

Impact of H⁺ Ion Beam Irradiation on Matrimid[®]. II. Evolution in Gas Transport Properties

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Received 10 March 2006; accepted 30 April 2006

DOI 10.1002/app.25359

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Ion beam irradiation is an easily controlled method to modify the chemical structure and microstructure of polymers including the fractional free volume, free volume distribution and chain mobility, thus altering the gas transport properties of the irradiated polymers. The previous paper focused on the impact of H⁺ ion beam irradiation on chemical structural evolution of the polyimide Matrimid[®]. This paper focuses on the impact of H⁺ ion beam irradiation on microstructure and gas permeation properties of Matrimid[®]. Irradiation at low ion fluence resulted in slight decreases in permeabilities for five gases (*i.e.*, He, CO₂, O₂, N₂, and CH₄) with increases in permeabilities

for some gas pairs (*e.g.*, He/CH₄ and He/N₂). In contrast, irradiation at relatively high ion fluences resulted in simultaneous increases in permeabilities and permselectivities for most gas pairs (*e.g.*, He/CH₄, He/N₂, O₂/N₂, and CO₂/CH₄). While Matrimid[®] has bulk gas permeation properties that are below the range of commercially interesting polymers, samples irradiated at high ion fluences exhibited significant improvement in gas separation performances. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1670–1680, 2007

Key words: ion beam irradiation; crosslinking; polyimide; gas separation membrane; modification

INTRODUCTION

Polymeric membrane-based gas separation is becoming increasingly attractive because of flexible design, lower energy expenditure, and ease of operation in comparison with conventional methods like cryogenic distillation or adsorption.¹ To be commercially feasible, four important factors, *i.e.*, permeability, permselectivity, stability at the operating conditions, and processibility, must be considered in selection of membrane materials.^{2,3} There have been numerous studies of the relationship between polymer chemical structure and gas transport properties, and have led to general rules of thumb that allowed tailoring of polymers with improved gas permeation properties. For example, introduction of bulky groups within the polymer backbone, which can hinder both segmental mobility and intersegmental packing, results in simultaneous increases in permeability and permselectivity.^{4–8} In addition, reorganization of the fractional free volume (FFV) of a polymer can result in significant changes in gas transport properties.^{1,2}

While considerable progress has been made in synthesis of polymers with improved permeabilities and permselectivities, new polymers appear to be approaching a new upper bound limit of transport behavior as demonstrated by Robeson.⁹ Moreover, polymers are typically limited to applications at fairly low temperature and in inert environments. At elevated temperature or presence of highly soluble gases, polymer chains have increased segmental mobility resulting in increased permeabilities with significant reduction in permselectivities.¹ Therefore, recent work has focused on developing alternative membrane materials and/or using postformation techniques for modification of pristine polymeric membranes to overcome these limitations. Two interesting examples of postsynthesis modification methods are pyrolysis of asymmetric polymeric membranes to form carbon molecular sieving (CMS) membrane and plasma modification of polymeric membrane surfaces.^{10–15} While these membranes have improved gas transport properties combined with thermal and chemical stability, they are challenging to process and have issues with mechanical stability. Therefore, alternative postsynthesis modification methods that focus on modifying the selective layer of a polymeric membrane are of interest.

Ion beam irradiation is an easily controlled and effective method that can be used to modify chemical structure, microstructure, and gas permeation properties of polymers.^{16–24} When an energetic ion

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Contract grant sponsor: National Science Foundation; contract grant number: Presidential Faculty Fellowships CTS-955367 and CTS 9975452.

penetrates a polymer surface, it transfers its energy to the polymer backbone. There are essentially two energy transfer mechanisms from the incident ion to the polymer for the ion energy used in this study²⁵: (i) electronic energy loss, which involves electronic excitation and exchange of electrons between incident ions and the polymer, and (ii) nuclear energy loss, which involves atomic collision between ions and atoms in the polymer. Ion beam irradiation through energy transfer from incident ions to the polymer can lead to a number of chemical reactions within a polymer layer, such as degradation of chemical bonds with formation of free radicals, release of small volatile molecules, and crosslinking between polymer chains. The release of small volatile molecules can leave small molecular size defects within the polymer matrix, which could increase the FFV of the polymer and therefore gas permeability. On the other hand, crosslinking of the polymer induced by ion beam irradiation can increase inhibition to segmental chain mobility, thereby increasing stability as well as diffusivity selectivity.^{26,27} Therefore, through the control of contribution from the crosslinking and the formation of small molecular size defects, ion beam irradiation could modify the microstructure of polymer material, including the FFV, free volume distribution, as well as chain mobility, thus resulting in modification of gas transport properties of the polymer.

Ion beam irradiation-induced modification on microstructure of polymeric membrane depend on a number of factors, such as the chemical structure of the virgin polymer, ion type, ion energy, and ion fluence.¹⁶ A detailed study of evolution in chemical structure and gas permeation properties of Matrimid[®] was undertaken by our group clarify the impact of ion type and irradiation conditions on structure evolution and properties. The evolution in chemical structure of the polyimide Matrimid[®] induced by H⁺ ion beam irradiation was reported in the first paper.²⁸ This paper presents results of an investigation of evolution in gas permeation properties of Matrimid[®] induced by H⁺ ion beam irradiation over a wide range of ion fluences. Matrimid[®] was chosen because it has superior gas permeation properties to many commercial polymers for industrially important gas pairs, well-characterized physical and transport properties and has been used successfully as a base material for CMS membranes.^{26–30}

EXPERIMENTAL

Materials

The chemical structure of Matrimid[®] is shown in Figure 1. Matrimid[®] was purchased from Ciba Specialty Chemicals Company (Brewster, NY). Meth-

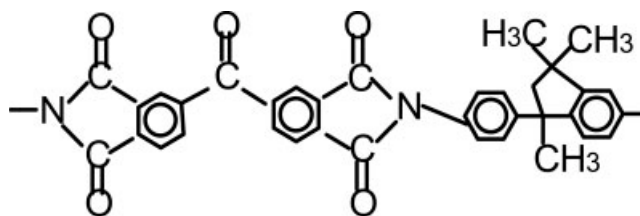


Figure 1 Chemical structure of monomer unit of the polyimide Matrimid[®]

ylene chloride (CH₂Cl₂) was used as a solvent for film formation and purchased from Fisher Scientific (Hanover Park, IL). The polymer and solvent were reagent grade and used without further purification. The five gases (He, CO₂, O₂, N₂, and CH₄) used in this study were obtained from O. E. Meyer Company (Maumee, OH). The purity of these gases was at least 99.95%. These gases were selected to represent a range of kinetic molecular diameter of penetrant molecules and condensability.

Preparation of Matrimid[®]-ceramic composite membranes

Permeation properties of pristine and irradiated Matrimid[®] were determined using composite membranes that consisted of a very thin polymer-selective layer on a porous ceramic membrane. Whatman[®] Anodisc membranes with pore diameter of 0.02 μm were used to provide mechanical support because they will not be modified by ions so that the impact of ion beam irradiation on the gas transport properties of Matrimid[®] was isolated. Prior to composite membrane formation, a solution of 3–6 wt % Matrimid[®] in methylene chloride was prepared and filtered. The polymer solution was cast on an Anodisc membrane using a spin-coating method developed in our lab using a P-6000 Spin Coater from Specialty Coating System, Inc. (Indianapolis, IN). An initial spinning speed of 75–80 rpm was used to prevent the polymer solution from penetrating into the pores of the membrane followed by spinning at 200–600 rpm. This provided very thin polymer-selective layers, which were required to ensure that the entire the polymer thickness was modified. The resulting composite membrane was masked immediately with aluminum foil tape and dried in a vacuum oven at 50°C for 24 h to remove residual solvent. The foil mask was used to make the sample easier to handle, and to define both permeation and irradiation areas. The O₂/N₂ ideal selectivity of each pristine Matrimid[®]-ceramic composite membrane was more than 85% of the reported bulk material value ($\alpha_{O_2/N_2} = 6.11$).²⁹ Thus, the polymer layer of the unmodified membranes was considered essentially defect-free. On the basis of O₂ permeability of the bulk material and O₂ permeances of the pristine membranes,

the thicknesses of the selective layers of all pristine membranes were estimated to be from 0.3 to 1.3 μm .

Ion beam irradiation

The implantation was performed at the Department of Physics and Astronomy, University of Western Ontario, Canada, using a Tandem Accelerator. All of the irradiation was performed at room temperature within a vacuum chamber at a pressure less than 1.9×10^{-7} torr. To avoid heating of the sample, a low beam-current density ($<1 \mu\text{A}/\text{cm}^2$) was used. The incident beam was perpendicular to the surface of the samples. The incident energy of 180 keV was determined using a well-known program titled "The Stopping and Range of Ion in Matter" (SRIM)³¹ to ensure that the entire thickness of the Matrimid[®]-ceramic composite membrane was modified.

Gas permeation measurements

The pure gas permeances of He, CO₂, O₂, N₂, and CH₄ were measured for the pristine and the irradiated membranes in a standard constant volume variable pressure permeation cell at 35°C with pressurized upstream and evacuated downstream.³² The permeance of each gas was measured for each composite membrane prior to and following ion beam irradiation so that direct comparison can be made. The standard method used for characterizing polymer membranes for a wide pressure range was modified to prevent stress on the fragile ceramic porous support.³² For these experiments, the upstream side of the membrane was not evacuated before pressurizing, but purged at low pressure with the feed gas. After purging the feed for several minutes, the downstream was slowly evacuated, the upstream purge was closed and the feed pressure slowly increased to 3.74 atm. The system was allowed to sit overnight to ensure that steady permeability was achieved. The pure gas permeabilities at 35°C can be estimated as a product of permeance and the thick-

ness of the selective layer estimated on the basis of the O₂ permeability of the bulk material and O₂ permeances of the pristine membranes.

RESULTS AND DISCUSSIONS

Results

As discussed in the previous paper,²⁸ H⁺ ion beam irradiation at very low ion fluences (below 5.0×10^{13} H⁺/cm²) induced little modification in chemical structure. However, there was progressive chemical structural evolution and crosslinking with increase of ion fluence. For ion fluence of 6×10^{14} H⁺/cm², irradiation resulted in not only the degradation of the *para*-disubstituted aromatic ring (see Fig. 1 for Matrimid[®]'s unit structure), but also the rapid degradation of CH₃, benzophenone C=O and the imide groups (such as imide C=O and CNC). In addition, following irradiation at ion fluence of 6×10^{14} H⁺/cm², the Matrimid[®] became totally insoluble, which indicated considerable crosslinking in the irradiated samples. As discussed earlier, crosslinking can lead to increased polymer chain rigidity, which typically results in the increased gas selectivity, resistance to chemical attack, and high temperature stability.^{26,27} Therefore, 6×10^{14} H⁺/cm² was chosen as the starting ion fluence to irradiate the Matrimid[®]-ceramic composite membranes in this study. Four Matrimid[®]-ceramic composite membranes were irradiated with 180 keV H⁺ at ion fluences ranging from 6×10^{14} to 2.5×10^{15} H⁺/cm². The pure gas permeances were measured at 35°C for each composite membrane before and after H⁺ ion beam irradiation. The measured permeances and permselectivities at 35°C for the pristine and the H⁺ ion beam irradiated membranes are summarized in Tables I and II, respectively. As mentioned earlier, since the O₂/N₂ selectivity of the pristine membranes was between 85 and 96% of the bulk value, the pristine membranes were considered defect free.

The normalized permeances for the five gases and the normalized permselectivities for several gas pairs are plotted as a function of H⁺ ion fluence in

TABLE I
Gas Permeation Properties of the Matrimid[®]-Ceramic Composite Membranes Prior to H⁺ Ion Beam Irradiation

Sample	Estimated thickness ^a	Permeance (GPU ^b)					Selectivity ^c		
		He	CO ₂	O ₂	N ₂	CH ₄	O ₂ /N ₂	CO ₂ /CH ₄	He/CH ₄
A	0.3	77.0	38.0	7.28	1.37	1.33	5.3	29	58
B	0.5	59.7	19.5	4.66	0.90	0.79	5.2	25	75
C	1.2	27.2	10.8	1.94	0.38	0.38	5.2	29	72
D	1.3	21.8	9.9	1.75	0.30	0.27	5.9	37	81

^a Unit: μm based on O₂ permeance of the pristine Matrimid[®]-ceramic composite membrane and O₂ permeability of the bulk material of 2.3 Barrer.

^b 1 GPU = 10^{-6} cm³ (STP)/cm² s cmHg, feed pressure: 3.74 atm.

^c Ratio of pure-gas permeance.

TABLE II
Gas Permeation Properties of the Matrimid[®]-Ceramic Composite Membranes Following H⁺ Ion Beam Irradiation

Sample	Ion fluence (H ⁺ /cm ²)	Permeance (GPU ^a)					Selectivity ^b		
		He	CO ₂	O ₂	N ₂	CH ₄	O ₂ /N ₂	CO ₂ /CH ₄	He/CH ₄
A	6.0 × 10 ¹⁴	61.4	19.4	4.34	0.82	0.72	5.3	27	85
B	9.0 × 10 ¹⁴	65.2	19.5	4.71	0.92	0.70	5.1	28	93
C	2.0 × 10 ¹⁵	37.0	13.6	2.68	0.48	0.35	5.6	39	106
D	2.5 × 10 ¹⁵	36.9	14.2	2.89	0.45	0.33	6.5	44	113

^a 1 GPU = 10⁻⁶ cm³ (STP)/cm² s cmHg; feed pressure: 3.74 atm.

^b Ratio of pure-gas permeance.

Figures 2–4. A normalized gas permeation property is defined as the ratio of the property of the irradiated membrane to that of the pristine membrane. Normalized values are used to allow a direct comparison of the modification induced by H⁺ ion beam irradiation and to account for any differences in transport properties of the pristine membranes. At the lowest ion fluence used in this study (6 × 10¹⁴ H⁺/cm²), there was a general decrease in the permeances for all gases studied with smaller decrease for the smallest size molecule and larger decreases for other four penetrants studied (see Fig. 2). For example, He permeance decreased to 80% of the initial value, and CH₄ permeance decreased to

55% of the initial value. As a consequence, the permselectivity of He/CH₄ increased to 85, which was about 150% of its initial value. There is no change in permselectivity of O₂/N₂ at this stage of modification (Fig. 3). At ion fluence of 9 × 10¹⁴ H⁺/cm², ion beam irradiation resulted in a slightly increased permeance for the smallest molecule and almost no change in the permeances for intermediate molecules (*i.e.*, CO₂, O₂, and N₂), with a decrease of about 10% in the permeance for the largest molecule (*i.e.*, CH₄). As a result, the permselectivity of He/CH₄ increased to 124% of its initial value while the permselectivity of O₂/N₂ remained almost unchanged (Fig. 3). As ion fluence was

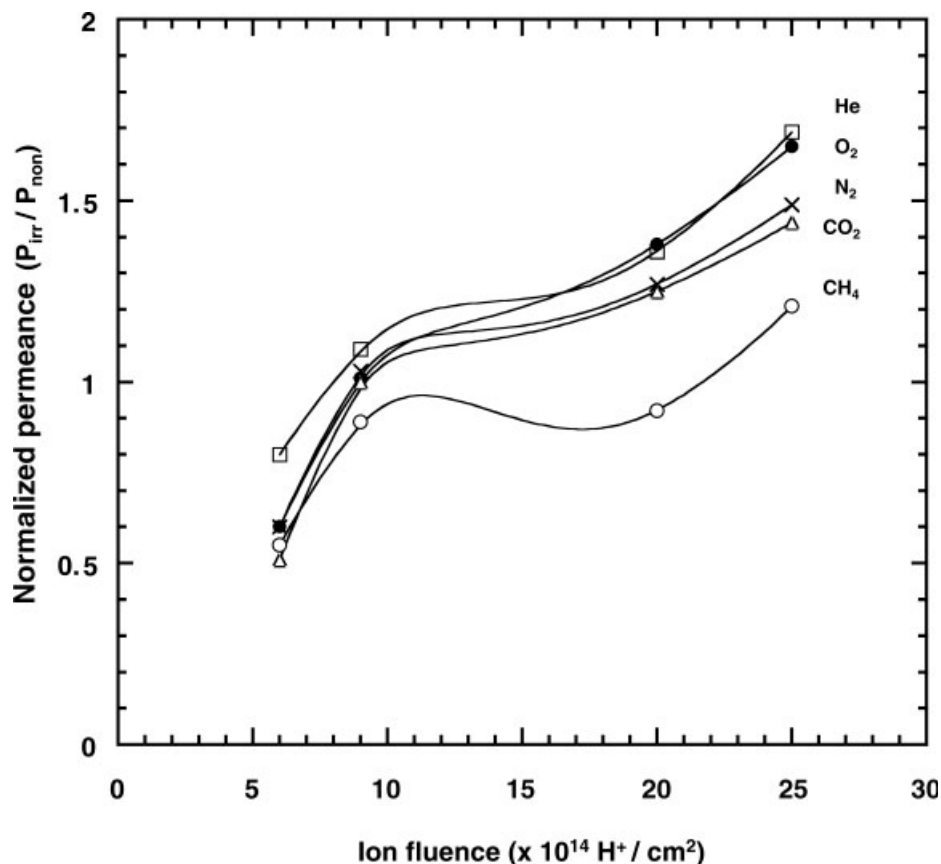


Figure 2 Impact of H⁺ ion fluence on the normalized permeances for He (□), CO₂ (△), O₂ (●), N₂ (×), and CH₄ (○) in the H⁺ ion beam irradiated Matrimid[®]-ceramic composite membranes.

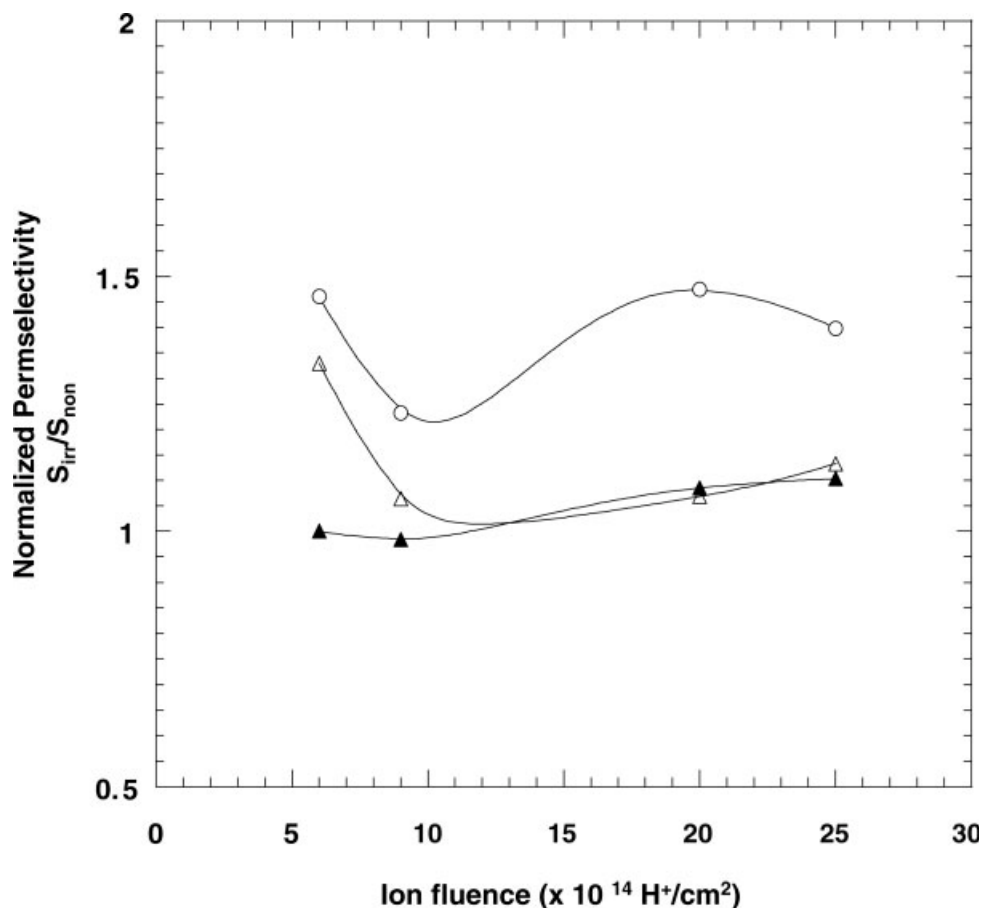


Figure 3 Impact of H^+ ion fluence on the normalized permselectivities for He/CH_4 (\circ), He/N_2 (\triangle), and O_2/N_2 (\blacktriangle) in the H^+ ion beam irradiated Matrimid[®]-ceramic composite membranes.

increased to $2 \times 10^{15} \text{ H}^+/\text{cm}^2$, there was a small reduction (about 8%) in the permeance for the largest size molecule (*i.e.*, CH_4), and a general increase in the permeances for other four gases studied. This resulted in increases in permselectivities for some gas pairs (such as O_2/N_2 , He/CH_4 , and CO_2/CH_4), as shown in Figures 3 and 4. As ion fluence was increased to $2.5 \times 10^{15} \text{ H}^+/\text{cm}^2$, irradiation resulted in increases in permeances for all gases studied. Since smaller molecules exhibited larger increases in permeances, there were simultaneous increases in permselectivities for several gas pairs. The increase in permeance is in the order of $\text{He} > \text{O}_2 > \text{N}_2 > \text{CO}_2 > \text{CH}_4$, which, with the exception of CO_2 , is inverse of the order of kinetic diameter of penetrant gases.

The impact of H^+ ion fluence on the normalized permselectivities for several gas pairs is shown in Figures 3 and 4. Following H^+ ion beam irradiation at $6 \times 10^{14} \text{ H}^+/\text{cm}^2$, there were increases in the permselectivities for the gas pairs He/CH_4 and He/N_2 but little change in the permselectivity for the gas pair O_2/N_2 . At ion fluence of $9 \times 10^{14} \text{ H}^+/\text{cm}^2$, the permselectivities for several gas pairs such as

He/N_2 , He/CH_4 , and CO_2/CH_4 were increased by H^+ ion beam irradiation, whereas the permselectivities for the gas pairs O_2/N_2 and CO_2/N_2 were slightly decreased. Following irradiation at $2 \times 10^{15} \text{ H}^+/\text{cm}^2$ or beyond, there was a general increase in permselectivities for most gas pairs (He/CH_4 , He/N_2 , CO_2/CH_4 , and O_2/N_2).

An unexpected result was observed for H^+ ion beam irradiation induced effects on CO_2 permeation properties of the Matrimid[®] composite membranes, as shown in Figures 2 and 4. The normalized permselectivities of three gas pairs (CO_2/CH_4 , CO_2/O_2 , and CO_2/N_2) are shown in Figure 4. There was a trend for the normalized CO_2/CH_4 permselectivity of an initial increase at low ion fluences, to a maximum value (about 1.47) followed by a decrease at very high ion fluence. Interestingly, both CO_2/O_2 and CO_2/N_2 permselectivities were lower than the values for pristine membrane over the whole range of ion fluences investigated. From the view point of microstructural evolution of the polymer induced by ion beam irradiation and size-exclusion mechanism of gas diffusion, a larger increase in permeance for CO_2 than that for O_2 or N_2 would be expected

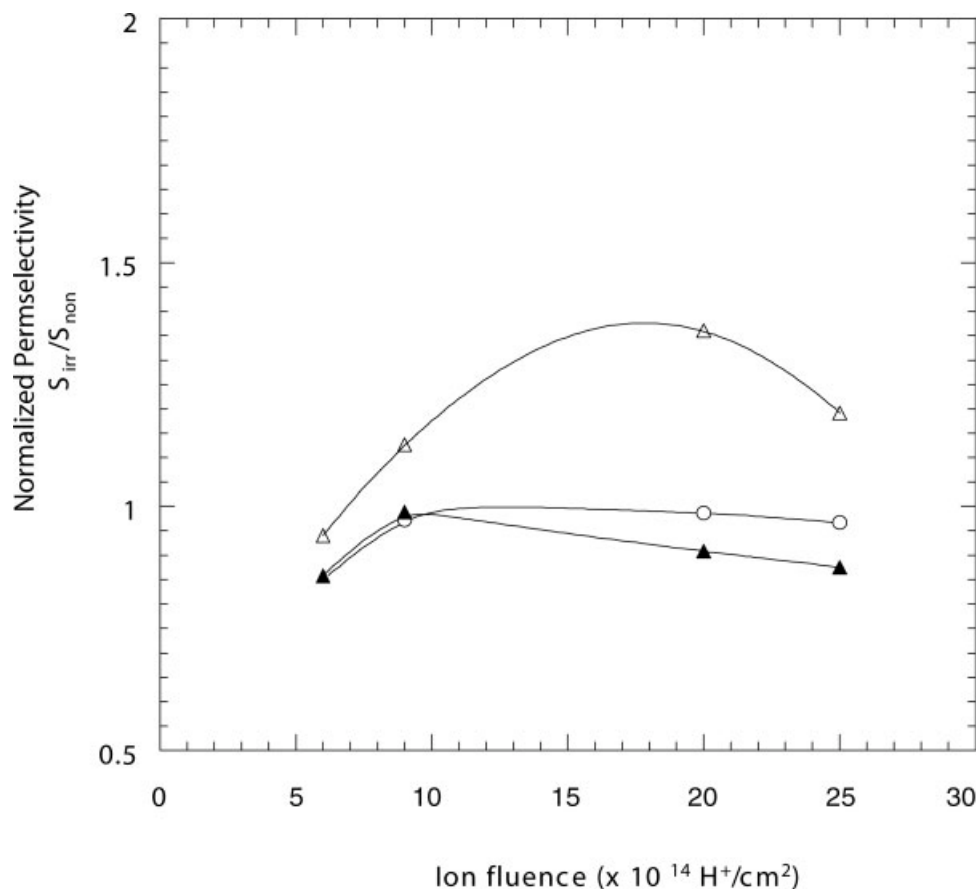


Figure 4 Impact of H⁺ ion fluence on the normalized permselectivities for CO₂/N₂ (○), CO₂/CH₄ (△), and CO₂/O₂ (▲) in the H⁺ ion beam irradiated Matrimid[®]-ceramic composite membranes

because of its smaller kinetic molecular diameter. However, over the whole range of ion fluences, there was a general decrease in the permselectivity for the gas pair CO₂/O₂ or CO₂/N₂, which implies that diffusion effects do not dominate in case of these molecules. These results will be discussed in terms of impact of irradiation on both diffusivity and solubility in following section.

Discussion of results

Hypothesis regarding the evolution in microstructure of Matrimid[®] induced by ion beam irradiation

The evolution in permeances of the Matrimid[®] composite membranes induced by H⁺ ion beam irradiation implied an evolution in microstructure, or the FFV and free volume distribution of the material following ion beam irradiation. Since the thickness of each membrane is not expected to change significantly following irradiation, the normalized permeability should be the same as the normalized permeance. Since permeation of a gaseous penetrant through glass polymer membrane is a solution-diffusion process, permeability of a gaseous penetrant

through the polymer membrane can be factored into diffusivity coefficient and solubility coefficient. While diffusivity coefficient and solubility coefficient were not measured for the individual gases in the irradiated sample, considering the impact of irradiation on permeability in terms of these values can provide valuable insight into material's properties. Specifically, diffusivity coefficient is a kinetic factor, which is determined by the FFV and free volume distribution of a polymer, as well as molecule size and shape of a penetrant. On the other hand, solubility coefficient is a thermodynamic term, which is determined by the FFV and free volume distribution of a polymer, penetrant condensability, and interactions between polymer and penetrant. In this paper, a general model of the evolution of microstructure in terms of the dynamic FFV and free volume distribution of Matrimid[®] induced by H⁺ ion beam irradiation is proposed.

The potential impact of irradiation on the dynamic FFV of Matrimid[®] is shown in cartoon form in Figure 5. In Figure 5, the solid line represents a general proposed FFV distribution for the pristine material. Following H⁺ ion beam irradiation at the lowest ion fluence (6×10^{14} H⁺/cm²) used in this study, there

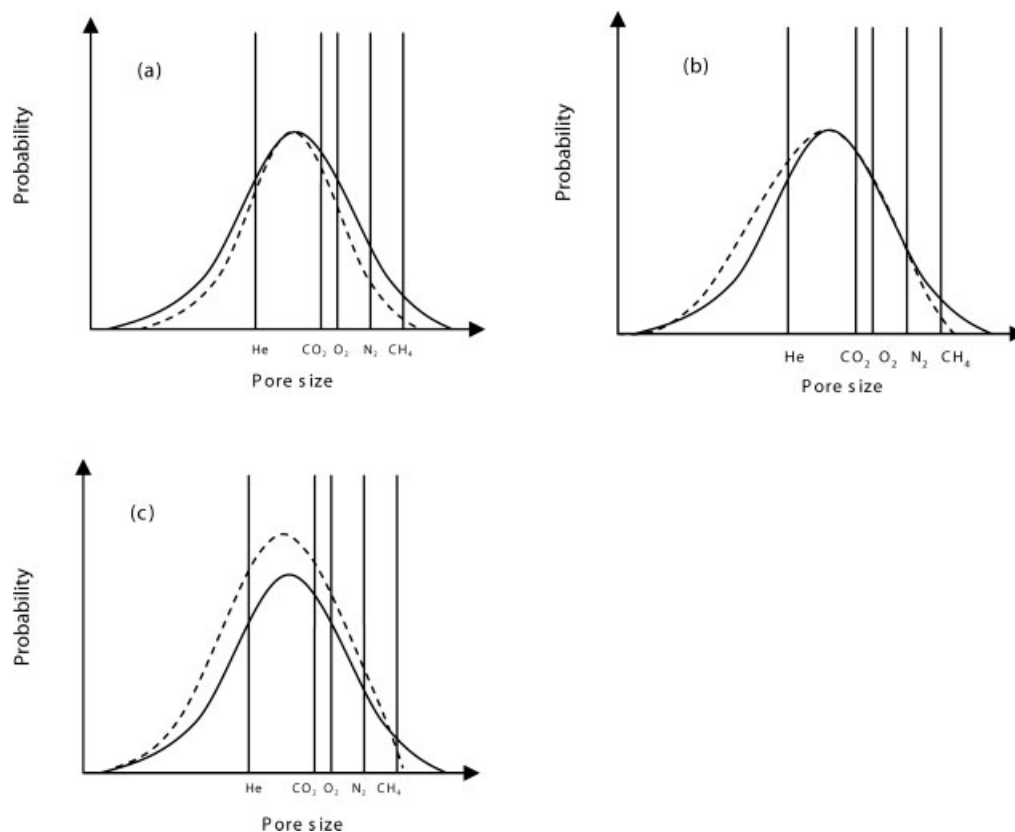


Figure 5 Cartoon of the evolution in the FFV and the free volume distribution of the polyimide Matrimid[®] resulting from H⁺ ion beam irradiation at increasing ion fluences where solid line represents the pristine Matrimid[®] and dashed line represents the H⁺ ion beam irradiated Matrimid[®]. (a) 6×10^{14} H⁺/cm², (b) 9×10^{14} H⁺/cm², (c) 2.0×10^{15} – 2.5×10^{15} H⁺/cm².

was a general decrease in the permeabilities for all gases studied with the smallest decrease for the smallest molecule (*i.e.*, He) and large decreases for other four molecules studied (*i.e.*, CO₂, O₂, N₂, and CH₄). The difference in the extent of decrease in permeability gave a rise to increases in permselectivities for the gas pairs with larger difference in the kinetic molecular diameter, such as He/CH₄ and He/N₂. This could reflect a decreased FFV with the narrowed free volume distribution induced by the irradiation, which is shown in Figure 5(a). The decreased FFV and the narrowed free volume distribution might result from an increased intersegmental or intrasegmental resistance to chain motions due to a high-level crosslinking between polymer chains that was induced by H⁺ ion beam irradiation. If crosslinking played a dominant role in modifying the microstructure of the Matrimid[®] selective layer compared with the formation of small molecular size defects due to release of some small molecules (such as CH₄ and H₂), there would be a slight decrease in the FFV with narrowing of free volume distribution. This is consistent with FTIR analysis of the evolution of chemical structure of Matrimid[®] induced by H⁺ ion beam irradiation at this stage. H⁺ ion beam irradiation of 6×10^{14} H⁺/cm² led to the degradations

of methyl CH₃ of branched structure with release of CH₄ and rapid degradation of benzophenone C=O without release of small molecules, which contributed to the high-level crosslinking in the irradiated Matrimid[®].²⁸

For H⁺ ion beam irradiation at intermediate ion fluence (9×10^{14} H⁺/cm²), there was a slight increase in permeability for the smallest molecule He and little change for medium size molecules with a large decrease in the permeability for the largest molecule CH₄ studied. This contributed to corresponding increases in permselectivities for most gas pairs. This could be indicative of a subtle change in the FFV with a slight shift of the free volume distribution to smaller size, which is illustrated in Figure 5(b). Among the five gases studied, only He could take advantage of this shift of the free volume distribution to small size so the permeability for He would be slightly increased. As reported in the first paper,²⁸ when ion fluence was increased to 9×10^{14} H⁺/cm², the level of crosslinking became much higher and simultaneously a larger number of small molecules were given off due to the degradation of many functional groups of Matrimid[®] induced by the irradiation. As discussed earlier, high crosslinking tends to increase the resistance to intersegmental

or intrasegmental mobility, which would result in the improved diffusivity selectivity. However, a large number of small molecules would generate a number of molecular size defects within polymer matrix, which tended to increase FFV. The counterbalance of the increase in FFV attributed to the formation of molecular size defects and the decrease in FFV due to crosslinking could result in an effective shift of free volume distribution to slightly small size. This would be expected to result in a slight increase in permeability for the smallest molecule He and little change for medium size molecules with a decrease in permeability for the largest molecule CH₄ studied. This variation in gas transport properties implied that the ion fluence of 9×10^{14} H⁺/cm² might be where a balance between the contribution from the formation of small molecular size defects and the formation of crosslinking to modifying the microstructure of Matrimid[®] composite membrane was achieved.

When ion fluence was increased to 2.0×10^{15} H⁺/cm² and beyond, considerably more release of small molecules such as CO occurred, with corresponding generation of a greater number of small molecular size defects. As a consequence of the formation of large number of molecular size defects, ion beam irradiation would increase the FFV. On the other hand, ion beam irradiation led to further crosslinking, which would decrease chain mobility. This might result in reduction in FFV at large molecule size, and hence narrow the free volume distribution, which would enable the polymer matrix to better discriminate penetrant.²⁶ For H⁺ ion beam irradiation in this range, a general increase in permeabilities with increases in permselectivities for most gas pairs reflected the increase in FFV and a slight shift of the free volume distribution toward smaller size, which is demonstrated in Figure 5(c). Therefore, it could be hypothesized that the formation of a great number of small size defects due to release of small molecules with different molecular size contributed fairly larger to the modification in gas transport properties relative to high-level crosslinking over this ion fluence range.

Effect of presence of polar carbonyl group on CO₂ sorption

As mentioned above, H⁺ ion beam irradiation over a full range of ion fluences resulted in reduction in permselectivities for both CO₂/O₂ and CO₂/N₂ gas pairs. The phenomenon cannot be explained simply from the viewpoint of the impact of microstructural evolution on diffusivity induced by ion beam irradiation. Diffusion of a penetrant through a polymer membrane is a size-selective process, which relies on chain packing and rigidity of the polymer. Therefore, considering only the diffusivity, CO₂ would be

expected to have slightly higher permeability than that of O₂. However, CO₂ is very condensable so it exhibits a higher solubility in typical polymers relative to O₂ or N₂. Therefore, the anomalous CO₂ separation behavior induced by the irradiation cannot be discussed solely in terms of the effect of ion beam irradiation on the diffusivity, and must include the impact of ion beam irradiation on the solubility coefficient.

The solubility coefficients of penetrants are typically determined by FFV, the distribution of FFV between packing defects and densely packed regions, penetrant condensability, and penetrant-polymer interactions. Since CO₂ is a highly condensable gas, it would be expected to exhibit large decrease in solubility with decrease in FFV following irradiation. However, the significant drop in CO₂ permeability may result from both changes in FFV and penetrant-polymer interactions. As reported in the literature,^{29,33,34} for a family of polymers, the presence of the polar carbonyl groups could promote favorable sorption of CO₂ in the polymer matrix. Therefore, a decrease in the presence of polar carbonyl group can contribute to a decrease in CO₂ sorption relative to base material.

As reported in the first paper,²⁷ at ion fluences of 6×10^{14} H⁺/cm², H⁺ ion beam irradiation resulted in considerable degradation of the benzophenone C=O, which contributed to the decrease in the presence of polar carbonyl groups relative to the pristine polymer. The reduction in the presence of polar carbonyl group might contribute to a large decrease in the sorption of CO₂ in the irradiated membrane, thus giving a rise to a greater decrease in the overall permeability for CO₂ than would be expected based on its kinetic diameter relative to O₂ or N₂ following irradiation at 6×10^{14} H⁺/cm². For ion beam irradiation at 9.0×10^{14} H⁺/cm² and beyond, both degradation of benzophenone C=O and imide carbonyl C=O resulted in much larger decrease in the presence of polar carbonyl group.²⁷ The large decrease in concentration of polar carbonyl group might greatly decrease sorption of CO₂ in the irradiated membrane. This would contribute to a smaller increase in the overall permeability for CO₂ than for O₂ or N₂. N⁺ ion beam irradiated Matrimid[®] composite membranes have been shown to exhibit similar anomalous behavior of CO₂/N₂ and CO₂/O₂ gas separation, which will be discussed in a later paper that compares the impact of irradiation of different ion type on the chemical structure, microstructure, and permeation properties of the polymer.

Trade-off curves for He/CH₄ and O₂/N₂

To compare gas transport properties of the irradiated Matrimid[®] composite membranes with the bulk

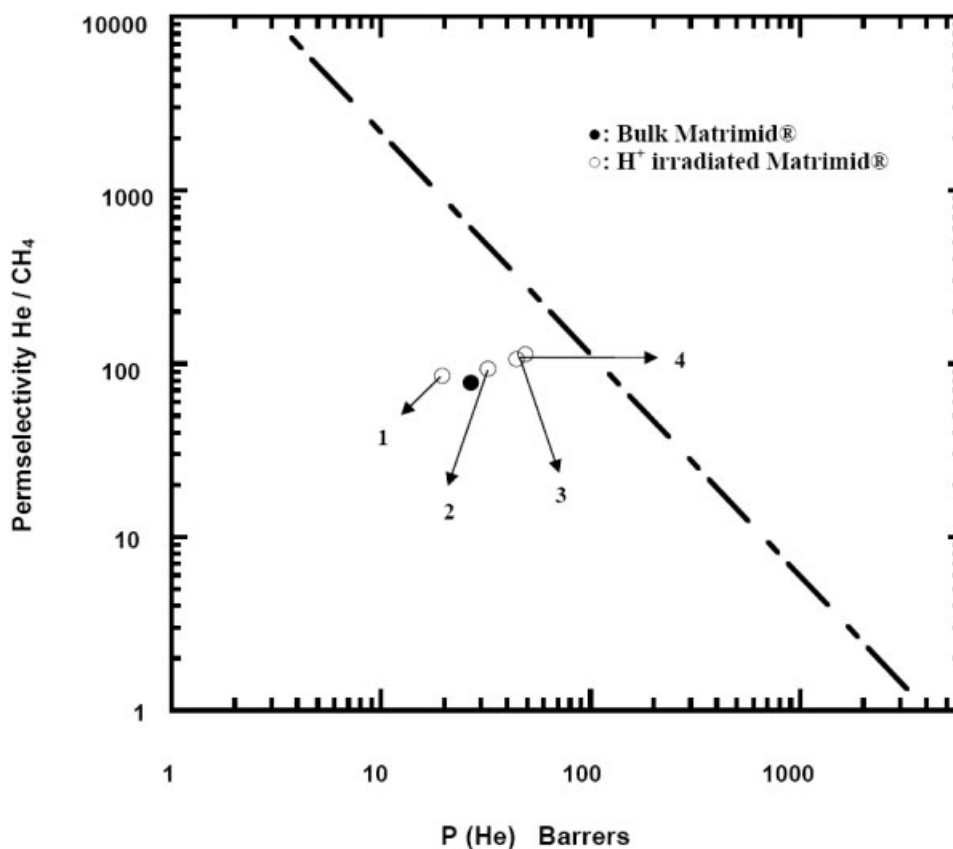


Figure 6 “Trade off” for the He/CH₄ separation system, the H⁺ ion beam irradiated Matrimid[®]-ceramic composite membranes (○) (1, 2, 3, and 4 for H⁺ ion fluence at 6.0×10^{14} , 9.0×10^{14} , 2.0×10^{15} , and 2.5×10^{15} H⁺/cm², respectively), and bulk Matrimid[®] (●). The dashed line represents the so-called “upper bound” of the performance trade-off reported by Robeson.

Matrimid[®], trade off curves for both He/CH₄ and O₂/N₂ gas pairs are shown in Figures 6 and 7, respectively. The He/CH₄ gas pair was chosen to illustrate the effect of irradiation on permeation properties of Matrimid[®] for the gas pair with large molecular size difference. In addition, the He/CH₄ system is a good model system for H₂/CH₄ for purification of H₂ streams. As shown in Figure 6, there was an improvement in He/CH₄ separation properties following H⁺ ion beam irradiation at 9×10^{14} H⁺/cm² and beyond. In addition, the H⁺ ion beam irradiated membrane at 2.5×10^{15} H⁺/cm² exhibited much better He/CH₄ separation properties relative to the bulk material, with an ideal permselectivity of 113 and a He estimated permeability of 49.0 Barrer approaching the upper bound proposed by Robeson. For O₂/N₂ gas separation system, as shown in Figure 7, when ion fluence was increased to 2.0×10^{15} H⁺/cm² and beyond, there was an increase in the O₂ permeability following the irradiation. Especially, at ion fluence of 2.5×10^{15} H⁺/cm², the H⁺ ion beam irradiated membrane exhibited much better O₂/N₂ separation properties than the bulk material. It showed an ideal permselectivity of 6.5 and an O₂ permeability of 3.8 Barrer, which was approaching

the O₂/N₂ upper bound as shown in Figure 7. Note that for both gas pairs best results were exhibited following irradiation at high ion fluence. These results implied that further increasing H⁺ ion fluence or using heavy ions (such as N⁺ ions) to irradiate Matrimid[®] may move He/CH₄ and O₂/N₂ separation properties of irradiated membrane beyond the upper bounds. Since irradiation at high ion fluences is time consuming so it is not commercially feasible. Therefore, N⁺ ions was used to irradiate the Matrimid[®]-ceramic composite membranes at higher energies, as will be discussed in subsequent paper.

CONCLUSIONS

The impact of H⁺ ion beam irradiation over a wide range of ion fluences (6×10^{14} H⁺/cm² to 2.5×10^{15} H⁺/cm²) on permeances and permselectivities of the Matrimid[®]-ceramic composite membranes for the five gases was reported. With the exception of H⁺ ion beam irradiation at the low ion fluences used in this study, there was an increase in permeability for most gases studied (e.g., He, CO₂, O₂, and N₂) following H⁺ ion beam irradiation. The small mole-

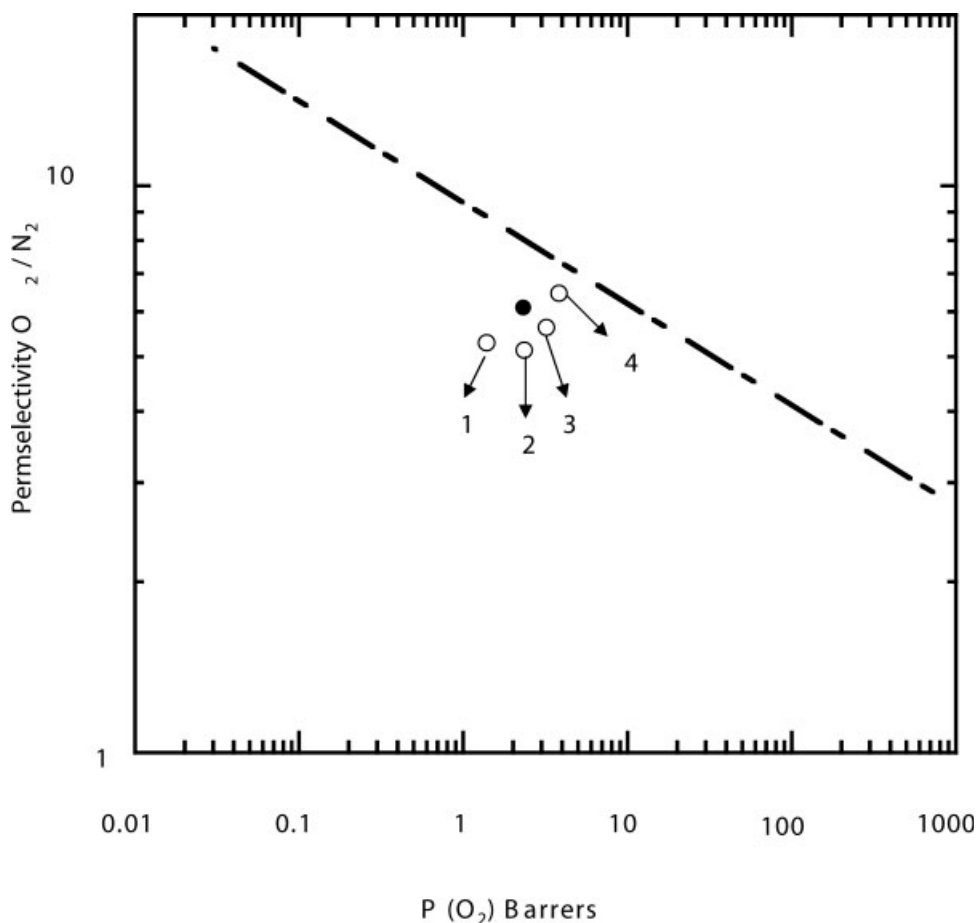


Figure 7 “Trade off” for the O₂/N₂ separation system, the H⁺ ion beam irradiated Matrimid[®]-ceramic composite membranes (○) (1, 2, 3, and 4 for H⁺ ion fluence at 6.0×10^{14} , 9.0×10^{14} , 2.0×10^{15} , and 2.5×10^{15} H⁺/cm², respectively), and the bulk Matrimid[®] (●). The dashed line represents the so-called “upper bound” of the performance trade off reported by Robeson.

cules (e.g., He and O₂) exhibited larger increase so there was an overall increase in selectivity for most gas pairs (He/N₂, He/CH₄, CO₂/CH₄, and O₂/N₂). Additionally, H⁺ ion beam irradiation at higher ion fluence significantly improved He/CH₄ and O₂/N₂ separation performances. The pristine Matrimid[®] exhibits gas transport properties well below the upper-bound of the trade-off between permeability and permselectivity proposed by Robeson. Following irradiation at high ion fluences, the Matrimid[®] approached this upper-bound.

The evolution in gas transport properties was discussed in terms of evolution in chemical structure and microstructure. While crosslinking appeared to dominate the modification of microstructure induced by H⁺ ion beam irradiation at the lowest ion fluence studied, the formation of small molecular size defects due to release of small molecules during irradiation became increasingly important at higher ion fluence. Moreover, H⁺ ion beam irradiation reduced the presence of polar carbonyl group of Matrimid[®], which might result in the decrease in sorption of

CO₂ in the irradiated Matrimid[®]. This would result in smaller increase in CO₂ permeability relative to other small molecules.

The authors thank Dr. Peter Simpson of the University of Western Ontario for providing irradiation of the samples.

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