Pervaporation Separation of Aqueous Alcohol Solution through the Membrane of *o*-Trimethylsilylphenylacetylene Initiated by a Tungsten Carbene Complex

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ABSTRACT: A poly(*o*-trimethylsilylphenylacetylene) [poly(*o*-TMSPA)] initiated by a tungsten carbene complex was investigated under various conditions. The molar mass of poly(*o*-TMSPA) increases with increasing the polymerization temperature and decreasing the initiator concentration. The X-ray diffraction measurements show that poly(*o*-TMSPA) has an amorphous structure. The water molecules preferentially permeate through the poly(*o*-TMSPA) membranes. The effects of feed compositions, degree of swelling, and the molecular size of alcohols on the pervaporation performances were investigated. The separation factor and the permeation rate increase with increasing ethanol concentration in the feed. The diffusivity contributes to a major part to selective transport. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 647–654, 1999

Key words: *o*-trimethylsilylphenylacetylene; tungsten carbene complex; pervaporation; membrane

INTRODUCTION

Pervaporation has been increasing attention as a method for separating liquid mixtures, such as azeotropic mixtures, close boiling point compounds, heat-sensitive compounds, and isomers.[1–5] This is a process involving permeation of liquid through a membrane and then evaporation of liquid from the downstream side of the membrane. The efficiency of the pervaporation process depends mainly on the intrinsic property of the polymer used to prepare the membranes. There-

fore, designing membranes with a high permeation rate and a suitable separation factor is an important issue. There are a lot of researchers related to many kinds of membrane materials for separation aqueous alcohol mixtures by pervaporation.[6–9] In addition, in order to improve the pervaporation performances (water permselectivity), many experimental attempts have been made to control the specific interaction between the membrane and the permeate by synthesis of a new hydrophilic polymer,[10] blending and crosslinking,[11] copolymerization,[12] and grafting a hydrophilic species onto an inert substrate.[13] Recently, several substituted polyacetylenes have been synthesized using groups V and VI transition metal catalyst.[14] Compared with hydrocar-

bon polyacetylenes, Si-containing polyacetylenes exhibit unique properties. For example, poly[1-(trimethylsilyl)-1-propyne] shows extremely high gas permeability and ethanol permselectivity in the pervaporation of ethanol–water mixtures.[15,16]

The present article is concerned with a detailed study on the polymerization of *o*-trimethylsilyl-phenylacetylene (*o*-TMSPA) with a tungsten carbene complex as a catalyst under various conditions. The effects of the concentration of the catalyst on the molar mass were examined. Moreover, the behavior of the poly(*o*-TMSPA) membrane in the pervaporation of aqueous ethanol solution were investigated.

EXPERIMENTAL

Monomer Preparation

The monomer (*o*-TMSPA) was prepared according to the methods of Brandsma and Masuda and their coworkers.[17,18] The monomer was carefully distilled [bp, 85°C (1.3 kpa); yield, 78.8%; purity, 99.9% (by gas chromatography)].

Catalyst Preparation

The catalyst, tungsten carbene complex, was prepared according to the method of Rudler and coworkers,[19] as shown in Scheme I, as follows:

Scheme 1

The crude solid obtained was purified on a chromatographic column of silica gel with hexane as the eluent and was recrystallized from pentane solution.

Polymerization

The polymerization was synthesized following the procedures reported in Liaw et al.[20] Mixtures of

tungsten carbene complex catalyst (0.01 g) and solvent CCl$_4$ (1.76 mL) were introduced into a Schlenk tube. The contents of the tube were flushed with nitrogen and sealed in vacuum by the freeze–thaw technique. The tube was kept in the dark and placed in a tank at a constant temperature 40°C for 15 min. The monomer (*o*-TMSPA, 0.5 mg) was added to the solution by a syringe. The mixtures was kept in the dark at 40°C for 20 h. The reaction solution was red and homogeneous at the beginning of polymerization but gradually changed from red to dark purple. The polymerization reaction was terminated with a toluene–methanol (volume ratio of 2 : 1) mixture; the viscous solution was diluted with toluene and poured into methanol with stirring to precipitate the dark purple polymer formed. The polymer was filtered and dried for about 24 h at 60°C under vacuum and weighed. The polymer was characterized by infrared (IR), ^{1}H nuclear magnetic resonance (^{1}H-NMR), ^{13}C-NMR, and ^{29}Si–NMR spectra.

IR: ν/cm^{-1} C=C, 1583; SiC–H, 1245; Si–C, 834. ^{1}H-NMR (in CDCl$_3$): δ/ppm 0.07 [9H, Si–(CH$_3$)$_3$]; 4.40–7.80 (=CH—). ^{13}C-NMR (in CDCl$_3$): δ/ppm 123–150 (C=C); 1.0 (Si–(CH$_3$)$_3$). ^{29}Si–NMR (in CDCl$_3$): δ/ppm 5.90 [Si–(CH$_3$)$_3$].

Molar Mass Measurement

The number-average and mass average molar masses (M_n and M_w) were determined by gel permeation chromatography (GPC).

Membrane Preparation

The poly(*o*-TMSPA) membrane was prepared from a casting solution containing 10 wt % polymer in CHCl$_3$. The membrane was formed by casting the solution on a glass plate to a predetermined thickness. The glass plate was then heated at 70°C for 40 min. The average thickness of the membranes was about 25–30 μm.

Pervaporation Experiments

A traditional pervaporation apparatus was used in this study.[21] The effective membrane area was 10.17 cm^2. A vacuum pump maintained the downstream pressure at 3–5 mm Hg. The permeation rate was determined by measuring the weight of the permeate. The compositions of the feed solutions, permeates, and solutions absorbed in the

Table I   Results of the Polymerization of *o*-Trimethylsilylphenylacetylene Under Various Conditions[a]

No.	Catalyst [I]	Solvent	$[M]_0/[I]_0$	Temperature (°C)	Yield (%)	$\overline{M_n}$[h] $\times 10^{-3}$	$\overline{M_w}$[h] $\times 10^{-3}$	$\overline{M_n}/\overline{M_w}$
						Polymer[g]		
1	AIBN	Toluene	40	60	0	—	—	
2	Noncoordinated carbene[b]	Toluene	40	60	0	—	—	
3	Fischer catalyst[c]	Toluene	40	60	0	—	—	
4	Coordinated carbene[d]	Toluene	10	60	53.2	2.4	6.9	2.88
5	Coordinated carbene[d]	Toluene	20	60	22.2	12	35	2.92
6	Coordinated carbene[d]	Toluene	40	60	8.4	22	63	2.86
7	Coordinated carbene[d,e]	Toluene	40	30	99.1	163	538	3.30
8	Coordinated carbene[d]	CCl_4	100	30	100	91	189	2.08
9	Coordinated carbene[d]	$CHCl_3$	100	30	88.3	40	74	1.85
10	Coordinated carbene[d]	CH_2Cl_2	100	30	25.0	26	56	2.15
11	Coordinated carbene[d]	$(CH_2Cl)_2$	100	30	0	—	—	
12	Coordinated carbene[d,f]	CCl_4	100	40	82.6	435	1145	2.63

[a] Polymerization time, 24 h; $[M]_0$, 1.0 mol/L.
[b] Noncoordinated carbene: [c] Fischer catalyst: [d] Coordinated carbene:

[e] Polymerization time, 20 h; $[M]_0$, 1.0 mol/L. $AlCl_3$ was used as catalyst. $[AlCl_3]/[I]_0 = 12$.
[f] Tungsten carbene complex was irradiated in CCl_4 for 60 min with a 365-nm Ushio 250-W high-pressure mercury lamp at a distance of 5 cm.
[g] Methanol-insoluble product.
[h] Measured by GPC in THF; polystyrene was used as the standard.

membrane were measured by gas chromatography (GC; China Chromatography 8700). The separation factor was calculated from

$$\alpha_{H_2O/EtOH} = \frac{Y_{H_2O}/Y_{EtOH}}{X_{H_2O}/X_{EtOH}}$$

where Y_{H_2O} and Y_{EtOH}, and X_{H_2O} and X_{EtOH} are the weight fraction of water and ethanol in the permeate and feed, respectively.

Sorption Measurement

A membrane was immersed in ethanol–water mixtures for 24 h. It was subsequently blotted between tissue paper to remove adherent solvent and placed in the left container of a twin-tube setup. The system was evacuated while the left container with the swollen membrane was heated to evaporate completely the liquid absorbed in the membrane. The evaporated vapor was trapped in the right one by cooling with liquid nitrogen. The composition of condensed liquid in the right tube was determined by GC.

RESULTS AND DISCUSSION

Polymer Synthesis

Table I shows the results of polymerization of *o*-trimethylsilyl phenylacetylene initiated with several catalysts. It shows that the coordinated carbene catalyst was clearly more efficient than other catalysts, such as AIBN or Fischer's catalyst. A greater yield and smaller molar mass of poly(*o*-trimethylsilylphenylacetatene) [poly(*o*-TMSPA)] were obtained when the polymerization was performed at a lower monomer-to-initiator ratio

Table II   Effect of Temperature on the Polymerization of *o*-Me₃SiPA in CCl₄ᵃ

Temperature (°C)	Yield (%)	$\overline{M_n}$ c × 10⁻³	$\overline{M_w}$ c × 10⁻³	$\overline{M_n}/\overline{M_w}$
30	100	92	189	2.05
40	100	128	208	1.63
60	100	226	575	2.54
80	100	257	585	2.28

ᵃ Polymerization time, 24 h; $[M]_0 = 1.0$ mol/L; $[M]_0/[I]_0 = 100$.
ᵇ Methanol-insoluble product.
ᶜ Measured by GPC in THF; polystyrene was used as the standard.

($[M]_0/[I]_0$) in toluene. The polymer obtained with coordinated carbene catalyst easily dissolved in organic solvents, such as hexane, benzene, and toluene, and chlorinated aliphatic hydrocarbon, such as methylene chloride, chloroform, and carbon tetrachloride. In addition, the effect of temperature on the polymerization of *o*-TMSPA in CCl₄ is shown in Table II. The molar mass increased with the temperature of polymerization. The polymer yield reached 100% at any temperature. The thermogravimetric analysis (TGA) curves for thermal degradation of the poly(*o*-TMSPA) heated at 10°C/min in nitrogen, air, and oxygen are shown in Figure 1. It shows that the loss of mass of poly(*o*-TMSPA) occurred above 300°C. In the presence of nitrogen, the onset of mass loss of poly(*o*-TMSPA) occurred at a slightly higher temperature than in oxygen. In the presence of oxygen, the decrease of mass showed down

Figure 1   TGA curves for poly(*o*-TMSPA) in nitrogen, air, and oxygen (heating rate: 10°C/min).

Figure 2   The effect of feed water concentration on the water concentration in the permeate and in the membrane.

considerably between 400 and 460°C before a second rapid mass loss step occurs. The amount of resides at 700°C exceeding 10% was probably SiO₂. This observation was also reported by Tang et al.[22] and Neoh et al.[23] Moreover, a X-ray diffractogram was recorded with the powder method. The broad diffraction line indicated that the poly(*o*-TMSPA) obtained from tungsten carbene complex has an amorphous structure.

Effect of Feed Solution Concentration on Pervaporation Performance

Figure 2 shows that the effect of feed water concentration on the water concentration in the permeate and in the membrane for the poly(*o*-TMSPA) membrane initiated by the tungsten carbene complex in CCl₄ at 60°C. It shows that the water composition in the membrane and in the permeate are higher than that in the liquid feed, indicating that water molecules are preferentially dissolved into the membrane and are also predominantly diffused through the membrane. Additionally, compared with water concentration in membrane, the water concentration in permeate is higher than that in membrane for pervaporation of ethanol–water mixture in the range of 10–90 wt %. These results can be explained by the very strong affinity between the ethanol molecules and the poly(*o*-TMSPA) membrane and also the water molecules size is rather small. Furthermore, in order to confirm the interaction between the feed solution and the poly(*o*-TMSPA)

Figure 3 The effect of feed water concentration on the contact angle.

Figure 5 The effect of feed water concentration on the permeation rate and the separation factor for the poly(*o*-TMSPA) membrane.

membrane, the contact angle measurement were made. The data are presented in Figure 3. It can be seen that the contact angle decreases with increasing the feed ethanol concentration. It indicated that the affinity between the ethanol molecules and the poly(*o*-TMSPA) membrane is higher than that between the water molecules and the poly(*o*-TMSPA) membrane. These results completely support the data shown in Figure 4; that

Figure 4 The effect of feed water concentration on the degree of swelling of the poly(*o*-TMSPA) membrane.

is, higher ethanol concentration in the feed results in a higher degree of swelling. Moreover, the effect of composition of feed mixtures on the pervaporation performances of the poly(*o*-TMSPA) membranes is shown in Figure 5. The permeation rate and separation factor decreased as the feed water concentration increased. These results can be explained by the plasticizing effect of ethanol. Generally, the hydrophobic membrane has a strong interaction with alcohol. When the ethanol concentration in the feed is higher, the amorphous regions of the membrane are more swollen. Hence, the polymer chain becomes more flexible, thus decreasing the energy required for diffusive transport through the membrane, resulting in permeation rate increases with the ethanol concentration in the feed solution. The degree of swelling of the poly(*o*-TMSPA) membranes decreased, and the contact angle increased with increasing water concentration, as shown in Figures 3 and 4, respectively. These results correspond well with the permeation rate of the poly(*o*-TMSPA) membrane, as indicated in Figure 5. In addition, when the degree of swelling of the membrane in the mixture was large, water permeated through the membrane, in spite of its low affinity toward the membrane. That is, excessive swelling due to the nonselective solvent (ethanol) causes a selective solvent (water) to permeate through the membrane and enhance the separation selectivity. Thus, the separation factor increased with increasing of the feed ethanol concentration.

Table III   Effect of Feed Compositures on the Sorption Amount, Sorption Separation Factor, and Pervaporation Factor

Feed H_2O Concentration (wt %)	Total Sorption (g/100 g Membr)	Water Sorption (g/100 g Membr)	Ethanol Sorption (g/100 g Membr)	α_{sorp}	α_{PV}
10	5.9	3.8	2.1	16.7	30
30	5.1	3.9	1.2	8.2	16
50	4.5	3.7	0.8	4.6	12
70	3.8	3.4	0.4	3.1	8
90	2.7	2.6	0.1	2.1	5

Effect of Feed Composition on the Properties of Sorption and Diffusion

According to the solution–diffusion model,[24] the permeability (P) of a permeant through a membrane is a product of the solubility (S) and the diffusivity (D). Sorption experiments were performed to determine the solubility of ethanol and water in the poly(o-TMSPA) membrane. The results of sorption amount are presented in Table III, and the water composition in the membrane is depicted in Figure 2. Comparing the separation factor from sorption and pervaporation (Table III) and comparing the water compositions in the membrane and in the permeate, it can be seen that water is preferentially dissolved into the membrane and diffuses faster through the membrane than ethanol, hence, resulting in the high water permselectivity. Additionally, the diffusivities of permeants through membranes can be de-

termined on basis of the solution-diffusion model: $P = D \times S$, P can be calculated from the permeation flux, and S can be determined from the sorption experiment. With P and S, D can be calculated. The results of the solubility and diffusivity ratios of water to ethanol are depicted in Figures 6 and 7, respectively. On basis of Figure 6, the solubility ratio of water to ethanol increases with an increase in the feed ethanol concentration. These phenomena might be due to the fact that the high affinity between the ethanol molecules and the poly(o-TMSPA) membrane results in the membrane structure being more swollen. Thus, the water molecules can easily dissolved into the membrane. The diffusivity ratio, shown in Figure 7, was in the range of 1.8–2.6. The diffusivity is related to membrane structure, as follows: a denser membrane structure results in a higher diffusivity ratio. From the results shown

Figure 6   The effect of feed water concentration on the solubility ratio of water to ethanol.

Figure 7   The effect of feed water concentration on the diffusivity ratio of water to ethanol.

Figure 8 Comparison of the performance of the various substituted polyacetylene membranes[25]: (●) poly-(dimethylsiloxane); (○) poly(1-chloro-1-octyne); (■) poly(1-chloro-2-phenylacetylene); (▲) poly(1-trimethylsilyl-1-propyne); (◆) poly(o-TMSPA); (□) poly(1-(n-hexyldimethylsilyl)-1-propyne); (▼) poly(1-methyl-2-phenylacetylene); (★) poly(1-(trimethylsilylmethyldimethylsilyl)-1-propyne).

in Figure 4, the degree of swelling of the poly(o-TMSPA) membrane decreases with the feed water concentration increases. Therefore, a denser poly(o-TMSPA) membrane structure was obtained at the high water concentration in the feed, resulting in the high diffusivity ratio. Obviously, the effect of solubility dominates the behavior of pervaporation because the separation factors of pervaporation follow the same trend as the solubility ratio but not the trend of diffusivity ratio.

Comparison with Previous Data of Various Substituted Polyacetylene

Compared with the performance of the various substituted polyacetylene membranes were shown in Figure 8. It shows that two analogues of poly(TMSP) with a longer and/or bulkier substituent were essentially ethanol-permselective, but an opposite phenomenon was obtained in this study. These results might be attributed to the less hydrophobic nature and/or the more denser structure of the poly(o-TMSPA) (aromatic polyacetylene). Similar results were previously obtained for the chlorine-containing polyacetylenes, that is, poly(1-chloro-1-octyne) and

poly(1-chloro-2-phenylacetylene), by Masuda et al.[25] It shows that the former is ethanol-permselective, whereas the letter is water-permselective.

CONCLUSION

An silicon-containing polyacetylene, poly(o-TMSPA), was successfully synthesized in this article. Water molecules preferentially permeate through the poly(o-TMSPA) membrane. The solubility of ethanol for the poly(o-TMSPA) membrane is higher than that of water, but the diffusivity or water across the membrane is much higher than that of the ethanol. The solubility contributes to a major part to selective transport.

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