

Polyimides and Their Derivatives for Gas Separation Applications

234th Annual ACS National Meeting

John R. Klaehn
Christopher J. Orme
Thomas A. Luther
Eric S. Peterson
Jagoda M. Urban-Klaehn

July 2007

The INL is a
U.S. Department of Energy
National Laboratory
operated by
Battelle Energy Alliance



This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint should not be cited or reproduced without permission of the author. This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, or any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use, or the results of such use, of any information, apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights. The views expressed in this paper are not necessarily those of the United States Government or the sponsoring agency.

Polyimides and Their Derivatives for Gas Separation Applications

John R. Klaehn¹, Christopher J. Orme¹, Thomas A. Luther¹,
Eric S. Peterson¹, Jagoda M. Urban-Klaehn²

¹Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415-2208

²Idaho Accelerator Center, 1500 Alvin Ricken Dr., Pocatello, ID 83201

INTRODUCTION

Fossil fuels will remain the core of energy production well into the 21st century. Availability of these fuels to provide clean, affordable energy is essential for the prosperity and security of the United States. Roughly one third of the United States' carbon emissions come from utilities, such as power plants. To stabilize and ultimately reduce greenhouse gas concentrations (especially carbon dioxide), DOE has established the Carbon Sequestration Program with the charge to develop methods for carbon emissions reductions. To be successful, carbon sequestration must meet the following requirements: 1) have effective separation and be cost-competitive, 2) have stable, long term storage, and 3) be environmentally benign.

A set of polyimide-based materials (trade name "VTEC") has been identified as an excellent membrane material. The VTEC polyimides (Kapton-like) possess thermal properties (up to 500 °C) and these polyimides are robust and flexible even after multiple thermal cycles (up to 400 °C). These polymers have proven to be very interesting for the carbon sequestration effort. Another aspect of the high performance polymers is polybenzimidazole (PBI, Figure 1). It is another attractive polymer for challenging high temperature gas separation applications.^{1,2} The INL has developed synthetic routes for a range of post-polymerization-modified PBI materials. Modification of the base PBI has been accomplished with polymer solubility in common organic solvents accomplished. This result makes possible application of membranes to complex shapes utilizing common membrane casting methods. The substituted PBI polymers were not advantageous for high temperature gas separation; however, these substituted polymers showed to be useful as blends with VTEC.

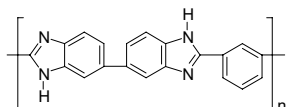


Figure 1. PBI (polybenzimidazole).

EXPERIMENTAL

Instrumentation. Proton and ¹³C{¹H} NMR spectra were recorded on a Bruker DMX 300WB spectrometer operating at 300 MHz (¹H), 75 MHz (¹³C). Thermal analyses were obtained using TA Instruments Model 2910 differential scanning calorimeter (DSC) and a Model 2950 thermogravimetric analyzer (TGA).

Pure Gas Testing/Pressure Rise Time-Lag Method. The gas-testing results were obtained using the pressure-rise time-lag method.³ Membranes were exposed to six different gases: He, H₂, N₂, O₂, CH₄ and CO₂. In a typical experiment, both sides of the membrane are evacuated to an equal vacuum. The test cell is then isolated and the pressure at zero time is used as the baseline. Next, the feed side is exposed to the test gas. Finally the pressure build up on the permeate side of the membrane is recorded as a function of time. The two gas transport properties that are determined directly from the pure gas test system are time lag and permeability. The permeability is the rate at which the gas permeates through the membrane after the gas has come to equilibrium in the polymer. The time lag is the time it takes the gas to permeate from the feed side of the membrane to the permeate side and is used to calculate the diffusivity.

The basic relationship of gas-transport properties, permeability (P), solubility (S), and diffusivity (D) in polymeric membranes is expressed in the following terms.

$$P = DS \quad (1)$$

Permeabilities for these experiments were calculated using the following equations where test system volume is *V* (cm³), test system feed gas initial pressure is *p*₁ (cm Hg), test system temperature is *T* (°C), membrane thickness is *l* (cm), and membrane area exposed to the feed gas is *A* (cm²). The slope was determined from a least squares fitted line of the time (sec) versus permeate gas pressure (cm Hg) steady-state data set (data during equilibrium flux) obtained using the above method.

$$P = \text{slope} \frac{V}{76} \frac{273}{(273 + T)} \frac{1}{A} \frac{l}{p_1} \quad (2)$$

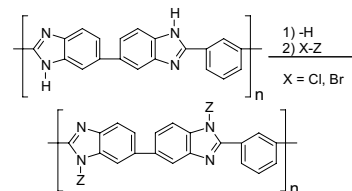
The time-lag is the intercept of the baseline and the least square fitted line for the data set. The determined value for the time lag is used to calculate the diffusivity *D*.

$$t = \text{timelag} = \frac{\text{baseline} - \text{intercept}}{\text{slope}} \quad D = \frac{l^2}{6t} \quad (3)$$

The gas solubility is algebraically calculated from the measured quantities of permeability and diffusivity using eq 1.

DISCUSSION

From previous work, INL has successfully synthesized, characterized and tested the following N-substituted PBI polymers where Z = RMe₂SiCH₂-, RO₂C-, RCO-, R-; R = alkyl, phenyl (Scheme 1). This synthetic pathway provides moderate yields with a high degree of substitution of -Z. These N-substituted PBI polymers are soluble in common solvents, such as tetrahydrofuran (THF).



Scheme 1. Z = RMe₂SiCH₂-, RO₂C-, RCO-, R-; R = Alkyl

There are few literature citations that describe N-substituted PBI materials that are soluble in common solvents.⁴ Our purified modified polymers will dissolve in THF and chloroform. The yields among the substitutions were approximately 50%. Overall, our gas testing data for N-substituted PBI polymers show that the gas permeabilities were higher, but the gas separations (like H₂/CO₂) were not as good as the parent PBI material.

A promising family of polymers for gas separation is VTEC polyimides. We are using VTEC polymers along with N-substituted PBI and other polymer systems to develop membranes that can provide better gas separation. Interestingly, VTEC polymers films do not change after being heated in a convection oven at 250 °C for days. Conversely, many organic polymers will degrade (carbonize) at high temperatures when exposed to the atmosphere for extended periods.

The gas transport data from the polymers is quite astonishing and competitive with the other high performance gas separation polymers. As we began to observe the transport properties of the polymers, it quickly became apparent that the polymer processing procedures for preparation of the membranes is critical. Thus, we developed a heat treatment regimen that gives reliable gas testing data and repeatable film casting techniques.

TGA data (Figure 2) were taken on the same VTEC PI 80-051 with and without ~10 wt% elemental bromine added to the polymer.

Over the 12-hour period of the experiment, at a temperature of 300°C, (all INL polymers were heat cycled before the TGA evaluation), very little weight loss was shown. The parent VTEC PI 80-051 shows a 1.06% weight loss and the same material with 10-wt% bromine at 300°C over 12 hours demonstrates only 1.5% weight loss. The weight loss difference between the two films is minor, less than 0.5%; therefore, the loss of the “remaining” bromine is not an issue. The team suggests that the “remaining” bromine is tightly held by the polymer by either van der Waals interactions or covalent bonding. In addition, several other INL’s experiments have shown no problems with the VTEC polymers operating at 300°C.

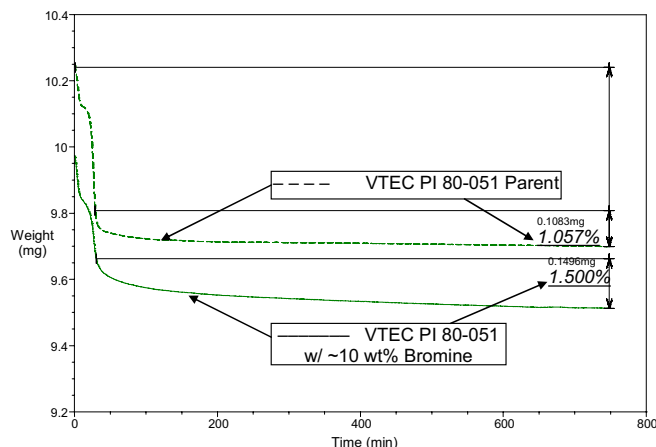


Figure 2. TGA composite of VTEC 80-051 Parent and VTEC 80-051 w/ ~10 wt% bromine at 300°C for 12 hours.

A critical variable when working with the glassy polymers is their moisture content. Moisture content of the polymer solutions plays a major role with the gas selectivity, especially when the gas permeation rates are low. It has been found that water entrapped within the polymer matrix (either as hydration molecules attached to salts in the polymer, left over solvent, or physisorbed) can also cause the polymer to change dramatically (Table 1). This is evident with the time lag (gas permeability) values determined in the gas permeation experiments. In some cases, the same membrane gave different gas permeation values simply because the membrane was exposed to a humid environment between tests. INL has found that the presence of moisture in the gas stream or in the polymer generally decreases the gas selectivity, while a scrupulously dried membrane will show better performance. Upon discovery that moisture from the environment was being absorbed into the membranes, additional effort was made to dry the films prior to testing. These efforts comprised drying at 150°C for longer periods (24-48 hours). In addition, the membranes were sometimes further dried at 250°C for another 24 hours, such as for VTEC PI 08-051 w/ 10 wt% LiCl. After the drying, the membrane was then quickly transferred to the gas testing apparatus and placed under vacuum for the gas permeation evaluation using dry gas streams.

Table 1. Pure Gas Data Collected at 30 °C

Polymer	Permeability (barrers) ^a						Selectivity α	
	H ₂	Ar	N ₂	O ₂	CH ₄	CO ₂	H ₂ /CO ₂	H ₂ /CH ₄
VTEC PI 80-051w/~10 wt% LiCl (wet)	4.20	0.35	0.11	0.20	1.01	1.38	3.0	4.2
VTEC PI 80-051w/~10 wt% LiCl (dry)	4.30	0.04	0.03	0.18	0.03	0.58	7.4	143.3

^abarrers - (10⁻¹⁰)(cm³ (STP) x cm)/(cm² x sec x cmHg))

Presence of molecular water in the polymer's void volume has been validated through Positron Annihilation Lifetime (PAL) spectroscopy for VTEC 80-051 (Table 2). From our PALS results, the

differences between the lifetimes and intensities of the spectra for unheated and heated samples are relatively small. Since the microporosity of these samples is low compared to other open volume polymers, their long lifetime and intensity values are low, thus their values have relatively high uncertainty. In the case of low statistics (less than 1 million counts in the spectrum), the software program may act in the unstable way. Therefore, the best indicator of any possible change in the structure is the product of both (intensity and lifetime). Since the free volume fraction is calculated based on both—lifetime (pore size) and the intensity (pore frequency, rate)—it is the most reliable value to consider while comparing the unheated and heated spectra of polymers. It is interesting to note that the free volume fraction for VTEC polymers increased after the polymer was heated. This may be caused by the fact that more positrons could be trapped inside the volume of the polymers due to the release of the bound water, since the intensity (I₃) has increased significantly.

Table 2. Estimation of Free Volume from PAL Measurements

Polymer	τ _L	τ _L error	I _L %	I _L error	Pore Radius [Å]	Pore Vol. [Å ³]	Free Volume Fraction ^c
VTEC PI 80-051 ^a	2.15	0.67	2.6	1.6	3.01 (2.33-3.55)	114 (53-187)	0.53 (0.10-1.42)
VTEC PI 80-051 ^b	1.8	0.26	4.42	0.86	2.69 (2.4-2.93)	82 (58-105)	0.65 (0.37-1.00)

^aNormal atmospheric humidity exposure (20-40% relative humidity)

^bHeated at 150°C for 1 hour

^cFree Volume Fraction calculated according to the formula:

$$v_f(\%) = 0.0018 \cdot I_3(\%) \cdot \sqrt{4/3\pi R^3}$$

ACKNOWLEDGEMENTS

The work described in this paper was supported by the United States Department of Energy's National Energy Technology Laboratory through Contract DE-AC07-99ID13727 and the Internal Research and Development (IR/D) Program at the National Science Foundation.

REFERENCES

- Vogel, H.; Marvel, C. S. *J. Polym. Sci.* **1961**, 50, 511.
- (a) Marvel, C. J.; Vogel, H. A. Re. 26065, Jul 19, 1966. (b) White, D. M. U.S. Patent 3,408,366, Oct 29, 1968. (c) Chenevey, E. C.; Conciatori, A. B. U.S. Patent 3,549,603, Dec 22, 1970. (d) Sayigh, A. A. R.; Tucker, B. W.; Ulrich, H. U.S. Patent 3,708,439, Jan 2, 1973. (e) Sheratte, M. B. U.S. Patent 4,154,919, May 15, 1979. (f) Choe, E. W. U.S. Patent 4,312,976, Jan 26, 1982. (g) Conciatori, A. B.; Choe, E. W.; Hall, H. K. U.S. Patent 4,483,977, Nov 20, 1984.
- (a) Barrer, R.M. *Trans. Faraday Soc.* **1939**, 35, 628. (b) Wijmans, J.G.; Baker, R.W. *J. Mem. Sci.* **1995**, 107, 1. (c) Rogers, C.; Meyer, J.A.; Stannett, V.; Szwarc, M. *Studies In The Gas And Vapor Permeability Of Plastic Films And Coated Papers, Parts I And II.* TAPPI **1956**, 39, 737. (d) van Amerongen, G.J. *J. App. Physics* **1946**, 17, 972.
- (a) Gieselman, M. B.; Reynolds, J. R. *Macromolecules* **1992**, 25, 4832. (b) Gieselman, M. B.; Reynolds, J. R. *Macromolecules* **1993**, 26, 5633.