Ion Beam Irradiation Effect on Gas Permeation Properties of Polyimide Films

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SYNOPSIS

This study deals with the ion beam irradiation effect on gas permeation properties of polyimide films. 2 MeV α, 500 keV, and 170 keV N^+ ions were used for modifying the membranes. It was found that there are two different effects according to the implantation dose. In the case of small-dose irradiation, ion implantation causes a raise of permeability both for CH_4 and H_2. When the implantation dose reaches a more important level, the implanted membranes have at the same time high permselectivity for H_2/CH_4 and high permeability for H_2. The relationships between the permeation properties and microstructure of the films are also discussed. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The study of gas permeation began during the '70s. In the past thirty years synthetic chemists provided a sophisticated array of polymers, giving a grand set of membrane processes and products.[1,2] It is well known that the chemical segment composition and the steric relationships between the segmental repeat units of polymeric membrances are determinant factors of gas permeability and gas permselectivity. Unfortunately as a general rule,[1] polymers with higher selectivities usually have lower permeabilities and those with higher permeabilities have lower selectivities. To obtain a polymeric membrane having at the same time high permselectivity and high permeability is always the aim of many synthetic chemists and membrane scientists. For a few years, the membranes obtained from polyimides have been raising a special interest for gas separation because they present not only a good resistance to temperature and chemical attacks but also a more interesting permeability/selectivity ratio than most polymers.[3-5] Especially the 6FDA-based polyimides have systematically higher selectivity at an equivalent value of permeability as compared to other polymers, showing a fundamental deviation from the conventional relationship between permeability and permselectivity. Several investigations have been undertaken in order to explain these particular gas permeation properties.[6,7]

Recently we have studied diffusion of iodine into polyimide films modified by ion bombardment.[8] Iodine atoms diffuse normally into the Kapton film up to 3 μm depth, according to Fick's laws, after keeping the films in iodine atmosphere at 45°C for 64 h. But in the case of small-dose implantations there are many more iodine atoms located at the energy deposition range of the ion beam, while there are few iodine atoms beyond this range. In the case of high-dose implantation, the ion beam modified layer becomes a stopping layer so iodine atoms can not diffuse into the Kapton film. This is a very interesting phenomenon and excites us to study ion beam irradiation effect on gas permeation properties.

In this work the authors present their preliminary research results concerning ion beam effects on gas permeation properties of polyimide films.

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EXPERIMENTAL

Materials

The polyimide films used for this study, prepared by Institut Français du Petrole (I.F.P.), were prepared by polycondensation from hexafluorodianhydride (6FDA) and a meta-phenylene diamine (mPDA) reaction. The polyimide was synthesized in metacresol or 1-methyl-2-pyrrolidone (NMP) at a temperature close to 200°C. The polymer was precipitated and washed with a non-solvent such as ethanol or water. After being crushed, the obtained powder still contains about 5–6% residual solvent. Cast polyimide films were prepared by phase inversion process with NMP or metacresol solvent, then annealed for 4 h at 180°C or 300°C under vacuum. The mean films' thickness varies from 15 μm to 39 μm.

Ion Implantation

Ion implantation was performed at a Van de Graaf accelerator for 2 MeV He^+ ion implantation and for 500 keV N^+ ion implantation. The 170 keV N^+ ion implantation was performed at an ion implantor. Small ion beam current densities were used (from 0.1 $\mu A/cm^2$ to 0.3 $\mu A/cm^2$) in order to avoid heating the samples during ion implantation. All implantations were done at room temperature and the incident ion beam was always perpendicular to the surface of the samples. The time required to perform an implantation (t) depends both on implantation fluence and on ion beam current density, and can be determined by a simple formula: $t = e\Phi/I$, where e is the charge of proton, Φ is the implantation fluence, and I is the beam current density. The thickness of ion beam modified layer was determined as ($Rp + \Delta Rp$) by TRIM'91 code[9] and was confirmed by RBS measurement. Tables I and II provide detailed ion implantation conditions.

Table I Ion Implantation Conditions for Small Dose Irradiation

Sample	Thickness (μm)	Ion Implantation Conditions (2 MeV α implantation, two faces of the film were implanted.)
Sample 1	22.5	Implantation fluence: 2 $\times 10^{13}/cm^2$, 0.1 $\mu A/cm^2$, 32 s 18 μm, i.e., 80% of total thickness of the film was modified by implantation.
Sample 2	29	Implantation fluence: 4 $\times 10^{13}/cm^2$, 0.13 $\mu A/cm^2$, 49 s 18 μm, i.e., 62% of total thickness of the film was modified by implantation.
Sample 3	18	Implantation fluence: 3.6 $\times 10^{14}/cm^2$, 0.1 $\mu A/cm^2$; 9 min, 36 s 18 μm, i.e., 100% of total thickness of the film was modified by implantation.

Table II Ion Implantation Conditions for Strong Dose Irradiation

Sample	Thickness (μm)	Ion Implantation Conditions
Sample 4	30	170 keV N^+ implantation, two faces of the film were implanted. Implantation fluence: 2 $\times 10^{15}/cm^2$, 0.3 $\mu A/cm^2$; 17 min, 48 s 1.12 μm, i.e., 3.7% of total thickness of the film was modified by implantation.
Sample 5	38.5	500 keV N^+ implantation, two faces of the film were implanted. 2.4 μm, i.e., 6.2% of total thickness of the film was modified by implantation. First implantation fluence: 1.5 $\times 10^{15}/cm^2$, 0.3 $\mu A/cm^2$; 13 min, 21 s Second implantation fluence: 3.5 $\times 10^{15}/cm^2$, 0.3 $\mu A/cm^2$; 31 minutes, 9 seconds; total dose: 5 $\times 10^{15}/cm^2$ Third implantation fluence: 4 $\times 10^{15}/cm^2$, 0.3 $\mu A/cm^2$; 35 min, 36 s; total dose; 9 $\times 10^{15}/cm^2$

Permeation Measurements

The permeation cell is made up of two compartments (upstream and downstream) which are separated by the polyimide membrane to be measured. The cell is thermostated in a chamber maintained at 20°C. A preliminary vacuum desorption is needed in order to ensure that the static vacuum pressure changes in the downstream compartment will be much smaller than pressure changes due to permeation. Then a 3-bar pressure is introduced in the upstream part. The pressure variation in the downstream volume is measured by a Datametrics pressure sensor and is very low compared to the pressure in the upstream part. By plotting the measured pressure versus time, the study-state line enables the calculation of both the permeability coefficient (P_e) from the slope and the diffusion coefficient D by extrapolation on the time axis, which gives the time-lag Θ. The permeability coefficient P_e is expressed in Barrers (10^{-10} $cm^3 cm/cm^2 \cdot s \cdot cm\,Hg$) and the diffusion coefficient D in cm^2/s. Two permeation measurements

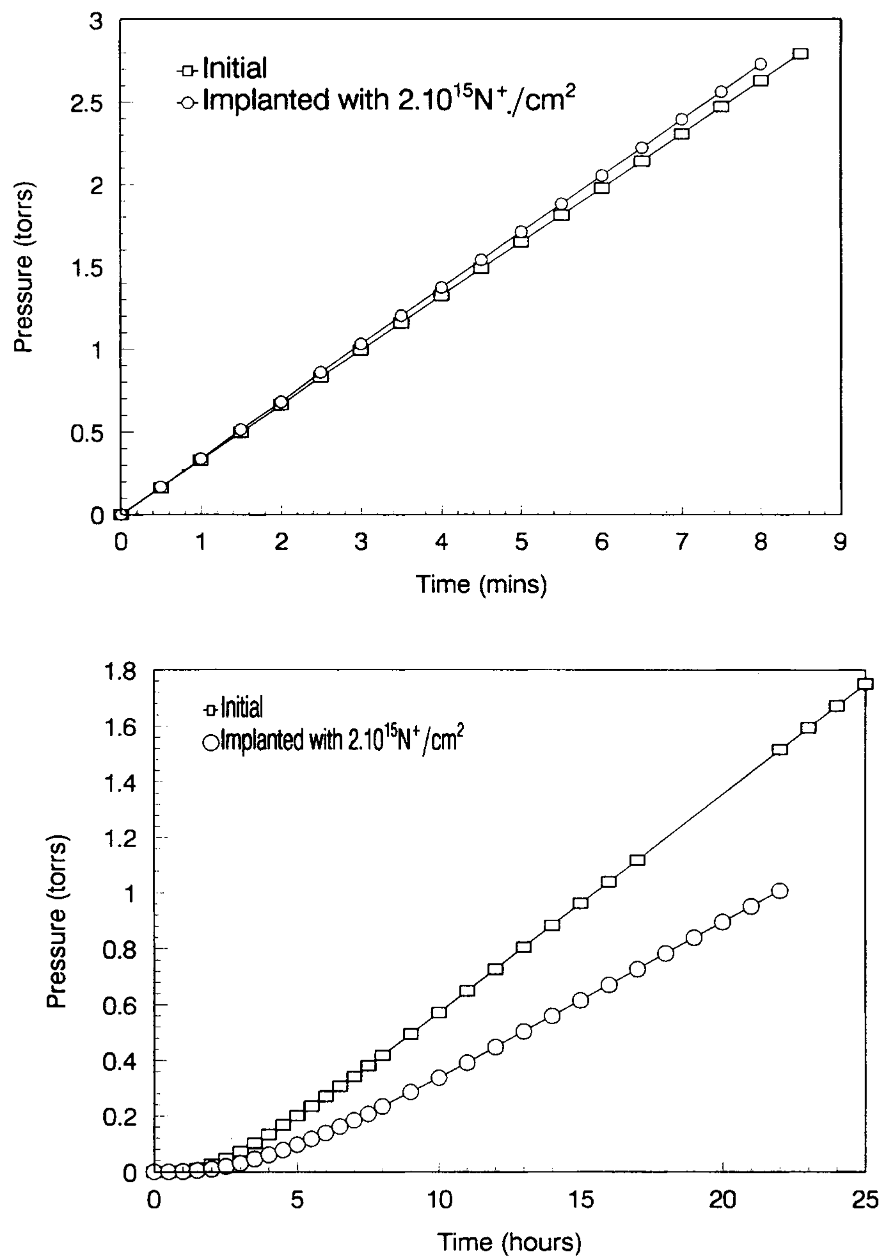

Figure 1 Typical permeation curves of ion implanted polyimide film for H_2 (a) and for CH_4 (b). The samples were implanted with 170 keV N^+ ions.

(before and after irradiation) were performed for each sample.

RESULTS AND DISCUSSION

Figure 1(a) and 1(b) show typical curves of $P_e = f(t)$. For methane, the time-lag allows a fine calculation of D. For H_2, the time-lag is always very short (< 15 seconds) and it can only be ensured, according to the films thicknesses, that D is $\geq 10^{-7}$ cm^2/s.

According to the results of our previous study on iodine diffusion into the ion beam modified polyimide films, we performed the gas permeation study of the implanted polyimide in two steps: the first step is small-dose irradiation effect, and the second is strong-dose irradiation effect.

Small-Dose Implantation Effect

Limited by the maximum available energy of the Van de Graaf accelerator and also by the available membranes, only one sample was irradiated throughout the whole thickness. The other membranes were partially irradiated, so the implanted samples present a sandwich structure. As schematically indicated in Figure 2, the samples were composed of three layers: the two outside layers modified by ion beams with the same implantation conditions, and a middle layer not affected by the ion beam irradiation. According to Fick's laws, the gas flux J through the membrane, which is identical in the different interfaces of the film, can be expressed as:

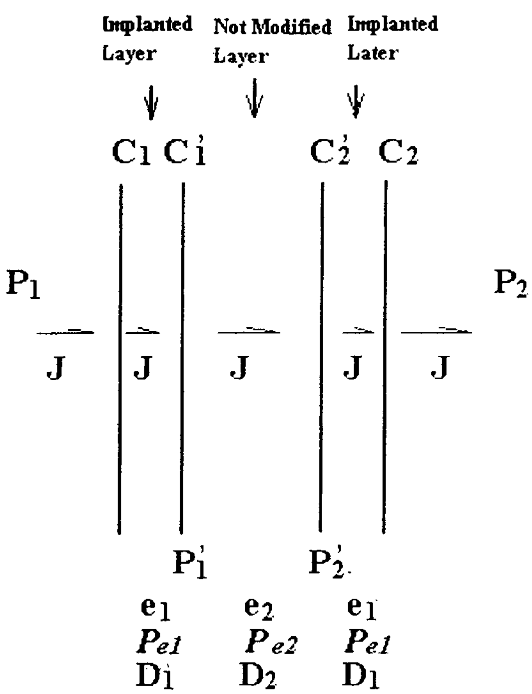

Figure 2 Structural schema of the ion beam irradiated polyimide membrane. Two outside layers are ion beam modified layers and middle layer was the core part which is not affected by ion beam irradiation.

$$J = \frac{-D_1(c'_1 - c_1)}{e_1} = \frac{-D_2(c'_2 - c'_1)}{e_2} = \frac{-D_1(c_2 - c'_2)}{e_1} = \frac{-(c_2 - c_1)D_{app}}{e_2 + 2e_1} \quad (1)$$

$$J = \frac{P_{e1}}{e_1}(P_1 - P'_1) = \frac{P_{e2}}{e_2}(P'_1 - P'_2) = \frac{P_{e1}}{e_1}(P'_2 - P_2) = \frac{P_{eapp}}{2e_1 + e_2}(P_1 - P_2) \quad (2)$$

where e_1, P_{e1}, D_1 are, respectively, the thickness, permeability, and diffusion coefficient of the modified layers. e_2, P_{e2}, and D_2 are, respectively, the thickness, permeability and diffusion coefficient of the unmodified layer. c_1, c_2, c'_1, c'_2, P_1, P_2, P'_1, P'_2, are the gas concentrations and gas pressures at different faces and interfaces indicated in Figure 2. D_{app} and P_{eapp} are the measured diffusion coefficient and the measured permeability of the sandwich structure, respectively. After resolving these two equations we obtain the following formulas:

$$\left(\frac{2e_1 + e_2}{P_{eapp}}\right) = \frac{2e_1}{P_{e1}} + \frac{e_2}{P_{e2}} \quad (3)$$

$$\left(\frac{2e_1 + e_2}{D_{app}}\right) = \frac{2e_1}{D_1} + \frac{e_2}{D_2} \quad (4)$$

Table III shows the principal permeation results of the polyimides membranes before and after ion implantation.

From equations (3) and (4) and the experimental values, i.e., e_1, e_2, P_{e2}, and P_{eapp}, we can obtain the permeability P_{e1} and diffusion coefficient D_1 of the ion beam modified layer which are mentioned in Table III. Figure 3 shows the evolution of gas permeation properties of the ion beam irradiated polyimide membrane as a function of the irradiation dose in the small-dose irradiation step. In this step permeabilities for both CH_4 and H_2 increase with the ion implantation dose, but the permeability for CH_4 increases more rapidly than that for H_2. So the permselectivity H_2/CH_4 decreases with the dose. At the dose of $3.6 \times 10^{14}/cm^2$, the permeability for CH_4 is greater than the initial value by a factor of 48; meanwhile, the permeability for H_2 is only 9.9 times more important than the initial value. This result is very much like the results obtained by K. Schaupert et al.[10] In their studies, the permeability of a uranium ion-irradiated region of polyethyleneterephtalate (PETP) samples for neon, oxygen, argon, carbon dioxide, and water is enhanced by factors of 60 to 290. The increase of gas permeability is comprehensive. As indicated by the different authors,[10,11,12] with small-dose irradiation the polymer films are gradually damaged through breakup of chemical bonding, reticulation, and formation of small molecules and free radicals. Hence there are gas emissions and formation of the stable defects. Thus the ion beam damaged layer is considered as a region of reduced density.[10] One could expect that after the small-dose irradiation the mean dimension of free volume and its density might become much more important than before irradiation. This structural change might not only give rise to the interesting phenomena of iodine diffusion into small-dose irradiated polyimide film but also cause the new behaviors of the permeation properties of irradiated polyimide films.

Strong-Dose Implantation Effect

Shown in Table IV are the permeation results of the polyimide membrane before and after implantation in the case of strong-dose implantation. The modified layer presents only 3.7% of total thickness for Sample 4 and only 6.2% for Sample 5. But for Sample 4 the permeability for CH_4 after implantation has only 0.705 of its initial value; meanwhile, the permeability for H_2 has 1.038 of its initial value. The permselectivity H_2/CH_4 raises from 249 of its initial value to 367 of its modified value, presenting an augmentation of 47%. If we apply eq. (3) to this case, the permeability of modified layer for CH_4 is 0.0128 Barrers and that for H_2 is 508 Barrers. The permselectivity H_2/CH_4 of the modified layer reaches almost 40,000. This is a very interesting result, especially if the process can be applied to asymmetrical membranes with thin dense layers on microporous supports.

Shown in Figure 4 is a representation of the relation between permeability for H_2 and permselectivity H_2/CH_4 of Sample 5 for different implantation

Table III Small Dose Irradiation Results

Sample	Thickness (μm)	Permeability for CH_4 Before Irradiation P_{e2} (CH_4) (Barrers)	Permeability for H_2 Before Irradiation P_{e2} (H_2) (Barrers)	Selectivity Before Irradiation $\alpha = \frac{P_{e2}(H_2)}{P_{e2}(CH_4)}$	Measured Permeability for CH_4 After Irradiation P_{eapp} (CH_4) (Barrers)	Measured Permeability for H_2 After Irradiation P_{eapp} (H_2) (Barrers)	Selectivity After Irradiation $\alpha = P_{eapp}$ (CH_4)	Calculated Permeability of Modified Layer for CH_4 P_{e1} (CH_4) (Barrers)	Calculated Permeability of Modified Layer for H_2 P_{e1} (H_2) (Barrers)	Calculated Selectivity of Modified Layer $\alpha = P_{e1}$ (CH_4)
Sample 1	22.5	0.132	29.7	225	0.1706	36.55	214.2	0.1841	38.79	210.7
Sample 2	29	0.155	39	251	0.238	51	214	0.3538	62.81	177.5
Sample 3	18	0.13	25	192	6.37	273.4	42.9	6.37	273.4	42.9

Table IV Principal Permeation Results in the Case of Strong Dose Irradiation

Sample & Implantation	Thickness (μm)	P_{e2} (CH_4)	P_{e2} (H_2)	$\alpha = \frac{P_{e2}(H_2)}{P_{e2}(CH_4)}$	P_{e1} (CH_4)	P_{e1} (H_2)	$\alpha = \frac{P_{e1}(H_2)}{P_{e1}(CH_4)}$
Sample 4							
2×10^{15} N^+/cm^2	30	0.156	38.9	249	0.110	40.4	367
Sample 5							
1.5×10^{15} N^+/cm^2	38.5	0.170	35.2	207	0.149	38.8	260
5×10^{15} N^+/cm^2					0.095	37.8	397.9
9×10^{15} N^+/cm^2					4	22	5.5

dose. An evident deviation from the general rule, which is that polymers with higher selectivities usually have lower permeabilities and those with higher permeabilities have lower selectivities, can be observed. This deviation is more important than those which can be obtained by using other physical or chemical methods.[1,7]

If we follow the structural evolution of similar polyimide film under ion beam irradiation, this phenomenon could be understood, although further studies are needed. In fact, when irradiation dose reaches $1 \times 10^{15}/cm^2$, the irradiated polyimide Kapton film has undergone a complete structural change and has lost almost all its characteristic absorptions.[13] A new type of material, consisting of small graphite-like grains embedded in amorphous carbon, formed.[11,14,15] The mean dimension of the free volume in the irradiated layer may become much smaller than the initial values and the density of the free volume maintain a high level. This is perhaps the reason why the implanted layer has at the same time high permselectivity and high permeability for H_2 but not for CH_4.

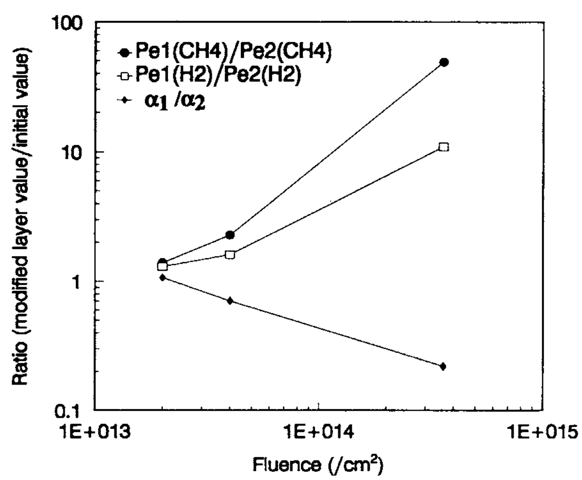

Figure 3 Permeation properties evolution of the polyimide samples as function of irradiation dose. Pem/Pei means the ratio of permeability after irradiation over the initial one. Sm/Si means the ratio of permselectivity after irradiation over the initial one.

CONCLUSION

Ion beam irradiation can greatly alter the gas permeation properties of the polyimide membrane. In the case of small-dose irradiation, ion implantation can raise the permeability for both CH_4 and H_2. In the case of strong-dose irradiation, ion bombardment causes a serious diminution of the permeability for CH_4 and an increase of the permeability for H_2, so the membranes thus modified have at the same time higher permselectivity and high permeability. These effects are related to the structural changes during ion irradiation.

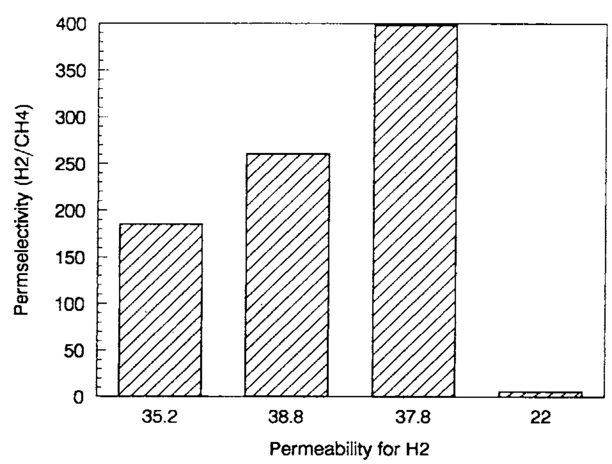

Figure 4 Relationship between permeability for H_2 and permselectivity (H_2/CH_4) of Sample 5 for different implantation dose.

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