

Particle-Beam Treatment of Organosilicon Gas Separation Membranes: A Novel Way of Controlling Their Mass Transport Properties

A. TÓTH,^{1,*} V. S. KHOTIMSKY,² I. BERTÓTI,¹ and G. MARLETTA³

¹Hungarian Academy of Sciences, Research Laboratory for Inorganic Chemistry, Budaörsi út 45, H-1112 Budapest, Hungary; ²Russian Academy of Sciences, A. V. Topchiev Institute of Petrochemical Synthesis, Leninsky prospekt 29, 117912 Moscow V-71, Russia; ³University of Basilicata, Department of Chemistry, via N. Sauro 85, I-85100 Potenza, Italy

SYNOPSIS

Fast atom bombardment applied in the low keV energy range to organosilicon gas separation membranes was found to modify their mass transport properties in a controllable manner. In particular, asymmetric polyvinyltrimethylsilane membranes and polydimethylsiloxane-based composite ones were treated by particle beams obtained from various gases like Ar, He, H₂, and NH₃, with particle energies of about 1 keV and doses of about 10¹⁵ particles cm⁻². In each case, improvements in the component selectivities for various gas mixtures coupled with decreases in the component permeances were obtained. The extent of modification of the mass transport properties increased with increase of the calculated average depth of penetration of the bombarding particles. The modification of the mass transport properties was considered to take place as a result of compaction of the surface layer due to reactions like crosslinking and loss of pendant groups. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The control of mass transport properties of polymers is an important topic in several fields of technological interest, e.g., packaging in microelectronics or packaging of food, pharmaceuticals, cosmetics, and fine chemicals,¹ controlled release delivery systems,² and gas separation membranes.³ In particular, the "barrier" properties of polymers may be improved by methods including sulfonation, fluorination, wet coating with other polymeric layers, dry coating by evaporation of aluminum or of silicon oxides, and plasma-enhanced chemical vapor deposition of silicon dioxide.¹ High values of permeance and component selectivity for gas separation purposes may be achieved by tailoring the macromolecular structure, considering the proper structure-performance-type relationships,^{4,5} as well as by applying appropriate membrane fabrication

methods like preparation of asymmetric integrally skinned membranes using phase inversion,³ preparation of thin-film composite membranes using transfer of thin films onto microporous support, plasma polymerization, interfacial polycondensation,^{3,6} and reactive modification of the membrane surfaces by fluorination and by exposure to various plasmas.⁷⁻¹¹

Although the particle-beam modification of polymers (see, e.g., Refs. 12-14 and references therein) is increasingly used to alter the wettability, adhesion, biocompatibility, mechanical, electrical, optical, etc., properties of polymers, it is only recently that we presented apparently the first evidence of the possibility of modifying the mass transport properties of organosilicon gas separation membranes by their particle-beam treatment applied in the low keV energy range.¹⁵ In the present article, we continue to explore this subject in more detail, demonstrating the possibility of *controlling* the permeance and the component selectivity of organosilicon gas separation membranes by low keV particle-beam treatment.

* To whom correspondence should be addressed.

Table I Gas Permeances (P/l) for the Untreated and the Particle Beam-treated Membranes

Membrane Material	Particle Source	P/l ($\text{cm}^3 \text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$) $\times 10^{-5}$					
		He	H ₂	O ₂	N ₂	CH ₄	
PVTMS	None	12.0	15.0	3.3	1.1	1.4	
	Ar	9.8	11.0	1.3	0.24	0.31	
	None	13.5	17.6	3.1	0.86	1.5	
	He	9.4	9.4	1.0	0.18	0.27	
	None	12.5	16.5	3.3	0.92	1.5	
	H ₂	5.3	4.3	0.26	0.06	0.07	
	PDMS	None	7.2	12.1	11.2	5.4	16.7
		Ar	7.4	10.2	6.2	1.9	3.4
		None	8.2	12.9	11.6	5.6	18.4
		He	5.9	9.1	2.2	0.40	0.66
None		7.8	12.4	11.3	5.4	17.8	
NH ₃		4.4	4.4	0.37	0.14	0.40	

EXPERIMENTAL

Materials

The membranes studied were as follows: (a) asymmetric polyvinyltrimethylsilane (PVTMS) gas separation membrane obtained by a continuous phase-inversion process on an industrial scale (type: PA-160-S-3,1, manufacturer: Kuskovo Chemical Plant,

Russia); (b) industrial three-layered composite gas separation membrane with a working layer containing polydimethylsiloxane (PDMS) and polymethylsilsesquioxane (PMSSO) with a ratio of the corresponding repeat units = 200 : 5 (type: MDK, manufacturer: Polimersintez, Russia). The following gases were used for particle generation: He (Linde Gas Hungary, 4.6 purity), Ar (Linde 4.8), H₂ (Linde 5.0), and NH₃ (UCAR Specialty Gases 4.8).

Table II Component Selectivities (α) for Some Gas Pairs for the Untreated and the Particle Beam-treated Membranes

Membrane Material	Particle Source	α						
		He/H ₂	H ₂ /O ₂	H ₂ /N ₂	H ₂ /CH ₄	He/CH ₄	O ₂ /N ₂	
PVTMS	None	0.8	4.6	13.6	10.7	8.6	3.0	
	Ar	0.9	8.5	45.8	35.5	31.6	5.4	
	None	0.8	5.6	20.3	11.8	9.1	3.6	
	He	1.0	8.9	53.2	34.7	34.7	5.9	
	None	0.8	5.0	17.9	11.3	8.6	3.6	
	H ₂	1.2	16.5	73.4	65.6	80.2	4.5	
	PDMS	None	0.6	1.1	2.3	0.7	0.4	2.1
		Ar	0.7	1.6	5.3	3.0	2.2	3.3
		None	0.6	1.1	2.3	0.7	0.4	2.1
		He	0.6	4.2	22.9	13.9	8.9	5.5
None		0.6	1.1	2.3	0.7	0.4	2.1	
NH ₃		1.0	11.9	31.4	11.0	11.0	2.6	

Table III Effective Diameters, d (Å) of the Test Gas Molecules and Their Solubility Coefficients, S ($\text{cm}^3_{\text{gas}} \text{cm}^{-3}_{\text{polym}} \text{cmHg}^{-1}$) $\times 10^{-3}$, in the Polymers PVTMS and PDMS¹⁷

Parameter	Polymer	He	H ₂	O ₂	N ₂	CH ₄
d	—	1.78	2.14	2.89	3.04	3.18
S	PVTMS	0.46	1.1	5.8	3.0	10.0
S	PDMS	0.7	1.5	4.2	2.5	8.8

Particle-beam Treatment

The particle-beam treatment of the gas separation membranes was performed in an equipment assembled from the following units: gas manifold, extrafine control needle valve, FAB 114-type saddle field source (Ion Tech Ltd., Great Britain), power supply, stainless-steel reaction chamber, magnetically operated shutter, sample holder, plate valve, vacuum system consisting of rotary and oil diffusion pumps, and Pirani and ionization gauges. The disk-shaped membranes with a diameter of 56 mm were fixed to the sample holder positioned at a distance of 170 mm from the beam aperture. The vacuum chamber was pumped down to 10^{-6} mbar, then purged by the actual treating gas for 5 min at 60 mL s^{-1} (STP). Accelerating voltages of about 1 kV and particle fluences of about 10^{15} particles cm^{-2} were applied. The beam densities for the various gases were determined in blank experiments by the equivalent beam currents measured from secondary emission electron fluxes. Adjusting with the needle valve the gas flow

(which implies also the discharge impedance within the source) and the output current at the power supply unit, both the accelerating voltage and the particle-beam current could be kept constant within limits of $\pm 10\%$.

Determination of the Gas Transport Properties

The permeances for a series of test gases (He, H₂, O₂, N₂, CH₄) for the untreated and the particle-beam-treated membranes were determined by the volumetric method applying a pressure difference of 1.5 bar, at 22°C, and using the known equations:

$$P/l = Q/\Delta p = V/(F \times t \times \Delta p) \quad (1)$$

The reproducibility of the measurement expressed in terms of random error is $\pm 5\%$.

The ideal selectivities for the various gas pairs were calculated as the ratios of the corresponding permeances:

Table IV Diffusivities (D/l) of the Test Gases of the Untreated and of the Particle-beam-treated Membranes, as Calculated by Eq. (3)

Membrane Material	Particle Source	D/l (cm s^{-1}) $\times 10^{-2}$				
		He	H ₂	O ₂	N ₂	CH ₄
PVTMS	None	26.1	13.6	0.57	0.37	0.14
	Ar	21.3	10.0	0.22	0.080	0.031
	None	29.4	16.0	0.54	0.29	0.15
	He	20.4	8.5	0.18	0.059	0.027
	H ₂	11.5	3.9	0.045	0.020	0.0066
PDMS	None	10.3	8.1	2.67	2.15	1.90
	Ar	10.6	6.8	1.48	0.76	0.39
	None	11.7	8.6	2.76	2.24	2.09
	He	8.4	6.1	0.52	0.16	0.075
	None	11.2	8.3	2.69	2.16	2.02
	NH ₃	6.3	2.9	0.088	0.056	0.046

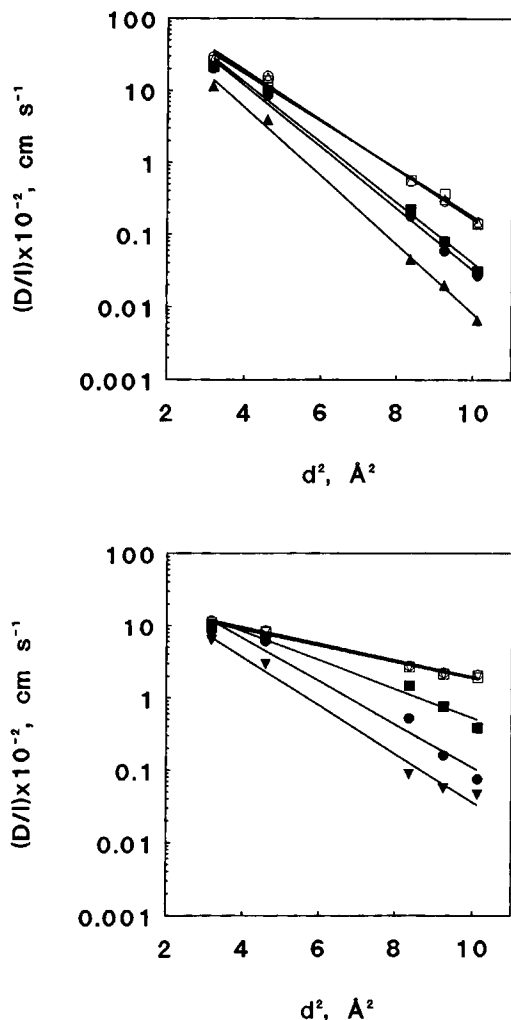


Figure 1 Effect of FAB treatment on the diffusivity of various gases through asymmetric PVTMS (top) and PDMS-based composite (bottom) membranes. Treatment by (■) Ar; (●) He; (▲) H₂; (▼) NH₃. No treatment: open symbols.

$$\alpha_{i,j} = (P/l)_i / (P/l)_j \quad (2)$$

The posttreatment-type oxidation effect was found to be the biggest source of inherent error in the effect of treatment (e.g., an immediate exposure of the FAB-treated membrane to air could result even in a complete loss of its selectivity). To minimize the posttreatment-type oxidation effect,¹⁴ each membrane was relaxed after treatment for at least 24 h in the vacuum chamber at about 10^{-6} mbar.

RESULTS AND DISCUSSION

Table I shows the permeances of various gases through each untreated organosilicon membrane

and through their particle-beam-treated variants. The corresponding selectivities are reported in Table II. From these tables, it can be seen that as a result of particle-beam treatment the gas permeances decrease (with the only exception of the fast Ar atom beam-treated PDMS-based membrane, where the permeance to He remains practically constant).

The extent of the decrease in permeance varies with the nature of the polymer and with that of the penetrant gas. It is remarkable, however, that the particle-beam treatment increases the selectivities for the various gas pairs. The selectivity for O₂/N₂, in particular, may increase by a factor of 1.8 and 2.6 for the particle-beam-treated PVTMS and PDMS-based membranes, respectively. In some cases, the increase in selectivity may reach very high factors (e.g., in the case of the PDMS-based composite membrane treated by fast particles obtained from NH₃, the selectivity for He/CH₄ becomes more than 25 times higher than that measured for the untreated membrane).

Expressing the gas permeance of a membrane as the product of diffusivity and of the solubility coefficient,

$$P/l = (D/l) \times S \quad (3)$$

the dependence of diffusivity on the effective diameters of the penetrant gases¹⁶⁻¹⁸ can be calculated, according to the equation

$$\log(D/l) = a - bd^2 \quad (4)$$

Table V Fit Coefficients of the Lines Representing Eq. (4) in Figure 1

Membrane Material	Particle Source	<i>a</i>	<i>b</i>	<i>R</i>
PVTMS	None	2.545	0.330	0.9967
	Ar	2.774	0.417	0.9967
	None	2.654	0.345	0.9970
	He	2.763	0.427	0.9977
PDMS	None	2.600	0.338	0.9971
	H ₂	2.655	0.475	0.9985
	None	1.389	0.112	0.9969
	Ar	1.716	0.200	0.9895
PDMS	None	1.440	0.115	0.9954
	He	2.017	0.299	0.9858
	None	1.417	0.114	0.9955
PDMS	NH ₃	1.893	0.334	0.9927

Table VI Parameters and Results of TRIM^{19,20} Calculation of the Average Depths of Penetration (*X*) of the Projectile Particles in the Fast Atom Beam-treated Membranes

Membrane Material	Polymer Density (g cm ⁻³)	Particle Source	Particle Considered	Particle Energy (keV)	<i>X</i> (Å)
PVTMS	0.836 ²¹	Ar	Ar	1	64
	0.836 ²¹	He	He	1	236
	0.836 ²¹	H ₂	H ⁺	0.8	254
PDMS	0.97 ²²	Ar	Ar	1	62
	0.97 ²²	He	He	1	234
	0.97 ²²	NH ₃	H ⁺	1	327

where *a* and *b* are constants and *b* is a parameter characteristic for the mobility selectivity. For clarity, the solubility coefficients¹⁷ for the polymer/gas pairs concerned and the effective diameters¹⁷ of the penetrants are collected in Table III. The diffusivities calculated by eq. (3) are reported in Table IV. The dependencies of diffusivities on the effective diameters of the penetrant gases according to eq. (4) are shown in Figure 1; the corresponding fit coefficients are listed in Table V.

It can be seen that straight lines with regression coefficients (*R*) in the ranges of 0.9954–0.9971 and 0.9858–0.9985 are obtained for the untreated and for the particle-beam-treated membranes, respectively. The fact that the deterioration of the linearity after particle-beam treatments is relatively small suggests that the solubility coefficients of the penetrants do not change to a great extent, and the improvements in the mobility selectivities must be mainly responsible for the improvements observed in the overall selectivities. The changes in the slopes of the lines in Figure 1 (*b* in Table V) clearly show that the mobility selectivity always increases as a result of the particle-beam treatment of the membranes studied.

The average depths of penetrations of the projectile particles (or mean projected ranges), *X*, in the polymer targets applied were calculated by the TRIM program^{19,20} and are listed in Table VI. The dependence of *b* on *X* is depicted in Figure 2, which reflects that *b* always increases with *X*. (The regression coefficients are 0.9127 and 0.9813 for the PVTMS and the PDMS-based membranes, respectively.) In other words, the extent of alteration of the mass transport properties of the membranes increases with the average depth of penetration of the projectiles. Such a dependence is certainly reasonable, but is also somewhat surprising, considering the clearly different chemical nature of the particle source gases, the evidently different densities of the

deposited energy, and that the thickness of the ion beam-modified surface layer may be higher than the penetration depth of the bombarding particles (due to dynamic factors like atomic displacement in the collision cascade, radical diffusion, chain motion, etc.).

Obviously, the alterations of the transport properties of the fast atom beam (FAB)-treated membranes are connected to the extensive structural changes induced by particle-beam treatment. In general, the particle bombardment of polymers is known to induce a high-yield, non-conventional chemistry due to the deposition of energy in a very high density in the topmost ultrathin layer.

The chemical processes induced by energetic particles in the surface layers of organosilicon polymers were investigated by X-ray photoelectron spectroscopy in several articles.^{14,23,24} In a recent XPS study¹⁴ of particle beam-induced surface chemical modification of PVTMS, a preferential elimination of Si-containing fragments was shown to occur, probably due to a partial loss of the pendant trimethylsilyl groups. Furthermore, a PVTMS sample slightly pretreated by a particle beam and relaxed in vacuum exhibited a response, qualitatively different from that of a pristine sample during a particle-beam treatment, which was explained by beam-induced crosslinking. Literature data²⁵ show that PDMS is a negative resist-type polymer, i.e., a polymer in which crosslinking predominates over chain scission under ionizing radiation. Consequently, processes like the loss of pendant groups and crosslinking can be considered responsible for the decrease in the permeances of the penetrant gases through the FAB-treated organosilicon membranes. Such processes are expected to lead to a kind of "compaction" of the surface layer manifested in the decrease in their free volume and in hindered segment mobility.

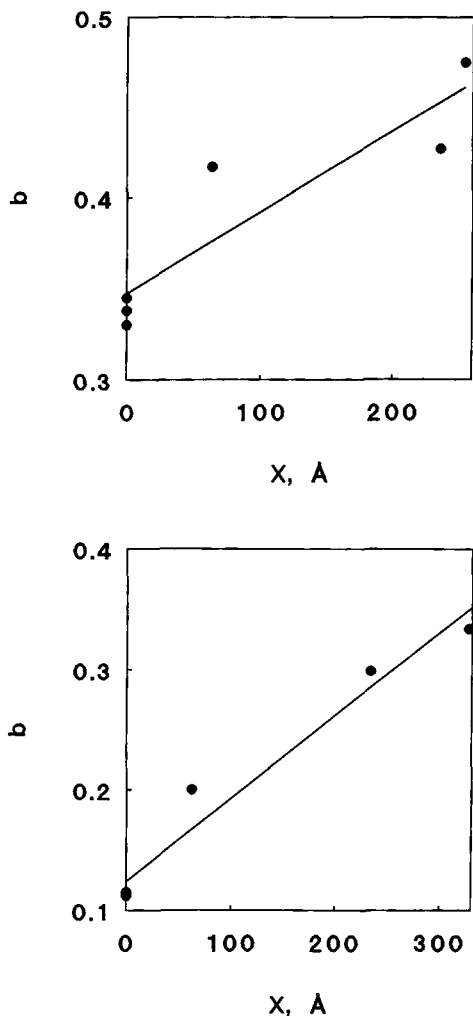


Figure 2 Dependence of the mobility selectivity parameter (b) on the average depth of penetration (X) of the bombarding atoms for asymmetric PVTMS (top) and PDMS-based composite (bottom) membranes.

CONCLUSION

Fast atom beam treatment applied in the low keV energy range modifies the mass transport properties (permeance and selectivity) of various organosilicon (asymmetric PVTMS and PDMS-based thin-film composite) gas separation membranes. Since organosilicon polymers, in general, are distinguished among the polymers by very high permeability coefficients, the observed increase in their selectivities—even if coupled with decrease in permeances—may lead to improvement in the performance of the related membranes in many applications. The particle beam-induced modification of the transport properties is considered to take place as a result of compaction of the surface layer due to processes like

crosslinking and loss of pendant groups, leading to the formation of a new, ultrathin, integral skin on the membrane. The extent of changes of the gas permeances and component selectivities increases with the average depth of penetration of the bombarding particles applied. This observation may serve as a basis of *controlling* the mass transport properties of the gas separation membranes, by offering the possibility of selecting the appropriate beam parameters like the mass of the projectile, its energy, etc. Finally, the induced decrease in permeance may be applied advantageously, e.g., in packaging, where the improvement of barrier properties of polymers is dramatically important.

NOMENCLATURE

Q	flux ($\text{cm}^3 \text{cm}^{-2} \text{s}^{-1}$)
Δp	pressure difference (cmHg)
F	area (cm^2)
P	permeability coefficient ($\text{cm}^3 \text{cm cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$)
D	diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
S	solubility coefficient ($\text{cm}^3_{\text{gas}} \text{cm}^{-3}_{\text{polym}} \text{cmHg}^{-1}$)
d	effective diameter of a penetrant gas molecule (Å)
X	average depth of penetration of a bombarding particle (Å)
V	volume (cm^3)
t	time (s)
l	thickness of the active layer (cm)
P/l	permeance ($\text{cm}^3 \text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$)
D/l	diffusivity (cm s^{-1})
$\alpha_{i,j}$	selectivity for a given gas pair

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