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Structural Characterization and Gas-Transport Properties of Brominated Matrimid Polyimide*

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ABSTRACT: The commercial polyimide Matrimid was modified by bromination for the purpose of improving its membrane-transport properties as a gas-separation material and providing functional group reactivity for further modifications. The unmodified and brominated polymers were characterized by elemental analysis and one-dimensional and two-dimensional NMR, which revealed that one bromine atom per repeat unit was incorporated regioselectively onto the indane aromatic ring. The thermal and physical properties of the polymers before and after bromination were also investigated. The gas-transport properties of the unmodified and brominated polymers were compared. © 2002 Government of Canada. Exclusive worldwide publication rights in the article have been transferred to Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 40: 4193–4204, 2002

Keywords: Matrimid polyimide; bromination; gas transport; functionalization of polymers; NMR; structure-property relations

INTRODUCTION

Matrimid 5218 is a commercially available thermoplastic polyimide (PI) from Ciba Specialty Chemicals Corp.¹ It is obtained by the polycondensation of 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and a mixture of two rigid cycloaliphatic indane-type monomers, 5- and

6-amino-1-(4'-aminophenyl)-1,3,3-trimethylindane, as shown in Scheme 1.² It is currently used in industry mostly for coatings because it is soluble in a variety of common solvents and gives durable, tough films with excellent adhesion, chemical resistance, and good thermal properties.

Matrimid is also interesting as a polymer for gas-separation membranes because it is readily soluble and exhibits an excellent combination of selectivity and permeability for many significant gas pairs that is superior to those of most other commercial polymers. Jones and Koros⁴ prepared ultrathin and defect-free hollow-fiber membranes from Matrimid 5218³ and prepared carbon molec-

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Scheme 1. Synthetic scheme showing the preparation of the commercial PI Matrimid 5218.

ular sieve membranes by the pyrolysis of other PIs. Fuertes et al.⁵ also prepared carbon membranes from Kapton and Matrimid membranes. Strathmann et al.^{6,7} prepared plasticization-resistant Matrimid membranes for the industrially attractive high-pressure CO₂/CH₄ separation. There are also examples of Matrimid gas-separation membranes in the patent literature.^{8–11}

The good solubility of Matrimid in common organic solvents enables bulk chemical modifications to be performed as long as the employed reagents do not induce chain degradation or crosslinking reactions with the more sensitive benzophenone and imide carbonyl structural segments present. In previously reported work, bromine atoms were introduced into other PIs either by the polymerization¹² of halogen-containing monomers or by the free-radical bromination of alkyl groups.¹³ The brominated PIs were prepared primarily for two purposes: increased processability, such as improved solubility by a reduction in chain packing and crystallinity,¹² and increased reactivity by the substitution of bromine with other useful functionalities for applications such as pervaporation¹³ and photorefractive¹⁴ materials.

The literature contains some examples of halogenated PI gas-separation membranes. Dichloro- and tetrachlorobenzidine monomers were used to prepare soluble chlorinated PIs from various dianhydrides such as 3,3',4,4'-biphenyl tetracar-

boxylic dianhydride, 4,4'-(hexafluoroisopropylidene)diphenyl dianhydride, and pyromellitic dianhydride, and the resulting polymers were fabricated into asymmetric hollow fibers for O₂/N₂ separation.¹⁵ Chlorine-containing diamine monomers were also used to prepare PI gas-separation membranes with improved O₂ permeability.¹⁶ Okamoto et al.¹⁷ reported the free-radical bromination of alkyl-containing PIs that were cast as films and subsequently treated with amines. The resulting partially aminated gas-separation films could be crosslinked by the reaction of amines with residual bromine. In related work, crosslinked pervaporation membranes were prepared by the thermal treatment of phosphorylated PIs, which, in turn, were prepared by the reaction of triethyl phosphite with PI containing CH₂Br groups.¹³ PI gas-separation membranes were also surface modified with chlorine or bromine vapor under reduced pressure, in the presence or absence of light.¹⁸ The resulting membranes exhibited enhanced O₂/N₂ permselectivity without a reduction in the oxygen permeability.

In this article, the preparation of modified Matrimid 5218 by electrophilic bromination on the aromatic ring is reported. The purpose of this work was to achieve an improvement in the gas-transport properties and to render the polymer more reactive for further modifications.

Scheme 2. Reaction scheme for the bromination of the PI Matrimid.

EXPERIMENTAL

Materials

The PI Matrimid 5218 was obtained from Ciba Specialty Chemicals. The polymer powder was stirred in hot water for several hours for the removal of residual *N*-methylpyrrolidinone, a solvent found in the sample. The bromine-modified polymers were prepared with bromine and chloroform as received. The reactions were conducted under a constant argon purge and with magnetic stirring.

Preparation of Brominated Matrimid 5218

Brominated Matrimid was prepared as shown in Scheme 2. The bromination was conducted by the addition of bromine (6 mL, 18.72 g, 117.13 mmol) to a yellowish solution of PI (2.00 g, 3.62 mmol)

dissolved in chloroform (13.3 mL, 15% w/v) in a 100-mL, round-bottom flask equipped with a condenser and a magnetic stirrer. The dark red solution was vigorously stirred for 6 h, during which time a dark gum precipitated from the reaction mixture. Methanol (~70 mL) was poured into the flask under vigorous stirring to precipitate the yellow, modified polymer. The precipitated polymer was filtered and stirred vigorously again in fresh methanol. This was repeated until no more bromine could be extracted, this being indicated by colorless methanol. The brominated PI was purified by redissolution in chloroform and precipitation from 95% ethanol. After vacuum drying, a yield of 90% (2.06 g) was obtained.

Characterization Methods

NMR spectra were recorded on a Varian Unity Inova spectrometer at a resonance frequency of

Table 1. ^1H NMR Data for Unmodified and Brominated Matrimid

Proton Number	Matrimid 5218 δ (ppm)	Brominated PI δ (ppm)
H5	8.20–8.34	8.21–8.38
H7	8.20–8.34	8.21–8.38
H8	8.08–8.18	8.08–8.20
H10	7.30–7.44	7.32–7.44
H11	7.30–7.44	7.32–7.44
H13	7.30–7.44	7.32–7.44
H14	7.30–7.44	7.32–7.44
H17	2.26–2.36	2.31
H17'	2.48–2.56	2.52
H21	7.18–7.44	7.13 ^a and 7.48 ^b
H22	7.18–7.44	—
H23	7.18–7.44	—
H24	7.18–7.44	7.58 ^a and 7.20 ^b
H25	1.76	1.70–1.84
H26	1.15 or 1.41	1.15 or 1.36–1.44
H27	1.41 or 1.15	1.36–1.44 or 1.55

^a Main chain in position 22.^b Main chain in position 23.

399.961 MHz for ^1H and 100.579 MHz for ^{13}C . For each analysis, an approximately 10 wt % polymer solution was prepared in CDCl_3 for ^1H NMR, and an approximately 20 wt % solution was prepared for ^{13}C NMR. Quantitative carbon spectra were obtained with appropriate acquisition parameters (long delay and acquisition time) with a 10-mm tunable broadband probe, and the solutions for carbon analysis contained chromium(III) acetylacetonate as a spin relaxation agent. Tetramethylsilane was used as the internal-standard chemical-shift reference. Carbon–hydrogen correlations were obtained for $^1\text{JC}-\text{H}$ set to 140 Hz and $^3\text{JC}-\text{C}-\text{C}-\text{H}$ set to 7.5 Hz.

A DuPont 951 thermogravimetric analyzer was used for measuring degradation temperatures by thermogravimetric analysis (TGA) and for measuring glass-transition temperatures (T_g 's) by differential scanning calorimetry (DSC). Polymer samples for TGA were ramped to 60 °C at 10 °C/min under a nitrogen atmosphere, held isothermally for 120 min, and heated to 800 °C at 10 °C/min for degradation-temperature measurements. Samples for DSC were initially heated above T_g , quenched with liquid nitrogen, held isothermally for 10 min, and reheated at 10 °C/min under a nitrogen atmosphere for the T_g measurements. Elemental analyses results were obtained in our laboratories (CHN) with a Leco CHN 1000

analyzer and from Galbraith Laboratories (CHNBr).

Dense membranes were prepared in the form of films, which were made from approximately 5 wt % polymer solutions in chloroform. Polymer solutions were filtered through Whatman 25-mm syringe filters, the pore size of which was 1 μm . The evaporation process was performed at room temperature under a nitrogen-enriched atmosphere. The films were evacuated for 3 days at 40 °C for the removal of residual solvent and then were annealed at 130 °C in a vacuum oven overnight. The resulting thickness of the films was about 100 μm . The gas permeability coefficients were obtained by the downstream pressure change being measured through the constant-volume method. A steady-state pressure rate was chosen in the time region above 10 more than the time lag. The permeability coefficients were calculated with the following formula:

$$P = \frac{(\text{Quantity of permeate}) (\text{Film thickness})}{(\text{Area}) (\text{Time}) (\text{Pressure drop across film})} \left(\frac{\text{cm}^3 (\text{STP}) \text{ cm}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}} \right)$$

X-ray diffraction was used to investigate d -spacing. A Macscience model M18XHF22 was used with Cu $K\alpha$ radiation, the wavelength (λ) of which was 1.54 Å. The scanning speed was 5 °/min. The d -spacing was calculated with Bragg's law ($d = \lambda/2 \sin \theta$), with θ of the broad peak maximum. The densities of the dried membranes were measured by the displacement method with a Mettler density kit with anhydrous ethanol at 23 °C. The fractional free volume (FFV) was calculated from

$$\text{FFV} = \frac{V_{\text{sp}} - V_o}{V_{\text{sp}}}$$

where V_{sp} is the specific volume calculated from the density and V_o is the occupied chain volume obtained with the Bondi group contribution method.^{19,20}

RESULTS AND DISCUSSION

Structural Characterization by ^1H NMR and ^{13}C NMR

Tables 1 and 2 list the chemical shifts (ppm) of proton and carbon signals, respectively, for the

Table 2. ^{13}C NMR Data for Unmodified and Brominated Matrimid

Carbon Number	Matrimid 5218 δ (ppm)	Brominated PI δ (ppm)
C1	166.10, 166.23	165.60
C2	132.19, 132.24	132.12, 132.28
C3	135.05, 135.11	135.01, 135.12
C4	166.10, 166.23	166.09
C5, C7	124.67 or 135.77	135.81 or 124.72, 124.90
C6	141.85	141.81
C8	124.25	124.29, 124.49
C9	128.90	129.06, 129.13
C10, C14, C11, C13	125.96 or 127.51	126.10 or 127.35, 127.49
C12	150.64, 150.76	149.84
C15	192.87	192.87
C16	50.80, 50.87	50.70, 50.96
C17	59.13, 59.20	58.96, 59.05
C18	43.03, 43.15	43.07, 43.28
C19	152.57, 153.37	153.15, 155.93
C20	148.76, 149.48	149.22, 152.26
C21	123.36, 123.53 or 125.68, 125.77	127.10(C22) 129.83(C23) ^b
C22	(Q)129.91 (T)121.03 ^a	129.25(C22) 120.98(C23) ^b
C23	(Q)130.55 (T)125.12 ^a	121.82(C22) 129.86(C23) ^b
C24	123.36, 123.53 or 125.68, 125.77	128.04(C22) 124.90(C23) ^b
C25	30.82	30.38 or 30.54 or 30.72
C26	30.62	30.38 or 30.54 or 30.72
C27	30.62	30.38 or 30.54 or 30.72

^a Q for quaternary carbon (attached to main chain); T for tertiary carbon (C—H).

^b C22 for main chain in position 22; C23 for main chain in position 23.

unmodified and brominated PI. ^1H and ^{13}C NMR spectra of unmodified and brominated Matrimid are shown in Figures 1 and 2, respectively. A combination of one-dimensional (1D) NMR, homonuclear decoupling, distortionless enhancement by polarization transfer (DEPT), and heteronuclear and homonuclear correlation experiments was used to unambiguously assign the majority of the absorption frequencies.

Matrimid

Matrimid PI is obtained from the reaction of BTDA and a mixture of cycloaliphatic diamines [5- and 6-amino-1-(4'-aminophenyl)-1,3,3-trimethylindane; Fig. 1]. The diaminated indane monomers used in the preparation of Matrimid have amine groups occupying two possible carbon sites. Therefore, the main polymer chains consist of two different repeat units depending on the amine position. The only NMR data on Matrimid of which we are aware are from Grobelny et al.²¹ with solid-state ^{13}C NMR for the miscibility of polyethersulfone (PES) and PI blends. In the following discussion on NMR spectroscopy, it is de-

termined that the commercial polymer Matrimid consists of repeat units attached to either one of the two benzene carbons opposite the cyclopentane ring in a ratio of approximately 4:3. The entire aliphatic region that resides in the indane portion of the PI was readily assigned. The three methyls and two hydrogens of CH_2 are all chemically nonequivalent because of the tetrahedral nature of the aliphatic carbons forming the indane cyclopentane ring. One H-17 is cis to the main polymer chain, whereas the other is trans, and this explains their different chemical shifts. The geminal coupling for both H-17 protons is $J = 13.6$ Hz. Similarly, in ^{13}C NMR, all aliphatic peaks were readily assigned: CH_2 by DEPT, the quaternary carbon C-16 by its single two-bond coupling (~ 7 Hz) with H-25, and the other quaternary C-18 by its two two-bond couplings (~ 7 Hz) with H-26 and H-27.

The aromatic regions of both ^1H and ^{13}C spectra of Matrimid are more complex not only because of the larger number of atoms but also because the amine of the indane monomer can occupy two different sites on the benzene ring, leading to two different repeat units for the poly-

Figure 1. ^1H NMR spectra (ppm) of unmodified and brominated Matrimid.

mer. As expected, the C-15 carbonyl group appeared at a low field and was three-bond-coupled with H-5 and H-7; similarly, the imide carbonyls (C-1 and C-4) were also at a low field and displayed long-range coupling with H-5 and H-8. Two predominant sets of aromatic hydrogen multiplets were observed from 7.18 to 7.44 ppm and from 8.08 to 8.34 ppm. On the basis of the ex-

pected electron-withdrawing effect of the ketone group on aromatic protons and on the intensity of the proton peaks, as well as homonuclear and heteronuclear (one-bond C—H and three-bond C—C—C—H) correlation, we were able to assign H-5 and H-7 (8.20–8.34 ppm) and H-8 (8.08–8.18 ppm) as well as all the benzophenone ring carbons C-2, C-3, C-5, C-6, C-7, and C-8. Aromatic carbons

Figure 2. ^{13}C NMR spectra (ppm) of unmodified and brominated Matrimid.

C-19, C-20, and C-12 were easily assigned on the basis of their three-bond couplings with the aliphatic indane protons. Information from 1D quantitative ^1H and ^{13}C NMR spectra and heteronuclear correlation led to the assignment of the protons and carbons of the symmetric benzene (CH-10 and CH-14, and CH-11 and CH-13) as well as the quaternary carbon (C-9). The indane benzene ring gave rise to several hydrogen and carbon peaks due to the two possible sites for the

main-chain attachment at either C-22 or C-23. Furthermore, C-22 and C-23 were either tertiary or quaternary carbons, depending on the chain attachment site. C-19 and C-20 were unambiguously assigned because of their multiple three-bond couplings with aromatic and aliphatic protons. The key component to the assignment of C-22-chain and C-23-chain versus CH-22 and CH-23 was the three-bond coupling information from heteronuclear chemical-shift correlation.

Figure 3. Carbon–hydrogen correlation NMR spectrum (ppm) of brominated Matrimid showing long-range (C—C—C—H) coupling between C19–H21 and C20–H24.

For the chain in position C-22, C-19 showed three-bond coupling to H-21 and H-23, whereas C-20 had only one three-bond coupling to H-24. Similarly, for the chain in position C-23, C-19 had only one three-bond coupling to H-21, whereas C-20 had two three-bond couplings to H-24 and H-22. Those peaks around 150 ppm in ^{13}C NMR are well resolved and were used to estimate the ratio of repeat units in position 22 to repeat units in position 23. Figure 2 illustrates a carbon spectrum of Matrimid with an enlargement window showing the indane aromatic C-19 and C-20; their integration values indicate a ratio of 4:3 in favor of the main chain in position 22.

Brominated Matrimid

The aliphatic cyclopentane portion of Matrimid PI was unaffected by bromination; therefore, the NMR spectra of the hydrogen and carbon aliphatic regions were almost identical to those of unmodified Matrimid. Only minor changes in the chemical shifts were observed as a result of conformational changes caused by the presence of bulky bromine atoms.

The same spectral analysis rationale applied to Matrimid was used for brominated Matrimid. It

was quite apparent from ^1H and ^{13}C NMR that no substitution occurred either on the benzophenone rings or on the benzene ring attached to C-16 on the indane moiety. The proton region for the indane aromatic ring was considerably changed, and DEPT indicated that some tertiary carbons had been converted into quaternary carbons. Key information was obtained by the three-bond C—C—C—H coupling of C-19 with H-26 and H-27 (as seen before in Matrimid) and two new proton singlet peaks at 7.13 and 7.48 ppm (Fig. 3). These new three-bond couplings originate from H-21, one being when bromine is in position 22 and the other when bromine is in position 23. Similarly, key information was obtained from three-bond coupling of C-20 with H-25 and also with new proton signals at 7.58 and 7.20 ppm, which could only originate from C-20 long-range-coupled with H-24. No other three-bond coupling was observed for both C-19 and C-20, and this indicated that carbon C-22 and C-23 were deprived of protons and, therefore, that bromination occurred at C-22 and C-23 sites, whereas none occurred at C-21 and C-24 sites. Two sets of two lower intensity quaternary carbons around 120 and 130 ppm had three bond couplings to H-21 and H-24 and were, therefore, assigned as C—Br or C chains. Chem-

Table 3. T_g and Degradation Temperatures for Unmodified and Brominated Matrimid

Polymer	T_g (°C)	Onset Degradation		
		1% Weight Loss (°C)	2% Weight Loss (°C)	Extrapolated (°C)
Matrimid	313.3	469.0	492.1	504.2
Brominated Matrimid	355.2	364.1	415.1	484.3

ical-shift predictions for brominated Matrimid were obtained with the help of Advanced Chemistry Development Laboratories NMR database software (ACD, Toronto, Canada). The software predicted a high-field shift for the carbon of C—Br (~107 ppm), whereas a much lower field shift (~146 ppm) was predicted for a carbon attached to a cyclodiimide. On the basis of these predictions, we suggest that the quaternary peaks around 120 ppm arise from the C—Br carbons and that the other quaternary peaks around 130 ppm arise from C-chain carbons. With three-bond correlation and the assumption from the database predictions, all CH-21, C-22, C-23, and CH-24 could be assigned.

Minor additional signals appeared in both ^{13}C NMR and ^1H NMR in the aliphatic regions. Their chemical shifts suggest that they are the result of a small degree of bromination occurring on the methyl groups of the indane cyclopentane. Elemental analyses also indicated that a total substitution of slightly more than one bromine per repeat unit occurred. It was observed that when stronger bromination conditions were used (higher polymer concentration and additional bromine), those peaks had slightly increased intensities; the total degree of substitution (DS) ranged from 1.1 to 1.3, depending on the experimental conditions. In all reactions, a small amount of bromination at the methyl sites occurred, and it was approximately 10–20% of the total aromatic ring bromination.

Determination of the Ratio of Chain Attachment Sites for Matrimid PI

The ratio of chains at C-22 to chains at C-23 in the commercial Matrimid was established with peak intensity data from quantitative ^{13}C NMR. C-19 had two different chemical shifts well resolved by 1 ppm that depended on the chain being located at either C-22 or C-23. The ratio of C-19 with chains at C-23 to C-19 with chains at C-22 is 4:3. The intensities of the proton peaks from 7.18 to

7.30 ppm (H-22 and H-23) confirmed the ratio measured by ^{13}C NMR. The carbon spectrum was preferred over the proton spectrum for the calculation of this ratio because of its better peak resolution.

Determination of the DS

The DS was estimated with ^1H NMR and elemental analysis. The intensity of the CH_2 signals was set to two, and the integration of the aromatic regions of Matrimid and brominated Matrimid were compared with that of the indane CH_2 . The integration values ranged from 13 for unmodified PI to 12 for bromine-substituted polymer. The DS at the methyl sites was estimated at 0.2 once again by a comparison of the intensities of the $\text{CH}_2\text{—Br}$ peaks between 3 and 4 ppm with the intensity of the indane CH_2 . The DS estimated from proton integration was, therefore, 1.2.

Elemental analyses were performed to confirm the presence of bromine and to obtain an estimate of the DS. The theoretical elemental percentages of CHNBr for brominated Matrimid with a DS of 1.2 were as follows: C, 64.95%; H, 3.55%; N,

Figure 4. Thermal degradation curves of unmodified and brominated Matrimid.

Table 4. Gas Permeability and Permselectivity of Unmodified and Brominated Matrimid

	$P(\text{He})^a$	$P(\text{CO}_2)^a$	$P(\text{O}_2)^a$	$P(\text{N}_2)^a$	$P(\text{CH}_4)^a$	O_2/N_2^b	CO_2/N_2^b	$\text{CO}_2/\text{CH}_4^b$
Matrimid	22	8.7	1.9	0.27	0.24	7.0	32	36
Brominated Matrimid	29	14	3.0	0.46	0.42	6.5	30	33

^a Permeability coefficients measured at 35 °C and 1 atm of upstream pressure. 1 barrer = 10^{-10} [cm³ (STP) · cm]/(cm² · s · cmHg).

^b Ideal selectivity = $(P_a)/(P_b)$.

4.33%; and Br, 14.81%. The experimental elemental analysis results were as follows: C, 64.05%; H, 3.86%; N, 4.45%; and halogen, 16.23%. It was observed that the Matrimid polymers had a tendency to strongly bond and trap solvents even when heated overnight at a high temperature (120 °C) in a vacuum oven. This could account for some of the discrepancies between theoretical and actual elemental analysis results because any residual chloroform or bromine trapped in the polymer would result in an increased halogen content. Elemental analyses were obtained for unmodified Matrimid, and the differences between the theoretical and experimental results were of the same order of magnitude as those for modified Matrimid PI.

Thermal Stability and T_g

The thermal stabilities of the Matrimid polymers were determined by TGA. Table 3 lists the actual onset of degradation temperatures for 1 and 2% weight losses, as well as the extrapolated onsets of degradation, at a heating rate of 10 °C/min in nitrogen. Figure 4 shows a plot of both degradation curves. Both unmodified and modified polymers had high degradation temperatures, well above 350 °C. As indicated in Table 3, Matrimid lost only 2% of its weight at 492 °C. Brominated Matrimid was thermally less stable, having lost 2% of its weight at 415 °C. T_g 's were determined from DSC measurements. T_g 's of brominated polymers increased compared with those of the unmodified polymers because of hindered rotation from the bulky bromine atoms. In the case of Matrimid, T_g increased from 313.3 to 355.2 °C for the brominated polymer. Because T_g of brominated Matrimid was close to its initial degradation temperature, precautions were taken not to exceed the degradation temperature during the first heating run before the liquid-nitrogen quench.

Gas Permeability

Matrimid exhibits some of the most attractive gas-transport properties of any commercially available polymer. In combination with its solubility in common solvents, it is an ideal candidate for gas-separation membranes, especially for O_2/N_2 separations, on account of its high permselectivity. Experimental gas permeability data for unmodified and brominated Matrimid are compared in Table 4. Matrimid films had a carbon dioxide permeability of 8.7 barrer with a CO_2/CH_4 permselectivity of 36. The oxygen permeability was 1.9 barrer with an O_2/N_2 permselectivity of 7.0. When Matrimid was substituted with a single bromine atom on the aromatic position, $P(\text{O}_2)$ and $P(\text{N}_2)$ increased by about 1.6 times. Simple molecular modeling indicated some conformational changes occurred in the brominated repeat units in comparison with the unmodified PI. However, an expected change in the dihedral angle between the imide ring and the aromatic ring at C-22 or C-23 was not apparent because the angle was approximately 50° in both the unmodified and C-22 or C-23 brominated derivative. The increase in permeability was attributed to a loosening of interchain packing by the bulky bromine group. The d -spacing values increased from 3.2 to 3.7 Å when the bromine group was introduced into Matrimid (Table 5). FFV also increased from 0.11 to 0.14. These results are supporting evidence that interchain packing was hindered by the bulky bromine group and that gas permeability was, therefore, increased.

Table 5. d -Spacing, V_{sp} , and FFV of Unmodified and Brominated Matrimid

	d -Spacing (Å)	V_{sp} (cm ³ /g)	FFV
Matrimid	3.2	0.79	0.11
Brominated Matrimid	3.7	0.73	0.14

Figure 5. Permeation properties of unmodified and brominated Matrimid: (a) permselectivity for oxygen/nitrogen versus oxygen permeability and (b) permselectivity for carbon dioxide/methane versus carbon dioxide permeability.

Although permeabilities increased, permselectivities decreased slightly when Matrimid was brominated. A logarithmic plot of permselectivity versus permeability in relation to Robeson's upper bound limit²² is presented in Figure 5 to show the tradeoff between selectivity and permeability. Figure 5(a) shows the data for the oxygen/nitrogen gas pair. The permselectivity for oxygen/nitrogen decreased from 7.0 to 6.5, although oxygen permeability increased from 1.9 to 3.0 barrer. The data for the carbon dioxide/methane gas pair is shown in Figure 5(b). The permselectivity for carbon dioxide/methane also decreased slightly from 36 to 33 barrer, although carbon dioxide permeability increased from 8.7 to 14 barrer. The im-

proved permeation properties could be attributed to a suppression of interchain packing by the addition of bulky bromine groups as well as some possible conformational changes in the backbone. This can result in the simultaneous inhibition of intrachain motion around flexible hinge points, which tends to increase permeability without unacceptable losses in permselectivity.²³

CONCLUSIONS

We modified Matrimid 5218 PI (Ciba Specialty Chemicals) by bromination to investigate changes in its gas-transport properties and to provide a reactive site for further modification. The unmodified and brominated polymers were fully characterized with NMR spectroscopy and elemental analysis, which showed that one aromatic hydrogen atom per repeat unit was substituted by a bromine atom with some additional minor amount of bromination of a methyl group. The aromatic substitution was regioselective to either one of the aromatic carbons of the indane moiety adjacent to the main-chain link. The brominated polymer retained the good solubility and thermal properties that it possessed before modification. Compared with unmodified PI, brominated Matrimid had a lower decomposition temperature but an increased T_g , most likely attributable to decreased chain mobility in the presence of bulky bromine atoms. The brominated polymer exhibited approximately 1.6-fold increases in gas permeabilities for O_2 and CO_2 , with some concurrent decreases in permselectivity of approximately 7–8% for the O_2/N_2 and CO_2/CH_4 gas pairs.

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