

# Microstructure of HTPB-Based Polyurethane Membranes and Explanation of Their Low O<sub>2</sub>/N<sub>2</sub> Selectivity

RUOH-CHYU RUAAN,<sup>1</sup> WEN-CHUNG MA,<sup>1</sup> SHIH-HSIUNG CHEN,<sup>2</sup> JUIN-YIH LAI<sup>1</sup>

<sup>1</sup> Department of Chemical Engineering, Chung Yuan University, Chung Li, Taiwan 302, Republic of China

<sup>2</sup> Department of Environmental Engineering and Health, Chia-Nan College of Pharmacy and Science, Tainan, Taiwan 717, Republic of China

Received 21 September 1999; accepted 19 September 2000

**ABSTRACT:** Polyurethane (PU) membranes usually have high gas permeability but low selectivity. It was supposed that an increase of the hard-segment content in PU membranes would enhance the selectivity since the hard segment has a higher oxygen affinity and could reduce the chain mobility. However, an attempt to increase the O<sub>2</sub>/N<sub>2</sub> selectivity by increasing the hard-segment content failed. It was found that increase of the hard-segment content did increase the gas solubility but the solubility ratio of oxygen to nitrogen was not increased. Increase of the hard-segment content also reduced the permeabilities of both oxygen and nitrogen, but no improvement of the O<sub>2</sub>/N<sub>2</sub> diffusivity ratio was observed. The microstructure of polybutadiene-containing PU was examined by DSC and FTIR measurements. It was found that hydrogen bonding between hard segments was the cause of the failure of selectivity improvement. Avoiding the formation of hydrogen bonds between the hard segments is the key for a successful improvement of the O<sub>2</sub>/N<sub>2</sub> selectivity of the PU membranes. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1307–1314, 2001

**Key words:** O<sub>2</sub>/N<sub>2</sub> selectivity; oxygen solubility; microphase separation

## INTRODUCTION

Polyurethane (PU) materials have many applications because of their good mechanical properties and chemical resistance, such as tensile strength, abrasion, oil resistance, and long fatigue life. However, there are only a few studies of gas separation by PU membranes.<sup>1,2</sup> Separation between oxygen and nitrogen by PU membranes has been rarely studied. Hsieh and Lai<sup>3,4</sup> measured the permeabilities of O<sub>2</sub> and N<sub>2</sub> through polyether and polyester-based PUs. They chose poly(butylene adipate)glycol (PBA), poly(caprolactone)gly-

col (PCL), and poly(tetramethylene oxide)glycol as the soft segments and 4,4'-diphenylmethane diisocyanate (MDI) as the hard segment. The oxygen permeability could reach as high as 36 Barrers but the O<sub>2</sub>/N<sub>2</sub> separation coefficients were mostly under 2.0. Pegoraro et al.<sup>5,6</sup> used poly(oxypropylene)glycol (PPG) and poly(tetramethylene)adipate (PTMA) as the soft segment and TDI as the hard segment. The O<sub>2</sub>/N<sub>2</sub> selectivity was improved, but was still lower than 3.0. Huang et al.<sup>7</sup> synthesized hydroxyl-terminated polybutadiene (HTPB)-based PU for O<sub>2</sub>/N<sub>2</sub> separation. The separation factor was still lower than 3.0. In general, PU membranes have excellent gas permeability but low selectivity. Improvement of the O<sub>2</sub>/N<sub>2</sub> selectivity of PU membranes is an important issue. To improve the selectivity, we need

Correspondence to: R.-C. Ruaan (ruaan@mbox.cycu.edu.tw).

*Journal of Applied Polymer Science*, Vol. 82, 1307–1314 (2001)  
© 2001 John Wiley & Sons, Inc.

to understand the mechanism of gas transport through PU membranes.

Galland<sup>8</sup> and Lam<sup>9</sup> demonstrated that the properties of segmented PUs are greatly influenced by the degree of microphase separation. In looking for a possible explanation for the relationship between gas transport and the microstructure of PU membranes, we synthesized HTPB-based PU with an increasing degree of microphase separation. The gas permeability and solubility were measured independently. The microstructure was characterized by  $T_g$  measurement and compared with the corresponding gas permeability and solubility.

## EXPERIMENTAL

### Materials

The chemicals used for this study were MDI, HTPB (average functionality 2.3 MW = 2000), 1,4-butanediol (1,4-BD) used as chain extender, and dibutyltin dilaurate (DBTDL) used as a catalyst. Tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) were used as solvents. The two-stage polymerization method employed, first, the polymerization of a —NCO-terminated prepolymer and then chain extension with 1,4-BD. The reaction procedure followed the report of Huang et al.<sup>10</sup> Four HTPB-based PUs, of which the hard/soft segment ratios were 4/1, 8/1, 12/1, and 16/1, were synthesized. The synthesized PUs were designated as PU 1/4/3, PU 1/8/7, PU 1/12/11, and PU 1/16/15, respectively.

### Gas-permeation Measurements

The apparatus and experimental procedure for gas-permeability measurements were described by Cheng and Lai.<sup>11</sup> The gas permeability was determined by the following equation:

$$\text{Permeability} = \frac{1}{\Delta P l} \left[ \frac{q}{A} \right]$$

where  $q$  is the volumetric flow rate of gas permeation [ $\text{cm}^3$  (STP) /s];  $l$ , the membrane thickness (cm);  $\Delta P$ , the pressure difference across the membrane (mmHg); and  $A$ , the effective membrane area ( $\text{cm}^2$ ). The gas permeability is expressed in Barrers [ $10^{-10} \text{ cm}^3$  (STP)  $\text{cm}/\text{cm}^2 \text{ s cmHg}$ ].

### Gas-sorption Measurements

The method for gas-sorption measurement was shown in our previous report.<sup>12</sup> A microbalance (Cahn Model D-202 electrobalance) was enclosed in a stainless chamber. The chamber was enclosed in a constant temperature box. The system pressure was then vacuumed to about  $4 \times 10^{-3}$  Torr before each measurement. The gas diffusivity was obtained by the ratio of gas permeability to gas solubility.

### Measurement of Glass Transition Temperature

A Perkin–Elmer DSC 7 was used for the  $T_g$  measurement. The heating rate for the  $T_{gH}$  measurement was  $5^\circ\text{C}/\text{min}$  from 30 to  $100^\circ\text{C}$ . For the amorphous soft phase, a cooling rate of  $20^\circ\text{C}/\text{min}$  was used from 30 to  $-150^\circ\text{C}$ . Each sample was tested over five runs. The difference of the  $T_{gH}$  measurements was within  $0.2^\circ\text{C}$  and that of the  $T_{gS}$  measurements was within  $0.5^\circ\text{C}$ .

### Measurement of Hydrogen-bonding Index

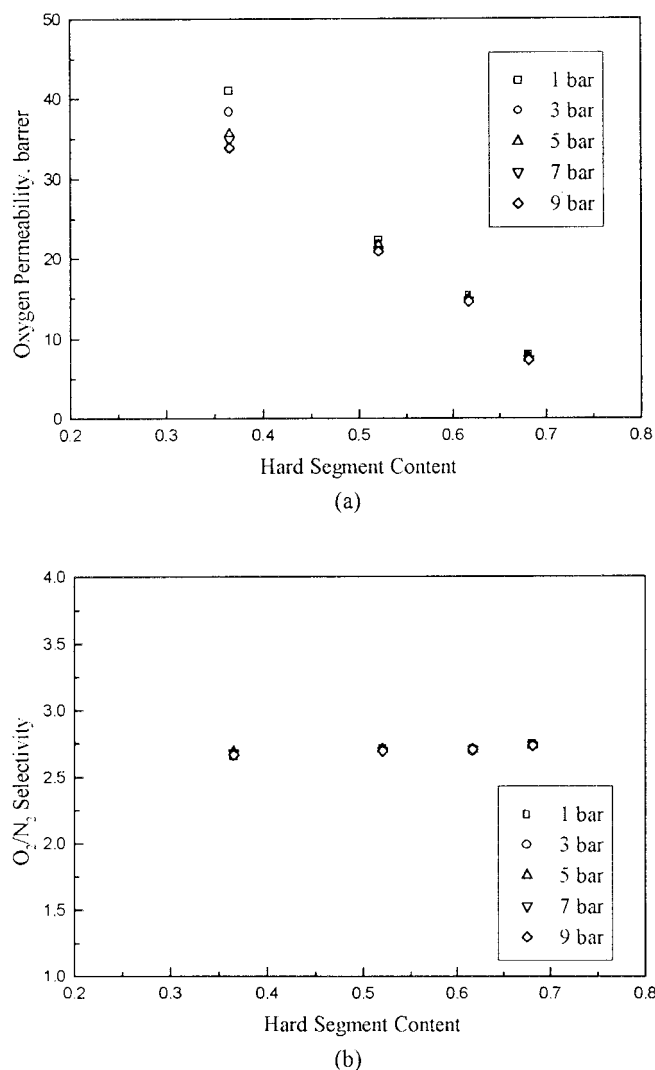
A Shimadzu FTIR/ATR spectrometer Model FT8000 was used for the FTIR–ATR analysis. The peak of hydrogen-bonded C=O stretching is centered at  $1700 \text{ cm}^{-1}$  and that of free C=O stretching is centered at about  $1717 \text{ cm}^{-1}$ . In the butadiene-containing PUs, hydrogen bonding can occur only between the C=O and N–H groups in the urethane segments. The extent of the carbonyl group participating in hydrogen bonding is expressed by the hydrogen-bonding index (HBI), which is defined as the relative absorbance of the two carbonyl peaks,<sup>13</sup> that is:

$$\text{HBI} = \frac{A_{\text{C=O,bonded}}}{A_{\text{C=O,free}}}$$

where  $A_{\text{C=O,bonded}}$  and  $A_{\text{C=O,free}}$  are the absorbance of bonded and free carbonyl groups, respectively.

### Specific Volume Measurements

The specific volume was estimated by dividing the membrane volume by the mass of the membrane. The membrane volume was calculated by multiplying the average membrane thickness by the area. The thickness of the membranes was measured by a thickness gauge (Teclock MS1201). The average membrane thickness was obtained by averaging 10 measurements.



**Figure 1** Effect of hard-segment content on the (a) oxygen permeability and (b)  $O_2/N_2$  selectivity at 35°C.

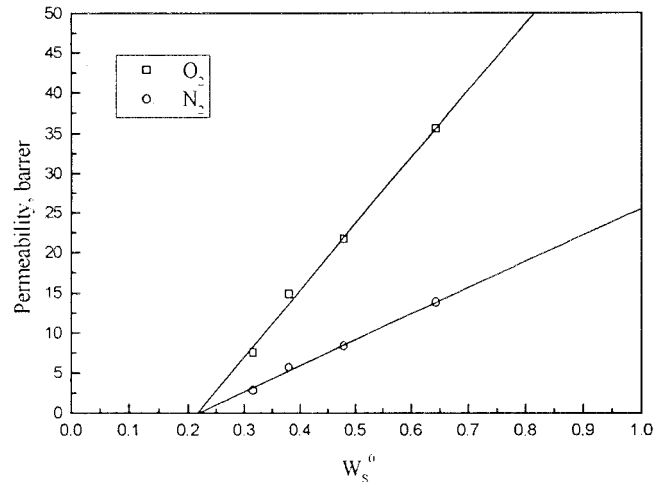
## RESULTS AND DISCUSSION

### Effect of Hard-segment Content on Gas Permeability and $O_2/N_2$ Selectivity

Four HTPB-based PUs, for which the hard/soft segment ratios were 4/1, 8/1, 12/1, and 16/1, were synthesized. The oxygen and nitrogen permeabilities were measured and the  $O_2/N_2$  selectivities were calculated. As shown in Figure 1(a), the oxygen permeability decreased as the hard-segment content increased. According to our past experience, the selectivity usually increases when gas permeability decreases. However, as shown in Figure 1(b), the hard-segment content had no observable effect on the  $O_2/N_2$  selectivity.

### Effect of Soft-segment Content on Gas Permeability

Figure 2 plots the gas permeability against the soft-segment content. It was found that both the oxygen and nitrogen permeabilities were extremely small when the soft-segment content was low, but increased linearly with increase of the soft-segment content when the soft-segment content was higher than 22 wt %. This result implied that most gases passed through the soft-segment-containing region of the membrane. A similar result was also found in polyether PUs.<sup>8</sup> This information provided an explanation of the phenomenon of gases transporting through the HTPB-based PU membranes. Actually, PU is a rather heterogeneous polymer. Because of hydrogen bonding



**Figure 2** Effect of soft-segment content on the gas permeability at 35°C and 5 bar.

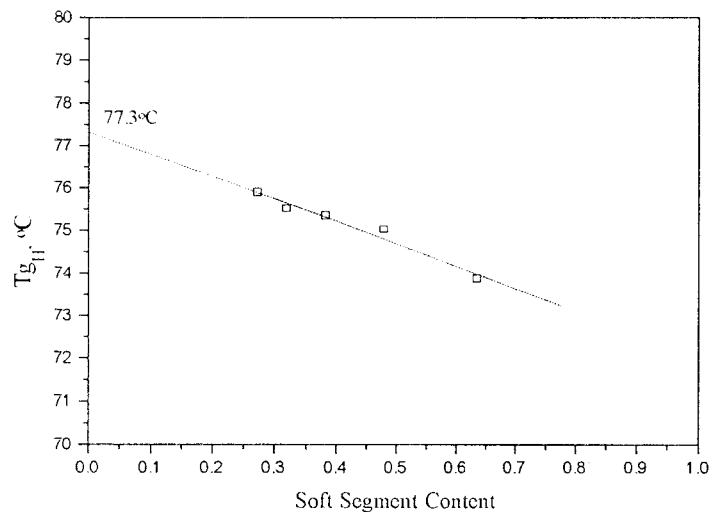
between the urethane linkages, the hard segments tend to aggregate together. Therefore, PU segregates into hard and soft domains. The gas-transport properties of different domains are different. To understand the transport properties of these HTPB-based PU membranes, the microstructure of these membranes need to be studied.

#### Microstructure of HTPB-based PU Membranes

The sizes of the hard and soft domains were estimated by the measurement of the glass transition temperatures of the hard and soft segments. The quantity of the soft and hard segments in the soft domain can be estimated by the Fox equation<sup>14</sup>:

$$\frac{1}{T_{gS}} = \frac{W_{SS}}{T_{gS}^0} + \frac{W_{HS}}{T_{gH}^0}$$

where  $T_{gS}$  is the glass transition temperature of the soft domain;  $W_{SS}$  and  $W_{HS}$ , the mass fraction of the soft and hard segments in the soft domain; and  $T_{gS}^0$  and  $T_{gH}^0$ , the glass transitions of pure the soft and hard segments, respectively. Similarly, the mass fraction of soft and hard segments ( $W_{SH}$  and  $W_{HH}$ ) in the hard domain could also be estimated by  $1/T_{gH} = W_{SH}/T_{gS}^0 + W_{HH}/T_{gH}^0$ , where  $T_{gH}$  is the glass transition temperature of the hard domain. The glass transition of pure polybutadiene ( $T_{gS}^0$ ) could be measured. The glass transition of the pure hard segment was esti-



**Figure 3** Estimation of the glass transition temperature of pure hard segment.

**Table I Morphological Characterization of HTPB-based PU**

Polymer	$W_H^0$	$W_S^0$	$T_{gH}$ (°C)	$T_{gS}$ (°C)	$W_H$		$W_S$	
					$W_{HH}$	$W_{SH}$	$W_{HS}$	$W_{SS}$
PU 1/4/3	0.356	0.644	73.9	-62.6	0.030 (0.025)	0.990 (1.0)	0.970 (0.975)	0.663 (0.661)
PU 1/8/7	0.520	0.480	75.0	-61.3	0.267 (0.262)	0.01 (0.0)	0.733 (0.738)	0.653 (0.424)
PU 1/12/11	0.617	0.383	75.3	-89.2	0.993 (1.0)	0.007 (0.0)	0.347 (0.349)	0.904 (0.903)
PU 1/16/15	0.681	0.319	75.5	-90.0	0.580 (0.576)	0.006 (0.0)	0.420 (0.424)	0.904 (0.903)
					0.994 (1.0)	0.006 (0.0)	0.096 (0.097)	0.904 (0.903)
					0.654 (0.650)	0.005 (0.0)	0.346 (0.350)	0.913 (0.911)
					0.995 (1.0)	0.005 (0.0)	0.087 (0.089)	0.913 (0.911)

$W_H^0$ : soft-segment content (wt %);  $W_S^0$ : hard-segment content (wt %);  $W_H$ : mass fraction of hard domain (wt %);  $W_S$ : mass fraction of soft domain (wt %);  $W_{HH}$ : mass fraction of hard segment in hard domain (wt %);  $W_{SH}$ : mass fraction of soft segment in hard domain (wt %);  $W_{HS}$ : mass fraction of hard segment in soft domain (wt %);  $W_{SS}$ : mass fraction of soft segment in soft domain (wt %).

mated by extrapolating. As shown in Figure 3, the  $T_{gH}$  decreased linearly with increase of the soft-segment content. The glass transition temperature of a pure hard segment,  $T_{gH}^0$ , could be obtained by extrapolating to a 0% soft-segment content. After  $W_{SS}$ ,  $W_{HS}$ ,  $W_{SH}$ , and  $W_{HH}$  were obtained, the mass percentages of the soft and hard domains ( $W_S$  and  $W_H$ ) could be calculated. Table I lists all the measured  $T_{gS}$  and estimated mass percentages. Since the variations of the  $T_{gH}$ 's were within the estimation error, we could assume that the hard domains were free of soft segments and took the average  $T_{gH}$  as  $T_{gH}^0$  to recalculate the mass fractions. Very similar results were obtained, which are shown within the parentheses in Table I. It was found that more than one-third of the soft domain was filled with hard segments when the hard-segment content was low (PU 1/4/3 and PU 1/8/7). But the mass fraction of hard segments in the soft domain was less than 10% when the overall hard-segment content was high (PU 1/12/11 and PU 1/16/15).

#### Effect of Hard Segment on the Diffusivity Ratio of Oxygen to Nitrogen

Table II shows that increase of the hard-segment content reduced the specific volume of the membrane. Normally, the decrease in specific volume favors the selection of smaller molecules because it greatly reduces the diffusivities of larger molecules. Therefore, it was expected that the increase of the hard segment would increase the  $O_2/N_2$

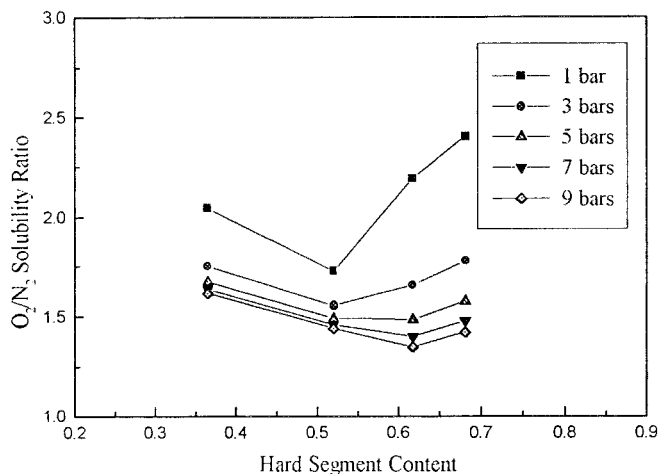
diffusivity ratio and, subsequently, the  $O_2/N_2$  selectivity would be improved. However, as shown in Figure 4(b), the diffusivity ratio did not increase along with the increase of the hard-segment content. By combining the results described in the above two sections, it became clear why the increase in hard-segment content failed to increase the  $O_2/N_2$  diffusivity ratio. Since most gases passed through the soft domain, the  $O_2/N_2$  diffusivity ratio was largely controlled by the microstructure of the soft domain. The increase of the hard domain might increase the tortuosity of the diffusion path; subsequently, the  $O_2/N_2$  diffusivity ratio would increase. However, the reduction of  $W_{HS}$  at a high hard-segment content, as shown in Table II, made the soft domain so flexible that the  $O_2/N_2$  diffusivity ratio decreased.

#### Effect of Hard Segment on the Solubility Ratio of Oxygen to Nitrogen

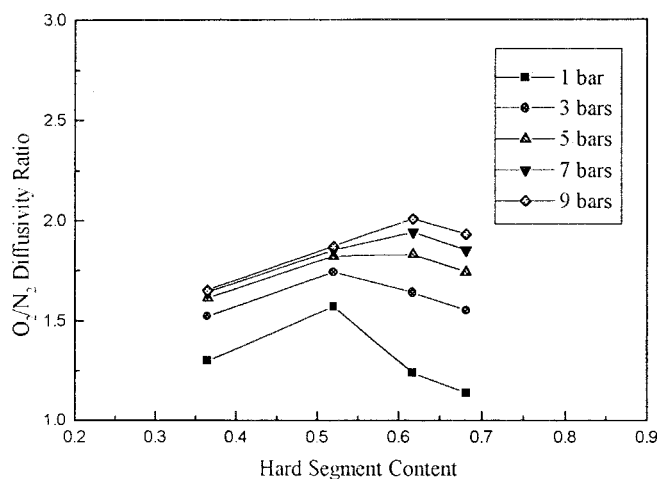
The hard segments appeared to have a higher affinity toward oxygen and nitrogen than that

**Table II Specific Volume of HTPB-based PU Membranes**

Polymer	Specific Volume (cm <sup>3</sup> /g)
PU 1/4/3	0.98
PU 1/8/7	0.92
PU 1/12/11	0.91
PU 1/16/15	0.88



(a)

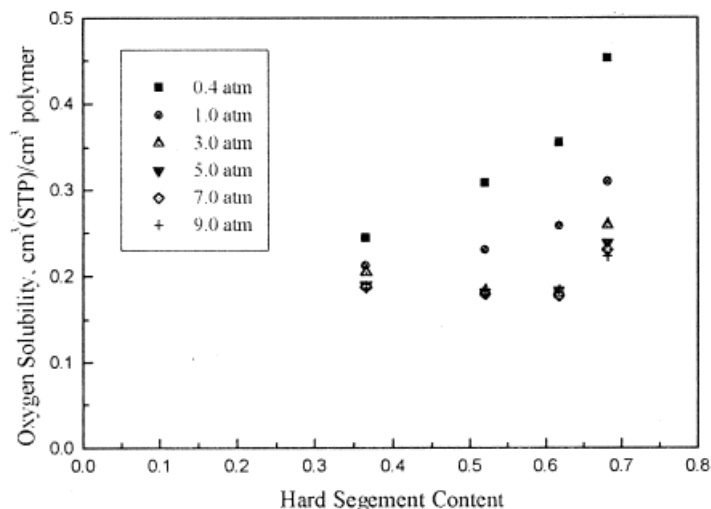


(b)

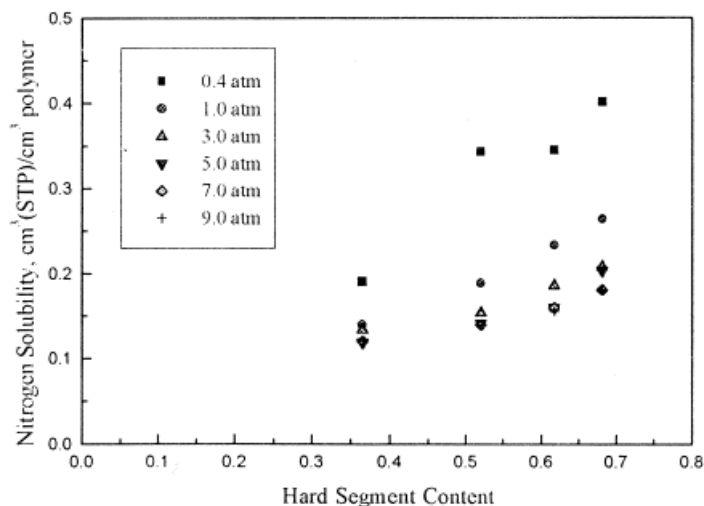
**Figure 4** Effect of hard-segment content on the  $O_2/N_2$  (a) solubility ratio and (b) diffusivity ratio at 35°C.

of the soft segments. As shown in Figure 5, both the solubilities of oxygen and nitrogen increased along with increase of the hard-segment content. The hard segment contained polar functional groups. The increase of gas solubility was probably due to the induced dipoles caused by the polarity of urethane linkages in the hard segments. The induced dipole of oxygen is usually stronger than that of nitrogen; therefore, the  $O_2/N_2$  solubility ratio was supposed to increase after more hard segments were introduced into the membrane. But, apparently, the  $O_2/N_2$  solubility ratio shown in

Figure 4(a) did not increase with increase of the hard-segment content. It is difficult to explain the sorption behaviors of oxygen and nitrogen without elucidation of the microstructure of PU. As mentioned in the above section, hard segments tended to aggregate when the hard-segment content was high. A hydrogen-bonding index, defined by Seymour et al.<sup>13</sup> as the ratio of bonded (at  $1717\text{ cm}^{-1}$ ) to free (at  $1700\text{ cm}^{-1}$ ) carbonyl groups, was used to characterize the aggregation of hard segments. Figure 6 shows the IR absorbance between 1600 and 1800  $\text{cm}^{-1}$ . It was found that the hydrogen-bonding



(a)



(b)

**Figure 5** Effect of hard-segment content on (a) oxygen and (b) nitrogen solubilities at 35°C.

index increased as the hard-segment content increased (Table III). The existence of hydrogen bonding greatly reduced the polarity of hard segments and subsequently decreased the solubility ratio of oxygen to nitrogen. This phenomenon was also found by Reimers and Barbari<sup>15</sup> when they studied the sorption of CO<sub>2</sub> in a vinyl alcohol/vinyl butyral copolymer. The increase of the O<sub>2</sub>/N<sub>2</sub> sorption ratio by the introduction of extra hard segments was eliminated by the formation of hydrogen bonds. The O<sub>2</sub>/N<sub>2</sub> sorption

ratio started to increase only when the hydrogen-bonding index stopped increasing.

## CONCLUSIONS

The increase of hard-segment content in HTPB-based PU reduced the gas permeability but did not improve the oxygen-to-nitrogen selectivity. It was found that most gases pass through the soft-segment-rich area of the membrane. The reduc-

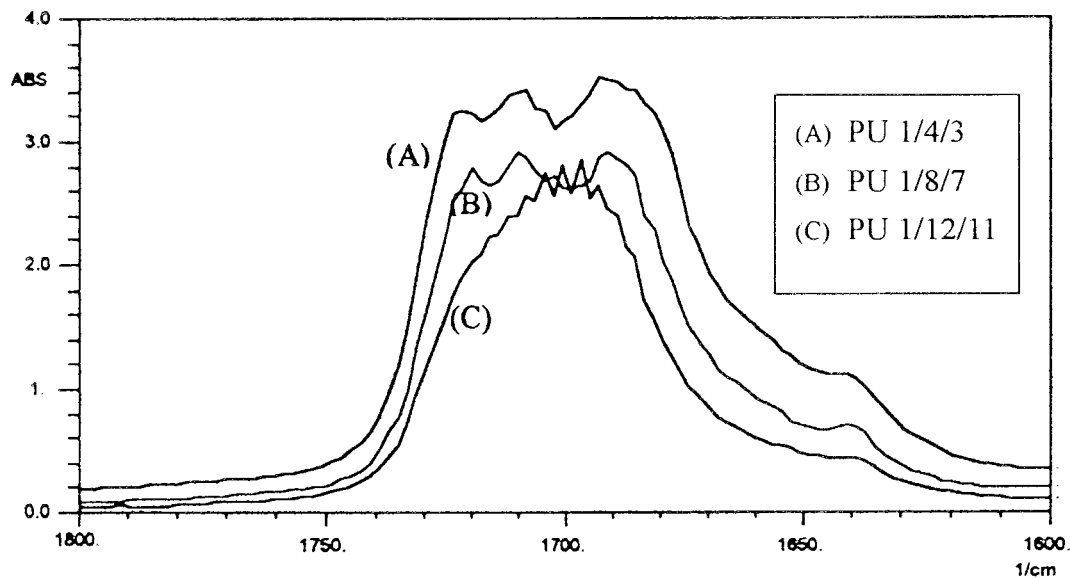


Figure 6 IR absorption spectrum between 1600 and 1800  $\text{cm}^{-1}$ .

tion in gas permeability by the increase of hard-segment content was due to the decrease in the more permeable soft segments. The hard segments did have higher affinity toward oxygen. However, the affinity toward oxygen was reduced after the hard segments aggregated. The increase of hard segments might not increase the  $\text{O}_2/\text{N}_2$  diffusivity ratio because the soft domain, where most gases passed through, contained fewer stiff hard segments as the hard-segment content increased. The increase of hard segments did not improve the oxygen-to-nitrogen sorption ratio because most hard segments formed aggregates at a hard-segment content higher than 60%. The analysis gave us a hint that, although the introduction of polarity might facilitate the transport of oxygen, the strong hydrogen bonding between polar functional groups should be avoided.

Table III Hydrogen-bonding Index of HTPB-based PU Membranes

Polymer	HBI
PU 1/4/3	2.1
PU 1/8/7	2.7
PU 1/12/11	4.0

## REFERENCES

1. McBride, J. S.; Massaro, T. A.; Cooper, S. L. *J Appl Polym Sci* 1979, 23, 201.
2. Knight, P. M.; Lyman, D. J. *J Membr Sci* 1984, 17, 245.
3. Hsieh, K. H. Tsai, C. C.; Chang, D. M. *J Membr Sci* 1991, 49, 341.
4. Hsieh, K. H.; C. C.; Tsai, D. M. Chang, *J Membr Sci* 1991, 56, 179.
5. Pegoraro, M.; Severin, F.; Gallo, R.; Zanderighi, L. *J Appl Polym Sci* 1995, 57, 421.
6. Pegoraro, M.; Zanderighi, L.; Penati, A.; Bianchi, F.; Cao, N.; Sisto, R.; Valentini, C. *J Appl Polym Sci* 1991, 43, 687.
7. Huang, S. L.; Lai, J. Y. *J Membr Sci* 1995, 105, 137.
8. Galland, G.; Lam, T. M. *J Appl Polym Sci* 1993, 50, 1041.
9. Li, F.; Hou, J.; Zhu, W.; Xu, M.; Luo, X.; Ma, D.; Kim, B. K. *J Appl Polym Sci* 1996, 62, 631.
10. Huang, S. L.; Ruaan, R. C.; Lai, J. Y. *J Membr Sci* 1997, 123, 71.
11. Cheng, S. H.; Lai, J. Y. *J Appl Polym Sci* 1996, 59, 1129.
12. Cheng, S. H.; Ruaan, R.-C. Lai, J. Y. *J Membr Sci* 1997, 134, 143.
13. Seymour, R. W.; Estes, G. M.; Cooper, S. L. *Macromolecules* 1970, 3, 579.
14. Fox, T. G.; Flory, P. J. *J Appl Phys* 1950, 21, 581.
15. Reimers, M. J.; Barbari, T. A. *J Polym Sci Polym Phys* 1993, 31, 537-543.