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Poly(*p*-substituted phenylacetylene) with perfluoroalkyloxydimethylsilyl side groups for oxygen and ethanol permselective membrane

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Summary

p-(1H,1H,2H,2H-perfluorodecyloxydimethylsilyl)phenylacetylene(**ACf8**) and *p*-(1H,1H,2H,2H-Perfluorohexyloxydimethylsilyl)phenylacetylene(**ACf4**) were synthesized and copolymerized with *p*-trimethylsilylphenylacetylene(**ASi**). The resulting copolymers, copoly(**ACf8/ASi**) and copoly(**ACf4/ASi**), were fabricated to tough membranes showing high oxygen permeabilities(Po_2) of 10^{-8} cc(STP)·cm/cm^2·s·cmHg and high oxygen permselectivities($\alpha=Po_2/P_{N_2}$) of more than 2.7. In particular, a copoly(**ACf4/ASi**) containing 15.1 mol% of **ACf4** unit showed the best result: $Po_2 = 3.51\times10^{-8}$ cc(STP)·cm/cm^2·s·cmHg and $\alpha = 3.04$. The values were in a top level and very close to those of 'upper bound' line in an $\alpha-Po_2$ plot of data in the literature. In addition, copoly(**ACfn/ASi**) membranes were ethanol permselective owing to water repellency of the perfluoroalkyl groups. Copoly(**ACf4/ASi**) membranes showed better oxygen and ethanol permselectivity than copoly(**ACf8/ASi**) membranes.

Introduction

For an oxygen-permselective membrane, a high oxygen permeability coefficient(Po_2:cc(STP)·cm/cm^2·s·cmHg) and a high oxygen separation factor($\alpha=Po_2/P_{N_2}$) are required. Only few kinds of polymer structures have shown high Po_2 of more than 1.0×10^{-8}. We have reported on the molecular design for highly oxygen permeable membranes(1-5). In general, Po_2 increases with decreasing α(6). When compared at a similar value of Po_2, poly(substituted acetylene)s showed higher α values than those of the other polymers(7). However, in these good oxygen-permselective poly(substituted acetylene)s, only limited polymers showed Po_2 of more than 1.0×10^{-8} : for example, poly-(1-trimethylsilylpropyne)(PTMSP)(7), poly(trimethylsilyldiphenylacetylene)(8), hepta-fluoropropylated poly(diphenylacetylene)(9), poly(*p*-trifluoromethylphenylacetylene)(3), and poly(t-butylacetylene)(7). We also found poly(*p*-trimethylsilylphenylacetylene) [poly(ASi)] and poly{bis(*o*-,*p*-trimethylsilyl)phenylacetylene} to show good oxygen permeability and permselectivity: $Po_2=1.71\times10^{-8}$ and 4.73×10^{-8}, α=2.70 and 2.65, respectively(4). In this paper, we report new poly(substituted acetylene)s having Po_2 of

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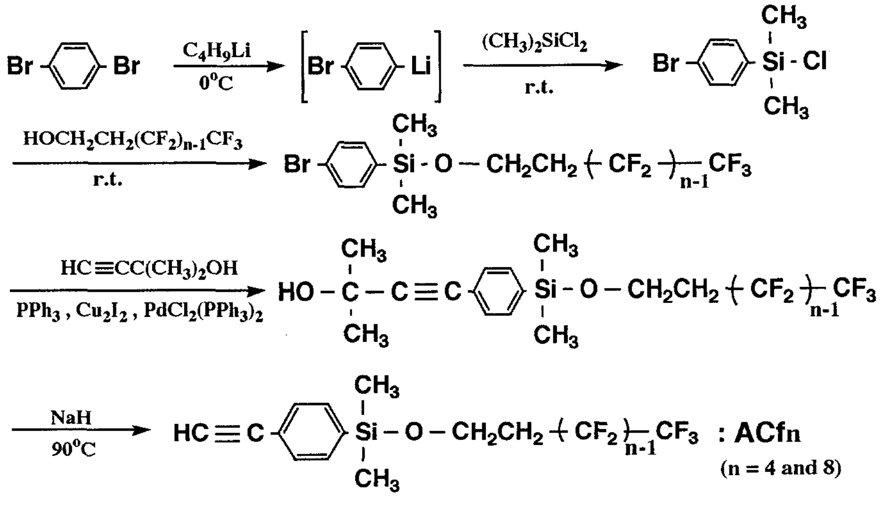
more than 1.0 x 10^{-8}.

In view of the fact that perfluorinated and polyfluorinated organic compounds have been utilized to artificial blood, the fluorine-containing compounds are expected to be oxygen permselective membrane materials. For example, a highly oxygen permselective membrane containing perfluorotributylamine was reported(10). Recently, two kinds of PTMSP based membranes modified by fluorine-containing compounds were reported to have very high α and Po_2 : one was surface-modified by fluorine gas(11) and the other was modified by imbibing hexafluorobutyl methacrylate(12). However, it has not been reported that the introduction of a fluorine-containing group to a membrane polymer via covalent bonds shows good effect for enhancing oxygen permselectivity. When a small amount of a fluorine-containing group such as a trifluoromethyl group was introduced, Po_2 increased but α decreased because of the bulkiness of the group(3,13,14), and in the case of a large amount of fluorine-containing group such as polytetrafluoroethylene, Po_2 was very low and α was not high because of its high crystallinity. Moreover, a polymer of a high fluorine content is apt to be insoluble and has poor membrane forming ability. Therefore, in order to make a membrane highly oxygen permselective, an appropriate chemical structure, which satisfies both high fluorine content and low crystallinity must be selected. We reported that poly[p-(1H,1H,2H,2H-perfluoroalkyldimethylsilyl)styrenes] [poly(S1,m)] showed relatively high α along with high Po_2 value(5). Simultaneous introduction of SiO bond and perfluoroalkyl chain as the side chains into polystyrene was effective for enhancing α without a drop in Po_2. α's for poly(S1,m) had a maximum value at a certain length of the perfluoroalkyl chain. This behavior was found to be affected by crystallizability of the perfluoroalkyl side chains. However, the membranes were so week as to need a supporting membrane and Po_2 was in a low level of 4 ~10x10^{-9}. In this study, in order to obtain a new polymer having a higher α, Po_2 of more than 10^{-8}, and good membrane forming ability, we synthesized a copolymer of *p*-(1H,1H,2H,2H-perfluoro-



Scheme 1. Synthetic route to ACfn.

decyloxydimethylsilyl)phenylacetylene(**ACf8**) or *p*-(1H,1H,2H,2H-perfluorohexyloxydimethylsilyl)phenylacetylene(**ACf4**) with *p*-trimethylsilylphenylacetylene(**ASi**) and evaluated their oxygen permeation performance for the resulting copolymer membranes.

Fluorine- and silicon-containing polymers have been applied to ethanol-permselective membranes as well. However, because diffusivity of water is higher than that of ethanol, examples of such membranes are very limited to those such as poly(dimethylsiloxane) (PDMS)(15), PTMSP(16), and poly(tetrafluoroethylene) derivatives(17). We have reported the efficient enhancement of the ethanol permselectivity (α^{EtOH}) of PDMS membrane by adding a small amount of poly(1H,1H,2H,2H-perfluoroalkyloxydimethylsilylstyrene) ($\alpha^{EtOH} = 22.3$, $[EtOH]_{Feed} = 2.70$ wt% at 25°C)(18,19). In this paper, therefore, the behavior of the above copolymers as new ethanol permselective membranes is also described.

Experimental

Materials

$[RhCl(norbornadiene)]_2$ was purchased from Aldrich Chemical Company, Inc. and used without further purification.

Synthesis of monomers(Scheme 1)

All the following reaction procedures were conducted under nitrogen.

p-(1H,1H,2H,2H-Perfluorodecyloxydimethylsilyl)phenylacetylene(ACf8)

p-Bromo(chlorodimethylsilyl)benzene(18): To a dry ether solution(100 ml) of p-dibromobenzene 11.8 g(50.0 mmol) was added dropwise a hexane solution(30 ml) of n-butyllithium(50.0mmol) at 0°C. After stirring for 1 hour the solution was added dropwise to dichlorodimethylsilane 19.4 g(150 mmol) and the mixture was stirred for 12 hours at room temperature. The usual work up and distillation gave the product in 68.6% yield(8.56 g). bp 64°C(0.48mmHg), ^1H-NMR(CCl_4): δ 0.67(s, 6H, $Si(CH_3)$), 7.52(dd,4H, phenylene protons).

p-Bromo(1H,1H,2H,2H-perfluorodecyloxydimethylsilyl)benzene(18): To a dry ether solution(70 ml) of 1H,1H,2H,2H-perfluorodecan-1-ol 19.2 g(41.3 mmol) and triethylamine 5.80 ml(41.3 mmol) was added dropwise p-bromo(chlorodimethylsilyl)benzene 10.3 g(41.3 mmol) at 0°C and the mixture was stirred for 12 hours at room temperature. The salt formed was filtered out and the solvent was evaporated. Recrystallization from 1,3-bis(trifluoromethyl)benzene(BTB) at -3~0°C gave slightly reddish viscous solid in 89.9% yield(25.2g). Rf 0.93(eluent:benzene/ethyl acetate = 3/1), ^1H-NMR(CCl_4): δ 0.40(s, 6H, $Si(CH_3)_2$), 2.36(tt, 2H, CH_2CF_2), 3.89(t, 2H, CH_2O), and 7.50(dd,4H, phenylene protons).

p-(3-Hydroxy-3-methyl-1-butynyl)(1H,1H,2H,2H-Perfluorodecyloxydimethylsilyl)-benzene(4,20): p-Bromo(1H,1H,2H,2H-perfluorodecyloxydimethylsilyl)benzene 25.8g (38.1 mmol), dry triethylamine(50ml), and 2-methyl-3-butyn-2-ol 6.41 g(76.2 mmol) were added to a mixture of triphenylphosphine 0.38g(0.15mmol), cuprous iodide 0.19g(0.10mmol), and bis(triphenylphosphine)palladium(II) chloride 0.23g(0.03mmol) and the solution was heated at 90 °C for 4 hours. The salt formed was filtered out and the solvent was evaporated. The crude product was purified by silica-gel chromatography(eluent: benzene / ethyl acetate = 3/1) and recrystallization(solvent:BTB) to give the pure product in 50.3% yield(26.1g). Rf 0.72, ^1H-NMR(CCl_4): δ 0.37(s, 6H, $Si(CH_3)_2$), 1.53(s, 6H,$C(CH_3)_2$), 1.97(b, 1H, OH), 2.31(tt, 2H, CH_2CF_2), 3.83(t, 2H, CH_2O), 7.38(dd,4H, phenylene protons), IR(cm^{-1}): 3388(OH), 2250(C≡C).

p-(1H,1H,2H,2H-Perfluorodecyloxydimethylsilyl)phenylacetylene(ACf8)(4,20): Sodium hydride 0.23g (9.7 mmol) was added to a toluene solution(20 ml) of 4-(3-hydroxy-3-methyl-1-butynyl)(1H,1H,2H,2H-perfluorodecyloxydimethylsilyl)benzene 3.63 g(5.83 mmol) and the solution was heated to 110°C and stirred for 1 hour. The unreacted sodium hydride was filtered out and the solvent was evaporated. The crude product was purified by silica-gel chromatography(eluent: heptane/benzene = 4/1) to give slightly brown viscous solid in 37.6% yield(1.36g). The total yield from *p*-dibromobenzene: 11.7%, Rf 0.58, ^{1}H-NMR(CCl_4) : δ 0.42(s, 6H, $Si(CH_3)_2$), 2.37(tt, 2H, CH_2CF_2), 3.11(s,1H, HC≡C), 3.94(t, 2H, CH_2O), 7.50(dd,4H, phenylene protons) , IR(cm^{-1}) : 3312(CH≡).

p-(1H,1H,2H,2H-Perfluorohexyloxydimethylsilyl)phenylacetylene(ACf4)

Reactions similar to those above were run with 1H,1H,2H,2H-perfluorohexan-1-ol. The crude product was purified by distillation to give slightly yellow liquid in 17.1% yield based on *p*-dibromobenzene. bp 68.0°C(0.6mmHg). Spectra similar to those above were observed in ^{1}H-NMR and IR.

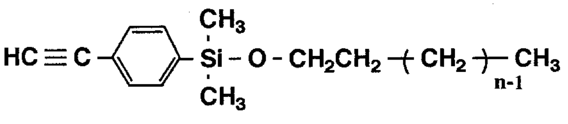
p-(Decyloxydimethylsilyl)phenylacetylene(ACh8)

Reactions similar to those above were run with 1-decanol. The crude product was purified by distillation to give colorless liquid in 11.5% yield based on *p*-dibromobenzene. bp 81°C(0.5 mmHg).

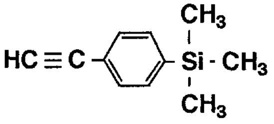
p-(Hexyloxydimethylsilyl)phenylacetylene(ACh4)

Reactions similar to those above were run with 1-hexanol. The crude product was purified by distillation to give colorless liquid in 17.2% yield based on *p*-dibromobenzene. bp 72°C(0.5 mmHg).

p-Trimethylsilylphenylacetylene(ASi) was synthesized according to our previous paper(4).



AChn (n = 4 and 8)



ASi

Copolymerization(Table 1)

To the monomer(M) and comonomer(**ASi**)(M') in dry triethylamine([M+M']=0.25 mol/l) was added the catalyst(C) $[RhCl(norbornadiene)]_2$ in dry triethylamine ([C]/[M+M']=0.005) and the solution was stirred under nitrogen for 4 hours at 30°C. The polymerization mixture was poured into methanol and the polymer was purified by reprecipitation from toluene solution into methanol and then dried *in vacuo*.

Membrane preparation

A chloroform solution(5wt%) of one of the polymers was cast on a polytetrafluoroethylene sheet. The solvent was evaporated at ambient temperature for 3h and the resulting membrane was dried *in vacuo* for 12h.

Oxygen permeation

Oxygen and nitrogen permeability coefficients(P_{O_2}, P_{N_2}: cc(STP)·cm/cm^2·s·cmHg) were measured at 25°C by gas chromatographic method using YANACO GTR-10. Diffusion constants(D_{O_2}, D_{N_2}: cm^2/s) were determined by time-lag method. Solubility coefficients(S_{O_2}, S_{N_2}: cc(STP)/cm^3·cmHg) were calculated using S=P/D.

Pervaporation of aqueous ethanol solution

Ethanol and water permeation rates(P_{EtOH} and P_{water}: g·m/m^2·h)were measured by gas chromatographic method using YANACO GTR-12L at 25°C. A 10.0wt% ethanol solution was fed. Ethanol permselectivity(α^{EtOH}) was expressed in the following equation:

$$\alpha^{EtOH} = (Y_{EtOH} / Y_{water}) / (X_{EtOH} / X_{water})$$

where X and Y are the weight fractions of the feed and permeate, respectively.

Results and discussion

Copolymerization of ACfn or AChn with ASi(Table 1)

New monomers synthesized were polymerized with $[RhCl(norbornadiene)]_2$ in triethylamine. Although the homopolymers of **ACf4** and **ACf8** were insoluble in ordinary solvents and fluorine-containing solvents, some of the copolymers with **ASi** were soluble and able to be fabricated to tough membranes: Those were copoly(**ACf8/ASi**) and copoly(**ACf4/ASi**) containing less than 6.0mol%(18.3wt%) of **ACf8** unit and 15.1mol% (30.1wt%) of **ACf4** unit, respectively. The copolymers with higher contents of **ACf8** or **ACf4** unit were insoluble in all solvents. The copoly(**ACf4/ASi**) membranes could have a higher fluorocarbon content (CF_2%) than copoly(**ACf8/ASi**) ones: the highest contents of the former and the latter were 17.4wt% and 12.3wt%, respectively. Their compositions were close to those of the feed and molecular weights were high(more than 3.6 x 10^5). In order to investigate the effect of the fluorocarbon on the oxygen and ethanol permselectivity, the corresponding hydrocarbon copolymers, copoly(**ACh8/ASi**) and copoly(**ACh4/ASi**), were also synthesized.

Oxygen permeation behavior of copoly(ACfn/ASi) membranes(Figure 1)

These copolymers showed a high oxygen permeabilities(P_{O_2}) of 10^{-8}

Table 1. Copolymerization[a] of ACfn or AChn with ASi(comonomer).

No.	Feed		Copolymer				
	Monomer	mol%(wt%)	Yield (%)	Monomer unit[b] mol%(wt%)	CF_2% (wt%)	Mw[c] ($\times10^5$)	Mw/Mn[c]
1	ACf8	6.5 (19.8)	44.1	6.0 (18.3)	12.3	3.97	2.12
2		3.3 (12.5)	45.8	3.2 (12.1)	8.2	4.11	2.01
3		2.6 (10.0)	48.7	1.9 (7.2)	4.9	4.16	1.86
4		1.3 (5.1)	51.4	0.9 (3.2)	2.2	4.20	1.99
5	ACf4	17.2 (34.1)	63.3	15.1 (30.1)	17.4	3.88	2.33
6		15.4 (30.6)	61.2	14.4 (28.7)	16.6	3.75	1.99
7		12.0 (24.8)	68.4	9.8 (20.4)	11.8	3.94	2.16
8		8.4 (18.1)	66.6	8.3 (17.9)	10.3	3.89	2.14
9		4.7 (10.6)	69.1	3.7 (8.3)	4.8	4.04	2.58
10	ACh8	12.4 (20.4)	80.4	11.4 (18.8)	0	2.85	3.04
11	ACh4	17.7 (12.6)	77.5	10.7 (15.0)	0	3.31	2.76
12[d]	ASi	0 (0)	92.0	0 (0)	0	6.51	3.23

a) In triethylamine with $[RhCl(norbornadiene)]_2$ at r.t. for 4h. b) By ^{1}H-NMR. c) By GPC. d) Homopolymerization of ASi.

cc(STP)·cm/cm^2·s·cmHg and moreover high oxygen permselectivities(α=P_{O_2}/P_{N_2}) of more than 2.7. In particular, copoly(**ACf4/ASi**) containing 15.1 mol% of **ACf4** unit showed the best performance: P_{O_2}=3.51x10^{-8} and α=3.04(No.5 in Figure 1). The values were very good, in a top level, and very close to those of 'upper boundary' line in an α-P_{O_2} plot of data in the literature(6). Both the P_{O_2} and α values of the copolymers were better than those of the polymers containing no fluorocarbon moiety such as poly(**ASi**), copoly(**ACh8/ASi**) and copoly(**ACh4/ASi**). Therefore, the fluorocarbon moiety in copoly(**ACfn/ASi**) was found to be effective for enhancing simultaneously the P_{O_2} and α value. In each copolymer series, the α increased with the increase in CF_2% accompanied with only a little decrease in the P_{O_2}(No.4 to No.1. No.9 to No.5) Therefore, the higher the CF_2 content, the better the performance. In comparison between the two series of copoly(**ACfn/ASi**)s having almost the same CF_2 content, copoly(**ACf4/ASi**) showed a higher P_{O_2} and lower α than copoly(**ACf8/ASi**)(Nos. 1 and 7, and 3 and 9 in Figure 1). Since the highest value of CF_2 content in which copoly(**ACfn/ASi**) was able to form a tough membrane was greater in copoly(**ACf4/ASi**) than that in copoly(**ACf8/ASi**), copoly(**ACf4/ASi**) could show a better performance than in copoly(**ACf8/ASi**). The lower values of the P_{O_2} and the highest value of CF_2 content in copoly(**ACf8/ASi**) may be due to the crystallization of the longer fluorocarbon chains.

In order to discuss the good oxygen permeation behavior, D_{O_2} and S_{O_2} were determined(Table 2). All the enhancement of α and P_{O_2} in copoly(**ACfn/ASi**)s (Run Nos.1~5) as a result of the substitution of one methyl group in poly(**ASi**)(Run No.6) by 1H,1H,2H,2H-perfluoroalkyloxy group were caused by D_{O_2}/D_{N_2} and S_{O_2}, respectively. Compared between copoly(**ACfn/ASi**)s having almost the same CF_2 content(Run Nos.1 and 5), P_{O_2} of copoly(**ACf8/ASi**) was lower than that of copoly(**ACf4/ASi**) owing to the lower D_{O_2}. The lower values of copoly(**ACf8/ASi**) may be due to the crystallization of the longer fluorocarbon chains. In fact, at an elevated temperature(No.3), the D_{O_2} and P_{O_2} increased to the level of those of copoly(**ACf4/ ASi**)(No.5).

Ethanol pervaporation behavior of copoly (ACfn / ASi) membrane (Figure 2)

Both the P_{EtOH} and α^{EtOH} values of the copolymers were better than those of the

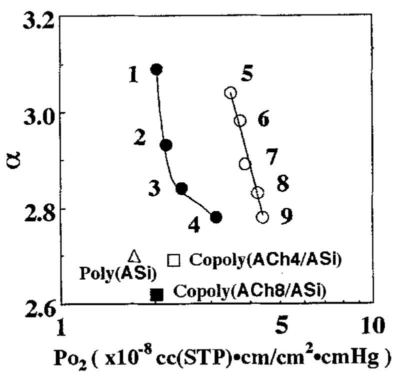


Figure 1. Plots of oxygen permselectivity versus oxygen permeability coeffcient.
●:Copoly(ACf8/ASi), ○:Copoly(ACf4/ASi)
The numbers in the figure correspond to those in Table 1.

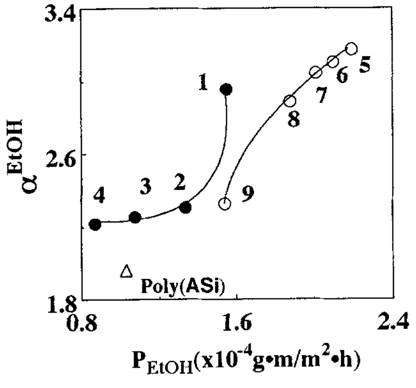


Figure 2. Plots of ethanol permselectivity versus ethanol permeation rate.
●:Copoly(ACf8/ASi), ○:Copoly(ACf4/ASi)
The numbers in the figure correspond to those in Table 1.

Table 2. Oxygen permeation behavior of Copoly(ACfn /ASi).

Run No.	Code	CF_2% (wt%)	Po_2 [a] ($x10^{-8}$)	α	Do_2 [b] ($x10^{-6}$)	$\frac{Do_2}{D_{N_2}}$	So_2 [c] ($x10^{-3}$)	$\frac{So_2}{S_{N_2}}$
1	Copoly(ACf8/ASi)	12.3	2.03	3.09	2.17	2.58	9.3	1.19
2		8.2	2.18	2.93	2.10	1.87	10.4	1.57
3 [d]		8.2	3.94	2.89	3.21	2.25	12.3	1.29
4	Copoly(ACf4/ASi)	17.4	3.51	3.04	3.48	1.69	10.1	1.78
5		11.8	3.88	2.89	3.23	1.88	12.0	1.54
6	Poly(ASi)	0	1.71	2.70	2.26	1.34	7.6	2.01

a) cc(STP)•cm/cm^2• sec•cmHg. b) cm^2/sec. c) cc(STP)/cm^3•cmHg. d) 29°C.

polymers containing no fluorocarbon moiety, poly(ASi). Therefore, the fluorocarbon moiety in copoly(ACfn/ASi) was found to be effective for enhancing simultaneously the P_{EtOH} and α^{EtOH} value. In order to discuss the effect of the fluorocarbon moiety, P_{EtOH}, P_{water}, and α^{EtOH} were plotted versus CF_2% in Figure 3. The enhancement of α^{EtOH} was caused by suppression of P_{water}. Copoly(ACf4/ASi) membranes had better P_{EtOH} and α^{EtOH} than copoly(ACf8/ASi) membranes. This behavior seemes to be affected by crystallizability of their perfluoroalkyl side chains.

Conclusions

1. Copoly(ACfn/ASi) membranes showed a high oxygen permeability(Po_2) of 2.0 ~ 4.4 $x10^{-8}$ cc(STP)cm/cm^2 s cmHg and moreover their oxygen permselectivity(α) were in the range of 2.7~3.1. The values were very good and very close to those of 'upper boundary' line in an α-Po_2 plot of reported data.
2. Copoly(ACfn/ASi) membranes were also ethanol permselective owing to water repellency of the perfluoroalkyl groups.
3. Copoly(ACf4/ASi) membranes had better oxygen and ethanol permselectivity than copoly(ACf8/ASi) membranes. This behavior may be attributed to a lower crystallizability of shorter perfluoroalkyl side chains.

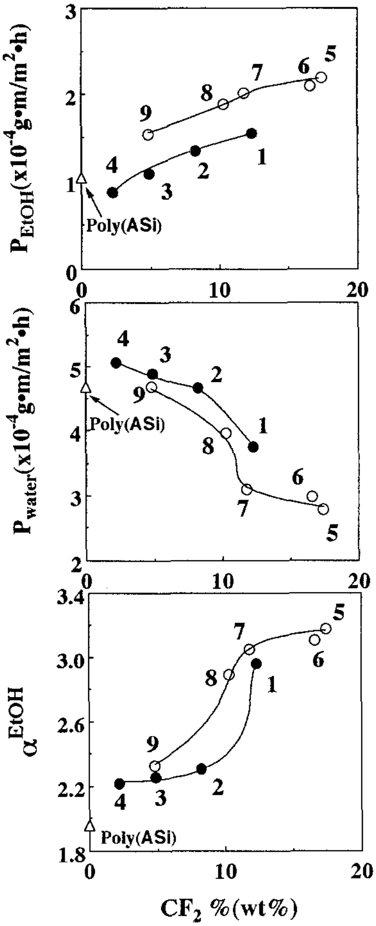


Figure 3. Plots of P_{water}, α^{EtOH} versus CF_2% of Copoly(ACfn/ASi).
● :Copoly(ACf8/ASi), ○ :Copoly(ACf4/ASi)
The numbers in the figure correspond to those in Table 1.

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