

ORGANIC PERMSELECTIVE PERVAPORATION CHARACTERISTICS OF POLY(SILYLPROPYLENE) AND COPOLYMER DENSE MEMBRANES

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ABSTRACT

An investigation into the organic permselective separation through poly [1-trimethylsilyl-1-propyne] (PTMSP) and (1-trimethylsilyl)-1-(1-penta-methyl-disilyl)-1-propyne copolymer (TMSP-PMDSP) dense membranes was made to gain an insight into the effect of the chemical structure of membrane materials on pervaporation (PV) characteristics. The results show that the copolymer has a higher separation factor $\alpha_{\text{org/water}}$ but with a relatively lower value of flux J_t ($\text{g/m}^2\cdot\text{h}$) than pure PTMSP. This phenomenon may be attributed to the introduction of side chain with large bulk volume in copolymer, which brought about a decrease of excess free volume and the improvement of diffusion selectivity to some extent. With the same molar concentration of organic liquids in feed, THF/water solutions have the highest value of $\alpha_{\text{org/water}}$ as well as J_t in comparison with ethanol/water, iso-propanol/water and THF/water mixtures.

INTRODUCTION

Poly(silylpropylene), a polymer family distinct from ordinary glassy polymers, has been investigated for use in gas separation in recent years. Based on these polymers, several papers were also reported for separating liquid mixtures^[1,2]. As an organic preferential permeating material, it is of use in fermentation extraction, alcohol-free beverage preparation, trace aroma compounds recovering, phenol removal from waste water and so on.

The fact that organic liquid usually has larger molecular size than water may set an obstruction for organic permselection over water, so that water diffuses faster than an organic component. Consequently, a membrane material for organic preferential permeation must have a closer affinity to organic liquids in order to overcome the disadvantage from the diffusion process. In a glassy polymer, it is well known

that the chain segments are difficult to move below the glass transition temperature, which leads to compact structure and difficulties in void migration within the polymer, and thus lowers the diffusion rate of penetrants. Thus, glassy polymers usually demonstrate such performances as preferential migration of water and low permeation rate. There are, however, always exceptions. PTMSP presents such a special case.

PTMSP is an amorphous polymer with high glass transition temperature ($T_g > 300^\circ\text{C}$), and shows a large value of flux. This unusual combination of properties intrigues us to study the correlation between the structure and PV performances. For the sake of simplicity, ethanol/water mixtures were used as the feed sources in this study.

Although PTMSP membrane has the property of high flux, low separation factor hinders its practical application. Therefore, many modifications of this polymer were carried out. Nagase did some modification of poly(silyl propyne) as follows: (1) the introduction of alkyl groups with different carbon numbers such as methyl, ethyl, propyl, hexyl into PTMSP^[3]; and (2) the synthesis of PTMSP-Polydimethylsiloxane (PDMS) graft polymer^[4]. Kang investigated the PV characteristics of PTMSP/PDMS blends^[5]. All these works showed an improvement of selectivity but a descent of flux at the same time. However, there is no work related to the elucidation of mass transport behaviors that mainly covers the contribution of sorption and the role of diffusion concerning this type of polymer as described by the solution-diffusion mechanism.

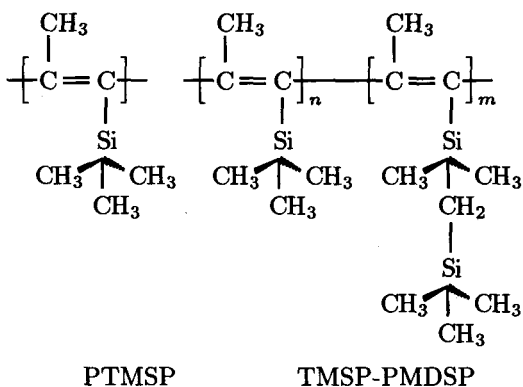


Fig. 1 The chemical structure of PTMSP and TMSP-PMDSP

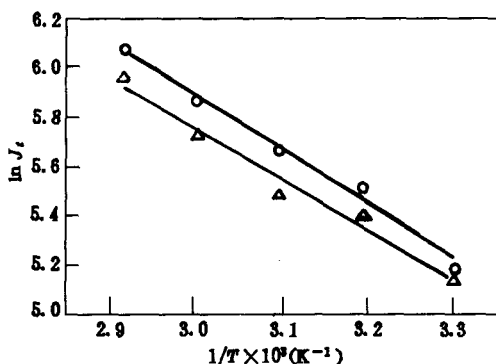


Fig. 2 The dependence of total flux on operating temperature for 10wt% ethanol/water feed

$\circ$ PTMSP $\Delta E_p = 18.36 \text{ KJ/mol}$;

$\triangle$ TMSP-PMDSP $\Delta E_p = 17.05 \text{ KJ/mol}$

In this paper, attempts have been made to compare the PV properties of PTMSP and TMSP-PMDSP, a copolymer with the different structure in the side chains shown in Fig. 1. We also attempt to give a comprehensive investigation about the PV characteristics/chemical structure relation, and attribute the high values of flux to excess free volume, which originates from the rigid and irregular main chain conformation and the low interchain attraction force of the side chains that shield the main chains.

EXPERIMENTAL

Membrane preparation

The weight average molecular weight ($\overline{M}_w$) of PTMSP determined by gel permeation chromatography is 7.45×10^5 . The copolymer consisting of 95% TMSP and 5% of PMDSP, is colorless, stable in air and even UV light, and dissolves easily in toluene. A toluene solution containing 1.0 wt% PTMSP was spread on a glass plate where the solvent was vaporized slowly at room temperature. After 48 hours, the cast membrane was floated off the plate.

PV characteristics measurement

PV properties were characterized by flux J_i and separation factor α . A membrane of 60 mm in diameter was put on a porous metal support plate. Penetrants were collected in a cold trap which was immersed in liquid nitrogen. The whole apparatus was linked to a vacuum pump.

Solution-diffusion behavior analysis under stable status

The diffusion coefficient and the solubility of penetrants as the important indexes reflecting the mass transfer process are approximately estimated by^[6]

$$\overline{D}_i = \frac{J_i \delta}{C_{i,f,m}} \quad (1)$$

where $\overline{D}_i$ is the mean diffusion coefficient of penetrant i , J_i is the partial flux and δ is the thickness of a dense membrane, and

$$\overline{K}_i = C_{i,f,m}/C_{i,f} \quad (2)$$

where $\overline{K}_i$ is the mean solubility of component i in the membrane. Herein $C_{i,f}$ is the feed concentration of component i , and $C_{i,f,m}$ determined by the same method in our previous work is the local concentration of component i at the upstream of the membrane under equilibrium status^[6]. And then the solubility selectivity (S_k)

and diffusion selectivity (S_d) which imply the contribution of sorption and diffusion process on permselectivity is conveniently obtained by the following equations

$$S_k = \bar{K}_i / \bar{K}_j$$

$$S_d = \bar{D}_i / \bar{D}_j \quad (3)$$

Thus the separation factor can be expressed by

$$\alpha_{o/w} = S_k S_d \quad (4)$$

Swelling degree test

We investigated swelling degree for its intimacy with the free volume, and the mobility of polymer segments. Swelling degree is usually defined as

$$S_w = (W_2 - W_1) / W_1 \times 100\% \quad (5)$$

where W_1 and W_2 are the weight of swollen and dry membranes, respectively. A dry membrane was immersed in a designed feed mixture until swollen equilibrium reached, and was weighed again after the water on the surface was removed with a dry filter paper.

Apparent density measurement of membranes

A prepared membrane after treated in a vacuum oven was weighed several times to calculate the average value W . A volume-actuated bottle filled with water had mass of M_1 at 20°C, then the membrane was put into the bottle carefully without bringing any bubbles to replace some volume occupied formerly by part of water. And the bottle which was kept at the same temperature for 2 hours was weighed again as M_2 . Then the volume of replaced water V , namely the volume of membrane, was obtained by the mass lost or increase of water and the apparent density of membranes ρ_a was thus obtained.

RESULTS AND DISCUSSION

PV characteristics

According to solution-diffusion mechanism, mass transfer through polymer membranes is significantly affected by the composition of feed mixtures, properties of organic solvent, the interaction between the penetrant and the membrane, operating temperature, chemical and physical structure of polymer materials, the flow regime of the feed and other conditions. Therefore, it is convenient to investigate some of the former factors.

Fig. 2 and Fig. 3 show the effect of operating temperature on the PV results. The overall flux increases according to the Arrhenius relation for both polymers. The permeation apparent activation energy is about 18.36 KJ/mol for PTMSP membrane and 17.05 KJ/mol for TMSP-PMDSP membrane, respectively. Both polymers allow organic components permeate preferentially and easily through membranes. The flux is similar to that of PDMS hollow fibre membrane (about 600 g/m²·h)^[9] though TMSP-PMDSP membrane demonstrates relatively minor values of flux than PTMSP. On the other hand, the copolymer membrane shows better selectivity for enriching ethanol at lower temperature as compared with PTMSP membrane. In this case, distinction of permselectivity originates only from the different chemical and physical structures. The increasing operating temperature which leads to the change of free volume in the membrane, tends to decrease separation factor as the swelling degree increases (shown in Fig. 4.)

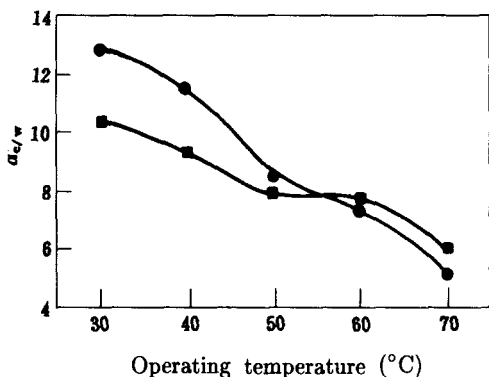


Fig. 3 The relationship between separation factor and operating temperature for concentrating ethanol from 10wt% EtOH feed solution

■ PTMSP ● TMSP – PMDSP

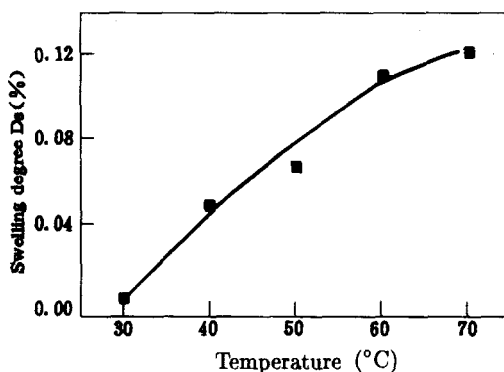


Fig. 4 The effect of temperature on swollen properties of PTMSP membrane

For a PV process, a preferential penetrant should not be the major constituent in the feed since it always has better affinity to membranes. A higher concentration of organic penetrant in feed facilitates the membrane swelling conspicuously, in that case, the repulsed component passes the membrane easily instead of suffering from the low affinity to membrane. Taking the results illustrated in Fig. 5 as an example, even equivalent ratio of ethanol to water in feed markedly lowers separation factor so that selective separation actually becomes meaningless, even if the flux is actually large. Lowering the content of ethanol in feed conduces to the improvement of permselectivity, but the flux becomes less simultaneously.

From the results of Fig. 6, we intend to clarify how the membrane thickness effects the PV characteristics since some studies reported contradictory results^[10,11]. From the PV behavior curves, the variation of permselectivity is the reverse of flux, that is to say, diminishing membrane thickness can not improve both the flux and selectivity when the membrane thickness is above 50 μm , selectivity does not show further improvement while the flux decreases continuously.

PV performances for separating iso-propanol/water and tetrahydrofuran (THF)/water solutions are listed in Table 1. Both polymers show somewhat better performance for separating THF aqueous solution. It is presumed that THF tends to have better affinity to polymers than iso-propanol and ethanol.

Table 1 PV characteristics for separating some organic/water mixtures

Organic penetrant	Organic content in feed (wt%)	PTMSP		TMSP-PMDSP	
		J_t ($\text{g}/\text{m}^2 \cdot \text{h}$)	$\alpha_{\text{org/w}}$	J_t ($\text{g}/\text{m}^2 \cdot \text{h}$)	$\alpha_{\text{org/w}}$
iso-propanol	12.15	201	9.1	336	12.9
THF	14.95	189	10.2	324	16.0

Tian proposed that the polymer adopts an rigid and irregular conformation which means that the secondary structure is of kinetic origin^[12]. During the film formation, the polymer-polymer interaction gradually alters polymer-solvent interaction. The rate of a polymer into its thermodynamically most stable equilibrium structure is much slower than the rate of cooling. Consequently excess free volume, which we believe affords primary contribution on flux is frozen into the polymer matrix.

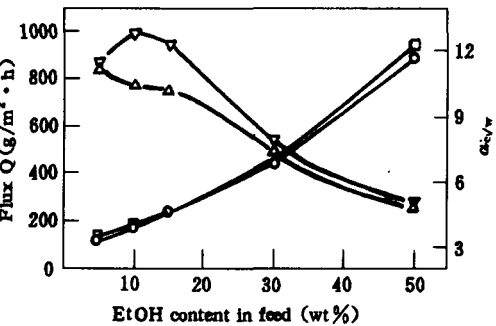


Fig. 5 The concentration dependence of PV characteristics through membranes at 30°C (membrane thickness is 35 μm)
Δ Selectivity of PTMSP; ▽ Selectivity of TMSP-PMDSP; □ Flux of PTMSP; ○ Flux of TMSP-PMDSP

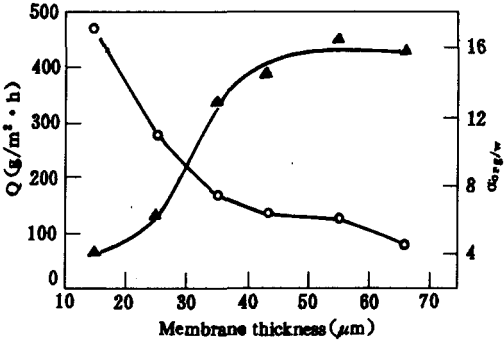


Fig. 6 The effect of membrane thickness on PV characteristics through PTMSP dense membrane at 30°C
▲ selectivity; ○ flux

Because both polymers are featured with the same main chain, therefore, the

pendent groups that might provide the difference of PV separation properties are examined to correlate with their chemical and physical structure. Pentamethyl-disilyl(PMDS-) groups which partly takes the place of trimethylsilyl groups in the copolymer impose at least the following effects on the polymer structure: (1) The relatively larger volume occupying the intersperse of polymer chains decreases the excess free volume for the occurrence of diffusion. This is confirmed by the membrane apparent density ratio (1.06:1) of copolymer to PTMSP, but due to its low molar content of 5% in copolymer, there is no significant decline of flux. (2) It is believed that PMDS-groups bring about not so better affinity of organic penetrant to polymer than TMS-groups as shown in Fig. 7. This, of course, leads to relatively low solubility selectivity as listed in Table 2.

Table 2 Solubility selectivity and diffusion selectivity at different temperature

Organic penetrant	Temp. (°C)	PTMSP			TMSP-PMDSP		
		S_k	S_d	$\alpha_{\text{org/w}}$	S_k	S_d	$\alpha_{\text{org/w}}$
EtOH	30	120	0.088	11.4	47	0.27	12.9
	40	86	0.11	9.3	34	0.33	11.2
	50	63	0.12	7.7	22	0.44	9.5
	60	47	0.17	7.9	14	0.52	7.3
	70	33	0.18	5.9	5.9	0.86	5.1
i-PrOH	30	210	0.043	9.1	150	0.066	10.2
THF	30	330	0.039	12.9	100	0.160	16.0

In general, bulk diffusion across solid membrane occurs through the defect mechanism. In some cases, diffusion process is achieved by a cooperative interchange of positions between neighboring groups of atoms. This is usually thought to occur by the planar rotation. For poly(silylpropyne), the chain with severe stereo hindrance is very rigid, thus the low mobility of chain makes such mechanism impossible. Vacancies, micro voids and other structural defects which provide the space for molecular diffusion across membrane result in a dominant status of defect mechanism. In that case, a small diffusion barrier means that a little of activation energy is required in the particular structure. As depicted in Fig. 8, there is not in much need of energy for water diffusion across the membrane. Actually, this activation energy is close to zero. The similar case occurs during ethanol migration. Therefore, mean diffusion coefficient of water remains constant in the range of operating temperature. As for ethanol, it just shows a slight increase.

However, it must be recognized that diffusion coefficients of water change more from PTMSP to TMSP-PMDSP membranes than those of ethanol. The fact deviates

from the proceeding prediction since free water has smaller size than free ethanol particle. In fact, the migration particles can not be looked upon just as free water or single ethanol molecule, inasmuch as it is possible that clusters are formed within feed mixtures or in polymer^[13]. This is true for the poor solvent of polymer, such as water. Furthermore, high concentration of water in feed facilitates an increase of water clusters. With reference to overall diffusion processes, since molecules within the clusters are generally less mobile than free water, additional energy is required to break the clusters into free water. For ethanol, it is assumed that a rapid exchange of molecules exists between the bound and free state originating from low concentration of ethanol in feed, or fewer clusters form in polymer matrix since a strong attraction between them destroys the tendency of the formation of clusters that gives little effect on ethanol diffusion.

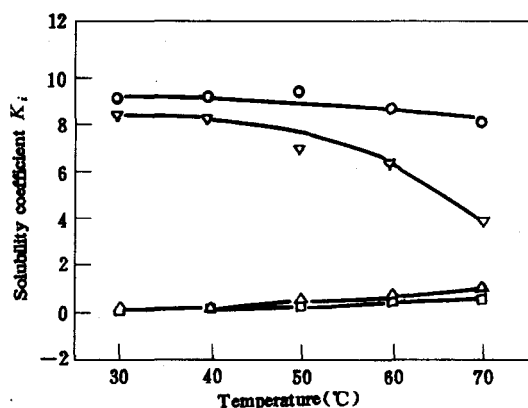


Fig. 7 The relationship of temperature and solubility coefficients at 10 wt% ethanol/water feed

□ Water in PTMSP; ○ EtOH in PTMSP;
△ Water in TMSP-PMDSP; ▽ EtOH in
TMSP-PMDSP

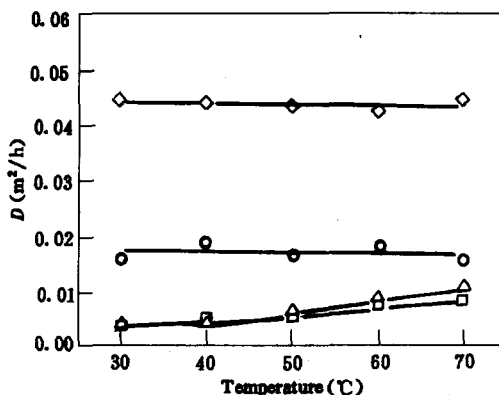


Fig. 8 The effect of temperature on diffusion coefficient at 10 wt% ethanol/water feed
△ EtOH in TMSP-PMDSP; □ EtOH in PTMSP; ○ Water in TMSP-PMDSP; ◇ Water in PTMSP

The long diffusion passage produced by the increased membrane thickness and the rigid chains within poly(silylpropyne) allow penetrants enter the polymer structure, weave and struggle their way in and around the polymer chains with more difficulties, which restrict the flow direction of penetrants, control the mass transport, and determine the overall pervaporation process finally. Apparently, diffusion will slow down, accompanied with decreasing permeate rate. It is true that the larger the particle size, the more hindrances it meets during diffusion process. Permeation rate of water (including free water and water clusters) herein lessens more markedly than ethanol with fewer clusters. Therefore, diffusion selectivity increases,

and higher permselectivity is anticipated for thick membranes.

For the purpose to discriminate the contribution of sorption from that of diffusion on permselectivity, separation factor is divided into solubility selectivity and diffusion selectivity. From the results illustrated in Table 2, we observe that selective separation primarily attributes to high solubility selectivity, and organophilic polymer preferentially combines with ethanol but repulses water onto the membrane surface contacting the feed. If the diffusion selectivity can be improved, the total selectivity will increase to a great extent. Thus, some approaches are anticipated to be operative to increase permselectivity, such as (1) increasing the concentration of water clusters in feed and polymer. In terms of cluster function^[14], high content of water in mixtures, low temperature in operating systems, and weak interaction, especially attraction force between water and polymer is necessary; (2) diminishing excess free volume. Effective modifications include introduction of long side chain into polymer in order to fill the micro voids, and thermal treatment that causes partial molecular chains move into a thermodynamically stable equilibrium state.

CONCLUSION

Poly(silylpropyne) dense membranes with preferential permeation of organic solvents were prepared and their PV characteristics for separating organic aqueous solutions were studied. Equilibrium composition of penetrants in a membrane was measured under the steady operating condition, then diffusion and solubility coefficients were obtained. Flux is considerably high and solubility selectivity is the major factor devoted to overall selectivity. Diffusion process across the membrane occurs easily so that additional energy is not much in need for water permeation through a membrane, the similar case occurs for ethanol. By diminishing excess free volume within a polymer membrane, an improvement of selectivity was satisfactorily predicted, though flux decreased to some extent.

Keywords:

Pervaporation separation; Poly [1-trimethylsilyl-1-propyne]; Dense membrane; Organic Permselectivity

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