Gas Separation, Free Volume Distribution, and Physical Aging of a Highly Microporous Spirobisindane Polymer

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The important parameters for membranes are gas solubility (*S*), diffusivity (*D*), permeability (*P*), and gas selectivity (α) with $P = DS$ and $\alpha_{A/B} = (P_A/P_B) = (D_A/D_B)(S_A/S_B)$. A polymer's permeability and selectivity are usually at odds with one another, and it is common for a polymer with high gas permeability to have poor selectivity and vice versa. Robeson observed this relationship for many polymers and several gas pairs and described it in terms of an upper-bound.[1] Freeman[2] has elucidated the upper-bound relationship as a function of polymer properties. He has shown that mobility selectivity (D_A/D_B) is related to chain flexibility and free volume, whereas solubility selectivity (S_A/S_B) is related to interactions of the gas molecules with the polymer matrix. Generally, high T_g amorphous polymers have offered the best permeability/selectivity combinations as their rigid nature provides a molecular sieving function. For this reason, a number of polymeric material investigations aim to mimic the molecular sieving characteristics of zeolites and carbon molecular sieves by modulating polymer chain packing and mobility. Koros et al. have shown permeability/selectivity can be optimized by changing the polymer packing and bulkiness for a series of polypyrrolone ladder-type structures.[3] Schmidhauser and Koros have shown that incorporating a spirobisindane moiety into the polymer backbone can lead to an increase in permselectivity for certain gas pairs because of inhibition of chain packing.[4,5] Recently, McKeown et al. built upon this finding by producing a series of ladder polymers based on the spirobisindane moiety.[6–8] The spirobisindane ring has been found to impact on the polymer chain intrasegmental mobility and increase pore volume.

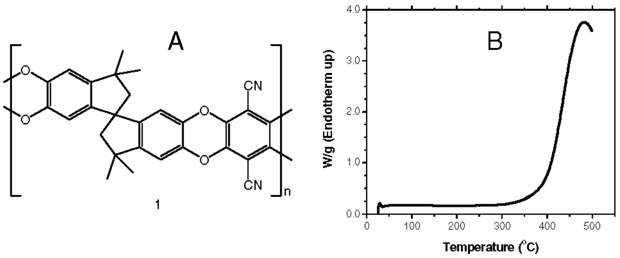

Figure 1. (A) Structure of spirobisindanepolymer **1** and (B) T_g.

Table 1. Single Gas Permeability, Diffusivity, Solubility, and Ideal Selectivity for Spirobisindane Polymer 1[a]

	He	H_2	CO_2	O_2	N_2	CH_4
P	1061	2332	3496	786	238	360
D	678	4.17	0.12	0.27	0.12	0.04
S	0.01	0.43	22.5	2.20	1.56	7.12
KD	2.60	2.89	3.30	3.46	3.64	3.80

Ideal Selectivity ($\alpha_{A/B}$)

He/N_2	4.5	H_2/N_2	9.8	CO_2/N_2	14.7	O_2/N_2	3.3
He/CH_4	2.9	H_2/CH_4	6.5	CO_2/CH_4	9.7	O_2/CH_4	2.2

[a] Average of three measurements with a 5% deviation in samples. *P* = Barrer, 1 × 10^{10} cm^3 (STP) cm/(cm^2 s cm Hg); *D* = 1 × 10^5 cm^2/s, *S* = cm^3 (STP)/(cm^3 atm), KD = Å.

In this contribution, we present results from the first direct measurement of the pore size distribution and physical aging of this class of polymer using positron annihilation lifetime spectroscopy (PALS), enabling us to conclusively compare this class of polymer with more traditional high free volume glassy polymers for the first time. Spirobisindane polymer **1** (Figure 1A) was prepared as described by McKeown et al.[7] Free standing films were formed with a 20 wt % polymer and CH_2Cl_2 solution that was evaporated over a 4 day period. Resultant films were tough, flexible, and fluoresced under UV light. Size exclusion chromatography revealed molecular weights of ~100 000 g mol^{-1} (M_w) with PDIs of 3.0–3.5 for polymer **1**.

A glass-transition temperature (T_g) of 436 °C was measured by DSC (TA Instruments 2950) at a scan rate of 10 °C/min in air (Figure 1B). A 5% weight loss was observed at 504 °C via gravimetric analysis (TA Instruments 2910). The time lag method[9] was used to measure the single gas permeability, diffusivity, and solubility of polymer **1**. Gas-transport properties were evaluated from an unaged sample using He, H_2, CO_2, O_2, N_2, and CH_4 as a probe gas at 35 °C and 4 atm (Table 1).

Changes in the gas permeability were also measured as a function of time to follow changes in the physical properties.

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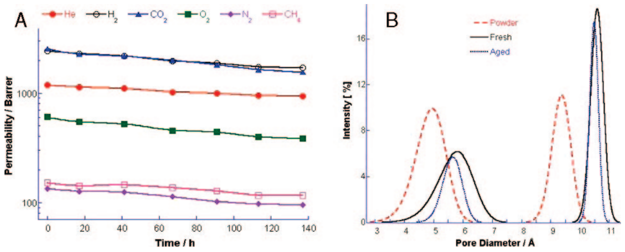

Figure 2. (A) Decrease inpermeability as a function of time. (B) Free volume distribution results obtained from PALS measurements of the spirobisindane polymer **1** in the powder form (- - -) and in the solution processed film before(—) and after (----) permeability measurements.

Although initial gas permeabilities were remarkable, further testing resulted in a slow degradation of gas permeability at the test conditions of 35 °C and 4 atm as a function of time (Figure 2A). Initial test conditions for this study began with an unaged sample that was tested continuously over a period of 140 h. During this test time, the permeability of individual gases declined between 20% (He) and 40% (CO_2) before the film failed. Interestingly, aged materials gave results, as reported in Table 1, similar to those previously reported for this polymer cast from tetrahydrofuran.[11] Because of the high T_g for this polymer, it is believed that plasticization may not be the reason for the rapid decline in permeability. These results suggest that solvent type may contribute significantly to the physical properties because of differences in polymer solubility, which affects many physical properties of polymers such as gas transport. Additional studies are warranted for elucidating the role of solvent and polymer molecular weight as it pertains to gas transport and the rapid loss in permeability and increase in density observed for this type of polymer.

The spirobisindane polymer **1** showed high permeability for each gas, with CO_2 having the highest permeability of all gases at 3496 barrer. This high CO_2 permeability is unusual when the kinetic diameter of CO_2 is compared to He and H_2 (3.30 Å and 2.6 Å and 2.89A, respectively). On the basis of the relative size of these gases, we expected He and H_2 to have a higher permeability than CO_2. Furthermore, CH_4 is 34% more permeable than N_2 and is 42% larger in size. Examination of the differences between D and S for these gas pairs reveals that S contributes significantly to the gas transport of CO_2 and CH_4, which explains why these large gas molecules have the highest apparent permeability of the gases used in this study. While high gas solubility is a typical property for "rubbery" polymers, it is not typical for "glassy" polymers. These results suggest that this high T_g material is readily placticized by CO_2 and CH_4 and that its "plasticization" may be a significant contributor to its enhancement in gas transport.

A reduction in permeability with increasing feed pressure is commonly observed in glassy polymers and typically described by the dual mode sorption model with partially immobilizing sorption.[12] However, the decreases in gas permeabilities reported here may be the result of a decrease in the free volume of the polymer while in operation. This phenomenon, termed physical aging, has been observed in other high free volume polymers such as PTMSP and AF1600.[13] The fractional free volume (FFV) of the polymer was calculated using Bondi's group contribution theory[14] and the bulk density of the film was measured before and after testing. The density increased from 1.12 to 1.16 g/cm^3(± 0.01 g/cm^3) after use. This increase in density translates to a 20% decrease in FFV between the fresh and used polymer film.

PALS measurements were performed using an automated EG&G Ortec fast−fast coincidence system with a resolution of 240 ps equipped and data were analyzed using PFPOSFIT. PALS spectra are composed of four lifetimes that can be extracted by a nonlinear least-squares fit of a weighted sum of discrete exponentials

$$N(t) = \sum_{i=1}^{k+1} \frac{I_i}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right) \qquad (1)$$

where τ_i denotes the mean lifetime of the positron state i and I_i is the relative intensity of the lifetime component. A component with lifetime longer than 600 ps is generally attributed to $o{-}P_s$. The $o{-}P_s$ wave function has a penetration depth of ΔR into the material surrounding the potential well and is equal to the thickness of the electron layer, which is approximately 1.656 Å. If the radius of the well is R, using quantum mechanics the $o{-}P_s$ pick-off lifetime can be related to the radius of the cavity.[15,16] Equation 2 provides the relationship between R and τ_3.

$$\tau_3 = \frac{1}{2}\left[1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right]^{-1} \qquad (2)$$

The interrelationship between the total fractional free volume (FFV) and τ_3 and I_3 is summarized by eq 3 with C equal to 1.80×10^{-3}/(ns × %).

$$\mathrm{FFV} = C\left(\frac{4\pi}{3}R\right)I_3 \qquad (3)$$

Overall, the PALS experiment uses the $o{-}P_s$ to determine the size and number I_3 of pores. Occasionally, especially in high free volume glassy polymers, two distinct $o{-}P_s$ lifetimes can be measured, τ_3, and τ_4, suggesting a bimodal or very broad pore size distribution. Figure 2B reveals that the solution processed spirobisindane polymer **1** has a bimodal pore distribution. The bimodal distribution has large pores of diameter approximately 10.6 Å and smaller pores of 5.8 Å.

Figure 2B also highlights that the broad distributions observed from the fresh film prior to permeability measurement are narrowed for the film after permeability measure-

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Table 2. PALS Results and O_2 Permeability for Spirobisindane Polymer 1 in the Fresh and Aged Condition Compared with PTMSP and AF1600[a]

	spirobisindane polymer **1**			PTMSP	
	fresh	aged	powder	fresh	aged
τ_3(ns)	2.06	1.98	1.62	1.7	1.7
I_3(%)	6.15	5.72	9.92	7.4	7.4
SPD	5.81	5.67	4.95	5.12	5.12
τ_4(ns)	6.28	6.15	4.88	8.8	8.8
I_4(%)	18.6	17.4	11.06	34	31
LPD	10.6	10.49	9.38	12.38	12.38
SG	1.13	1.16		0.75	
FFV	0.15	0.12		0.34	
PO_2	786	340		9700	

	AF1600		AF2400	PMP
	fresh	aged	fresh	fresh
τ_3(ns)	1.2	1.2	1.32	2.3
I_3(%)	5.51	5.85	4.87	8.4
SPD	3.93	3.93	4.25	6.23
τ_4(ns)	5.11	5.21	5.78	7.6
I_4(%)	17.3	15.1	13.6	29.4
LPD	9.6	9.69	10.19	11.58
SG	1.8		1.7	0.78
FFV	0.28		0.32	0.28
PO_2	350		1290	2700

[a] FFV, fractional free volume; SPD, small pore diameter; LPD, large pore diameter; SG, specific gravity.

ment with slightly smaller pore sizes and lower intensities, especially for the larger pores.

This reduction in free volume is similar to the physical aging process observed for other high free volume polymers such as PTMSP,[17] AF1600,[18] AF2400,[19] and PMP.[20] PALS has been successfully employed to provide detailed information on the size and concentration of free volume elements of each of these well-known high free volume glassy polymers, and these results are included in Table 2. In comparison to PTMSP, the spirobisindane polymer **1** has larger small pores and smaller large pores and much less of both of them. It may be concluded that the increase in density and decrease in gas permeabilities observed in Figure 2A are most likely the result of physical aging. It is also noteworthy that the fractional free volume of the spirobisindane polymer **1** in Table 2, calculated using the Bondi contribution method, is much lower than for the other high free volume polymers listed. On the basis of the PALS and oxygen permeability results in Table 2, a fractional free volume closer to that of AF1600 would be expected for the spirobisindane polymer **1**. The fractional free volume calculated for the spirobisindane polymer **1** is more like the values commonly obtained for polysulfone (0.16) or polyimide (0.17) membranes.

Figure 2B also illustrates the effect of film processing on the free volume charecteristics of the spirobisindane polymer **1**. It can be seen that the as-precipitated powder of the spirobisindane polymer **1**, compared to the fresh solution processed spirobisindane polymer **1** film, has a significantly lower number of large pores, which are smaller and very broadly distributed around the mean. Previously reported nitrogen adsorption experiments on spirobisindane polymer **1** showed that the powder has a larger surface area than the solution processed film.[6,21] In light of the PALS results in Table 2, it can be suggested that the previously reported nitrogen adsorption results reflect a greater externally accessible surface area of the powder, rather than the internal pore structure. These PALS results indicate that solvent processing increases the microporosity of the processed polymer from the intrinsic microporosity of the powder. Indeed, although part of this enhanced free volume relaxes during the permeation experiments over time, the free volume distribution following aging is still greater than that measured in the powder. Thus the use of an appropriate solvent, along with methods to mitigate physical aging, may provide a future route for improving the performance of this class of polymers.

A highly contorted ladder polymer was prepared and evaluated for gas transport. The membrane permeabilities were consistent with those of a polymer containing a large amount of free volume. Permeabilities were high for all gases tested and ideal selectivities were also good, particularly for O_2/N_2, H_2/CH_4, H_2/N_2, and CO_2/CH_4 separations. However, degradation of gas permeability and an increase in bulk density was observed during extended testing, suggesting a collapse of free volume within the polymer film. PALS was shown to be a reliable method for determining free volume distributions in this class of polymer and revealed, similar to PTMSP, a bimodal pore size distribution. PALS also revealed that, again similar to PTMSP, the observed decrease in gas permeability is the result of physical aging and is primarily due to the collapse of the larger pores. It was also shown that the solution processing necessary to form free-standing membranes of the polymer, resulted in an increase in free volume when compared to the intrinsic free volume of the powder. This discovery may point to methods of manipulation of polymer functionality or structure which could result in improved performance of this class of polymer.

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