

# Chemical Modification of Poly(substituted-Acetylene). V. Alkylsilylation of Poly(1-Trimethylsilyl-1-Propyne) and Improved Liquid Separating Property at Pervaporation

YU NAGASE,\* YURIKO TAKAMURA, and KIYOHIDE MATSUI

Sagami Chemical Research Center, Nishi-Ohnuma, Sagamihara, Kanagawa, 229 Japan

## SYNOPSIS

In order to improve the separation characteristic at pervaporation, the introduction of several kinds of trialkylsilyl groups into poly(1-trimethylsilyl-1-propyne) (PTMSP) was achieved via metalation of PTMSP followed by treating with trialkylchlorosilanes to afford trialkylsilylated PTMSP. Ratio of TMSp monomer unit and trialkylsilylated unit,  $x/y$ , was in the range of 95/5 to 80/20. All the chemically modified PTMSP membranes showed ethanol permselectivity at pervaporation of aqueous ethanol solution. Introduction of appropriate length of alkyl groups (methyl, ethyl, propyl, butyl, hexyl, octyl, and decyl groups) into PTMSP effectively enhanced the selectivity. However, excess introduction of octyl and decyl groups or introduction of dodecyl and octadecyl groups caused decrease of selectivity, of which the value was smaller than that of PTMSP membrane. Furthermore, acetone, acetonitrile, dioxane, and isopropanol were efficiently separated from their aqueous solutions at pervaporation through trimethylsilylated PTMSP membrane.

## INTRODUCTION

In the past few years, we have been investigating alcohol permselective membrane for the liquid separation by using pervaporation technique.<sup>1-5</sup> It is more practical to separate alcohol by alcohol permselective membrane, since it is usually a minor component in the alcohol production, for example, fermentation of biomass such as starch, sugar, and cellulose.

Poly(1-trimethylsilyl-1-propyne) (PTMSP) has been known to show the greatest permeability coefficients of several gases among the polymer membranes.<sup>6,7</sup> This polymer also has a good membrane forming ability according to its extremely high molecular weight, so that a very thin membrane can be prepared. In addition, PTMSP membrane has also been known to show preferential permeation of ethanol at pervaporation of aqueous ethanol solution.<sup>3,8</sup> The separation factor is 10 to 12, when the feed concentration of ethanol is about 7 wt %, and

the flux is also very high. These properties are according to its peculiar membrane structure. PTMSP membrane has been considered to contain excess free volume,<sup>9</sup> and ethanol permselectivity of this membrane is thought to be due to the existence of free volume and the hydrophobicity of the membrane surface. On the other hand, Fusaoka et al. has prepared poly(1-alkyldimethylsilyl-1-propyne) and evaluated the separation property of aqueous ethanol solution as compared with PTMSP membrane.<sup>10</sup> He 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. It is an interesting result of suggesting that the peculiar membrane structure of PTMSP is very important to achieve ethanol permselectivity, and the permselectivity is extremely alterable even by the slight change of the chemical structure.

In our previous study, chemical modification of PTMSP was achieved by introducing polydimethylsiloxane chain to afford graft copolymer.<sup>11</sup> Further, the graft copolymer membrane showed improved selectivity and stability at gas permeation and excellent permselectivity of ethanol from aqueous

\* To whom correspondence should be addressed.

ethanol solution by pervaporation technique.<sup>4</sup> Such a high selectivity for ethanol was induced by a delicate alteration of membrane structure, which was the introduction of short polydimethylsiloxane side chain into PTMSP backbone to bring about the increase of hydrophobicity. Therefore, we expected that introduction of alkyl group into PTMSP would be also effective to increase hydrophobicity of the membrane and to improve the separation property at pervaporation. In this study, we studied a chemical modification of PTMSP to introduce several kinds of alkyl groups by polymer reactions. These substituents were partly introduced in order to maintain the peculiar membrane structure of PTMSP. Thus, we describe our investigation upon the permeation and separation characteristics of aqueous ethanol solution through these membranes.

## EXPERIMENTAL

### Materials

Starting material, PTMSP, was prepared by the method according to Masuda et al.<sup>6</sup> (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  $7.72 \times 10^5$  and  $1.56 \times 10^6$ , 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. All the silicone containing compounds were purchased from Chisso Corporation, and freshly distilled before use. A part of chlorosilane compounds, *n*-decyldimethylchlorosilane, *n*-dodecyldimethylchlorosilane, and *n*-hexyldimethylchlorosilane, were synthesized as described below, because they were not commercially produced. Tetrahydrofuran used in the polymer reaction was twice distilled from calcium hydride and sodium to remove small amount of water.

### Preparations of Chlorosilane Compounds

*n*-Decyldimethylchlorosilane, *n*-dodecyldimethylchlorosilane, and *n*-hexyldimethylchlorosilane were easily prepared by hydrosilylation of dimethylchlorosilane with 1-decene, 1-dodecene, and 1-hexene, respectively, by using Pt catalyst.

To a mixture of 25 g of 1-decene (0.18 mol) and 50 mL of dimethylchlorosilane (0.46 mol), 0.1 mL of 0.1 M isopropanol solution of chloroplatinic acid was added. The reaction mixture was stirred for 2

h at 60°C, and then distilled under vacuum. *n*-Decyldimethylchlorosilane (28.3 g) (b.p. = 112–115°C/5 mm Hg) was obtained (67.7% yield).

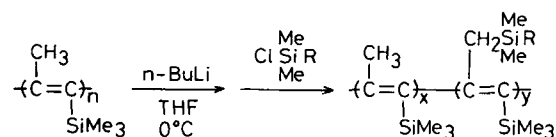
In the above reaction, 25 g of 1-dodecene (0.15 mol) and 25 g of 1-hexene (0.20 mol) were used instead of 1-decene. Then, 32.4 g of *n*-dodecyldimethylchlorosilane (b.p. = 95–96°C/0.3 mm Hg, 82.4% yield) and 26.7 g of *n*-hexyldimethylchlorosilane (b.p. = 66°C/15 mm Hg, 74.7% yield) were obtained, respectively.

### Alkylsilylation

Alkylsilylation of PTMSP was carried out via metalation of PTMSP with *n*-butyllithium followed by treating with chlorosilane compounds as shown in Scheme 1. The following describes a typical procedure.

PTMSP (1.0 g, 8.90 mmol) was dissolved in 100 mL of dry tetrahydrofuran under an argon atmosphere. To this solution 5.60 mL of 1.6 M *n*-hexane solution of *n*-butyllithium (8.96 mmol) was added at 0°C, whereupon color of the reaction mixture turned to red. After stirring for 2 h at 0°C, 5.2 g of *n*-decyldimethylchlorosilane (22.1 mmol) was added. Then, the reaction mixture was poured into 1.0 l of methanol, and the resulting polymer was reprecipitated several times from its toluene solution to excess methanol. *n*-Decyldimethylsilylated PTMSP (1.15 g) was obtained. The content of *n*-decyldimethylsilyl group of the product was about 5 mol %, which was determined by <sup>1</sup>H-NMR spectrum. When, in the above reaction, 10.1 mL of 1.6 M *n*-hexane solution of *n*-butyllithium (16.2 mmol) was used, the content of *n*-decyldimethylsilyl group was 11 mol %.

In this reaction, trimethylchlorosilane, ethyldimethylchlorosilane, triethylchlorosilane, *n*-propyldimethylchlorosilane, *n*-butyldimethylchlorosilane, *n*-hexyldimethylchlorosilane, *n*-octyldimethylchlorosilane, *n*-dodecyldimethylchlorosilane, and *n*-octadecyldimethylchlorosilane were used instead



$$\text{R} = \text{-(CH}_2\text{)}_m\text{CH}_3 \quad (m = 0 \sim 17)$$

**Scheme 1** Synthetic scheme of the preparation of trialkylsilylated PTMSPs by using polymer reaction.

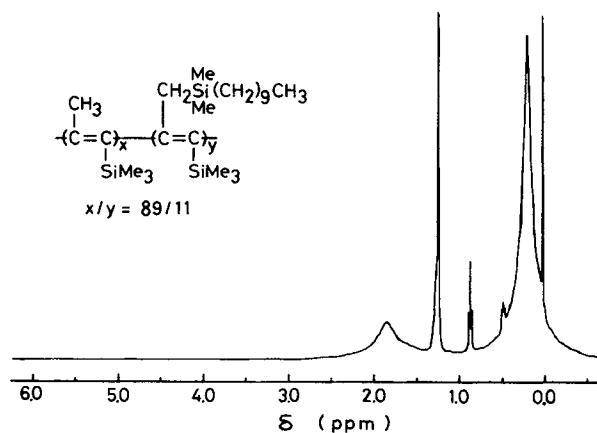
of *n*-decyldimethylchlorosilane. Then, several kinds of trialkylsilylated PTMSPs were prepared.

### Membrane Preparation

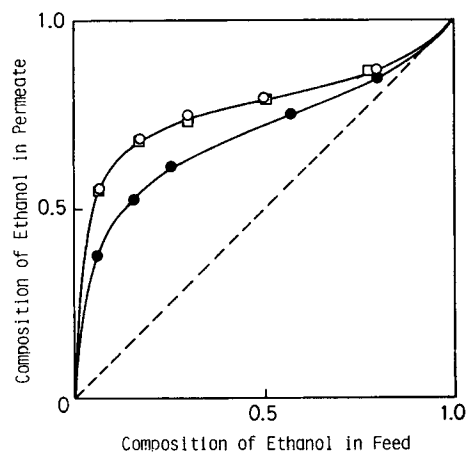
Toluene solution containing about 3 wt % of the polymer was cast on a polytetrafluoroethylene sheet and the solvent was evaporated over the period of 24 h. For the measurement of pervaporation the polymer membrane formed was then dried *in vacuo* and cut into a square piece of 50 mm in each length. The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

### Pervaporation

Pervaporation of aqueous organic liquid solution through the membrane was carried out by an ordinary method using a stainless steel cell at 50°C.<sup>1</sup> The permeation area of the membrane was 9.6 cm<sup>2</sup>. The feed solution was circulated on the upper side of the membrane, and the pressure of the lower side was kept at about 0.5 mm Hg. Composition and flux of the permeating mixture were determined by a gas chromatograph connected directly to the pervaporation cell, in order to avoid the effect of moisture on the determination of pervaporation characteristics. The permeation rate,  $P$  in g m/m<sup>2</sup> h, was calculated by a correction of the flux for the thickness of the membrane. The separation factor, 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.



**Figure 1** 400 MHz <sup>1</sup>H-NMR spectrum of decyldimethylsilylated PTMSP in CDCl<sub>3</sub>.

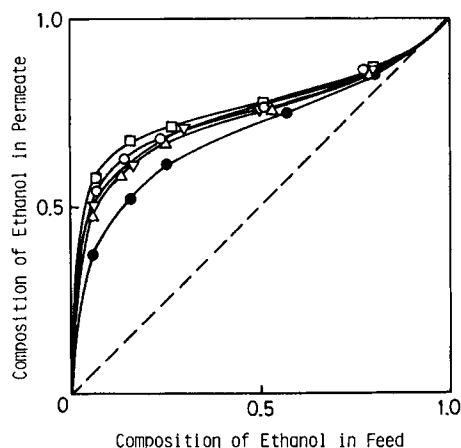


**Figure 2** Permeation composition curves of aqueous ethanol solution at pervaporation through trimethylsilylated PTMSP (O), triethylsilylated PTMSP (□), and PTMSP (●) membranes.

## RESULTS AND DISCUSSION

### Characterizations

In the reaction of Scheme 1, methyl protons connected to carbon-carbon double bond of PTMSP would be attacked by *n*-butyllithium to afford polyanion of PTMSP.<sup>11</sup> Next, the polyanion was reacted with trialkylchlorosilanes and the resulting product was trialkylsilylated PTMSP. The remaining excess trialkylchlorosilanes were easily removed by reprecipitation of the obtained product from its toluene



**Figure 3** Permeation composition curves of aqueous ethanol solution at pervaporation through *n*-butyldimethylsilylated PTMSP ( $\Delta$ ), *n*-hexyldimethylsilylated PTMSP ( $\square$ ), *n*-octyldimethylsilylated PTMSP ( $y = 11$  mol %) (O), *n*-decyldimethylsilylated PTMSP ( $y = 5$  mol %) ( $\nabla$ ), and PTMSP (●) membranes.

solution into excess methanol. Ratio of TMSP monomer unit and trialkylsilylated PTMSP unit,  $x/y$ , was in the range of 95/5 to 80/20, which was determined by  $^1\text{H-NMR}$  spectrometry. The rate of silylation was controlled by the amount of *n*-butyllithium to some extent. However, the limit of the content of silylated unit,  $y$ , was about 20 mol %.

$^1\text{H-NMR}$  spectrum of decyldimethylsilylated PTMSP was shown in Figure 1 as an example. This spectrum supported the chemical structure of the product. Methyl groups of PTMSP monomer unit

showed broad peaks at 0.2 and 1.8 ppm, and methylene and methyl groups of decyl group were observed at around 1.2 and 0.8 ppm, respectively. The value of  $x/y$  was determined by the ratio of integration of the peaks at 1.2 and 1.8 ppm. The similar spectra were observed for the other trialkylsilylated PTMSPs.

Weight-average molecular weight was more than 1 million by the measurement of gel permeation chromatography, but the molecular weight of the product was slightly smaller than that of starting

**Table I Results of Pervaporation of 6–7 wt % Aqueous Ethanol Solution through PTMSP and Alkylsilylated PTMSP Membranes at 50°C**

Sample	$x : y$ (molar ratio)	Ethanol Composition (wt %)		$\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$	$P$ (g m/m <sup>2</sup> h)
		Feed	Permeate		
1. PTMSP	—	6.58	41.9	10.3	$1.91 \times 10^{-2}$
2. PTMSP— $\begin{matrix} \text{Me} \\ \text{SiMe} \\ \text{Me} \end{matrix}$	90 : 10	6.23	53.9	17.6	$2.36 \times 10^{-2}$
3. PTMSP— $\begin{matrix} \text{Me} \\ \text{SiEt} \\ \text{Me} \end{matrix}$	92 : 8	6.15	50.4	15.5	$2.24 \times 10^{-2}$
4. PTMSP— $\begin{matrix} \text{Et} \\ \text{SiEt} \\ \text{Et} \end{matrix}$	94 : 6	6.25	52.1	16.3	$2.06 \times 10^{-2}$
5. PTMSP— $\begin{matrix} \text{Me} \\ \text{Si}-n\text{-C}_3\text{H}_7 \\ \text{Me} \end{matrix}$	92 : 8	6.25	50.0	15.0	$1.79 \times 10^{-2}$
6. PTMSP— $\begin{matrix} \text{Me} \\ \text{Si}-n\text{-C}_4\text{H}_9 \\ \text{Me} \end{matrix}$	94 : 6	6.18	49.8	15.1	$1.74 \times 10^{-2}$
7. PTMSP— $\begin{matrix} \text{Me} \\ \text{Si}-n\text{-C}_6\text{H}_{13} \\ \text{Me} \end{matrix}$	93 : 7	6.19	51.8	16.3	$1.72 \times 10^{-2}$
8. PTMSP— $\begin{matrix} \text{Me} \\ \text{Si}-n\text{-C}_8\text{H}_{17} \\ \text{Me} \end{matrix}$	89 : 11 80 : 20	6.81 6.74	52.0 32.9	14.9 6.77	$1.81 \times 10^{-2}$ $3.17 \times 10^{-3}$
9. PTMSP— $\begin{matrix} \text{Me} \\ \text{Si}-n\text{-C}_{10}\text{H}_{21} \\ \text{Me} \end{matrix}$	95 : 5 89 : 11	6.13 6.42	53.8 38.2	17.8 9.01	$1.72 \times 10^{-2}$ $5.08 \times 10^{-3}$
10. PTMSP— $\begin{matrix} \text{Me} \\ \text{Si}-n\text{-C}_{12}\text{H}_{25} \\ \text{Me} \end{matrix}$	92 : 8	6.36	29.4	6.12	$5.89 \times 10^{-3}$
11. PTMSP— $\begin{matrix} \text{Me} \\ \text{Si}-n\text{-C}_{18}\text{H}_{37} \\ \text{Me} \end{matrix}$	94 : 6	6.31	26.1	5.23	$1.99 \times 10^{-3}$

PTMSP. Chain scission of very small part of PTMSP was suspected under the reaction with *n*-butyllithium. At membrane preparation, however, such a decrease of molecular weight hardly affected the membrane forming ability of the trialkylsilylated PTMSP.

No glass transition temperature nor melting temperature was detected for trialkylsilylated PTMSP in the temperature range between  $-150$  and  $300^{\circ}\text{C}$  by DSC. Thermal degradation or oxidation occurs above  $180^{\circ}\text{C}$  as evidence by a DSC exotherm. The thermal properties of all the trialkylsilylated PTMSPs were very similar to that of PTMSP.

The obtained polymers 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 solvent casting method. On the other hand, they were insoluble in polar solvents, such as methanol, ethanol, dioxane, acetone, acetonitrile, acetic acid, DMF, DMSO, pyridine, ethyl acetate, etc.

### Pervaporation

Figures 2 and 3 show permeation composition curves of aqueous ethanol solution through trialkylsilylated PTMSP membranes in comparison with PTMSP. Membranes of trimethyl and triethylsilylated PTMSPs and *n*-butyl, *n*-hexyl, *n*-octyl, and *n*-decyldimethylsilylated PTMSPs were evaluated. Preferential permeation of ethanol was observed for all the membranes at every component in feed. Every alkylsilylated PTMSP membrane has higher selectivity than 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. Through PTMSP membrane, 6.58 wt % feed solution was concentrated to 41.9 wt % ethanol, and the separation factor,  $\alpha$ , was calculated as 10.3. The permeability coefficient  $P$  was  $1.91 \times 10^{-2} \text{ g m m}^{-2} \text{ h}^{-1}$ . On the other hand, through trimethylsilylated PTMSP membrane, 6.23 wt % feed solution was concentrated to 53.9 wt %, and the  $\alpha$  was 17.6. This value is higher than that of PTMSP membrane. And also, the permeability coefficient  $P$  was increased to  $2.36 \times 10^{-2} \text{ g m m}^{-2} \text{ h}^{-1}$ . For the other two membranes, ethyldimethylsilylated and triethylsilylated PTMSP membranes, a similar tendency was observed. Furthermore, *n*-propyl, *n*-butyl, *n*-hexyl, *n*-octyl, and *n*-decyldimethylsilylated PTMSP membranes also showed improved separation factors, around 15 or 16. Such an increase of separation factor is considered to be due to the increase of hydrophobicity of the membrane by these alkyl groups.

In the case of octyl and decyl groups, the composition,  $x/y$ , was changed in order to observe the effect of composition upon the permeation. In each case,  $\alpha$  and  $P$  were decreased as the  $y$  component increased. Moreover, the introduction of dodecyl and octadecyl groups greatly decreased  $\alpha$  and  $P$  as shown in Table I. Such a decrease of separation factor would be due to the reduction of the free volume of membrane by a long alkyl group. Actually, the density of membrane increased by the introduction of a long alkyl group. The high permeability coefficient is necessary to achieve the high selectivity of ethanol. If the permeability coefficients of these membranes largely decreased than that of PTMSP membrane, the separation factor remarkably decreased. Consequently, moderate introductions of appropriate lengths of alkyl groups effectively enhanced the selectivity according to the increased

**Table II Results of Pervaporation of 6–7 wt % Aqueous Organic Liquid Solution Through PTMSP and Trimethylsilylated PTMSP Membranes at  $50^{\circ}\text{C}$**

Organic Liquid	PTMSP				Trimethylsilylated PTMSP			
	Composition (wt %)		$\alpha_{\text{H}_2\text{O}}^{\text{Org}}$	$P$ (g m/m <sup>2</sup> h)	Composition (wt %)		$\alpha_{\text{H}_2\text{O}}^{\text{Org}}$	$P$ (g m/m <sup>2</sup> h)
	Feed	Permeate			Feed	Permeate		
Acetone	7.10	75.1	39.4	$6.66 \times 10^{-2}$	6.95	82.4	62.8	$9.92 \times 10^{-2}$
Acetonitrile	6.95	69.6	30.6	$4.39 \times 10^{-2}$	6.68	81.6	62.0	$8.65 \times 10^{-2}$
Dioxane	7.47	63.6	21.7	$2.98 \times 10^{-2}$	7.62	69.2	27.2	$4.37 \times 10^{-2}$
<i>i</i> -Propanol	6.24	51.1	15.7	$2.52 \times 10^{-2}$	5.29	57.0	21.1	$2.91 \times 10^{-2}$
Ethanol	6.58	41.9	10.3	$1.91 \times 10^{-2}$	6.23	53.9	17.6	$2.36 \times 10^{-2}$

hydrophobicity without change of the peculiar membrane structure of PTMSP.

Table II indicates typical pervaporation results of aqueous low concentrating solutions of organic liquid through PTMSP and trimethylsilylated PTMSP membranes. Acetone, acetonitrile, dioxane, isopropanol, and ethanol were used as organic liquids. Such a difference of selectivities for organic liquids are mainly attributed to a difference of solubilities of the liquids to the membrane surface.<sup>5</sup> In every case, the separation factors,  $\alpha$ , of the trimethylsilylated PTMSP membrane were improved as compared with those values of PTMSP membrane. For example, about 7 wt % aqueous solutions of acetone and acetonitrile were concentrated to over 80 wt % by one step of permeation. Further, the permeability coefficients,  $P$ , were also improved. Increases of both  $\alpha$  and  $P$  may be according to the increase of not only hydrophobicity but also free volume of the membrane. Actually, the density of membrane decreased by the introduction of trimethylsilyl group. Therefore, the high selectivity toward organic liquids of trimethylsilylated PTMSP membrane is probably due to increased hydrophobicity and excess free volume of membrane, and also to maintenance of the high permeability coefficient of PTMSP membrane.

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