

Surface Modification of Polyimide and Polysulfone Membranes by Ion Beam for Gas Separation

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ABSTRACT: The surface carbonization of polyimide (PI) and polysulfone (PSf) by ion beam has been performed to adapt the carbon molecular sieve properties on the skin of the polymeric membranes without the deformation of the membrane structure. In order to control the structure of membrane skin and to improve gas transport properties, the irradiation conditions, such as the dosage and the source of ion beams, have been varied. The ideal separation factor of CO₂ over N₂ through the surface-modified PI and PSf membranes increased threefold compared to those of the untreated, pristine membranes, whereas the permeability decreased with almost two orders of magnitude. This appears to be due to the fact that the structure of membrane skin has been changed to a barrier layer. The formation of barrier layer was confirmed by comparing the calculated values of a simple resistance model with the experimental results, and the estimated permeability of this barrier was 10⁻⁴ barrer. It was concluded that ion beam irradiation could provide a useful tool for improving selectivity for gas separation membranes. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1554–1560, 2000

Key words: ion beam irradiation; gas separation membrane; polyimide; polysulfone; carbonaceous surface modification

INTRODUCTION

Membranes for gas separation need to be highly permeable to one of the mixture components while rejecting the other component significantly, for practical uses of high permeability and high selectivity. However, the permeability and selectivity are in conflict in most polymeric membrane materials, as demonstrated with the trade-off curve by Robeson.¹ Molecular sieving materials, such as zeolites and carbon molecular sieves

(CMS), have received much attention recently because their permeability and selectivity lie above the upper bound of the trade-off curve. Although these molecular sieving inorganic materials have advantage of chemical and thermal stability, membrane modules mostly rely on polymeric materials, because of their cost.

CMS have been commonly prepared by the carbonization of polymer membranes through pyrolysis. However, pyrolysis most likely brings some fractures and/or deformations, owing to the large inhomogeneous shrinkage of the polymer membranes. Moreover, CMS obtained by pyrolysis are difficult to handle due to their brittleness. One way to avoid these problems is the modification of the surface

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into a carbonaceous material, expecting high selectivity without sacrificing permeance.

Surface modification of membranes is an attractive approach since it changes the surface properties of a polymer; thus, interactions with solutes can be changed specifically. For this approach, either a novel selective property is achieved or a new selective layer is created. For example, ultraviolet light irradiation has been used for the improvement of chemical resistance and thermal stability as well as the selective transport of gases at high rates.² Plasma techniques also have been used to modify various types of membranes³ as well as to induce graft polymerization.⁴

Ion beam irradiation has become an integral part in the modification of surface layers (a few micrometers or less) of polymers.⁵⁻⁷ Phenomena associated with ions and polymers depend on target parameters (e.g., composition, molecular weight, and temperature) and on ion beam parameters (energy, mass, and ion dosage). Chain scission, chain aggregation, double-bond formations, and molecular emissions occur at low ion dosages.⁵ At high ion dosages, an enrichment of carbon generally occurs, leading to a more or less complete carbonization (even to the formation of graphite), and the final sample composition may have little memory of the original chain structure.⁸ Marletta et al.⁹ modified 3,3',4,4'-benzophenonetetracarboxylic dianhydride-4,4'-oxydianiline polyimide films by bombarding with Ar⁺ with 150 keV at various dosages from 5×10^{12} to 2×10^{17} ions/cm². The modification of polymer seems to carbonize the polyimide and to produce an amorphous carbon network still containing significant amount of residual N and O atoms in the original polymer structure after 5×10^{15} ions/cm² doses. Similar results obtained using high ion beam energy have been observed in the other references.^{6,7,10} Marletta et al.¹¹ also used the low energy ion beam in the surface modification of polymer with low ion dosages. Recently, low-energy ion beams received attention because of the feasibility of the industrial range of surface modification.

In this paper, we demonstrate the possibility of controlling the gas transport properties of polymeric gas separation membranes using a low keV ion beam. The surface of polymeric membranes has been modified by an ion beam to form the carbonaceous surface, expecting the properties of the CMS on the top of the membranes. In this

surface treatment, the parameters, such as the ion beam source, ion beam energy, and irradiated ion dosages, have been varied in order to improve the gas separation performance of polyimide (PI)- and polysulfone (PSf)-dense membranes.

EXPERIMENTAL

The preparation of polyimide (PI, Matrimid 5218; Ciba-Geigy)- and polysulfone (PSf, P-3500; Amoco)-dense membranes was as follows: a pre-filtered 4 wt % of polymer in tetrahydrofuran solution was poured into a Petri dish, and the solvent was allowed to evaporate slowly at room temperature for 24 h. Then, the membrane was put into an oven at 120°C for 5 days. The final thickness of the membrane thus obtained was in the range of 30–40 μm.

A main chamber was evacuated with both a rotary pump and a diffusion pump. The base pressure and working pressure were 1×10^{-5} and 1×10^{-4} Torr, respectively. A 5-cm-diameter cold-hollow cathode ion source was used to generate ions. The ions were irradiated onto the polymer surface at room temperature. An applied ion beam potential was varied from 0.3 to 1.2 keV. The ion beam current was controlled by a discharge current and was measured by a Faraday cup-biased -30 V to prevent secondary electrons from entering it. The amount of irradiated ions was changed from 5×10^{14} to 5×10^{17} ions/cm² at a fixed ion beam current. Most experiments were performed with 1 keV Ar⁺ ions. We also studied the effects of varying the ionic species (e.g., He or N₂) and the ion beam energy.

Gas permeability coefficients were obtained by measuring downstream pressure change through the constant volume method. Temperature of the whole test system was maintained at 35°C, and the upstream pressure was 1 atm. Ideal separation factors of CO₂/N₂ (hereafter referred to as selectivity) were obtained from the ratio of pure CO₂ permeability over that of N₂.

RESULTS AND DISCUSSION

Effect of Ion Dosages

After the ion beam treatment, the surface of all PI and PSf membranes became visually black, im-

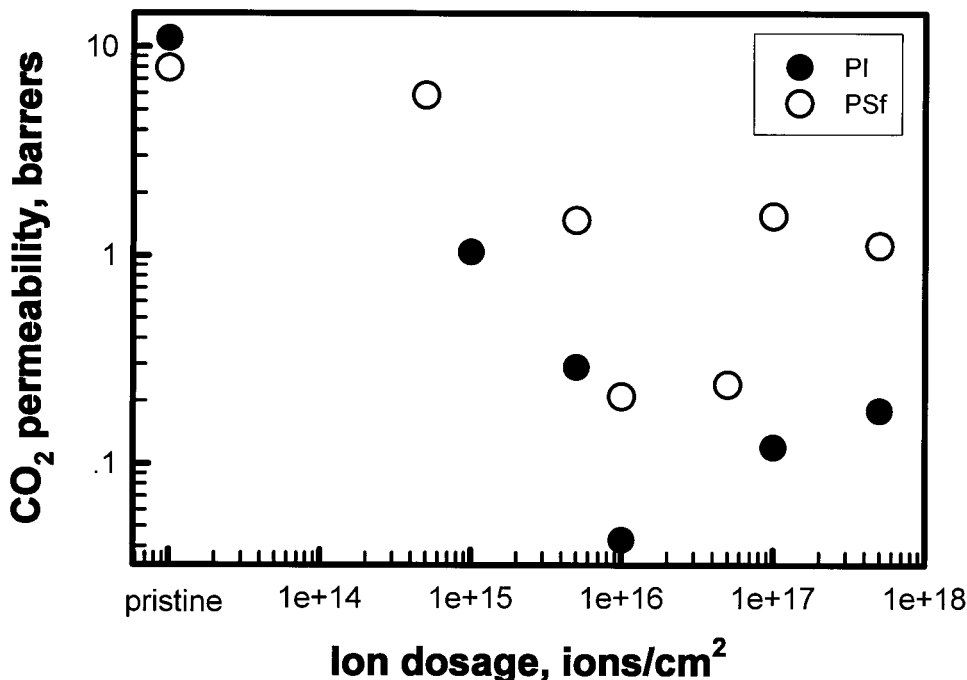


Figure 1 CO₂ Permeabilities of pristine and surface-modified PSf- and PI-dense membranes with ion dosages.

plying a carbonaceous phase. Carbonaceous layer formation has been well known after ion beam irradiation.¹² The pure gas permeabilities and selectivities of PI as well as PSf-dense membranes are plotted as a function of irradiated ion dosages with 1 keV Ar⁺ in Figures 1 and 2, respectively. The permeabilities of both PI and PSf membranes decrease with ion dosages and reach the minimum at about 1×10^{16} ions/cm² and then increase. This trend is more significant for PI than PSf at the same ion dosages. Detailed research of this trend is under study in this laboratory. The selectivities of modified membranes increased with irradiation, but this increase in the selectivity was accompanied by a drastic decrease in the permeability.

It is known that CMS have higher selectivity [$P(\text{CO}_2)/P(\text{N}_2) > 60$] than that of common polymeric materials, without a major sacrifice of permeability. Therefore, it is expected that the selectivity would improve for the carbonaceous surface-modified membranes. However, the current experimental results showed that the selectivity was increased approximately threefold, but the permeability was decreased unexpectedly more than an order of magnitude with increasing ion

dosages. This result implies that the modification of the polymer membrane by an ion beam leads to the formation of a barrier layer on the membrane surface.

Estimation of Permeability through the Surface Modified Layer

When a dense PI membrane was surface-modified with ion beam irradiation, a two-layer membrane comprising a surface-modified and matrix layer can be assumed. The effective permeability through the two-layer membrane can be calculated readily by the resistance model:

$$\frac{1}{P} = \frac{x_C}{P_C} + \frac{x_M}{P_M}$$

where P , P_C , and P_M are the effective permeability, the permeabilities through the surface-modified layer, and the matrix, respectively, and x_C and x_M are fractional thickness of the surface-modified and matrix layers, respectively.

In order to estimate the permeability of the surface-modified layer, the calculated results were compared with the experimental results. For the

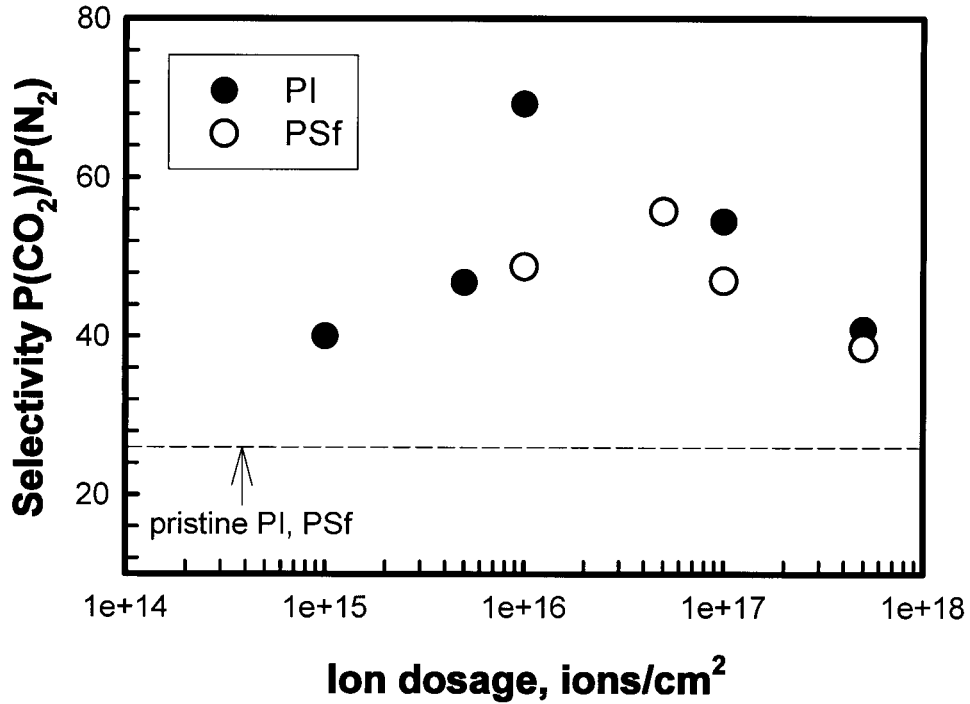


Figure 2 Selectivities of surface-modified PSf- and PI-dense membranes with ion dosages.

numerical calculation, the CO₂ permeability and CO₂/N₂ selectivity of the PI matrix were fixed at 10 barrer and 30, respectively, which were measured

in this laboratory. The CO₂/N₂ selectivity of the carbon layer was determined to be 70, which was close to the value reported by Koros.¹³ Because the

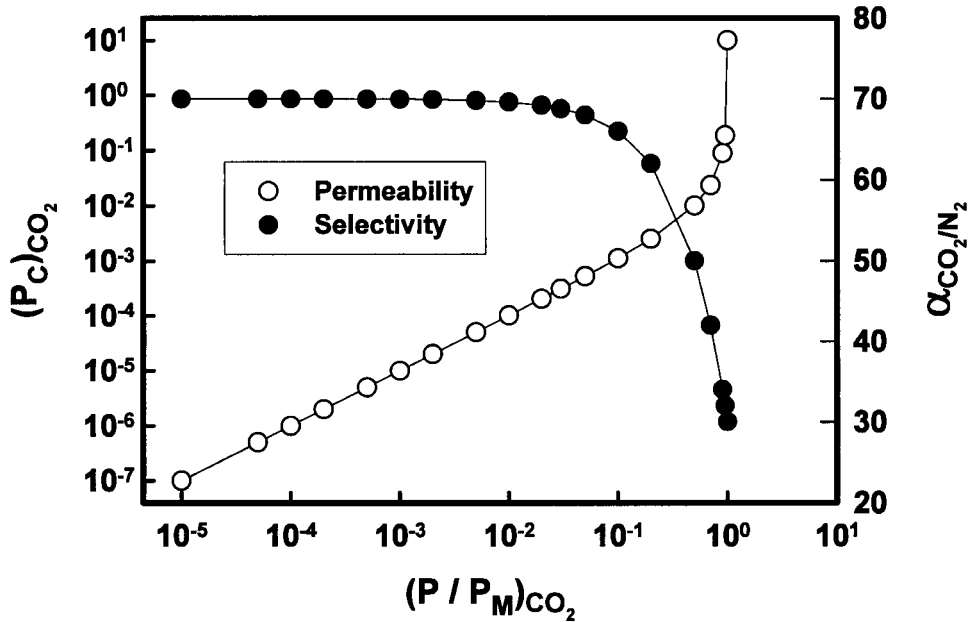


Figure 3 Theoretical prediction of $(P_c)_{CO_2}$ and α_{CO_2/N_2} as a function of $(P/P_M)_{CO_2}$, calculated by the simple resistance model.

Table I Gas Permeabilities of Surface-Modified PI Membranes Irradiated by Different Ion Sources with Ion Dosages

Ion Beam	Ion Dosage	Permeability (barrers)				Selectivity ^a $P(\text{CO}_2)/P(\text{N}_2)$
		He	CO ₂	O ₂	N ₂	
Ar	None		11.0	2.2	0.36	30.6
	1×10^{15}		1.04		0.0256	40.6
	5×10^{15}		0.294		0.00615	47.8
	1×10^{16}		0.043		0.000627	68.6
	1×10^{17}	3.86	0.198		0.0047	42.1
	3×10^{17}	4.54	0.174		0.0028	62.1
	5×10^{17}	4.26	0.178		0.0044	40.5
He	1×10^{15}		8.98	2.02	0.29	30.9
	1×10^{16}		1.40		0.047	29.8
	1×10^{17}		0.51	0.019	0.0092	55.4
N ₂	1×10^{15}		6.09	1.34	0.27	22.3
	1×10^{16}		0.65	0.14	0.020	32.5
	1×10^{17}		0.22	0.051	0.0035	63.7

^a Ideal separation factor.

depth of the surface-modified layer by the ion beam irradiation is estimated to be less than 0.01 μm (ca. 0.05% modification of the total membrane thickness), x_C was fixed at 0.001. Under this condition, the $(P_C)_{\text{CO}_2}$ was calculated as a function of $(P/P_M)_{\text{CO}_2}$ and is plotted in Figure 3. $(P/P_M)_{\text{CO}_2}$ was measured to be in the range of 10^{-2} ; thus, the $(P_C)_{\text{CO}_2}$ value is approximately 1×10^{-4} barrer. This value is much smaller than that reported for the amorphous carbon; therefore, it is consistent with the possible formation of graphite on the top surface.

Surface Modified Layer

At low ion dosage with low ion energy, the ion beam induces the compaction of the surface layer, due to the processes such as crosslinking and loss of pendant groups, leading to the formation of an ultrathin, integral skin on the membrane.¹¹ Upon ion bombardment on membrane surface, its structure can be modified to amorphous carbon or graphite, depending on the energy, the dosage of ion beams, and the polymer.

In this work, the irradiation amounts were high enough to form the carbonaceous layer in the skin, even though a low energy ion beam was used, which was proved by X-ray photoelectron spectroscopy. There are reports on the graphitization of the ion-irradiated films.^{14–17} Polystyrene films exhibited properties close to those of hydrogenated amor-

phous carbon when irradiated with 10^{15} ions/cm² at keV to MeV heavy ions, and graphitization occurred at about $\sim 10^{16}$ ions/cm² dosages.¹⁴ From these experimental results, it is expected that the carbonaceous top skin could be a graphite-like barrier, which was also shown in the carbon membrane obtained by pyrolysis.¹⁸ The graphite-like barrier formation is consistent with the results of ion irradiation of Kapton, yielding a glassy or graphite-like carbon phase due to the condensation of carbon aromatic rings.¹⁶

The identification of the amounts and mechanism of graphitization is not feasible, although many spectroscopic techniques have been used to characterize the modified surface induced by ion bombardment on polymeric films [e.g., ref. 15]. The formation of a graphite-like phase actually has been a controversial point, because the chemical nature of the materials produced by ion irradiation is difficult to characterize. Moreover, the relationship between the irradiation amounts of low-energy ion beam and the structure of the polymer surface are not understood yet and will not be discussed further because it is beyond our interest at this moment.

Effect of Ion Beam Source

The gas permeabilities of surface-modified PI membranes irradiated at 1 keV with different ion

Table II Gas Permeabilities of Surface-Modified PI and PSf Membranes Irradiated by 300 eV Ar⁺

Polymer	Ion Dosages	Permeability (barrers)			Selectivity ^a $P(\text{CO}_2)/P(\text{N}_2)$
		CO ₂	O ₂	N ₂	
PI	None	11.0	2.20	0.36	30.6
	1×10^{14}	10.2	—	0.32	31.9
	5×10^{14}	10.7	2.16	0.32	33.0
	1×10^{15}	11.4	2.10	0.33	34.5
PSf	None	7.92	1.50	0.26	30.5
	1×10^{14}	5.08	—	0.16	31.8
	5×10^{14}	5.89	0.58	0.16	36.8
	1×10^{15}	5.12	—	0.14	36.6

^a Ideal separation factor.

beams (Ar, He, and N₂) were measured, and their selectivities were calculated and summarized in Table I. The permeabilities decrease with increasing irradiation amounts. These permeability decreases were compensated for by the increase in selectivity. Due to the different mass of irradiation ions, it is expected that the permeability decreases with the increase of the proportion of the energy dissipated by collisions with the bombarding particles. However, there is not a significant discrepancy in the membrane modified by He and N₂ ion beams, whereas a strong reduction in the CO₂ permeability is observed from the one irradiated by Ar⁺ at 1×10^{15} ion dosage. However, for the membranes irradiated with sufficiently high enough dosages, such as more than 1×10^{17} , the effect of different ion beams became negligible. These results probably rely on the limitation of the film densification when the ion dosages are significantly high enough.

Effect of Ion Beam Energy

A series of PI and PSf membranes have been irradiated from 1×10^{14} to 5×10^{15} Ar⁺/cm² at low energy of 300 eV, and the results are summarized in Table II. The effect on the gas permeability of the membrane was negligible compared with those membranes irradiated by Ar⁺ at 1 keV. As can be seen, the permeability remains almost constant with increasing ion dosages at low-energy irradiation, whereas it decreases markedly at high energy (1 keV) irradiation (Fig. 1). The selectivity shows a similar behavior, which increased from 30 to 33 and 30 to 37 when the surface was irradiated at ion dosage range of

1×10^{14} to 5×10^{15} for PI and PSf membranes, respectively. This result implies that the ion irradiation of high ion energy is more effective to modify the surface than that of lower ion beam energy.

CONCLUSIONS

The surface carbonization by ion beam has been performed to adapt the carbon molecular sieve properties on the skin of the polymeric membranes without the deformation of the membrane structure. The result of the surface-modified membrane was that the selectivity was increased at the expense of a drastic decrease in the gas permeability. This can be a consequence of the formation of a barrier with irradiation, which was confirmed by the predictions of the simple resistance model. It also was found that irradiation using ion beams could provide a useful tool for improving the performance of selectivities for gas separation membranes.

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