

# Gas Permeability and Permselectivity of Photochemically Crosslinked Copolyimides

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**ABSTRACT:** A series of copolyimides were prepared from 2,4,6-trimethyl-1,3-phenylenediamines (3MPDA), 3,3',4,4'-benzophenone tetracarboxyl dianhydride (BTDA), and pyromellitic dianhydride (PMDA). Modification of the copolyimides by ultraviolet irradiation were carried out. Gas permeabilities of H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> through the copolyimides and photochemically crosslinked copolyimides were measured at temperatures from 30 to 90°C. The relationships between gas permeabilities and temperature are in agreement with the Arrhenius equation. The structure of photochemically crosslinked copolyimides were characterized by Fourier transform infrared and gel measurement methods. Linear relationships between both log *P* and *E<sub>p</sub>*, and the volume fraction of PMDA–3MPDA exist. Photochemically crosslinking modification result in a decrease in gas permeability and an increase in *E<sub>p</sub>* and α(H<sub>2</sub>/N<sub>2</sub>) for all the copolyimides. For H<sub>2</sub>/N<sub>2</sub> separation, photochemically crosslinked copolyimides are of higher gas permeabilities and permselectivities simultaneously than normal polyimides. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 73: 521–526, 1999

**Key words:** copolyimide; ultraviolet light irradiation; crosslinking; gas separation

## INTRODUCTION

Polyimides as gas separation material have attracted much attention because of their gas separation properties and excellent physical properties. In order to prepare gas separation membrane with both high gas permeability and permselectivity, a series of polyimides with systematically changed chemical structure were synthesized, and the effect of the structure on the gas permeation properties were investigated.<sup>1–9</sup> Recently, a series of highly permeable polyimides were obtained by introduction of bulky substitu-

tion groups to the backbone of polyimides (such as trifluoromethyl, methyl, halogen, etc.), but their gas permselectivities are low, especially for the separation of gases with large difference in molecular size and/or shape, such as H<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/CO, H<sub>2</sub>/CH<sub>4</sub>, and CO<sub>2</sub>/CH<sub>4</sub>.<sup>6,10–12</sup>

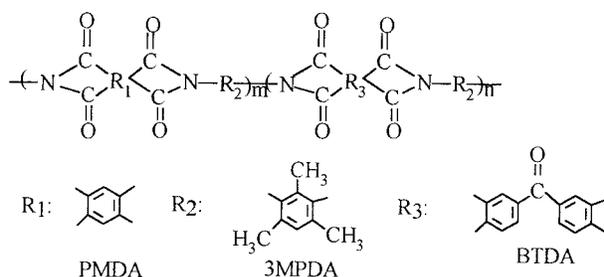
On the other hand, gas permselectivity of polyimides prepared from 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) could be improved effectively by the photochemically crosslinking method, and gas permeation properties of photochemically crosslinked polyimides could be further modified by copolymerization.<sup>10,11,13–15</sup> Gas permeabilities of polyimide prepared from pyromellitic dianhydride (PMDA) and 2,4,6-trimethyl-1,3-phenylenediamines (3MPDA) are higher than these of polyimide from BTDA

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**Figure 1** Chemical structure of copolyimides.

and 3MPDA.<sup>12</sup> Hence, it is expected that gas permeabilities of photochemically crosslinked copolyimides from PMDA, BTDA, and 3MPDA would be higher than that of BTDA-3MPDA; meanwhile, high gas permselectivity could be maintained by photocrosslinking modification, so a series of copolyimides were prepared from 3MPDA, BTDA, and PMDA, then modified by ultraviolet (UV) irradiation. The relationships between the structure and gas permeation properties were investigated.

## EXPERIMENTAL

### Materials

The chemical structures and components of copolyimides are given Figure 1 and Table I, respectively.

The copolyimides were synthesized by condensation of 3MPDA with the mixture of BTDA and PMDA in molar ratio, as listed in Table I, in *N*-methyl-2-pyrrolidone (NMP) for 24 h, and by chemical imidization with acetic anhydride/pyridine for 6 h under nitrogen at ambient temperature. The polymers were recovered by precipitation in methanol and purified by reprecipitation from dimethylacetamide (DMA) solution. The chemical structures of the polyimides were confirmed by Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) analysis.

### Preparation of Samples

Membranes were prepared by casting the 5 wt % solution of copolyimides in DMF at 50°C onto an optical flat-glass plate to remove most of the solvent, then drying at 200°C under vacuum for 48 h in order to remove residual solvent. The membranes were stripped from the glass plate and dried under vacuum at 100°C for 24 h. The thickness was around 30 μm. Photochemically

crosslinking modification was carried out by placing the films at a distance of 8 cm from the UV light source (high mercury lamp, type PRK-II, 375 W, with a water-circulated cylindrical quartz filter). The extent of crosslinking was controlled by the irradiation time.

### Characterization of the Extent of Photocrosslinking

The extent of crosslinking was followed by FTIR, performed on FTS-TMX (U.S.A.) using 2-μm-thickness films. In FTIR spectra, the peaks at 1678 and 863 cm<sup>-1</sup> are attributed to benzophenone carbonyl group and the phenyl ring unit, respectively. The strength of the former decreased, but the latter kept constant with the progress of crosslinking. Therefore, the percentage of reacted benzophenone unit percentage [C=O%(*r*)], which implies the crosslinking degree, can be calculated by eq. (1), as follows:

$$\text{C=O}\%(r) = 1 - \frac{(I_{1678}/I_{863})_t}{(I_{1678}/I_{863})_o} \quad (1)$$

where  $I_{1678}$  and  $I_{863}$  are the strengths of the peaks at 1678 and 863 cm<sup>-1</sup>, respectively. The  $(I_{1678}/I_{863})_t$  is for UV-irradiated samples, and  $(I_{1678}/I_{863})_o$  is for unirradiated samples.

The gel fraction of samples in DMF were determined based on the ratio of the weight of the sample insoluble in DMF to the weight of the sample. Unirradiated samples dissolved completely in DMF.

### Gas Permeability Measurement

Permeability measurements of membrane samples were performed on a low vacuum manometric apparatus<sup>16</sup> at temperatures from 30 to 90°C for hydrogen, oxygen, and nitrogen, whose purities were higher than 99.999%.

**Table I** Chemical Compositions of Copolyimides

Copolyimides	<i>m</i> : <i>n</i> (mol) <sup>a</sup>
PB3070	3 : 7
PB5050	5 : 5
PB8020	8 : 2
PB9010	9 : 1

<sup>a</sup> The same as in Figure 1.

**Table II Gas Permeation Properties of Copolyimides Modified by UV Irradiation for Various Times at 30°C**

Polyimide	Time (h) <sup>a</sup>	P(H <sub>2</sub> ) <sup>b</sup>	P(O <sub>2</sub> ) <sup>b</sup>	α(H <sub>2</sub> /N <sub>2</sub> )	α(O <sub>2</sub> /N <sub>2</sub> )	E <sub>p</sub> (H <sub>2</sub> ) <sup>c</sup>	E <sub>p</sub> (O <sub>2</sub> ) <sup>c</sup>	E <sub>p</sub> (N <sub>2</sub> ) <sup>c</sup>
PMDA–3MPDA	0	235.0	36.3	28	4.3	4.7	6.0	10.2
PB9010	0	156.0	22.3	30	4.3	5.0	6.5	11.0
PB9010	2	95.0	4.35	125	5.7	7.7	16.0	21.0
PB9010	6	41.0	0.67	410	6.7	14.0	22.0	25.0
PB8020	0	162.0	21.4	33	4.3	5.4	6.8	11.0
PB8020	2	119.0	9.10	82	6.3	8.9	12.0	22.0
PB8020	10	21.2	0.21	731	7.2	16.0	23.0	27.0
PB5050	0	92.6	12.1	37	4.9	7.1	8.60	14.0
PB5050	2	83.8	7.40	65	5.6	10.0	13.0	18.0
PB5050	6	25.7	0.40	696	11.0	17.0	23.0	30.0
PB3070	0	78.8	9.42	40	4.9	8.4	11.0	16.0
PB3070	2	38.0	1.15	368	11.0	12.0	21.0	31.0
BTDA–3MPDA	0	46.4	5.00	47	5.0	9.8	14.0	19.0
BTDA–3MPDA	2	20.6	0.84	268	11.0	15.0	24.0	— <sup>d</sup>

<sup>a</sup> UV irradiation time.<sup>b</sup> In barrer.<sup>c</sup> In kJ/mol.<sup>d</sup> There were an abrupt slope changes in Arrhenius plots of gas permeability of nitrogen versus temperature for this sample.<sup>13</sup>

## RESULTS AND DISCUSSION

### Gas Permeabilities of Copolyimides

The gas permeabilities and permselectivities of copolyimides, P(H<sub>2</sub>) and P(O<sub>2</sub>), and α(H<sub>2</sub>/N<sub>2</sub>) and α(O<sub>2</sub>/N<sub>2</sub>) are given in Table II. The relationships between gas permeabilities and temperature are in agreement with the Arrhenius equation; the apparent activation energies for the gas permeation were calculated and are listed in Table II. Compared to BTDA–3MPDA, higher methyl substitution density in the backbone of PMDA–3MPDA results in large openness of the polymer matrix, therefore leading to higher gas permeabilities, lower gas permselectivities, and apparent activation energies for gas permeation.

The results listed in Table II show that as the PMDA content in copolyimides increases, the gas permeabilities increase. The relationships between the gas permeabilities *P* and the compositions of copolyimides shown in Figure 2 are in agreement with eq. (2), proposed by D. R. Paul,<sup>17</sup> as follows:

$$\log P = \Phi_1 \log P_1 + \Phi_2 \log P_2 \quad (2)$$

where Φ<sub>1</sub> and Φ<sub>2</sub> are the volume fraction, which were determined based on the density of PMDA–3MPDA (1.267 g/mL) and BTDA–3MPDA (1.268 g/mL),<sup>11</sup> and *P*<sub>1</sub> and *P*<sub>2</sub> are the gas permeabilities

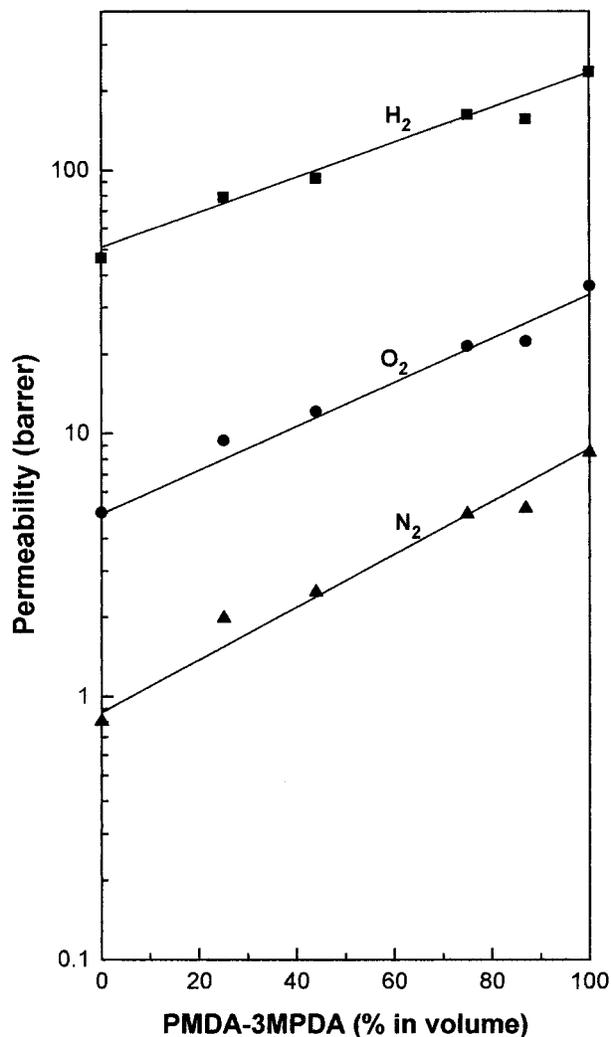
of PMDA–3MPDA and BTDA–3MPDA, respectively. In addition, the relationships between the apparent activation energies *E<sub>p</sub>* and the compositions of the copolyimides can be described by eq. (3), as shown in Figure 3:

$$E_p = \Phi_1 E_{p1} + \Phi_2 E_{p2} \quad (3)$$

where Φ<sub>1</sub> and Φ<sub>2</sub> are the same as in eq. (2) and *E<sub>p1</sub>* and *E<sub>p2</sub>* are the apparent activation energies for gas permeation of PMDA–3MPDA and BTDA–3MPDA, respectively.

### Characterization of Photochemically Crosslinked Copolyimides

The crosslinking structure of UV-irradiated copolyimides was characterized, and the results are listed in Table III. The content of crosslinked benzophenone unit [C=O%(*r*)] and gel content (gel %) were too low to be detected in UV-irradiated PB9010 and PB8020, even with 6–10 h of irradiation, because only benzophenone groups in BTDA can form crosslinking photochemically. When PB5050 and PB3070 were irradiated by UV light, C=O%(*r*) and gel % could be detected, and the results are listed in Table III. The longer irradiation time results in higher C=O%(*r*) and gel % in PB5050, the same results obtained for BTDA–3MPDA.<sup>13</sup>

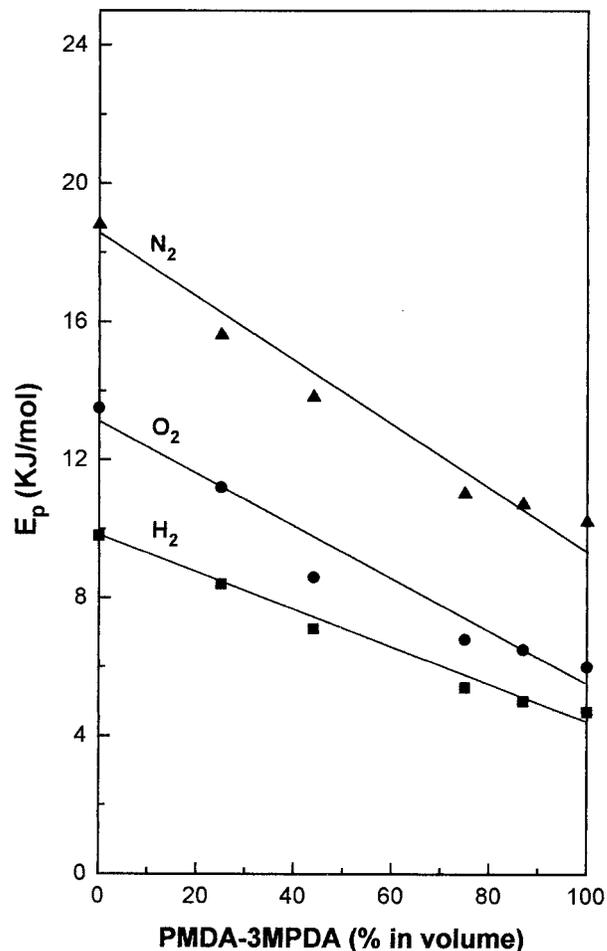


**Figure 2** Relationships between gas permeabilities and volume compositions of copolyimides.

#### Gas Permeation Properties of Photochemically Crosslinked Copolyimides

The gas permeabilities and permselectivities and the apparent activation energies for gas permeation of the photochemically crosslinked copolyimides are given in Table II.

UV irradiation of the copolyimides lower their gas permeabilities and increase gas permselectivities and apparent activation energies for gas permeation, as shown in Table II, although the change in the chemical structure of UV-irradiated PB9010 and PB8020 could not be detected by FTIR and the gel measurement method, as shown in Table III. By comparing the sample of BTDA-3MPDA after being irradiated for 2 h with that of PB9010 for 6 h,



**Figure 3** Relationships between apparent activation energies for gas permeation through copolyimides and volume compositions of copolyimides.

PB8020 for 10 h, and PB3070 for 2 h, the results listed in Table II show that the latter ones are of higher gas permeabilities for hydrogen and

**Table III** Characterization of Photochemically Crosslinked Copolyimides

Polyimide	Time (h) <sup>a</sup>	C=O%(r) <sup>b</sup>	Gel % <sup>c</sup>
PB9010	2	0	0
PB9010	6	0	0
PB8020	2	0	0
PB8020	10	0	0
PB5050	2	10	13
PB5050	6	27	28
PB3070	2	12	74

<sup>a</sup> UV irradiation time.

<sup>b</sup> Photochemically crosslinked benzophenone unit percentage measured by FTIR.

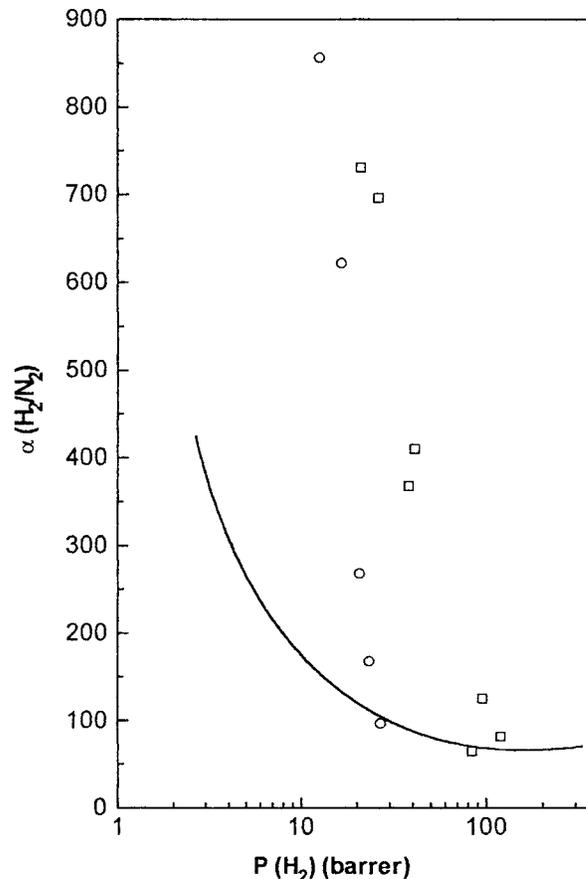
<sup>c</sup> Gel fraction.

gas permselectivities for  $H_2/N_2$ . The permeation of gas molecules through the polymer matrix must be accompanied by the motion of several segments of the polymer. The larger the gas molecules are, the longer the intrasegment involved in the motion of gas molecules is. The crosslinking decreases the mobility of intrasegment and the openness of the polymer matrix, leading to a decrease in gas permeabilities, especially for the gases with large size, such as  $O_2$  and  $N_2$ . Therefore, the crosslinked polyimides are of high gas permselectivities if the change in ratio of gas solubilities resulted from the photochemically crosslinking is negligible. In comparison with BTDA-3MPDA, the methyl substitution group densities in the backbone of copolyimides are higher, and the openness of the polymer matrix between crosslinking points in the crosslinked products should be higher, which leads to higher gas permeabilities.

The trade-off relationships of gas permeabilities with permselectivities for  $H_2/N_2$  separation of crosslinked copolyimides are shown in Figure 4. It can be seen that these are well above the typical trade-off relationships, that is, high permeability for low permselectivity as observed by many polymers. In addition,  $P(H_2)$  of the photochemically crosslinked copolyimides can be adjusted in a more wide range than photochemically crosslinked BTDA-3MPDA.<sup>13</sup> In all, the photochemically crosslinked copolyimides are good gas separation materials for  $H_2/N_2$  separation.

## CONCLUSIONS

Linear relationships between both  $\log P$  and  $E_p$  and volume fraction of PMDA-3MPDA hold for copolyimides prepared from PMDA, BTDA, and 3MPDA. UV irradiation led to an appreciable gel fraction in DMF and change in the strength of the peak at  $1678\text{ cm}^{-1}$  in FTIR for PB3070 and PB5050. However, no gel and the corresponding change in FTIR for PB2080 and PB9010 were found. Photochemically crosslinking modification results in decrease in gas permeability and increase in both  $E_p$  and  $\alpha(H_2/N_2)$  of all the copolyimides. The crosslinked copolyimides obtained are of higher gas permeabilities and permselectivities than normal polymers for  $H_2/N_2$  separation, and their gas permeability can be adjusted



**Figure 4** Trade-off relationships between gas permeabilities and permselectivities of the copolyimides: (□) photochemically crosslinked copolyimides; (○) photochemically crosslinked BTDA-3MPDA.<sup>13</sup>

in a wider range than photochemically crosslinked BTDA-3MPDA.

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