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Pervaporation of ethanol/water and benzene/cyclohexane mixtures using novel substituted polyacetylene membranes

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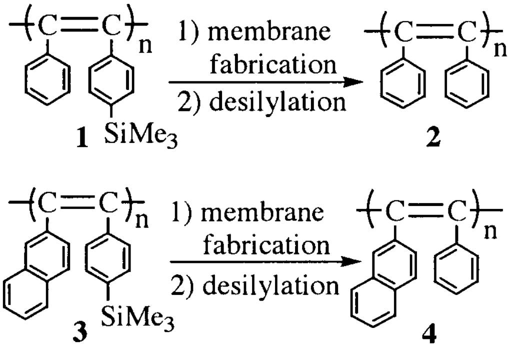
Summary

In the ethanol/water pervaporation using membranes of Si-containing polymers, poly[1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene] and poly[1-β-naphthyl-2-(*p*-trimethylsilyl)phenylacetylene], these polymer membranes permeated ethanol preferentially; $\alpha_{EtOH/H2O}$ 6.86 and 5.30, respectively, at 10 wt% EtOH content in the feed. Membranes of hydrocarbon-based polymers, poly(diphenylacetylene) and poly(1-β-naphthyl-2-phenylacetylene), which were prepared by desilylation of the two Si-containing polymer membranes, also exhibited ethanol permselectivity in ethanol/water pervaporation; $\alpha_{EtOH/H2O}$ 5.95 and 3.79, respectively. Further, in benzene/cyclohexane pervaporation, these desilylated membranes, which were insoluble in any organic solvent, showed rather low benzene permselectivity but very large fluxes. The results of the present study are attributed to the presence of many microvoids and, in turn, sparse structures.

Introduction

Although poly(diphenylacetylene) is insoluble in any solvents, its derivatives with bulky ring-substituents are usually soluble in common solvents such as toluene and chloroform and give membranes by solution casting [1]. Recently, a membrane of poly(diphenylacetylene) (**2**) has been prepared by the complete desilylation of a membrane of poly[1-phenyl-2-[*p*-(trimethylsilyl)phenyl] acetylene] (**1**) catalyzed by trifluoroacetic acid (Scheme 1) [2]. The obtained polymer membrane shows high thermal stability, insolubility in any solvent, and very high gas permeability (e.g., an oxygen permeability of 6000 barrers at 25 °C), which is comparable to that of poly[1-(trimethysilyl)-1-propyne] [poly(TMSP)] (Chart 1), the most gas-permeable polymer [3]. Further, a membrane of poly(1-β-naphthyl-2-phenylacetylene) (**4**) was prepared from a membrane of poly[1-β-naphthyl-2-[(*p*-trimethylsilyl)phenyl]-acetylene] (**3**) in a similar way [4]. This polymer membrane was also insoluble in any solvent and thermally very stable, and its Po_2 value at 25 °C reached 4300 barrers.



Scheme 1. Preparation of membranes of polymers **2** and **4**

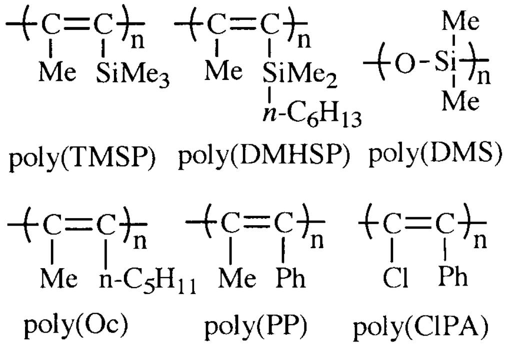


Chart 1. Polymer structure

Membrane separation processes have been extensively investigated as promising energy-saving separation techniques. Among them, pervaporation, where a membrane separates an upstream liquid mixture from downstream permeates in the gaseous state with a reduced pressure, is expected to have potential applications in liquid mixture separations, especially in the separation of azeotropic mixtures, heat-sensitive compounds, and organic mixtures with close boiling points [5–7]. The following three categories are considered in the application of pervaporation in chemical industry: 1) dehydration of organics, 2) separation of organics from water, and 3) organic/organic separation [8]. Since the first report of the synthesis of poly(TMSP) [9], it has been revealed that the membranes from poly(TMSP) and its homologous polymers such as poly[1-(dimethyl–*n*-hexylsilyl)-1-propyne] [poly(DMHSP)] are applicable to category 2, especially the separation or concentration of various types of alcohols from aqueous alcohol mixtures [10–13]. For instance, poly(TMSP) shows ethanol permselectivity and a fairly large flux in ethanol/water pervaporation; e.g., separation factor of ethanol against water ($\alpha_{\mathrm{EtOH/H2O}}$) is 17.0 at 10 wt% of ethanol in the feed [10–12]. This $\alpha_{\mathrm{EtOH/H2O}}$ value is similar to that of poly(dimethylsiloxane) [poly(DMS)] which is known as an ethanol-permselective conventional polymer [14]. On the other hand, poly(2-octyne) [poly(Oc)], an aliphatic polyacetylene, is practically non-permselective, while aromatic polyacetylenes such as poly(1-phenyl-1-propyne) [poly(PP)] and poly(1-chloro-2-phenylacetylene) [poly(ClPA)] exhibit rather water permselectivity [12]. The ethanol permselectivity of poly(TMSP) has been attributed to the presence of molecular-scale voids (microvoids) in this polymer. In organic/organic pervaporations, the benzene/cyclohexane (Bz/Chx) combination is the most common and has been investigated extensively [15]. However, no membranes of substituted polyacetylenes have been examined in this separation, because of the problem of their high solubility in many solvents.

In the present study, we investigated the performances of membranes of polymers **1**–**4** in ethanol/water pervaporation and those of polymers **3** and **4** in benzene/cyclohexane pervaporation. It has been found that all of polymers **1**–**4** are ethanol-permselective in the former system and that both polymers **3** and **4** show appreciably large fluxes in the latter system.

Experimental

Polymer synthesis

Polymers **1** and **3** were synthesized according to the literature methods [1, 4]. The polymerization conditions were as follows: 80 °C, 24 h, $[M]_0 = 0.10$ M, $[TaCl_5] = 20$ mM, $[n\text{-}Bu_4Sn] = 40$ mM. Polymers were isolated by precipitation into a large amount of methanol, and polymer yields were determined by gravimetry. The weight-average molecular weights (M_w) and polydispersity indices (M_w/M_n) of the polymers were determined by gel permeation chromatography ($CHCl_3$ as eluent, polystyrene calibration).

Membrane preparation

Membranes (thickness ca. 20–40 μm) of **1** and **3** were fabricated by casting toluene solution of the polymers (concn. ca. 1.0–1.5 wt%) onto a glass plate. Membranes of **2** and **4** were prepared by desilylation of membranes of **1** and **3** according to the literature method [2].

Pervaporation procedures

The permeation experiments of ethanol/water and benzene/cyclohexane mixtures were performed by an ordinary pervaporation technique [16]. The membrane area in contact with the liquid feed was 17.3 cm^2. The downstream pressure applied was around 267 Pa (2.0 mmHg), and the temperature of upstream mixture was kept at 30 °C. The permeates were analyzed by a Shimadzu GC-8APT gas chromatograph equipped with a 3.0-m long column packed with polyethylene glycol 20M [Chromosorb W (AW-DMCS)].

The performance of membranes in pervaporation was evaluated by the specific permeation rate (R; in $g\ m\ m^{-2}\ h^{-1}$) and the separation factor of component i against component j ($\alpha_{i/j}$). R and $\alpha_{i/j}$ are defined as follows:

$$R = F\theta/at$$

$$\alpha_{EtOH/H2O} = 1/\alpha_{H2O/EtOH} = (Y_{EtOH}/Y_{H2O})/(X_{EtOH}/X_{H2O})$$

$$\alpha_{Bz/Chx} = (Y_{Bz}/Y_{Chx})/(X_{Bz}/X_{Chx})$$

where F denotes the collected amount of the whole permeate, and θ, a, and t are membrane thickness (m), membrane area (m^2) and time (h), respectively. Y_i is the weight fraction of component in the permeate, and X_i is the one in the feed.

Results and discussion

Pervaporation of ethanol/water mixtures through membranes of Si-containing polymers, *1* and *3*

In ethanol/water pervaporation, membranes of Si-containing poly(diarylacetylenes) **1** and **3** were found to possess separation factors $\alpha_{EtOH/H2O}$ reaching 6.86 and 5.30, respectively (Table 1). Although these values are smaller than those of poly(TMSP) and poly(DMS) (17.0 and 11.9, respectively) [12, 14], they indicate ethanol permselectivity. These results are quite interesting when the following points are taken into account. That is, the $\alpha_{H2O/EtOH}$ values of polymers having polar groups such as cellulose acetate, nylon, and polyacrylonitrile, are 8.5–70, indicating high water permselectivity [17, 18], and even the $\alpha_{H2O/EtOH}$ values of hydrocarbon-based polymers such as polyethylene and polystyrene, are roughly 1.5–15, and hence they are also water-permselective. These results are explained by considering that the ethanol molecule is bulkier than the water molecule and so more difficult to permeate. The observed high ethanol permeability of polymers **1** and **3** should originate from the presence of molecular-scale voids (microvoids), which is also the case of poly(TMSP).

Table 1. Pervaporation of ethanol/water mixtures through membranes of Si-containing polyacetylenes and poly(DMS)[a]

membrane	X_{EtOH}[b]	Y_{EtOH}[c]	$\alpha_{EtOH/H2O}$[d]	10^3 R g m m^{-2} h^{-1}
1[e]	0.0975	0.426	6.86	4.17
3[f]	0.110	0.397	5.30	6.92
poly(TMSP)[g]	0.100	0.650	17.0	7.10
poly(DMHSP)[g]	0.100	0.250	3.00	0.027
poly(DMS)[h]	0.100	0.568	11.9	6.08

[a] Pervaporation was carried out at 30 °C; downstream pressure 267 Pa (2 mmHg). [b] Weight fraction of ethanol in the feed. [c] Weight fraction of ethanol in the permeate. [d] $\alpha_{EtOH/H2O} = (Y_{EtOH}/Y_{H2O})/(X_{EtOH}/X_{H2O})$. [e] Membrane thickness 53.2 μm. [f] Membrane thickness 32.0 μm. [g] Cited from ref. 12. [h] Cited from ref. 14.

Pervaporation of ethanol/water mixtures through membranes of desilylated polymers, 2 and 4

Both membranes of poly(diarylacetylenes), **2** and **4**, which were obtained by desilylation, also proved to permeate ethanol preferentially in ethanol/water pervaporation (Table 2). The $\alpha_{EtOH/H2O}$ values of polymers **2** and **4** were 5.95 and 3.79, respectively, which are smaller than that of poly(TMSP) and poly(DMS), but larger than unity. In general, common hydrocarbon polymers show water permselectivity; e.g., polystyrene $\alpha_{H2O/EtOH}$ 12 [19], polyethylene $\alpha_{H2O/EtOH}$ 1.7 [20]. The reason is that, despite their hydrophobicity, the diffusivity of bulky ethanol is rather small. Poly(Oc) and poly(PP), which are hydrocarbon-based substituted polyacetylenes, also show water permselectivity; i.e., their $\alpha_{EtOH/H2O}$ values are 0.72 and 0.28, respectively [10]. When these facts are taken into consideration, it is very interesting to note that hydrocarbon-based polyacetylenes **2** and **4** permeate ethanol in preference to water. This finding is explained by the idea that the microvoids that were present in the Si-containing polymers **1** and **3** are maintained even after desilylation.

Pervaporation of benzene/cyclohexane mixtures through membranes of desilylated polymers, 2 and 4

Previously unavailable were substituted polyacetylenes which are insoluble in common, low-polarity, organic solvents such as benzene, cyclohexane, etc. However, the desilylation method recently developed has enabled to provide such

Table 2. Pervaporation of ethanol/water mixtures through membranes of desilylated polyacetylenes and a few other polyacetylenes[a]

				10^3 R
membrane	X_{EtOH}[b]	Y_{EtOH}[c]	$\alpha_{EtOH/H2O}$[d]	g m m^{-2} h^{-1}
2[e]	0.0975	0.391	5.95	5.88
4[f]	0.0956	0.286	3.79	14.1
poly(Oc)[g]	0.100	0.0741	0.720	0.57
poly(PP)[g]	0.100	0.0302	0.280	0.24
poly(ClPA)[g]	0.100	0.0228	0.021	0.23

[a] Pervaporation was carried out at 30 °C; downstream pressure 267 Pa (2 mmHg). [b] Weight fraction of ethanol in the feed. [c] Weight fraction of ethanol in the permeate. [d] $\alpha_{EtOH/H2O} = (Y_{EtOH}/Y_{H2O})/(X_{EtOH}/X_{H2O})$. [e] Membrane thickness 46.3 µm. [f] Membrane thickness 45.0 µm. [g] Cited from ref. 10.

polymers [2, 4]. Thus, the pervaporation of benzene/cyclohexane mixtures was examined by using membranes of polymers **2** and **4** (Table 3). The $\alpha_{Bz/Chx}$ values of polymers **2** and **4** were 1.84 and 2.99, respectively, indicating benzene permselectivity though rather small compared to other polymers; e.g. cellulose acetate 19.0 [21], poly(vinylidene fluoride) 5.4 [22], poly(acrylonitrile-*co*-styrene) 23 [23]. Interestingly, the *R* values of polymers **2** and **4** were 106x10^{-3} and 22.5x10^{-3} g m m^{-2} h^{-1}, respectively, which are considerably large among the polymers so far examined; e.g., R (g m m^{-2} h^{-1}): cellulose acetate 0.34x10^{-3} [21], poly(vinylidene fluoride) 1.5x10^{-3} [22], poly(acrylonitrile-*co*-styrene) 2.6x10^{-3} [23]. Both high affinity of these membranes to organic solvents and the presence of many microvoids seem responsible for these results. In benzene/cyclohexane (50/50 wt%) pervaporation, polymers **2** and **4** showed even lower permselectivity, but larger fluxes, which is ascribed to a higher extent of swelling of the membranes. Polymer **4** behaves similarly to polyethylene in benzene/cyclohexane pervaporation, while polymer **2** appears to have a more sparce structure.

Table 3. Pervaporation of benzene/cyclohexane (Bz/Chx) mixtures through membranes of desilylated polyacetylenes and a few other polymers[a]

				10^3 R
membrane	X_{Bz}[b]	Y_{Bz}[c]	$\alpha_{Bz/Chx}$[d]	g m m^{-2} h^{-1}
2[e]	0.0951	0.162	1.84	106
2[e]	0.486	0.602	1.60	191
4[f]	0.097	0.243	2.99	22.5
4[f]	0.492	0.626	1.73	115
cellulose acetate[g]	0.500	0.950	19.0	0.34
polyethylene[h]	0.100	0.217	2.49	30.0

[a] Pervaporation was carried out at 30 °C; downstream pressure 267 Pa (2 mmHg). [b] Weight fraction of benzene in the feed. [c] Weight fraction of benzene in the permeate. [d] $\alpha_{Bz/Chx} = (Y_{Bz}/Y_{Chx})/(X_{Bz}/X_{Chx})$. [e] Membrane thickness 46.3 µm. [f] Membrane thickness 45.0 µm. [g] Pervaporation was carried out at reflux temperature, cited from ref. 21. [h] Pervaporation was carried out at 35 °C, cited from ref. 24.

In summary, membranes of the two kinds of Si-containing poly(diarylacetylenes) and the desilylated polymers derived from them turned out to show ethanol permselectivity in ethanol/water pervaporation. Furthermore, the desilylated polymer membranes exhibited considerably large fluxes in benzene/cyclohexane pervaporation. Investigations of pervaporation of various organic mixtures with these desilylated membranes will be interesting future subjects.

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