

Pervaporation Performance of PTMSP Membranes at High Temperatures

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Received 26 August 2002; accepted 13 March 2003

Published online 23 September 2003 in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/app.12895

ABSTRACT: The separation of ethanol–water mixtures by pervaporation has been carried out through poly(1-trimethylsilyl-1-propyne) (PTMSP) membranes. This polymer is known to be alcohol-selective and shows high selectivity and ethanol permeation rate. The performance of this polymer was studied at high temperatures over long periods of time to examine deterioration of its transport properties. The PTMSP membrane shows an initial separation factor ($\alpha_{\text{EtOH}}^{\text{H}_2\text{O}}$) of about 10.7 and specific permeation rate (R) of $0.054 \text{ g m m}^{-2} \text{ h}^{-1}$ for a 10 wt % ethanol solution. Although this polymer has good char-

acteristics for the separation of gases and liquid mixtures, its selectivity decreases with operating time, reaching a value of 8 after 450 h. On the other hand, the specific permeation rate remains almost constant except during the swelling period, in which it decreases to a value of $0.035 \text{ g m m}^{-2} \text{ h}^{-1}$. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2255–2259, 2003

Key words: degradation; membrane; polyacetylene; pervaporation; ethanol–water mixtures

INTRODUCTION

Pervaporation is a fractionation process that uses a polymer membrane between the liquid phase and the vapor phase of a mixture. This technique has experienced growing acceptance for separation of organic liquid mixtures, especially ethanol–water systems. Membranes used for pervaporation of alcohol–water mixtures are classified into two categories, namely water-selective and alcohol-selective membranes. It is more practical to permeate alcohol through the membrane when it is a minor component; nevertheless, most polymeric membranes are water permselective^{1–16} because the molecular size of water is smaller than that of the ethanol.

Ethanol-permselective membranes have been limited to silicon- and fluorine-containing polymers, for example, polydimethylsiloxane (PDMS), poly(1-trimethylsilyl-1-propyne) (PTMSP), and poly(tetrafluoroethylene) derivatives.^{17,18}

The PDMS was considered to be the most ethanol-permselective¹⁹ until the PTMSP was synthesized. Both of them show similar separation factor ($\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$) and specific permeation rate (R),^{20,21} but with the PT-

MSP polymer very thin membranes can be fabricated because of its high molecular weight.^{20,22} Therefore, this polymer is an attractive material for the production of membranes for gas separation, pervaporation, and vapor permeation.

The PTMSP is a polyacetylene that contains alternating double bonds along the main chain and bulky trimethylsilyl [$\text{Si}(\text{CH}_3)_3$] side groups, which severely hinder rotation of the polymer chains. This polymer has the lowest density of any known polymer and an extremely high free volume of 20 to 25% compared with free volume values of 2 to 6% for conventional glassy polymers. The extraordinarily high free volume fraction of the PTMSP produces numerous free volume elements that appear to be connected, forming a finely microporous network.²³ The ethanol permselectivity of this membrane is thought to be due to the existence of free volume and the hydrophobicity of the membrane surface.²⁴ Although PTMSP sorbs ethanol preferentially, it diffuses water faster than ethanol because the solubility selectivity dominates the overall permeability selectivity.²⁵

Additional advantages of glassy PTMSP over PDMS include higher possible transmembrane operating pressure, greater chemical stability, limited swelling of the glassy polymer resulting in a greater durability, and limited fouling of the membrane surface by using copolymers or surface fluorination.²⁶

On the other hand, this polymer shows the drawbacks of low selectivity at the separation of gases and ethanol–water mixtures and declining transport properties in time with aging.²⁷ Some authors have re-

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Contract grant sponsor: Universidades e Investigación del Gobierno Vasco; contract grant number: PI-1999-97 and QUI-1999-0758.

ported that the decrease in transport properties is ascribed to relaxation processes that change the structure and morphology of the membranes.^{28–31}

The objective of this work was to study the degradation of transport properties of PTMSP membranes with operating time in the separation of 10 wt % ethanol–water mixtures by pervaporation

EXPERIMENTAL

Materials

1-trimethylsilyl-1-propyne (TMSP, 99%) and TaCl₅ (99.9%) were purchased from Aldrich; toluene (analytical grade) and methanol (analytical grade) were purchased from Panreac (Barcelona, Spain), and ethanol (analytical grade) was purchased from Merck. TaCl₅ was used as received, with care being taken not to allow decomposition from exposure to moisture and/or air. TMSP and toluene were distilled in the presence of calcium hydride under nitrogen before use.

Polymerization procedure

The PTMSP was synthesized by using the method previously described,³² adapted from the Masuda et al.'s method.^{33,34} Polymerization of PTMSP was carried out under dry nitrogen at 80°C for 24 h. The catalyst, TaCl₅, was dissolved in toluene and after 10 min the solution became deep yellow. Then the monomer was added to this solution that turned into dark brown. The reaction mixture was poured into a large amount of methanol where the catalyst was deactivated. The polymer was purified by the solution-precipitation method by using a toluene-methanol system and was dried to constant weight.

Measurement of molecular weight

The molecular weight of the samples was determined by gel permeation chromatography (Water 510 Pump, Waters 410 Differential Refractometer, Waters Styragel HR column). Tetrahydrofuran was used as solvent and standard polystyrenes were used for calibrating molecular weight. The PTMSP membrane presented a number-average molecular weight of 1.2×10^6 .

Membrane preparation

Membranes were fabricated by casting polymer-toluene solutions (1–2 wt %) into a Petri dish, and the solvent was allowed to evaporate slowly over a few days at room temperature. The membrane thickness was determined through direct measurement of its weight and a reported density value of 0.75 g cm⁻³.^{23,35–37} The thickness of the membrane resulted in about 100 μm.

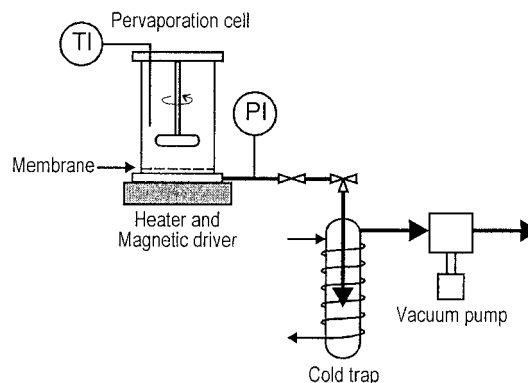


Figure 1 Schematic diagram of pervaporation system.

Pervaporation procedure

A schematic diagram of the system used to carry out the pervaporation experiments is shown in Figure 1. It consisted of a detachable stainless steel cell where the feed was maintained at 75°C for each run. The upper part of the cell holds the feed solution at atmospheric pressure, and the lower part holds the PTMSP membrane. The effective area of the membrane is 14 cm². The feed solution was kept vigorously stirred during the pervaporation runs with a magnetic stirrer. The cell was provided with an inlet port for the temperature measurement. The permeate was condensed and collected in a liquid nitrogen trap and the permeation rate was determined from the weight of the collected samples. Composition of the feed, the permeate, and the retentate is determined by refractive index measurements by using a calibration curve (Refractometer RX-5000, Atago). The permeate pressure is kept at about 2 mmHg by a rotary vacuum pump.

The performance of PTMSP membranes in ethanol–water pervaporation was evaluated by the separation factor ($\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$) and the specific permeation rate (R) defined by eqs. 1 and 2, respectively:

$$\alpha_{\text{H}_2\text{O}}^{\text{EtOH}} = \frac{Y/(1-Y)}{X/(1-X)} \quad (1)$$

$$R = \frac{F\delta}{At} \quad (2)$$

where X and Y are the weight fractions of ethanol in the feed and in the permeate, respectively, F is the collected amount of permeate (g), δ is the membrane thickness (m), A is the area of the membrane (m²), and t is the time (h).

Swelling measurement

The membrane is weighted before and after pervaporation runs so as to determine the swelling degree.

Both sides of the membrane have been carefully wiped with filter paper to eliminate the adhering solution. After their use, the membranes were stored in a solution with the same composition as that of the feed mixture. The degree of swelling is determined by using the relation:

$$DS (\%) = \frac{(W_s - W_0)}{W_0} \times 100 \quad (3)$$

where W_0 and W_s are the weights of dry and swollen PTMSP films, respectively.

RESULTS AND DISCUSSION

Separation factor

Pervaporation performance of PTMSP membrane is evaluated with 10 wt % ethanol solutions at 75°C. The initial value of this variable is of about 12, and after 450 h it has decreased to approximately 8, so it can be considered that the separation factor decreases slowly with operation time.

This decreasing tendency has been fitted to an exponential equation that is characteristic of degradation processes:

$$\alpha_{H_2O}^{EtOH} = A - B(1 - e^{-Ct}) \quad (4)$$

where A is the initial value of the variable, B is a residual value at infinite time, and C is a measurement of the degradation rate.

The parameters A , B , and C have been estimated by means of nonlinear regression of the separation factor data. The values reported for these parameters are 10.7, 4.6, and 0.0027 h^{-1} for A , B , and C , respectively. The variation of the separation factor and the fitting of the function to the experimental values are shown in Figure 2.

Masuda et al.³⁸ reported that the separation factor of a 30- μm PTMSP membrane remained unaffected with

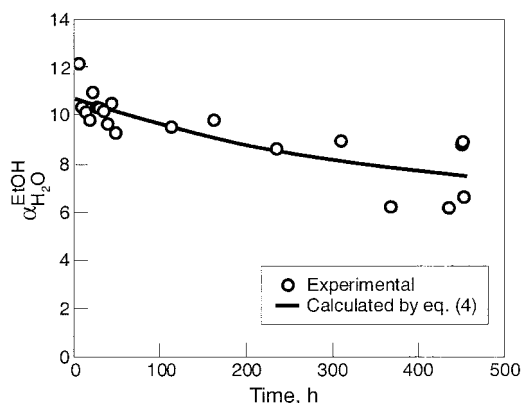


Figure 2 Separation factor as a function of operating time.

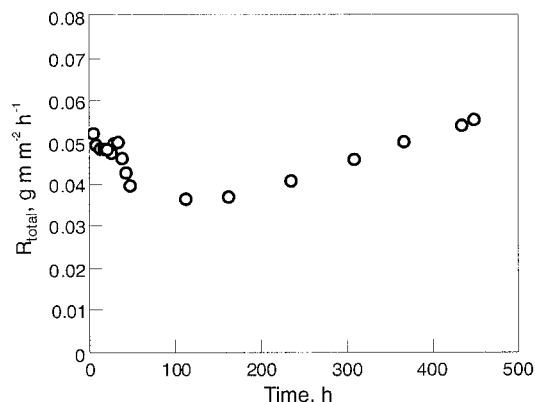


Figure 3 Specific permeation rate as a function of operating time.

time over a period of 40 h. Figure 2 shows a decrease in the separation factor with operation time. From the initial value of 10.7, after 450 h it decreased to an average value of 8, although up to 40 h the separation factor can be considered practically constant. The performance of thinner membranes (15–90 μm) has also been studied for shorter periods of time, and in all of the cases it has been observed that the separation factor was constant over 40 h.

Kang et al.³⁹ observed that for a 5 wt % ethanol-water mixture at 30°C the separation factor and the flux decreased simultaneously with time and determined that it was due to the decrease of the excess of free volume. The ethanol flux was more affected than the water flux because ethanol has a larger kinetic diameter and was more permeable than water.

Specific permeation rate

The evolution of the specific permeation rate with operation time is shown in Figure 3. This variable decreased from 0.054 to $0.035 \text{ g m}^{-2} \text{ h}^{-1}$, and after approximately 100 h of operation it increased slightly, reaching its initial value at 450 of operation time.

Some authors reported that the membrane performance was affected by temperature.²⁶ Hence, to analyze the influence of this variable on the specific permeation rate, the evolution of the cell temperature has been represented (Fig. 4). It can be seen from comparison of Figures 3 and 4 that while the temperature of the cell increased in the temperature range 50–250°C, the specific permeation rate decreased. Therefore, there is no evidence that the temperature of the cell is responsible for the variation of the specific permeation rate. Thus, the increase in this variable was related to a swelling process of the membrane during the pervaporation process. As the membrane was in contact with the liquid mixture, the mobility of polymer chains allowed the molecules to cross the membrane faster, making the specific permeation rate increase.

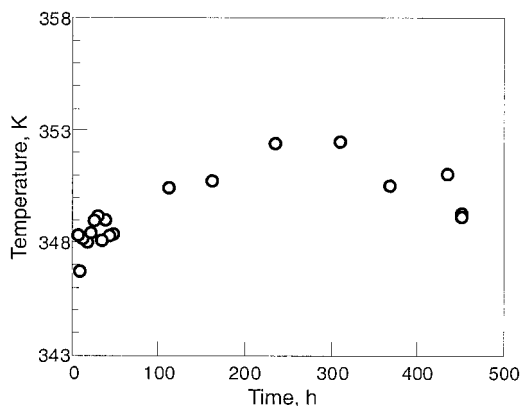


Figure 4 Evolution of temperature as a function of operating time.

Masuda et al.²⁰ reported the behavior of some substituted polyacetylenes in the pervaporation of ethanol–water mixtures (Table I). The separation factor obtained in this work is similar to those of the PTMSP and PDMS reported by these authors; nevertheless, the specific permeation rate is about one order of magnitude higher. After comparing the operation conditions, we have considered that the variable that allows us to obtain a higher value of R is temperature because low pressures (0.1–10 mmHg) do not seem to have any effect on flux or on the permeate concentration so the separation factor and the specific permeation rate are constant.^{20,38,40,41} On the other hand, Masuda et al.³⁸ showed no dependence of the total specific permeation rate with membrane thickness up to 150 μm .

From Table I it can also be observed that the other substituted polyacetylenes exhibit separation factors smaller than the unity, so they are water-permselective. Masuda et al. pointed out that aromatic polyacetylenes showed smaller separation factors and spe-

TABLE II
Swelling Degree of PTMSP Membranes

Membrane	W_0 (g)	W_s (g)	DS (%)
2	0.1322	0.1389	5
3	0.1160	0.1255	8
4	0.0192	0.0187	3
5	0.0260	0.0277	6

cific permeation rates than those of aliphatic polyacetylenes because of the fact that the former presents a tighter structure, which makes the permeation of ethanol more difficult.

Swelling measurements

In pervaporation, membranes are often swollen by feed solution because the polymer membrane directly contacts it. In our study we have observed a slight increase in the weight of the membrane after pervaporation experiments and it results in a swelling degree of about 8%.

In 1990, Masuda et al.³⁸ studied the swelling degree of a 30- μm membrane at 30°C by using solutions with different ethanol content as feed. For a 10 wt % ethanol solution the swelling degree observed was of about 8%. They reported that the membrane was not fairly swollen in water and the swelling degree increased with the ethanol content in the feed, the membrane showing a strong affinity for ethanol.

Likewise, we have studied the swelling behavior of some other membranes that have been used in our series for shorter periods of time under the same operation conditions (Table II). The swelling degree observed is, in all cases, less than 10%. Thus, it can be considered that the values obtained are similar to those of Masuda et al.³⁸

TABLE I
Separation Factor ($\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$) and Specific Permeation Rate (R) of Substituted Polyacetylenes and Some Other Polymers^a

Polymer	Polymer		$\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$	$R \cdot 10^3$ ($\text{g m}^{-2} \text{h}^{-1}$)
	R_1	R_2		
$\begin{array}{c} \text{-(C=C)-}_n \\ \quad \\ R_1 \quad R_2 \end{array}$	CH ₃	Si(CH ₃) ₃	10.7 ^b	54 ^b
	CH ₃	Si(CH ₃) ₃	12	4.50
	H	<i>t</i> -Bu	0.58	0.65
	H	CH(<i>n</i> -C ₅ H ₁₁)Si(CH ₃) ₃	0.52	0.40
	CH ₃	<i>n</i> -C ₅ H ₁₁	0.72	0.57
	Cl	<i>n</i> -C ₆ H ₁₃	1.10	0.41
	CH ₃	C ₆ H ₅	0.28	0.24
	Cl	C ₆ H ₅	0.21	0.23
	Others	Poly(dimethylsiloxane)		10
	Cellulose acetate		0.10	25
	Poly(methyl acrylate- <i>co</i> -diethylene triamine)		0.10	130
	Poly(maleimide- <i>co</i> -acrylonitrile)		0.02	0.90

^a Operating conditions for the membranes of polyacetylenes: EtOH, 10 wt %; 30°C; downstream pressure, 1.0 mmHg.

^b Operating conditions in this work: EtOH, 10 wt %, 75°C, permeate pressure, 2.0 mmHg.

CONCLUSION

The separation factor decreases with operating time at low rate, so that the study of the membrane degradation process would require long experimental runs. On the other hand, the total flux through the membrane, and thus the specific permeation rate, decreased with operation time, but after 100 h it increased and reached a value similar to the initial one. As there was no evidence that the temperature affected this variable, the decrease of the specific permeation rate was ascribed to a swelling process.

From the swelling measurement it can be deduced that the thickness variation of the studied membranes is low during the operating time, and therefore the polymer can be considered stable in the operating conditions.

The authors thank the Departamento de Educación, Universidades e Investigación del Gobierno Vasco for the financial support (PI-1999-97, QUI-1999-0758).

NOMENCLATURE

A	Area of the membrane (m^2)
DS	Swelling degree (%)
F	Collected amount of permeate (g)
R	Specific permeation rate ($\text{g m}^{-2} \text{h}^{-1}$)
t	Time (h)
X	Weight fraction of ethanol in the feed (%)
Y	Weight fraction of ethanol in the permeate (%)
W_0	Weight of the dry PTMSP films (g)
W_s	Weight of the swollen PTMSP films (g)

Greek symbols

$\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$	Separation factor
δ	Membrane thickness (m)

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