also the hydrophobic alkyl chains existed in PDMS matrix.²⁴ However, the alkyl chain length had negligible effect on water flux, especially at high alkyl grafting ratio.

In order to evaluate the overall pervaporation performance, the PSI for alkyl grafted PDMS membranes was calculated by Eq. (6) and presented in Figure 8. Compared with PDMS membrane, alkyl grafted PDMS membranes showed a higher PSI. The PSI increased with the increase of alkyl grafting ratio, and then decreased. Besides, when grafting ratio was above 6.9%, the PSI increased with the decrease of alkyl chain length. Overall, the highest PSI was achieved by 9% octyl grafted PDMS membrane, which was 42.5% higher than that of PDMS membrane. Those results suggest that alkyl grafting was an effective method to improve the pervaporation performance of PDMS membrane in separation of EA/water mixture.

Homogeneous Membranes in Separation of Other Organics/Water Mixtures

The PDMS and 9% octyl grafted PDMS membranes were further employed in separation of three different organics (BA, MTBE, and BuOH) from water. These organics are typical VOCs involved in chemical industry and their physicochemical properties are summarized in Table (VI).⁴ The feed concentrations were 0.1, 1, and 1% for BA, MTBE, and BuOH, respec-

tively. Compared with PDMS membrane, the 9% octyl grafted PDMS membrane exhibited higher separation factor for all organics tested due to its better hydrophobic affinity to organics [Figure 9(A)]. It is worth mentioning that the separation factors of BA and MTBE were much higher than that of BuOH since the BA and MTBE with weaker polarity had stronger hydrophobic interactions with octyl groups. At the same time, the improvement of separation factor due to the introduction of octyl groups into PDMS membrane were more significant in separation of BA/water and MTBE/water (67.04 and 53.26%, respectively) than BuOH/water (38.10%), as seen in Figure 9(A).

The flux of PDMS and 9% octyl grafted PDMS membranes is shown in Figure 9(B). The flux for MTBE/water was the largest because of the highest saturated vapor pressure of MTBE (Table VI). Compared with PDMS membrane, the 9% octyl grafted PDMS membrane showed a lower flux for all the feed solutions owing to the reduced free volume. The PSI in separation of these organics from water was summarized in Table VI, showing that the PSI for 9% octyl grafted PDMS membrane was higher than that of PDMS membrane for all the organics tested. It means that alkyl grafting was efficient in improving the pervaporation performance of PDMS membranes.

Composite Membranes in Separation of Organics/Water Mixtures

Composite membranes are always employed in industry to achieve high flux and sufficient mechanical strength. Therefore, the 9% octyl grafted PDMS composite membranes were prepared and their SEM images were shown in Figure 10. The skin layer thickness of the two composite membranes was 13.5 and 6.4 μm determined from SEM images. Such thin skin layer led to a much higher flux and a relatively lower separation factor for composite membranes compared with homogenous membranes (thickness about 100 μm), as shown in Figure 11. Similar phenomenon was reported by Jadav *et al.*⁵⁰ for PDMS membranes in separation of benzene from water. Overall, the PSI for 9% octyl grafted PDMS composite membranes ($>300000 \text{ gm}^{-2} \text{ h}^{-1}$) was much higher than that of the homogenous one (around $100000 \text{ gm}^{-2} \text{ h}^{-1}$), implying that the 9% octyl grafted PDMS composite membranes outperformed the homogenous one.

A comparison of pervaporation performance for removal of EA and MTBE from water in previous and present work was shown in Figure 11.^{4,7,51,52} Composite membranes in present work was located on the upper right of other membranes reported in literature, and was comparable to the inorganic silica membranes

Table VI. Physicochemical Properties of Organics and PSI of Membranes

Organics	Solubility in water (g/100 g H ₂ O)	Boiling point (°C)	Saturated vapor pressure ^a (kPa, 40 °C)	PSI _{PDMS} (gm ⁻² h ⁻¹)	PSI _{C8-PDMS} (gm ⁻² h ⁻¹)
BA	0.7	126.3	3.53	93762 ± 7647	123578 ± 8789
MTBE	4.8	55.2	59.97	91566 ± 4784	110117 ± 5749
BuOH	9.0	117.5	2.40	2904 ± 314	3248 ± 338

^a Calculated by Antoine equation.

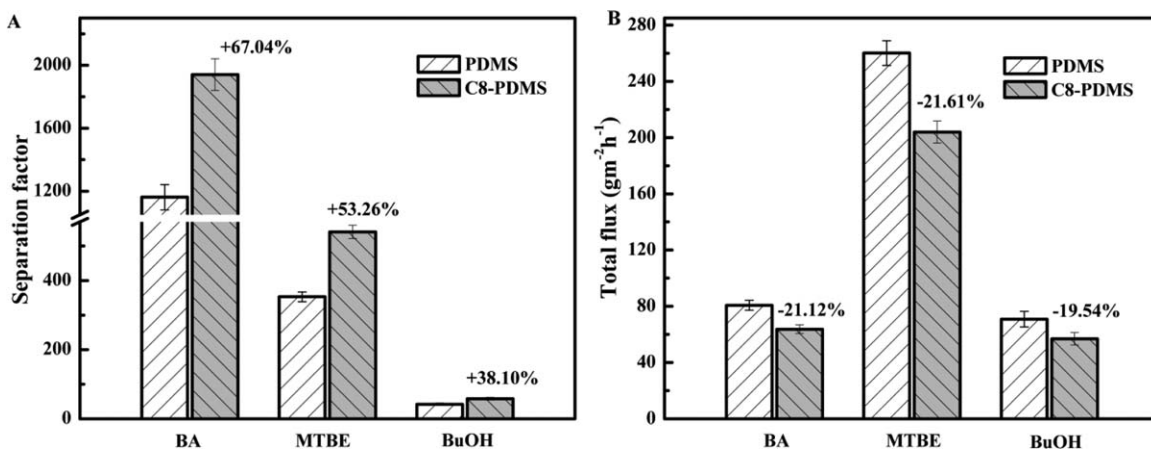


Figure 9. Separation factor (A) and total flux (B) for pristine PDMS and 9% octyl grafted PDMS membranes (C8-PDMS) in separation of BA, MTBE, and BuOH from water.

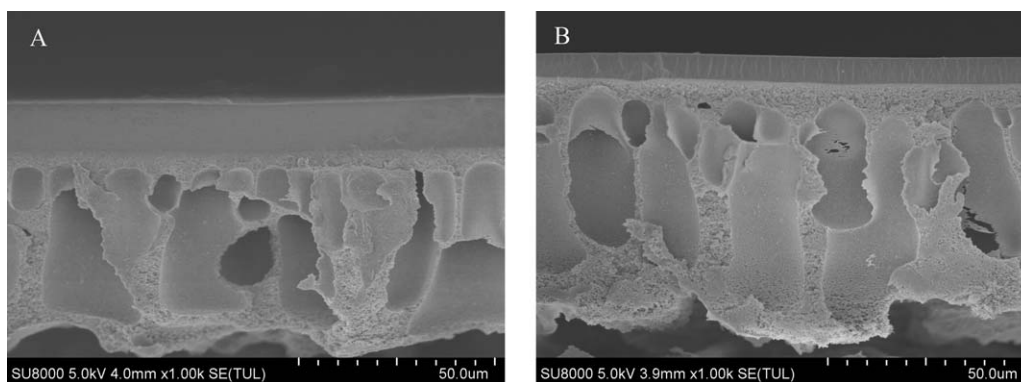


Figure 10. SEM images of 9% octyl grafted PDMS composite membrane with a skin layer thickness of 13.5 μm (A) and 6.4 μm (B).

in the separation of EA from water ($\text{PSI} > 300000 \text{ gm}^{-2} \text{ h}^{-1}$).⁷ The highest flux ($>2000 \text{ gm}^{-2} \text{ h}^{-1}$) was obtained for hydrophobic ceramic membranes while the corresponding separation

factor was quite low (<100).⁴ The PDMS and zeolite filled PDMS composite membranes (PV-1060 and PV-1070) from ref. 51 displayed high separation factor but low total flux. Interestingly, zeolite filling improved the separation factor of PDMS membranes toward EA, but had less effect on the separation factor toward MTBE. Octyl grafting in present work improved the separation factor of PDMS membranes for both EA and MTBE separation, and the corresponding composite membranes displayed outstanding performance in removal of EA and MTBE from aqueous solution.

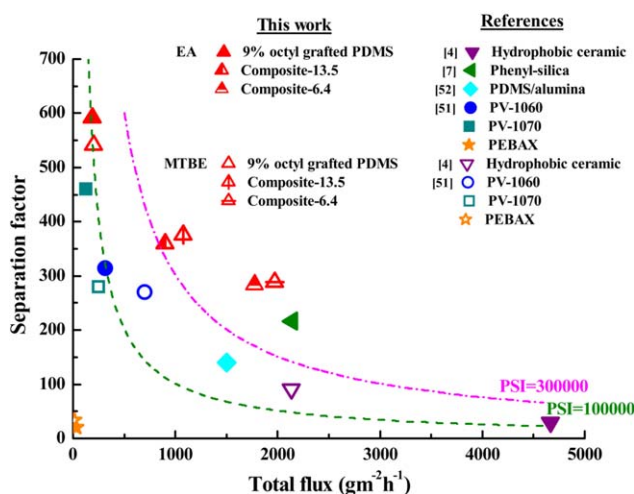


Figure 11. Separation efficiency of pervaporative removal of EA and MTBE from aqueous solution. Composite-13.5 in this work refers to 9% octyl grafted PDMS composite membrane with a skin layer thickness of 13.5 μm . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

Alkyl grafted PDMS membranes with different alkyl chain length were prepared. The membranes showed a higher tensile strength but lower toughness after moderately introduction of alkyl groups. The alkyl grafting ratio and alkyl chain length had great effects on the pervaporation performance of membranes in separation of EA/water mixture. With increasing alkyl grafting ratio, the separation factor increased rapidly and then decreased because of a tradeoff between preferential sorption (i.e., solution selectivity) and free volume (i.e., diffusion selectivity), while the flux decreased monotonously. At higher grafting ratio ($>6.9\%$), both the separation factor and flux decreased with the increase of alkyl chain length due to the

reduced free volume. Generally, the PSI of PDMS membranes was increased by alkyl grafting. The maximum PSI was achieved by 9% octyl grafted PDMS membrane, which was 42.5% higher than that of PDMS membrane in separation of EA/water mixture. Moreover, this octyl grafted PDMS membrane also showed improved separation performance in removal of BA, MTBE, and BuOH from water, and the corresponding composite membranes displayed outstanding performance in separation of EA or MTBE from aqueous solution. This study provides candidate membranes for efficiently removal of VOCs from aqueous solution.

NOMENCLATURE

τ	lifetime of positronium (ns)
I	intensity of positronium (%)
r	radius (Å)
V	volume (Å ³)
f	apparent fraction free volume
J	flux (gm ⁻² h ⁻¹)
W	weight (g)
d	thickness (μm)
A	membrane area (cm ²)
t	time interval (h)
α	separation factor
Y_o	organic concentration in permeate (wt %)
Y_w	water concentration in permeate (wt %)
X_o	organic concentration in feed (wt %)
X_w	water concentration in feed (wt %)
PSI	pervaporation separation index (gm ⁻² h ⁻¹)
δ	solubility parameters (MPa ^{0.5})

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