SHORT COMMUNICATIONS

Ethanol–Water Separation by Pervaporation through Substituted-Polyacetylene Membranes

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In the present short communication, we report on the behavior of substituted-polyacetylene membranes in the pervaporation of ethanol–water mixtures, especially on our finding that poly[1-(trimethylsilyl)-1-propyne] membrane permeates ethanol preferentially.

Since pervaporation can potentially be a much more effective process of separating liquid mixtures than distillation, it is recently under intensive research.[1-8] The concentration of an aqueous ethanol solution produced by the fermentation of biomass is usually lower than 10%. In order to separate ethanol from such a dilute solution, it is favorable to use a membrane which permeates ethanol preferentially (ethanol-permselective membrane). Few polymers, however, are known to be ethanol-permselective; e.g., poly(dimethylsiloxane),[1-3] FT30[4] (composition unpublished).

We have synthesized a number of substituted polyacetylenes by use of groups 5 and 6 transition metal catalysts.[9,10] Unlike polyacetylene, many of these substituted polyacetylenes are stable in air at room temperature over a long period of time, and are soluble in organic solvents to form films by solution casting. Hence we investigated their behavior in pervaporation in search of new functions of the substituted polyacetylenes.

EXPERIMENTAL

Substituted polyacetylene $[\{CR_1=CR_2\}_n]$ were synthesized using catalysts based on group 5 (Nb, Ta) and 6 (Mo, W) transition metals.[9,10] The polymers were obtained in over 50% yields, and had molecular weights of 10^5—10^6. Membranes were prepared by casting toluene solutions of polymers, extending them with a doctor knife, and allowing the solvent evaporate at room temperature.

The pervaporation experiment was carried out with ordinary apparatus.[5-7] The thickness of membranes was $\sim 20\,\mu\text{m}$ and their effective area was $7.07\,\text{cm}^2$. A $10\,\text{wt}\%$ aqueous ethanol solution was used as feed mostly at $30°\text{C}$. The downstream pressure was measured with a Pirani vacuum gauge, and maintained usually at $1.0\,\text{mmHg}$. Permeates were sampled after the steady state had been reached.

The performance of membranes for the pervaporation of ethanol–water mixtures was evaluated by separation factor $\alpha_{H_2O}^{EtOH}$ and specific permeation rate R. $\alpha_{H_2O}^{EtOH}$ is defined by eq 1, where X_{EtOH} and Y_{EtOH} are the weight fractions of ethanol in the feed and in the permeate, respectively. The ethanol fraction in the permeate was measured by gas chromatography. R is expressed by eq 2, where F, θ, a, and t are the permeate flux (g), mem-

Table I. Separation factor ($\alpha_{H_2O}^{EtOH}$) and specific permeation rate (R) of substituted polyacetylenes and some other polymers in the ethanol-water pervaporation[a]

Polymer		$\alpha_{H_2O}^{EtOH}$	$\dfrac{10^3 R}{g\,m\,m^{-2}\,h^{-1}}$	References
R_1	R_2			
CH_3	Si(CH_3)_3	12	4.5	
H	t-Bu	0.58	0.65	
H	CH(n-C_5H_{11})Si(CH_3)_3	0.52	0.40	
CH_3	n-C_5H_{11}	0.72	0.57	This work
Cl	n-C_6H_{13}	1.10	0.41	
CH_3	C_6H_5	0.28	0.24	
Cl	C_6H_5	0.21	0.23	
Others	Poly(dimethylsiloxane)	10	5.4	3
	Cellulose acetate	0.10	25	5
	Poly(methyl acrylate-co-diethylene triamine)	0.10	130	6
	Poly(maleimide-co-acrylonitrile)	0.022	0.9	7

(The polymer structure shown at left: $\{C=C\}_n$ with R_1 R_2)

[a] Operating conditions for the membranes of polyacetylenes: EtOH 10 wt%, 30°C, downstream pressure 1.0 mmHg.

brane thickness (m), membrane area (m²) and time (h), respectively. The amount of permeate was determined by gravimetry.

$$\alpha_{H_2O}^{EtOH} \equiv \frac{Y_{EtOH}/(1 - Y_{EtOH})}{X_{EtOH}/(1 - X_{EtOH})} \qquad (1)$$

$$R \equiv \frac{F \cdot \theta}{a \cdot t} \qquad (2)$$

RESULTS AND DISCUSSION

As Table I demonstrates, the $\alpha_{H_2O}^{EtOH}$ value of poly(dimethylsiloxane) is about 10,[1-3] while those of most conventional polymers are known to be smaller than unity [e.g., cellulose acetate, poly(phenylene oxide), nylon, polyethylene, and polyacrylonitrile[3,5,8]]. It is noteworthy that membranes with very high separation factors for water, $\alpha_{EtOH}^{H_2O}$ ($\equiv 1/\alpha_{H_2O}^{EtOH}$) [e.g., poly(maleimide-co-acrylonitrile)][7] have recently been developed.

Very interestingly, poly[1-(trimethylsilyl)-1-propyne] proved to permeate ethanol preferentially (Table I). Its $\alpha_{H_2O}^{EtOH}$ value is ap-

proximately the same as that of poly(dimethylsiloxane). The specific permeation rate, R, of this polyacetylene is also similar to that of poly(dimethylsiloxane). These coincidences are rather surprising, since the former polymers is glassy ($T_g > 200°C$), while the latter is rubbery around room temperature. Here, it should be mentioned that poly[1-(trimethylsilyl)-1-propyne] can be easily fabricated into a thin membrane, while poly(dimethylsiloxane) cannot owing to this morphological difference.

All the other substituted polyacetylenes examined were found to have $\alpha_{H_2O}^{EtOH}$ values close to or smaller than unity; that is, they were hardly permselective or water-permselective (Table I). In general, the aromatic polyacetylenes were more water–permselective ($\alpha_{H_2O}^{EtOH}$ smaller) and less permeable (smaller R) than the aliphatic polyacetylenes. This suggests that the more rigid and tighter structure of aromatic polyacetylenes makes the permeation of ethanol, which is bulkier than water, more difficult.
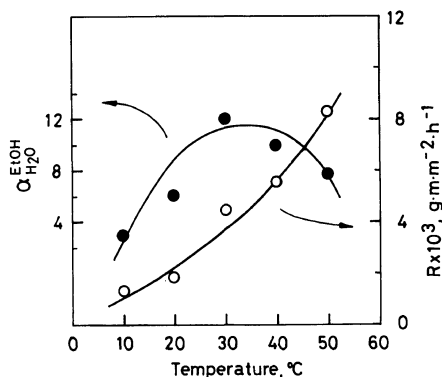
Figure 1 shows temperature dependences of

Figure 1. Effect of temperature on the ethanol–water pervaporation through poly[1-(trimethylsilyl)-1-propyne] membrane (EtOH 10 wt%, downstream pressure 1.0 mmHg).

Figure 2. Effect of downstream pressure on the ethanol–water pervaporation through poly[1-(trimethyl-silyl)-1-propyne] membrane (EtOH 10 wt%, 30°C).

$\alpha_{H_2O}^{EtOH}$ and R in the pervaporation through poly[1-(trimethylsilyl)-1-propyne] membrane. In the temperature range of 10—50°C, the $\alpha_{H_2O}^{EtOH}$ value showed a maximum of 12 at 30°C. On the other hand, the higher the temperature, the larger was the R value. The reason why $\alpha_{H_2O}^{EtOH}$ shows a maximum is not clear at present, but should be associated with some change in the swollen state of membrane with temperature. The increase in R with increasing temperature corresponds to the general tendency.

Figure 2 shows the dependences of $\alpha_{H_2O}^{EtOH}$ and R on the downstream pressure in pervaporation through poly[1-(trimethylsilyl)-1-propyne] membrane. The $\alpha_{H_2O}^{EtOH}$ value was unaffected by the downstream pressure in a range of 0.10 to 100 mmHg. The R value was virtually constant below 10 mmHg, whereas it decreased sharply with increasing pressure from 10 to 100 mmHg. Thus, the downstream pressure of 1.0—10 mmHg is the most practical.

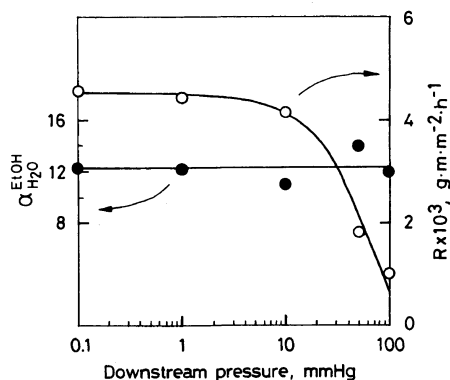In conclusion, poly[1-(trimethylsilyl)-1-propyne] was found to permeate ethanol preferentially in ethanol–water pervaporation. Thus, like poly(dimethylsiloxane), this polymer is one of rare examples of ethanol-perm-selective membrane. A more detailed study on the pervaporation through substituted polyacetylenes is underway.

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