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Gas Permeation Studies of Silylated Derivatives of Poly(methylphenylphosphazene)

Patty Wisian-Neilson* and Guo-Feng Xu

Department of Chemistry, Southern Methodist University, Dallas, Texas 75275-0314

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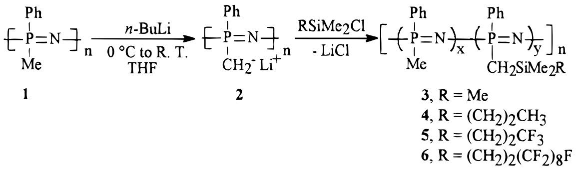
ABSTRACT: Several silylated derivatives of poly(methylphenylphosphazene) $[Me(Ph)PN]_x[RMe_2SiCH_2(Ph)PN]_y$ [R = CH_3, **3**; $(CH_2)_2CH_3$, **4**; $(CH_2)_2CF_3$, **5**; and $(CH_2)_2(CF_2)_8F$, **6**] were prepared via deprotonation of the methyl group of $[Ph(Me)PN]_n$ with *n*-BuLi followed by the treatment with chlorosilanes. Three new terpolymers, $[Me(Ph)PN]_x[Me_3SiCH_2(Ph)PN]_y[RMe_2SiCH_2(Ph)PN]_z$ [R = $(CH_2)_2(CF_2)_8F$; $x = 0.44$, $y = 0.14$, $z = 0.42$, **7**; $x = 0.46$, $y = 0.27$, $z = 0.27$, **8**; $x = 0.33$, $y = 0.54$, $z = 0.13$, **9**], were also prepared via cosubstitution using varying ratios of Me_3SiCl and RMe_2SiCl. Structural characterization and purity of each of these polymers were established by ^1H and ^{31}P NMR spectroscopy, elemental analysis, and differential scanning calorimetry. The gas permeabilities of membranes of these polymers were determined at 35 °C and compared to that of the parent polymer $[Me(Ph)PN]_n$, **1**, for which permeabilities to N_2, O_2, CH_4, and CO_2 were 0.6×10^{-10}, 1.8×10^{-10}, 0.7×10^{-10}, and 6.5×10^{-10} $cm^3(STP)\cdot cm^{-1}\cdot cmHg^{-1}\cdot s^{-1}$, respectively. The incorporation of the silyl groups generally increased permeabilities relative to $[Me(Ph)PN]_n$ without significant changes in selectivity. Polymers from the cosubstitution reactions had as much as a 15-fold increase in gas permeabilities with selectivity ratios (e.g., $\alpha_{CO_2/CH_4} = 8.9$) similar to those of **1**. The trimethylsilyl groups also increased the T_g values of the terpolymers **7**−**9** relative to the simple derivative **6**. The gas permeation properties of these polymers are discussed with respect to the lengths and concentration of the side groups.

Introduction

One of the fastest growing applications of polymeric materials is as membranes for gas separation and liquid separation.[1, 2] Although many factors, including physical structure, membrane history, and nature of the permeant, greatly affect both permeability and selectivity of a given membrane, the relationship between these properties and chemical structure is of fundamental importance in the design of membrane materials.[1] The very versatile polyphosphazenes offer unusual opportunities for examining these structure−property relationships because of the great range of substituents that are easily attached to the flexible inorganic phosphorus−nitrogen backbone. Despite the fact that several hundred phosphazene polymers have been reported, the gas permeabilities of only about a dozen have been studied.[3−5] Allcock[3] et al. and Hirose and co-workers[4] have shown that the fluorine-containing polyphosphazene $[(CF_3CH_2O)_2PN]_n$ has high gas permeabilities as well as attractive permselectivities. Allcock et al.[3] also reported a range of permeabilities and variable selectivities for phosphazenes with silyl-substituted aryloxy and ferrocenyl side groups.

Over a 100 new polyphosphazenes have been prepared in our laboratory by modification of preformed poly(alkyl/arylphosphazenes).[6−10] Through simple, one-step reactions at either methyl[6−9] or phenyl side groups,[10] the thermostability,[7] glass transition temperature,[8,9] charge transport efficiency,[11] and surface tension of polyphosphazene materials can readily be controlled.[8] In this report, we address the gas permeation properties of several recently reported silylated poly(methylphenylphosphazene) derivatives, $[Me(Ph)PN]_x[RMe_2SiCH_2(Ph)PN]_y$, and related terpolymers with mixed silyl substituents, all of which were prepared by the deprotonation−substitution reactions of **1** (eq 1).[8] The attachment of RMe_2Si moieties has been shown to facilitate control of properties such as T_g and hydrophobicity by simple variations of the substituents R. For example, as the length of R increased from 3 to 18 carbons, the T_g generally became lower and hydrophobicity increased significantly. The latter was even more pronounced with the incorporation of fluorinated groups; the water contact angle increased from 73° for $[Me(Ph)PN]_n$ to as high as 101° for the $[F(CF_2)_8(CH_2)_2]Me_2Si$ substituted derivative, **6**.[8]



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The pronounced changes in properties resulting from simple variations in the silyl side groups suggested that the gas permeation properties of polymeric membranes made from this series of polymers might also vary significantly. Several specific factors supported this assumption. First, the introduction of bulky pendent moieties generally increases the fractional free volume (V_f), which is directly proportional to the gas permeability in membrane materials.[1,12] Second, fluorine-containing groups have been shown to enhance both gas permeability of carbon dioxide and permselectivity for carbon dioxide versus methane ($\mathbf{P}_{CO_2}/\mathbf{P}_{CH_4}$).[1, 4, 12] Finally, the high oxygen permeability of poly(organosiloxanes) suggested that silyl side groups might also impart favorable gas permeation properties to these materials. Thus, the study of the gas permeation properties of the silylated polyphosphazenes with side groups of different lengths, chemical compositions, and concentrations offered a straightforward means for studying the relationship between structure and permeation properties of polymer membranes.

Results and Discussion

The silyl-modified polymers **3**−**6** (eq 1) synthesized for this study were characterized by NMR spectroscopy,

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Table 1. Physical and Elemental Analysis Data for Polymers 1 and 3−6

		composition[a]		elemental anal.[b]				
polymer	T_g (°C)	*x*	*y*	% C	% H	% N	density[c] (g/mL)	free volume[d]
1	37	1	0				1.2091	0.1574
3	50	0.40	0.60	58.66	7.02	7.77	1.1179	0.1873
				(58.58)	(7.15)	(7.76)		
4	13	0.35	0.65	60.83	7.79	7.14	1.0846	0.1911
				(60.86)	(7.87)	(6.92)		
5a	24	0.45	0.55	52.82	5.90	6.07	1.1992	0.2075
				(52.77)	(5.88)	(6.31)		
5b	25	0.35	0.65	51.64	6.01	5.70	1.2199	0.1985
				(51.87)	(5.88)	(5.90)		
6	19	0.50	0.50	39.90	3.23	3.86	1.4303	0.2423
				(40.11)	(3.24)	(3.60)		

[a] Determined by best fit of elemental analysis data with different degrees of substitution; generally these values were within 10−20% of those obtained by integration of ^{1}H NMR spectra. [b] Calculated values in parentheses. [c] Densities were measured at 35 °C. [d] Free volume $= (V_T - V_0)/V_T$, where V_T is the specific molar volume at temperature T and V_0 is 1.3 times[13] the van der Waals volume calculated by the group contribution method of Bondi.[14]

elemental analysis, and GPC to establish composition and sample purity. Both the ^{1}H and ^{31}P NMR spectra contained only the expected signals for the silylated polymers and corresponded to those reported earlier.[8] Of particular importance were the integration data for the ^{1}H NMR spectra which established the degrees of substitution (i.e., *x*:*y* ratios). These compared favorably with the degrees of substitution obtained by best fits of the elemental analyses data (Table 1). GPC indicated that the molecular weights increased as reported previously for the attachment of the silyl moieties.[8] It should be noted, however, that the silylated derivatives prepared here had significantly higher molecular weights than reported earlier because the parent polymer **1** (M_w = 236 000, M_n = 140 000, M_w/M_n = 1.7) used in this study had molecular weight at least double that of the parent polymers used in the previous work. A special effort was made to use higher molecular weight polymers because these possessed improved mechanical strength which facilitated preparation of good films. Thus the samples used for the gas permeation studies are well-characterized, high molecular weight polymers with good purity.

The chemical modifications of [Me(Ph)PN]$_n$ have been shown to significantly alter physical properties such as glass transition temperatures (T_g). The T_g, which is related to the mobility of the polymer chain, generally decreases as longer side chains are attached to the polymer backbone.[8] This trend is shown for **3**−**6** in Table 1 and suggests that longer side groups prohibit the close stacking of the polymer chains, thus increasing free volume and chain mobility. Polymers **1**−**6** should, therefore, provide opportunities to examine the relationship between side group length and gas permeabilities which are also related to free volume.

Gas permeation studies were carried out using films cast from THF solutions of the silylated polymers. Measurements were made for the permeation of nitrogen, oxygen, methane, and carbon dioxide using a pressure of 3 atm at 35 °C. Permeabilities (**P**) and selectivities (α) for **1** and **3**−**6** are shown in Table 2. Since the steady-state flux for these samples was reached very rapidly, the time lag could not be accurately measured. Thus, the diffusivities, **D**, were relatively high. For carbon dioxide, where the time lag, *θ*, was the longest and thus could be estimated, the diffusivity ($\mathbf{D}_{CO_2}$) ranged from 1 × 10^{-8} to 50 × 10^{-8} cm^2/s. While the permeation properties of the parent polymer **1** are comparable to polyethylene,[1] the gas permeabilities of films of the silylated derivatives **3**−**6** were somewhat higher. Despite the high oxygen permeability of poly(organosiloxanes), no preferential increase in oxygen permeation was observed. The presence of the Me$_3$Si group in **3** resulted in fairly uniform (ca. 2−3-fold) increases in permeabilities for all gases; i.e., the selectivities, $\alpha_{O_2}/_{N_2}$, $\alpha_{CO_2}/_{CH_4}$, and $\alpha_{N_2}/_{CH_4}$ changed negligibly from 3.1, 8.8, and 0.9 for **1** to 4.6, 10.2, and 0.6 for **3**.

Table 2. Permeability and Selectivity Data for Poly(methylphenylphosphazene) and Derivatives 3−6[a]

polymer	$\mathbf{P}_{N_2}$	$\mathbf{P}_{O_2}$	$\mathbf{P}_{CH_4}$	$\mathbf{P}_{CO_2}$	α_{O_2/N_2}	α_{CO_2/CH_4}	α_{N_2/CH_4}
1	0.6	1.8	0.7	6.5	3.1	8.8	0.9
3	1.1	5.0	1.7	16.9	4.6	10.2	0.6
4	2.0	7.1	5.1	25.2	3.7	4.5	0.4
5a	2.2	5.1	3.7	28.2	2.3	7.7	0.6
5b	2.7	8.7	4.9	43.5	3.2	8.8	0.6
6	5.2	13.7	6.3	60.4	2.6	9.7	0.8

[a] **P** is in barrer = 10^{-10} cm^3(STP)·cmHg^{-1}·cm^{-1}·s^{-1} at 35 °C.

Increasing the length of the side group had an important effect on the gas permeabilities of these silylated polymers. This is illustrated by the increased permeabilities of polymer **4**, which contained a Me$_2$(CH$_3$CH$_2$CH$_2$)Si group, versus polymer **3** with a Me$_3$Si group and of polymer **6** versus polymer **5a** with fluorodecyl and fluoropropyl substituents, respectively. Polymer **6**, which has the longest alkylsilyl group, had the best permeabilities to all four gases. These values were 8−10 times those of the parent polymer **1** and may due both to the presence of fluorine and to the increase in free volume[13,14] (Table 1) caused by the longer side group. The effect of fluorine is demonstrated by a comparison of the permeabilities of polymers **4** and **5b**. Both of these polymers have 65% of the monomer units substituted with side-groups of the same length, but **5b** contains the partially fluorinated CH$_2$CH$_2$CF$_3$ group instead of a simple propyl group. As shown in Table 2, the permeabilities to O$_2$ and N$_2$ for **5b** were slightly higher and the permeability to CO$_2$ for **5b** was almost twice that of **4**. However, the permeability to CH$_4$ was very similar for both **4** and **5b**. Consequently, the permselectivity of carbon dioxide versus methane ($\alpha_{CO_2}/_{CH_4}$ = 8.8) for **5b** is twice that of **4**. Higher permselectivities ($\alpha_{CO_2}/_{CH_4}$) have also been reported for other fluorinated polymer systems.[1,4,12] On the other hand, the introduction of the fluorine-containing groups in **5a**, **5b**, and **6** did not increase the permselectivity of oxygen versus nitrogen ($\alpha_{O_2}/_{N_2}$).

The degree of substitution on the polymer backbone also affected the gas permeabilities. This is shown by comparing the permeabilities of **5a** and **5b** where

Table 3. Characterization Data for Terpolymers 7−9

		composition[a]			elem anal[b]					
polymer	T_g (°C)	x	y	z	% C	% H	% N	XPS[b] F:Si[c]	density[d] (g/mL)	free volume[e]
7	12	0.44	0.14	0.42	41.83 (41.82)	3.80 (3.64)	3.91 (3.94)		1.3838	0.2414
8	30	0.46	0.27	0.27	45.43 (45.33)	4.49 (4.33)	4.66 (4.78)	8.9 (8.5)	1.3110	0.2328
9	49	0.33	0.54	0.13	50.52 (50.42)	5.76 (5.59)	5.58 (5.75)		1.1668	0.2450

[a] Determined by best fit of elemental analysis data. [b] Calculated values are in parentheses. [c] Ratio of moles of F to moles of Si. [d] Densities were measured at 35 °C. [e] Free volume = $(V_T - V_0)/V_T$ where V_T is the specific molar volume at temperature T and V_0 is 1.3 times[13] the van der Waals volume calculated by the group contribution method of Bondi.[14]

Table 4. Permeability and Selectivity Data for Terpolymers 7−9[a]

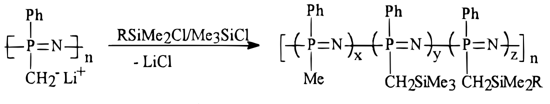
polymer	$\mathbf{P}_{N_2}$	$\mathbf{P}_{O_2}$	$\mathbf{P}_{CH_4}$	$\mathbf{P}_{CO_2}$	α_{O_2/N_2}	α_{CO_2/CH_4}	α_{N_2/CH_4}
7	11.7	26.6	14.5	101.5	2.3	7.0	0.8
8	7.0	20.1	10.4	92.1	2.6	8.9	0.7
9	3.0	9.5	4.2	34.1	3.2	8.1	0.7

[a] **P** is in barrer = 10^{-10} cm^3(STP)· cmHg^{-}·cm^{-1}·s^{-1} at 35 °C.

degrees of substitution of the $Me_2(CF_3CH_2CH_2)Si$ groups were 55 and 65%, respectively. The permeability of **5b** to each of the gases was higher than that of **5a**. Among the simple silyl derivatives in this series, polymer **6** showed the highest permeability with selectivities (e.g., $\alpha_{CO_2}/_{CH_4} = 9.7$) typical of rubbery polymer systems.[1] Both the length of the (1*H*,1*H*,2*H*,2*H*-perfluorodecyl)dimethylsilyl substituent and the high concentration of fluorine appear to be important factors in these properties.

Hence, for this set of polymers where only one type of silyl side group is attached, the permeabilities generally increased with increased fluorine content and with increased length of the side group. This corresponds to the decreases in T_g observed here and in previously reported silylated phosphazene polymers[8] and may be explained by increased free volume and backbone mobility.

Although the gas permeabilities of the polyphosphazenes were increased by introducing silyl moieties with long substituents and high fluorine content, the corresponding reductions in glass transition temperatures resulted in films that were difficult to handle and use as gas separation membranes. The bulky trimethylsilyl group, however, increases the T_g substantially while also providing some of the highest permselectivities in the monosilylated series, **3**−**6**. Thus, the three new silylated polymers, **7**−**9**, with both trimethylsilyl and (1*H*,1*H*,2*H*,2*H*-perfluorodecyl)dimethylsilyl groups were prepared in order to raise the T_g, to improve the mechanical properties of the polymer membranes, and to preserve selectivity. This was accomplished by treatment of the polymer anion **2** with a mixture of the two chlorosilanes (eq 2). The stoichiometric ratios of Me_3SiCl to $Me_2[F(CF_2)_8(CH_2)_2]SiCl$ were 1:3, 1:1, and 3:1 for **7**, **8**, and **9**, respectively.



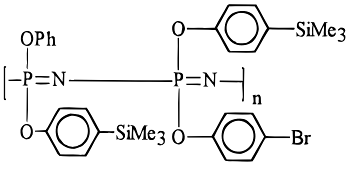
$$[-P(Ph)(CH_2^- Li^+)=N-]_n \xrightarrow[-\ LiCl]{RSiMe_2Cl/Me_3SiCl} [(P(Ph)(Me)=N)_x(P(Ph)(CH_2SiMe_3)=N)_y(P(Ph)(CH_2SiMe_2R)=N)_z]_n \quad (2)$$

2 R = $(CH_2)_2(CF_2)_8F$ **7 - 9**

These new terpolymers were characterized by NMR spectroscopy and elemental analyses. The ^{31}P NMR spectra of each contained two signals at ca. δ 1.0 ppm and δ −3.0 ppm, which are similar to the two signals observed for the simple silyl derivatives **3**−**6**. The ^1H NMR spectra also contained the expected signals at δ 6.8−8.2 (Ph), 0.6−2.1 (PCH_2, PCH_3, PCH, CH_2), and −0.3 to +0.1 (CH_3Si). The degrees of substitution (Table 3) of the silyl groups were estimated from integration of the ^1H NMR spectra and are consistent with the elemental analysis data. By NMR spectroscopy, the degree of substitution $[(y + z)/(x + y + z)]$ for **7**, **8**, and **9** are 55%, 52%, and 62%, respectively, as compared to 56%, 54%, and 67% calculated from elemental analyses. The y:z ratios (i.e., the relative amounts of each of the two silyl groups) for these polymers were estimated based on the best fit of the elemental analysis data. For polymer **9** this was 4:1 rather than the 3:1 expected from the reaction stoichiometry, but for polymers **7** and **8** these ratios matched the stoichiometry of the chlorosilane mixture. This conclusion was further supported by X-ray photoelectron spectroscopy (XPS). In **8**, the calculated atomic ratio of F to Si is 8.5 when y:z equals 1:1. The experimental result from XPS was 8.9. DSC data for the three new polymers confirmed that our initial premise was largely accomplished, i.e., that the T_g could be manipulated by varying the ratio of two substituents. As shown in Table 3, the glass transition temperatures for **7**, **8**, and **9** were 12, 30, and 49 °C, demonstrating that the greater the concentration of the trimethylsilyl group, the higher the T_g of the polymer.

The gas permeabilities of membranes prepared by cosubstitution were also substantially altered (Table 4). For sample **7**, where one in four of the silyl side-groups were the bulky $SiMe_3$ group, $\mathbf{P}_{CO_2}$ and $\mathbf{P}_{O_2}$ reached a maximum of 101 and 27 barrers, respectively. These are substantially higher than any of the permeabilities measured for polymers **3**−**6** with simple substitution of one type of silyl group. Increasing the proportion of $SiMe_3$ groups to 50%, as in polymer **8**, raised the T_g to slightly above room temperature but caused only a small decrease in permeabilities. These were still significantly higher than the best sample (polymer **6**) in the first set of polymers. Polymer **9**, in which 80% of the silyl groups were the $SiMe_3$ group, had the highest T_g and the lowest permeability of the cosubstituted polymers. Tradeoffs between permeability and selectivity also existed as illustrated for the gas pair of O_2 and N_2. As the concentration of the trimethylsilyl groups increased, permeability decreased and selectivity increased. Nonetheless, the $\alpha_{CO_2}/_{CH_4}$ was still a reasonable 8.8 for **8**. All polymer membranes in the study showed a higher permeability to methane than to N_2. This phenomenon was also observed in other membrane studies and has been attributed to the fact that methane has a higher condensibility than nitrogen.[15]

The gas permeabilities and permselectivities of the silyl derivatives reported here are comparable to those of the silylphenoxy polyphosphazenes (e.g., **10**) recently reported by Allcock et al.[3]



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For example, polymers **10** and **7** had permeabilities to CO_2, N_2, O_2, and CH_4 that differed by less than ca. 20%. The permselectivities were also similar for these two polymers. However, although some of the silylated polymers have permselectivities comparable to that of poly[bis(trifluoroethoxy)phosphazene], the permeabilities are significantly lower {e.g., $P_{CO_2} \approx 600$ barrers for poly[bis(trifluoroethoxy)phosphazene]}.

In summary, the polymers prepared by deprotonation of poly(methylphenylphosphazene) followed by substitution of alkylsilyl and fluoroalkylsilyl groups allowed the systematic study of the relationships between gas permeation properties and chemical structures of phosphazene polymers. Both increased length and concentration of silyl substituents on the backbone tend to increase the gas permeability. Fluorine-containing moieties further increase gas permeability while maintaining the permselectivity of CO_2 versus CH_4. Finally, the cosubstitution of the trimethylsilyl group and the (1*H*,1*H*,2*H*,2*H*-perfluorodecyl)dimethylsilyl group provides for additional control of both the gas permeation and the mechanical properties of polymer. With proper balance of cosubstituents, the highest permeabilities and improved mechanical properties were obtained without significant decrease in permselectivities.

Experimental Section

Materials. *n*-Butyllithium (2.5 M in hexane) was purchased from Aldrich Chemical Co. (Milwaukee, WI) and was used as received. Trimethylchlorosilane, *n*-propyldimethylchlorosilane, (3,3,3-trifluoropropyl)dimethylchlorosilane, and (1*H*,1*H*,2*H*,2*H*-perfluorodecyl)dimethylchlorosilane were dried over molecular sieves prior to use. Tetrahydrofuran (THF) was freshly distilled from Na/benzophenone, and hexanes were distilled from CaH_2.

Poly(methylphenylphosphazene), **1**, was synthesized via condensation polymerization according to the literature procedure[16] and was dried in a vacuum oven at 50 °C for 24 h prior to use. To get films with sufficient mechanical strength to withstand permeability measurements, parent poly(methylphenylphosphazene) with a number-average molecular weight (M_n) above 100 000 was chosen for the modification reactions. This was most efficiently and reproducibly obtained when sodium phenoxide was used as a polymerization catalyst.[17]

Modification Reactions. All of the modification reactions were carried out under an inert atmosphere according to the procedures described in our previous publication.[8] A representative procedure involved dissolution of 2 g of **1** in 10 mL of THF in a two-neck round-bottomed flask. Then 7 mL (1.2 equiv) of 2.5 M *n*-BuLi was added to the solution at 0 °C, the mixture was stirred at 25 °C for 1 h, and 1.2 equiv of alkyldimethylchlorosilane was added at 0 °C. This solution was stirred overnight and the polymer was isolated and purified by precipitations from THF into water and into hexane. For polymers **3**, **5a,** and **6** only 0.6 equiv of *n*-BuLi and the chlorosilanes were used, while 1.2 equiv of these reagents was used for polymers **4** and **5b**. The preparations of **7**, **8**, and **9** were done in the same manner using 1.2 equiv of *n*-BuLi followed by addition of a total 1.2 equiv of a mixture of trimethylchlorosilane and (1*H*,1*H*,2*H*,2*H*-perfluorodecyl)dimethylchlorosilane with stoichiometric ratios of 1:3, 1:1, and 3:1, respectively.

Polymeric films for gas permeation studies were cast by pouring THF solutions (ca. 30% w/v) of each polymer onto a smooth Teflon plate. The thickness of the films ranged from 0.1 to 0.2 mm. The films were dried slowly in a THF vapor chamber at ambient temperature for 2 days to avoid forming bubbles in the films, which hamper the gas permeation studies. The films were removed from the Teflon plate at 0 °C and then dried under vacuum at ambient temperature for 4 days prior to characterization and gas permeability measurements.

Characterization. NMR spectra were obtained on an IBM WP-200SY FT system, and elemental analyses were carried out using a Carbo Erba Strumentazione 1106 CHN elemental analyzer. Gel permeation chromatography measurements were performed as described previously using polystyrene standards.[8,16b] The glass transition temperatures were determined using a Dupont DSC Model 910 instrument equipped with a TA operating software module and data analysis system. The 5−10 mg samples were crimped in a small aluminum boat and were heated from −80 to 120 °C at 10 °C/min. Measurements were made against an aluminum reference. Glass transition temperatures listed in this study were the average of data obtained from second and third heating circles.

The X-ray photoelectron spectrum was obtained at Texas A&M University using a Perkin-Elmer (PHI) Model 5500 ESCA spectrometer (Mg Kα X-rays, 15 kV, 300 W). The incident angle was 45°. Atomic concentrations on the film surface were calculated from integrated signal intensities from multiplex XPS spectra and atomic sensitivity factors.[18]

A solution of calcium nitrate, water, and ethanol was made to measure the density of each polymer sample. The density of the solution was adjusted to the point that a piece of polymer sample did not float or settle to the bottom of the solution. The density of the solution was then determined and used as the density of the polymer sample.

Gas Permeation Studies. Generally, the permeability of polymeric membranes to gases can be interpreted as classical solution diffusion equilibria and kinetics.[1] Based on Fick's first law of mass transport, the transmission rate, **J**, which has the dimension of gaseous volume per film area (A_0) per permeation time (t) can be expressed as

$$\mathbf{J} = \mathbf{D}\cdot\mathbf{S}\cdot(P_1 - P_2)/l \tag{3}$$

where **D** is the diffusivity of the gas in the polymer and **S** is a solubility constant expressing the volumetric gas solubility (at 0 °C and 1 atm) per unit volume of polymer per unit pressure. $P_1 - P_2$ is the external gas pressure difference across the polymeric membrane of thickness l. Under steady-state conditions, the permeability **P** is expressed as

$$\mathbf{P} = \mathbf{D}\cdot\mathbf{S} \tag{4}$$

Equation 4 is true for rubbery polymer membranes. For glassy state membranes, dual mode sorption theory and dual mobility mode apply.[1]

Gas permeation studies were carried out using a specially designed permeation cell similar to that described in the literature.[19] The polymer film was tightly sealed in the cell which was placed in a thermostated bath at 35 °C. The downstream face of the cell was connected to the entrance of the column of a Gow-Mac 350 gas chromatograph through a four-port valve. The GC was equipped with a thermal conductivity detector (TCD), and helium was the carrier gas.[20] The upstream driving pressures of the permeant gases, nitrogen, oxygen, methane, and carbon dioxide, were 3 atm.

The permeation rate of the gas increased with time until solution diffusion equilibrium was reached. The volume (ΔV) of gas permeated in a certain length of time (Δt) was measured from the peak area on the chromatogram. This volume was corrected to the volume (ΔV_0) at 0 °C and 1 atm and was used to calculate the permeability of the gas under standard conditions as shown by eq 5.

$$\mathbf{P} = l\Delta V_0/A_0\Delta t\Delta P \tag{5}$$

ΔP is the experimental pressure difference of penetrant gas between upstream and downstream sides of the polymer membrane. Since the partial pressure of the penetrant gas on the downstream side is negligible as compared to that on the upstream side, ΔP practically equals the pressure of the penetrant gas on the upstream side. For the measurements of permeabilities, the deviation from parallel experiments was less than 10%.

Since the steady-state flux was reached very rapidly, it was difficult to measure the diffusivity, **D**. However, the chromatograms indicated that CO_2 permeation took a relatively long time to reach the steady state. Thus, the time lag, θ, could be estimated from the chromatogram and the diffusivity for carbon dioxide, $\mathbf{D}_{CO_2}$, was obtained by eq 6.

$$\mathbf{D}_{CO_2} = (l^2/6)\theta \qquad (6)$$

For rubbery materials, **D** obtained from eq 6 is true. However, for glassy materials, the diffusion coefficient in eq 6 is the apparent diffusion coefficient, $\mathbf{D}_{\mathbf{app}}$.[21] For the membranes in this study, carbon dioxide had the longest time lag and its diffusivity ($\mathbf{D}_{CO_2}$) ranged from 1×10^{-8} to 50×10^{-8} cm^2/s. Because **D** was relatively high, an accurate value could not be obtained by the technique described here.

Permselectivity, $\alpha_{A/B}$ is defined as

$$\alpha_{A/B} = \mathbf{P}_A/\mathbf{P}_B \qquad (7)$$

where $\mathbf{P}_A$ and $\mathbf{P}_B$ represent the permeability of membrane to gas A and gas B, respectively.

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