

Chemical Modification of Poly(substituted-Acetylene). VI. Introduction of Fluoroalkyl Group into Poly(1-Trimethylsilyl-1-Propyne) and the Improved Ethanol Permselectivity at Pervaporation

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SYNOPSIS

In order to improve the separation characteristics of membranes for pervaporation, the introduction of fluoroalkyl groups into poly(1-trimethylsilyl-1-propyne) (PTMSP) was achieved by two methods. First, 3,3,3-trifluoropropyldimethylsilylated PTMSP was prepared via metalation of PTMSP followed by treating with 3,3,3-trifluoropropyldimethylchlorosilane. About 6 mol % of 3,3,3-trifluoropropyldimethylsilyl group was introduced by the polymer reaction. Second, the copolymerizations of 1-trimethylsilyl-1-propyne (TMSP) with 1-(3,3,3-trifluoropropyldimethylsilyl)-1-propyne (FPDSP) or 1-(1H,1H,2H,2H-tridecafluorooctyldimethylsilyl)-1-propyne (FODSP) were carried out to afford TMSP/FPDSP or TMSP/FODSP random copolymers. The ratio of TMSP monomer unit and the comonomer unit, x/y , was in the range of 99/1–85/15. All the chemically modified PTMSP membranes showed ethanol permselectivity for pervaporation of aqueous ethanol solution. In particular, the introduction of less than about 5 mol % of fluoroalkylsilylated units into PTMSP effectively enhanced the selectivity. However, excess introduction of FODSP comonomer unit caused a decrease of the selectivity, with the value being smaller than that of PTMSP membrane. Furthermore, tetrahydrofuran, acetone, acetonitrile, dioxane, and isopropanol were efficiently separated from their dilute aqueous solutions using a TMSP/FPDSP copolymer membrane.

INTRODUCTION

Recently, we investigated the chemical modification of poly(substituted-acetylene), in order to achieve the improved selectivity and stability at gas permeation or to attain the higher permselectivity of alcohol for the separation of aqueous alcohol solution by the pervaporation technique.^{1–5} In particular, the introduction of short polydimethylsiloxane (PDMS) chain² or trialkylsilyl group⁵ into poly(1-trimethylsilyl-1-propyne) (PTMSP) caused excellent alcohol permselectivity at pervaporation, which was higher than that of a PTMSP membrane. The high selectivity for alcohol with our modified

PTMSP membrane was considered to be induced by a delicate alteration of membrane structure, which was brought about by an increase of hydrophobicity and the maintenance of high permeability coefficient of the original PTMSP membrane with the introduction of short PDMS chain or trialkyl group.

PTMSP membrane has been known to contain excess free volume.⁶ The greatest gas permeability and the ethanol permselectivity of this membrane is thought to be due to the existence of free volume.^{6,7} Fusaoka et al. has prepared poly(1-alkyldimethylsilyl-1-propyne) and evaluated the separation property of aqueous ethanol solution as compared with PTMSP membrane.⁸ He also suggested that if the alkyl group was changed to ethyl, hexyl, or octyl group, the separation factor was below 1. Thus, the membranes showed water permselectivity at pervaporation. This interesting result suggests that the

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specific membrane structure of PTMSP is very important to achieve ethanol permselectivity and that the permselectivity is readily alterable even by a slight change of the chemical structure of the monomer unit.

Therefore, we expected that the introduction of fluoroalkyl group into PTMSP would be also effective to increase hydrophobicity of the membrane and improve the separation property at pervaporation. In this article, we wish to present a chemical modification of PTMSP to introduce the fluoroalkyl group by a polymer reaction and a copolymerization. These substituents were partly introduced in order to maintain the peculiar membrane structure of PTMSP. In addition, we describe our investigation of the permeation and separation characteristics of aqueous ethanol solution and other aqueous organic mixtures through the modified membranes.

EXPERIMENTAL

Materials

Starting material, PTMSP, was prepared by the method according to Masuda et al.⁹; i.e., 1-trimethylsilyl-1-propyne was polymerized in toluene with tantalum pentachloride as a catalyst. The number-average and weight-average molecular weights were 7.72×10^5 and 1.56×10^6 , respectively. PTMSP thus obtained was reprecipitated several times from its toluene solution into excess amount of methanol, and was dried *in vacuo* at 80°C for 24 h before use. 3,3,3-Trifluoropropyltrimethylchlorosilane was supplied from Torey Silicone Co. and freshly distilled before use. 1-Trimethylsilyl-1-propyne (TMSP) and 1H,1H,2H,2H-tridecafluorooctyltrimethylchlorosilane was purchased from the Chisso Corp. and also freshly distilled before use. Tetrahydrofuran (THF) used as a solvent was twice distilled from calcium hydride and sodium to remove small amounts of water. Toluene was also distilled over sodium. Tantalum pentachloride and tetraphenyltin were commercially obtained from Alfa, Morton Thiokol, Inc. and Tokyo Kasei Co., respectively, and employed without further purification.

Alkylsilylation

PTMSP (1.0 g, 8.90 mmol) was dissolved in 100 mL dry tetrahydrofuran under an argon atmosphere. To this solution 5.60 mL 1.6M hexane solution of *n*-butyllithium (8.96 mmol) was added at 0°C, where-

upon the color of the reaction mixture turned red. After stirring for 2 h at 0°C, 5.2 g of 3,3,3-trifluoropropyltrimethylchlorosilane (22.1 mmol) was added. The reaction mixture was poured into 1.0 L methanol, and the resulting polymer was reprecipitated several times from toluene solution into excess methanol. 3,3,3-Trifluoropropyltrimethylsilylated PTMSP (0.98 g) (FPS-PTMSP) was obtained.

The number-average and weight-average molecular weights were 6.91×10^5 and 1.45×10^6 , respectively. The content of the monomer unit containing 3,3,3-trifluoropropyltrimethylsilyl group was about 6 mol %, which was determined by elemental analysis.

ELEMENTAL ANAL. Found: C, 62.33%; H, 10.55%.

Preparations of 1-(3,3,3-Trifluoropropyltrimethylsilyl)-1-Propyne (FPDSP) and 1-(1H,1H,2H,2H-Tridecafluorooctyltrimethylsilyl)-1-Propyne (FODSP)

Propyne gas (2.7 g, 67 mmol) was trapped in a 200 mL three-necked flask equipped with dry ice condenser at -78°C, and dissolved in 40 mL dry THF under an argon atmosphere. To this solution 37 mL 1.6M hexane solution of *n*-butyllithium (59 mmol) was added at -78°C and stirred for 30 min. After additional stirring for 40 min at RT, 5.8 g of 3,3,3-trifluoropropyltrimethylchlorosilane (30 mmol) was added, and the solution was stirred for overnight at 50°C. The reaction mixture was poured into 200 mL of iced water. The product was extracted with diethyl ether, and purified by distillation. FPDSP (4.7 g) was obtained as a colorless liquid (bp 140–141°C, 81% yield).

¹H-NMR δ (CDCl₃, ppm); 0.25 (6H, s), 0.85 (2H, m), 1.98 (3H, s), 2.21 (2H, m).

ELEMENTAL ANAL. C₈H₁₃F₃Si (194.27): Calcd: C, 49.46%; H, 6.76%. Found: C, 49.38%, H, 6.81%.

FODSP was prepared by the same procedure described above using 13.2 g 1H,1H,2H,2H-tridecafluorooctyltrimethylchlorosilane (30 mmol) instead of 3,3,3-trifluoropropyltrimethylchlorosilane. The desired product, FODSP (13.2 g), was obtained as a colorless liquid (bp 99°C/22 mm Hg, 99% yield).

¹H-NMR δ (CDCl₃, ppm); 0.25 (6H, s), 0.85 (2H, m), 1.97 (3H, s), 2.24 (2H, m).

ELEMENTAL ANAL. C₈H₁₃F₃Si (194.27): Calcd: C, 35.14%; H, 2.96%. Found: C, 35.11%, H, 2.81%.

Copolymerization

Copolymerizations of TMSP monomer with FPDSP or FODSP comonomers were carried out under an argon atmosphere. All monomers were distilled over calcium hydride just before use. A typical procedure is as follows (cf. Table I, Copoly-1, comonomer 2 mol %): A monomer solution was prepared by adding 10.8 g TMSP (96.6 mmol) and 0.380 g FPDSP (1.96 mmol) to 50 mL dry toluene. A catalyst solution was prepared by mixing 0.891 g tantalum pentachloride (2.49 mmol) and 1.063 g tetraphenyltin (2.49 mmol) in 150 mL toluene and aged by keeping at 80°C for 30 min. Then, the monomer solution was added to the catalyst solution at 80°C. After 24 h, the reaction mixture was diluted with 1 L of toluene and poured into 10 L of methanol. The product was filtered off, reprecipitated several times from its toluene solution into excess methanol, and dried *in vacuo* at 60°C for 24 h. TMSP/FPDSP random copolymer (9.90 g) was obtained (89% yield).

The number-average and weight-average molecular weights were 6.27×10^5 and 1.78×10^6 , respectively, which were determined by gel permeation chromatography. The content of FPDSP unit was about 2 mol %, which was determined by elemental analysis.

ELEMENTAL ANAL. Found: C, 63.71%; H, 10.68%.

Other copolymers, containing different compo-

sitions or comonomer units, were prepared by the same procedure as described above by changing the amount of FPDSP or the kind of comonomer to FODSP.

Characterization

¹H-NMR was recorded on a Bruker AM-400 (400 MHz) NMR spectrometer using CDCl₃ as the solvent. The number-average and weight-average molecular weights were determined with Toyo Soda HLC-802A gel permeation chromatograph. Tetrahydrofuran was used as the solvent and standard polystyrenes were used for calibrating molecular weight.

Membrane Preparation

Toluene solution containing about 3 wt % of the polymer was cast on a polytetrafluoroethylene sheet and the solvent was evaporated over a period of 24 h. For the measurement of pervaporation the polymer membrane formed was then dried *in vacuo* and cut into a square piece of 50 mm in each length. The thickness of membrane was in the range of 30–50 μm.

Pervaporation

Pervaporation of aqueous organic liquid solution through the membrane was carried out by the nor-

Table I Results of Pervaporation of 6–7 wt % Aqueous Ethanol Solution through the Membranes of PTMSP, FPS–PTMSP, and TMSP/FADSP Copolymers at 50°C

Sample	Comonomer Content (mol %)	Ethanol Composition (wt %)		$\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$	P (g m/m ² h)
		Feed	Permeate		
PTMSP	—	6.58	41.9	10.3	1.91×10^{-2}
FPS–PTMSP	—	6.21	55.3	18.7	2.11×10^{-2}
Copoly-1 ^a (R = CH ₂ CH ₂ CF ₃)	1.0	6.08	56.1	19.8	2.00×10^{-2}
	2.0	6.89	61.2	21.3	2.25×10^{-2}
	3.0	6.23	53.5	17.3	1.98×10^{-2}
	5.0	6.26	51.0	15.7	1.73×10^{-2}
	10.0	6.22	48.8	14.4	1.52×10^{-2}
Copoly-2 ^b (R = CH ₂ CH ₂ C ₆ F ₁₃)	15.0	6.23	42.2	11.0	1.37×10^{-2}
	1.0	6.33	54.1	17.4	1.97×10^{-2}
	5.0	6.18	46.7	13.3	1.61×10^{-2}
	10.0	6.14	39.3	9.91	1.05×10^{-2}
	15.0	6.39	21.3	3.96	2.63×10^{-3}

^a TMSP/FPDSP copolymer membranes.

^b TMSP/FODSP copolymer membranes.

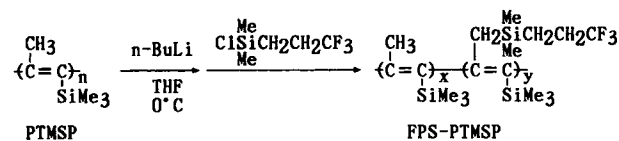
mal method using a stainless steel cell at 50°C.¹⁰ The feed solution (about 300 mL) was circulated on the upper side of the membrane at a flow rate of 1.2 mL/min, and the pressure on the downstream side was kept at about 0.5 mm Hg. After 30 min permeation, vapor in the down stream was stored in a 500 mL tank connected to the cell for 2–5 min. Composition and flux of the permeating mixture were determined by a gas chromatograph connected directly to the vapor tank, in order to avoid the effect of moisture on the determination of pervaporation characteristics. The permeation rate P (g m/m² h) was calculated with a correction of the flux for the thickness of the membrane. The separation factor α , which was a measure of the preferential permeation of component A, was also defined as the concentration ratio Y_A/Y_B in the permeate divided by the concentration ratio X_A/X_B in the feed.

RESULTS AND DISCUSSION

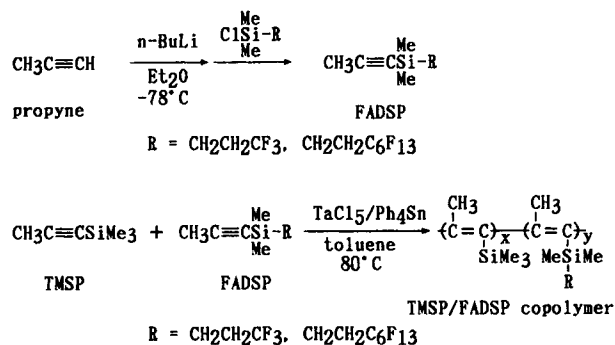
Preparations of the Modified PTMSP

The fluoroalkyl groups were introduced into PTMSP by two methods. One of them was the polymer reaction of PTMSP with *n*-butyllithium followed by treating with 3,3,3-trifluoropropyl dimethylchlorosilane as shown in Scheme 1, and another was the copolymerization of 1-trimethylsilyl-1-propyne (TMSP) with 1-fluoroalkyldimethylsilyl-1-propyne (FADSP) comonomers, as shown in Scheme 2. These comonomers were easily prepared from propyne gas dissolved in diethyl ether reacted with *n*-BuLi followed by treating with the corresponding chlorosilane compounds as also shown in Scheme 2.

In the case of the polymer reaction, the molecular weight of the product, 3,3,3-trifluoropropyl dimethylsilylated PTMSP (FPS-PTMSP), was slightly less than that of the starting PTMSP. Chain scission of a very small part of the PTMSP was suspected during the reaction with *n*-butyllithium. This decrease of molecular weight hardly affected the membrane forming ability of FPS-PTMSP. In addition, the rate of silylation was controlled by the amount



Scheme 1 Introduction of trifluoropropyl group into PTMSP by a polymer reaction.



Scheme 2 Preparations of FADSP monomers and TMSP/FADSP copolymers.

of *n*-butyllithium to some extent. However, accurate control of the rate of silylation was very difficult to achieve, and the limit of the content of silylated unit, y , was about 10 mol %.

Therefore, the accurate introduction of fluoroalkyl groups into PTMSP was carried out by the copolymerization of TMSP monomer with FADSP comonomers to afford TMSP/FADSP copolymers. The ratio of TMSP monomer unit to FADSP unit, x/y , was in the range of 99/1–85/15. It was difficult to confirm the composition of the resulting copolymer; however, the content of FADSP unit was almost equal to the content of FADSP comonomer in the copolymerization, which was determined by elemental analysis. Furthermore, absorption bands at 1210, 1120, and 1060 cm⁻¹ were observed in the IR spectra of the copolymers, which were due to the C–F bond.

The polymers obtained were soluble in several kinds of organic solvents, such as tetrahydrofuran, benzene, toluene, xylene, *n*-hexane, cyclohexane, methylene chloride, chloroform, carbon tetrachloride, etc. Tough and thin membranes could be obtained by a solvent casting method. On the other hand, they were insoluble in polar solvents, such as methanol, ethanol, propanol, acetone, acetonitrile, acetic acid, DMF, DMSO, etc.

Pervaporation

Figure 1 shows the permeation composition curves of aqueous ethanol solution through TMSP/FPDSP and TMSP/FODSP copolymer membranes, of which the contents of FPDSP and FODSP comonomer units were 1 mol %, in comparison with PTMSP homopolymer membrane. Preferential permeation of ethanol was observed for all the membranes for all ethanol feed concentrations. Interestingly, each copolymer membrane showed

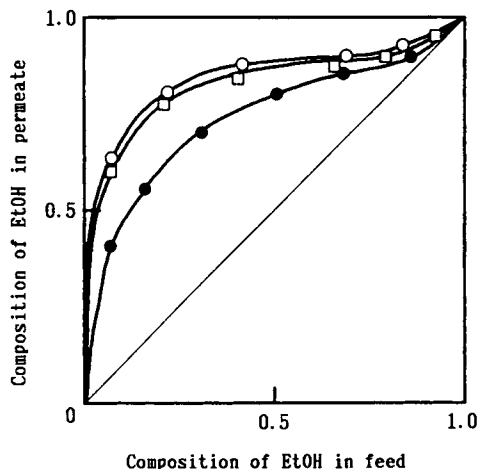


Figure 1 Permeation composition curves of aqueous ethanol solution through PTMSP (●) homopolymer, TMSP/FPDSP (○), and TMSP/FODSP (□) copolymer membranes at 50°C. The contents of FPDSP and FODSP units in the copolymers were both 1 mol %.

higher selectivity than the PTMSP membrane, especially at low concentration of feed solution.

Table I summarizes the results of pervaporation of 6–7 wt % aqueous ethanol solution through these membranes. As shown in this table, the ethanol permselectivity was observed in the pervaporation through all the modified PTMSP membranes. In addition, FPS-PTMSP, Copoly-1, and a part of Copoly-2 membranes showed higher selectivity of ethanol than the PTMSP membrane. In the case of Copoly-1 membranes, the separation factor α and the specific permeation rate P were influenced greatly by the content of comonomer unit: The maximum values of α and P were observed at 2 mol % of FPDSP content and their values decreased with the increase of FPDSP content over 2 mol %. Figure 2 shows the effect of FPDSP content of Copoly-1 membranes on α , P , and the contact angle of water on the surface of the membranes. A slight increase in the contact angle was observed over 5 mol % of FPDSP content. However, in the range of 5 mol % of FPDSP, α and P decreased considerably, even though the hydrophobicity of the membrane surface increased. On the other hand, for Copoly-2 membranes, α and P decreased with the increase of the comonomer component as shown in Table I. Moreover, the introduction of excess FODSP over 10 mol % caused a great decrease of α and P . Such a decrease in separation factor would be due to the reduction of the free volume of membrane by the long fluoroalkyl group. It is probable that the increase of FODSP units gradually fills the microvoids to reduce the free volume of the membrane and resists the

permeation through the voids to lower P . Actually, the density of the copolymer membrane increased by the introduction of such a long fluoroalkyl group. When the free volume of the membrane reduced, the differences between diffusivity of water and ethanol is considered to play a more important role.

Consequently, a high permeability coefficient seems to be necessary to achieve the high selectivity for ethanol. If the permeability coefficients of these membranes decreased significantly below that of PTMSP membrane, the separation factor also decreased significantly. Therefore, the moderate introduction of appropriate lengths of the fluoroalkyl groups effectively enhanced the selectivity according to the slight increase of hydrophobicity without changing the peculiar membrane structure of PTMSP.

Table II indicates typical pervaporation results for low concentrations of aqueous organic solutions through Copoly-1 membrane (FPDSP content = 2 mol %). Tetrahydrofuran (THF), acetone, acetonitrile, dioxane, isopropanol, and ethanol were used as organic liquids. As shown in this table, those organic liquids could be efficiently concentrated from their dilute aqueous solutions by using this membrane. For example, about 7 wt % aqueous solutions of THF, acetone, and acetonitrile were concentrated

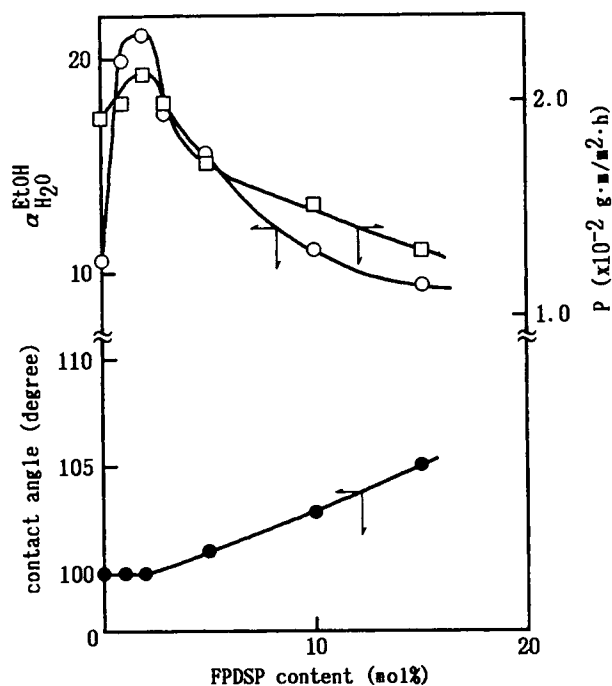


Figure 2 Plots of separation factor (α), specific permeation rate (P), and the contact angle of water against the content of FPDSP unit in TMSP/FPDSP copolymer membrane.

Table II Results of Pervaporation of 6–7 wt % Aqueous Organic Liquid Solution through TMSP/FPDSP Copolymer (Copoly-1, Comonomer Content = 2.0 mol %) Membrane at 50°C

Organic Liquid	Composition (wt %)		$\sigma_{H_2O}^{Org}$	P (g m/m ² h)
	Feed	Permeate		
THF	6.52	84.3	77.0	1.63×10^{-1}
Acetone	6.74	81.5	61.0	9.95×10^{-2}
Acetonitrile	6.48	80.0	57.7	8.95×10^{-2}
Dioxane	7.12	65.3	24.5	5.44×10^{-2}
2-Propanol	6.55	63.3	24.6	2.95×10^{-2}
Ethanol	6.89	61.2	21.3	2.25×10^{-2}

to over 80 wt % by one step of permeation. In every case, the separation factors α of the copolymer membranes were improved as compared with those values of PTMSP membrane.⁵ Such a difference in selectivities for organic liquids are mainly attributed to a difference of solubilities of the liquids at the membrane surface.⁴ Although the copolymer was soluble in THF and largely swollen in acetone and acetonitrile, the copolymer membrane was not destroyed by the feed solutions because the concentrations of the organic components were less than 10 wt %. Therefore, this type of copolymer membrane is expected to be useful, for example, for the

recovery of the organic components from their dilute aqueous solutions.

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