Fifth Annual Conference on Carbon Capture & Sequestration

Steps Toward Deployment

Capture – Membranes (May 9, 2006)

Polyimide and Polybenzimidazole Derivatives for Gas Separation Applications

John R. Klaehn, Christopher J. Orme, Thomas A. Luther, Eric S. Peterson*, *Idaho National Laboratory*

Kathryn A. Berchtold, Jennifer S. Young, *Los Alamos National Laboratory*

Alan R. Greenberg, Sudhir Brahmandam, *Department of Mechanical Engineering, University of Colorado*

Jim Acquaviva, Frank Onorato, Scott D. Hopkins, *Pall Corporation*

May 8-11, 2006 • Hilton Alexandria Mark Center • Alexandria, Virginia

**on Detail at National Science Foundation*

CO_2 Separation Using Thermally Optimized Membranes (DOE-Fossil Energy)

- Purpose — Develop high-temperature membranes for more efficient separation of CO_2 from methane and nitrogen streams
  - Develop and test thin, dense film polymer membranes at temperatures of 100 to 400ºC to take advantage of enhanced gas diffusion
  - Develop polymer membranes that have tunable permeability at an optimum temperature range for separation
  - Functional sites will be added to the structure of the polymer chain to facilitate transfer of CO_2 through the membrane
  - Develop polymer/porous metal composite membranes and modules that are chemically and physically robust for use in industrially relevant separation components

Project Roles

- LANL **(Kathryn A. Berchtold and Jennifer S. Young)**
  - **Polymer chemistry expertise**
  - **High temperature membrane testing of composites and films**
  - **Safe handling of flammable and toxic gases**

- CU **(Alan R. Greenberg and Sudhir Brahmandam)**
  - **Novel simultaneous compaction and permeation measurement capability and modeling expertise**

- Pall Corp. **(Jim Acquaviva, Frank Onorato, and Scott Hopkins)**
  - **Unique porous metal tubular support**
  - **Thin film formation**
  - **Membrane and module design and manufacturing capabilities**

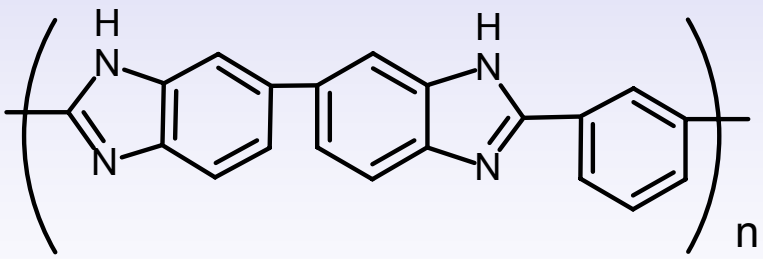
- INL **(John R. Klaehn, Christopher J. Orme, Thomas A. Luther, Eric S. Peterson)**
  - **Synthetic polymer chemistry expertise**
  - **Membrane formation and testing expertise**

Previous Work:

New Soluble N-Substituted Polybenzimidazoles by Post-Polymerization Modification

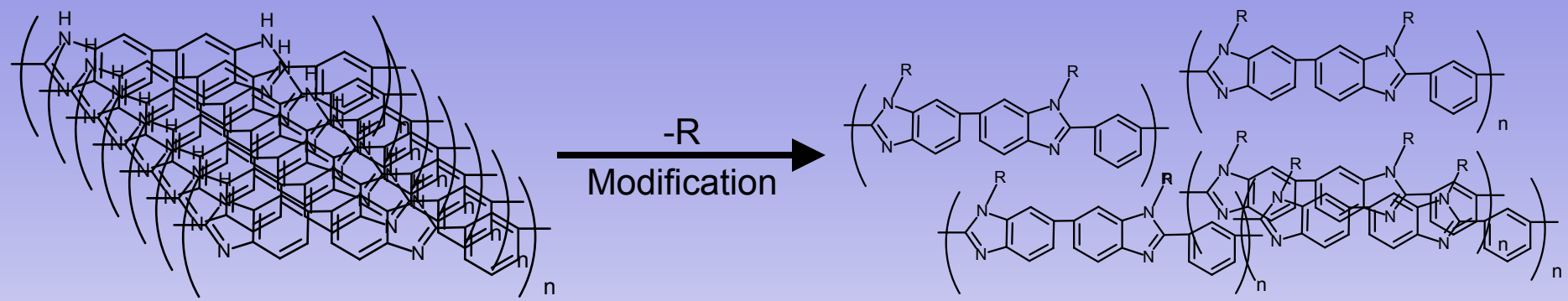
Polybenzimidazole (PBI)
Commercial product trademark – Celazole®

- Thermally stable (Tg ~ 425 ºC)
- Chemically resistant
- Not easily processed



PBI

INL Synthetic Approach: Post-Polymerization Polymer Modification



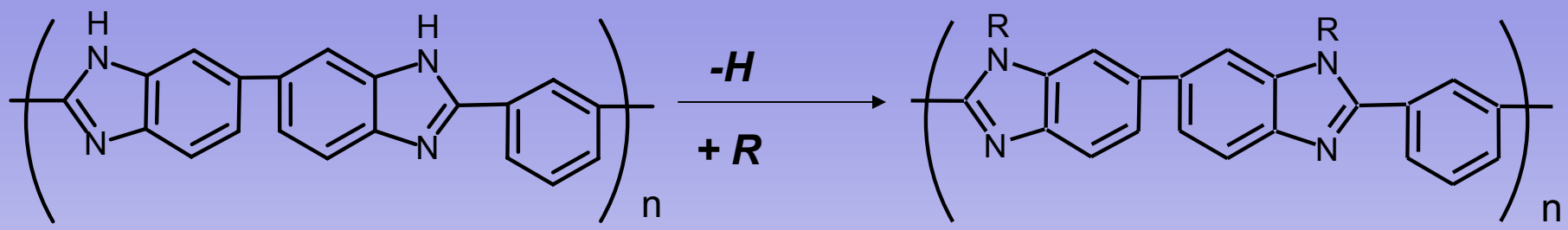
Molecular stacking: increases crystallinity, high Tg, and low free volume

Pi-Pi interactions provide very stable molecular stacking properties and highly crystalline behavior

Molecular stacking is decreased and the structure is opened up

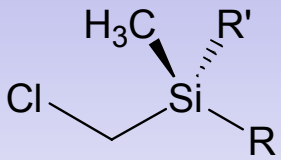
Larger substituent groups break up stacking and crystallinity.

Post-Polymerization Polymer Modification General Reaction*



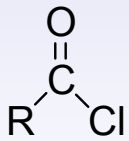
Two different classes of PBI substituents (-R) were developed.

1) **Organosilane functional groups**
(*U.S. Patent Application No. 10/862,921*)

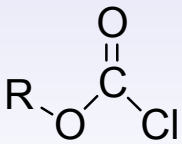


R,R' = alkyl, aromatic

2) **Organo functional groups** (*U.S. Patent Application No. 10/969,456*)
Organo acid chlorides (**1**); Organo chloroformates (**2**); Organo halides (**3**).



(**1**)



(**2**)

R—Br

(**3**)

R = alkyl, aromatic

***U.S. Patent Application No. 10/862,921**
***U.S. Patent Application No. 10/969,456**

PBI Post-Polymerization Modification Product Selection

Total PBI Synthetic Products — **41** PBI Products

↓

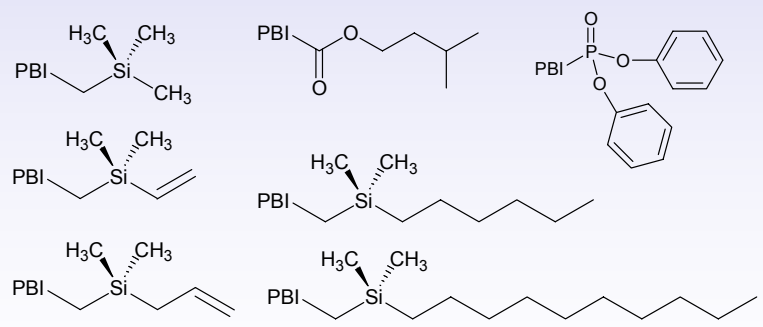
Isolated yields (>10%) coupled with solubility in common solvents (e.g. THF) — **16** PBI Products

↓

Good film formation properties — **13** PBI Products

↓

Final PBI synthetic products selected for gas permeability testing



U.S. Patent Application No. 10/862,921
U.S. Patent Application No. 10/969,456

Summary of Previous Work:

Needs:

- **Decrease crystallinity of polymer**
- **Increase free volume of polymer**
- **Enhance solubility in more volatile solvents**
- **Maintain high glass transition temperatures**
- **Maintain or increase molecular weight of polymer**
- **Must be a good film former for testing/applications**

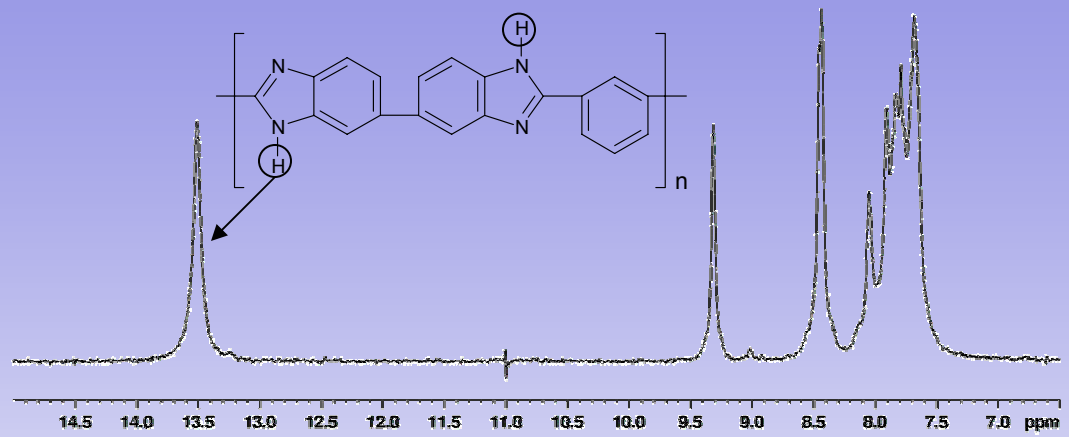
Accomplishments:

- **Decreased crystalline properties**
- **Substituted polymer is freely solubility in common solvents (i.e. THF, $CHCl_3$, Methanol)**
- **Adding ligands gave greater free volume (PALS)**
- **Some functionalized polymers form good films**
- **Membranes casted**
- **Membranes tested (at ambient)**
- **Molecular weights determined**

Overall, the functionalized PBI polymers can give better gas permeabilities; however, H_2/CO_2 separation is not improved compared to the parent PBI polymer.

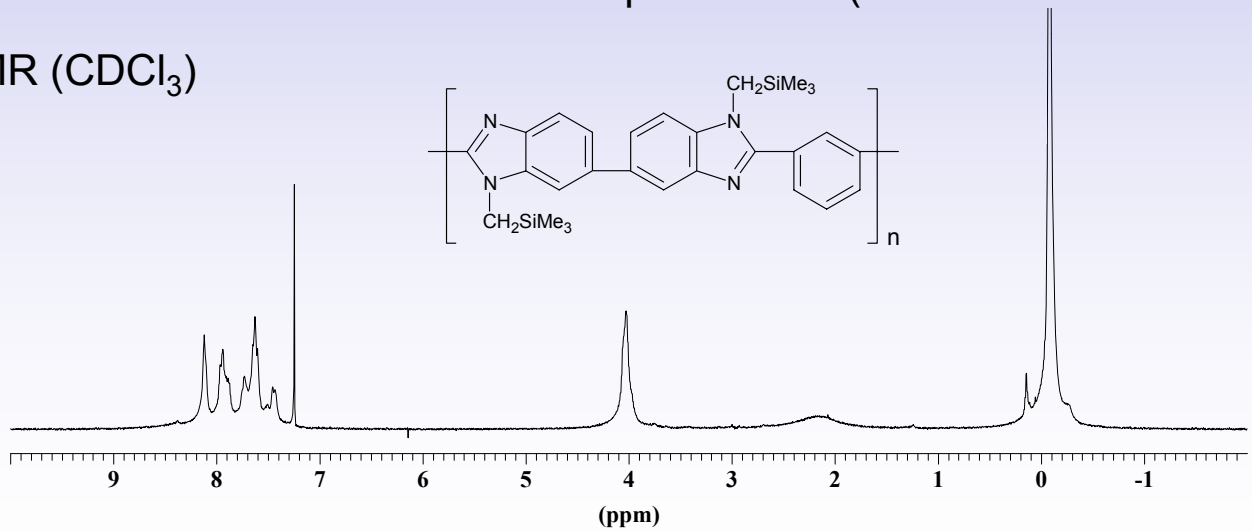
Functionalized PBI vs. Parent PBI

The dominate bonding force for Parent PBI is hydrogen bonding.
^{1}H NMR (DMAc-d_9): Benzimidazole protons are at 13.7 ppm

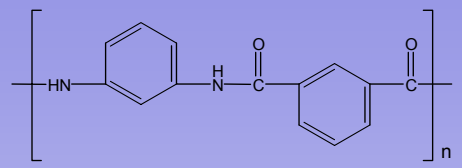


Functionalize PBI does not exhibit this bonding, and it will be difficult to form stable films without other additives or plasticizers (after solvent removal).

^{1}H NMR ($CDCl_3$)

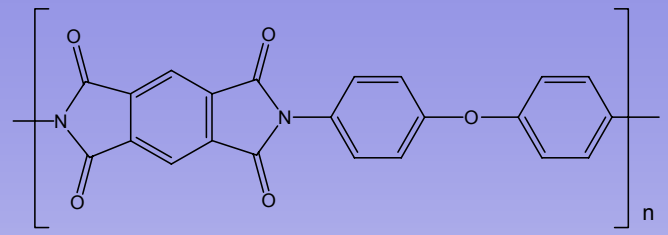


Different High Performance Polymer Classes
Alternative Polymers for Carbon Sequestration at High Temperature



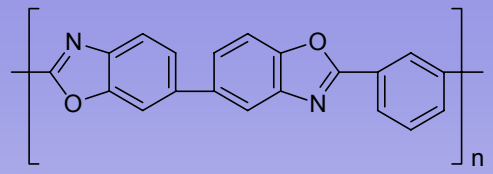
Nomex

Polyamides
(Nylon, Nomex)



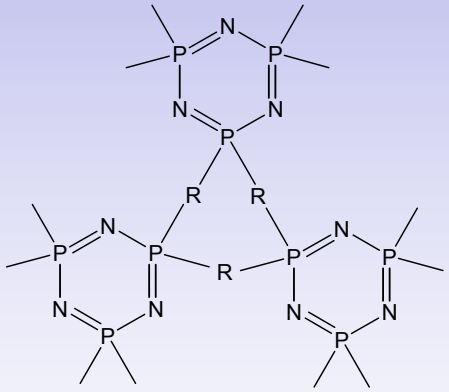
Kapton

Polyimides
(Kapton, VTEC)



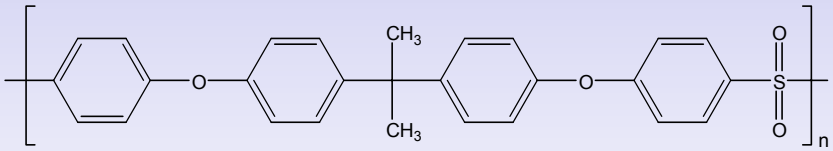
PBO

Polyazoles
(PBI, PBO)



Cyclomatrix

Phosphazenes
(Cyclomatrix derivatives)



Poly (ether sulfone)

Polysulfones
(Polyphenylsulfone)

VTEC Polyimide (RBI, Inc.): Presently Testing

VTEC polyimide (like Kapton) has desirable properties

- No apparent thermal decomposition up to 500 °C
- Good mechanical stability
- Good film formation for high temperature gas separation membranes

Three different VTEC polymers are being tested: PI 851, PI 080-851 and PI 1388.

PI 080-851
Film at 25 °C

PI 080-851 Film after
heated at 250 °C

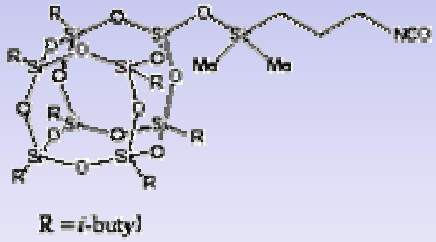
Other High Performance Polymers and Various Polymer Blends

Nomex

Kapton
(directly from manufacturer)

VTEC blended with POSS

- Successfully formed films with other high performance polymers.
- Able to obtain films from the manufacturer.
- Able to blend POSS (Polyhedral oligomeric silsesquioxane) with VTEC polyimides and form films with these blends.
- Able to obtain polybenzimidazole (PBI) from PBI Performance Products, Inc. for blending along with other high performance polymers, like VTEC.

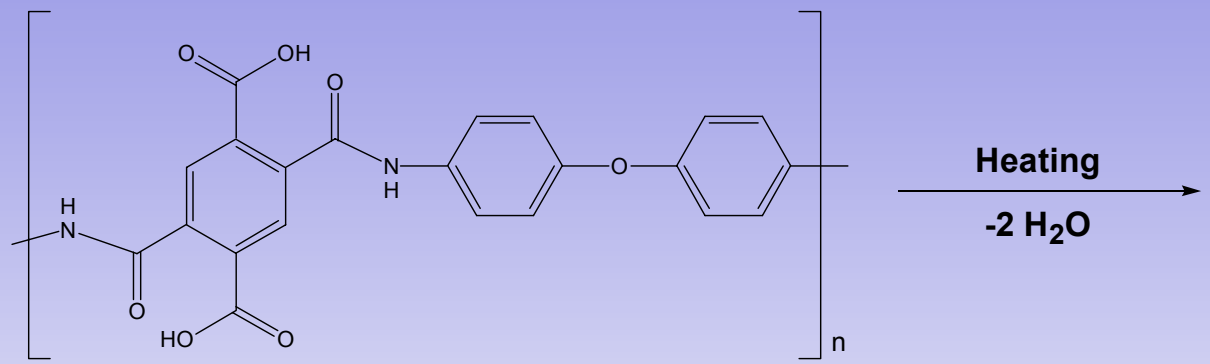


POSS

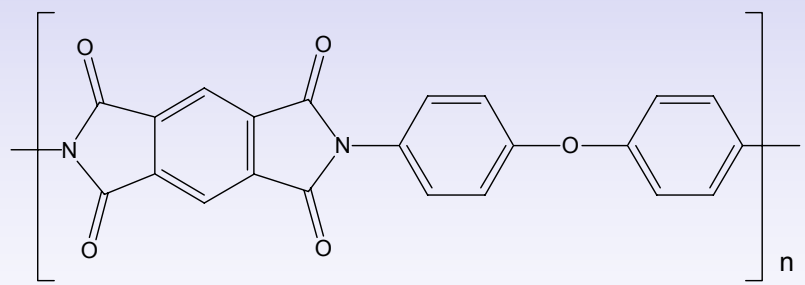
These polymers and polymer blends will help find other polymers that can be useful for high temperature gas separation and carbon separation

Polyimide Polymers

The polymer is the polyamide (or pre-polymer) before heat treatment



Pre-polymer to Kapton



Kapton

A heat treatment regimen is needed to yield polyimide

VTEC Polyimide Polymer

We verified through ^{1}H NMR that the VTEC polymers have carboxylic acid groups (pre-polymer), therefore heat processing is needed.

Thermal Decomposition is beyond 500 °C for all of the heat processed VTEC polyimide films.

Polymer Films	TGA Weight Loss under Nitrogen not heat processed	TMA Thermal Transition heat processed (dimensional change)
VTEC PI 851	243 ºC (-H_2O); 512 ºC	243 ºC (~2.5 µm; to 400 ºC)
VTEC PI 80-851	237 ºC (-H_2O); 524 ºC	255 ºC (~5.0 µm; to 400 ºC)
VTEC PI 1388	241 ºC (-H_2O); 529 ºC	285 ºC (~1.0 µm; to 400 ºC)

VTEC Polyimide Polymer Processing

Preparation of the membranes is critical for reliable gas testing data

A heat treatment regimen was used

- Casting the polymer membrane
- Evaporating the solvent from the polymer film over night, and heating to 100 °C to remove any water from the system
- Heating to 150 °C to remove any additional solvent from the system
- Heating to 250 °C for the polyimide to cure
- Lifting of the films from the plates in water
- Final drying at 150 °C followed by testing

Pure Gas Data Collected at 30° C for VTEC Polyimides

Polymer	Permeability (GPU, *[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 1388 No Heat Treatment	0.019 *[1.50]*	*b*	*b*	*b*	0.001 *[0.08]*	0.002 *[0.15]*	10.0	18.8
VTEC PI 80-851 No Heat Treatment	0.041 *[3.68]*	*b*	*b*	*b*	0.007 *[0.59]*	0.005 *[0.43]*	8.6	6.2
VTEC PI 851 No Heat Treatment	0.062 *[4.36]*	*b*	*b*	*b*	0.004 *[0.25]*	0.007 *[0.48]*	9.1	17.4
VTEC PI 1388 Heated to 250° C	0.041 *[3.30]*	*b*	*b*	*b*	0.001 *[0.10]*	0.004 *[0.3]*	11.0	33.0
VTEC PI 80-851 Heated to 250° C	0.084 *[7.59]*	*b*	*b*	*b*	0.003 *[0.27]*	0.008 *[0.68]*	11.2	28.1
VTEC PI 851 Heated to 250° C	0.043 *[3.01]*	*b*	*b*	*b*	0.008 *[0.53]*	0.005 *[0.32]*	9.4	5.7

[a]Permeabilities measured in GPU: $(10^{-6})(cm^3(STP)\ cm^{-2}\ sec^{-1}\ cmHg^{-1})$;
barrers: $[(10^{-10})((cm^3\ (STP)\ x\ cm)/(cm^2\ x\ sec\ x\ cmHg))]$
[b]not tested

Pure Gas Data Collected at 30° C[a]

Polymer	Permeability (GPU, *[barrers]*)[b]						Selectivity α	
	H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2	H_2/CH_4
VTEC PI 80-851	0.089 *[3.56]*	0.005 *[0.20]*	0.002 *[0.06]*	0.005 *[0.19]*	0.001 *[0.03]*	0.012 *[0.48]*	7.4	121.6
VTEC PI 1388	0.099 *[3.97]*	0.001 *[0.055]*	0.001 *[0.035]*	0.004 *[0.168]*	0.001 *[0.05]*	0.013 *[0.53]*	7.5	30.8
VTEC blend PI 80-851/ ~17 wt% PBI	0.173 *[3.45]*	0.002 *[0.047]*	0.001 *[0.020]*	0.008 *[0.168]*	0.001 *[0.02]*	0.031 *[0.61]*	5.7	172.5
VTEC blend PI 1388/ ~17 wt% PBI	0.156 *[3.12]*	0.002 *[0.045]*	0.002 *[0.041]*	0.008 *[0.151]*	0.002 *[0.03]*	0.025 *[0.49]*	6.4	30.8
VTEC blend PI 1388/ ~17 wt% POSS	0.072 *[6.5]*	*c*	*c*	*c*	0.009 *[0.8]*	0.023 *[2.1]*	3.1	8.1

[a]All polymers in this table were heat cycled prior to testing.
[b]Permeabilities measured in GPU: $(10^{-6})(cm^3(STP)\ cm^{-2}\ sec^{-1}\ cmHg^{-1})$;
barrers: $[(10^{-10})((cm^3\ (STP) \times cm)/(cm^2 \times sec \times cmHg))]$
[c]not tested

Mixed Gas Data Collected at 250° C.[a]

Polymer	Permeability (GPU, *[barrers]*)[b]						Selectivity α	
	H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2	H_2/CH_4
VTEC PI 80-851	1.66 *[83.0]*	0.062 *[3.1]*	*c*	*c*	0.046 *[2.3]*	0.19 *[9.3]*	8.9	36.1
VTEC PI 851	1.46 *[55.4]*	0.074 *[2.8]*	*c*	*c*	0.047 *[1.8]*	0.15 *[5.6]*	9.9	30.8
VTEC blend PI 1388/ ~17 wt% PBI	3.05 *[30.5]*	0.11 *[1.1]*	*c*	*c*	0.08 *[0.8]*	0.40 *[4.0]*	7.6	38.1

[a]All polymers in this table were heat cycled prior to testing.
[b]Permeabilities measured in GPU: $(10^{-6})(cm^3(STP)\ cm^{-2}\ sec^{-1}\ cmHg^{-1})$;
barrers: $[(10^{-10})((cm^3\ (STP) \times cm)/(cm^2 \times sec \times cmHg))]$
[c]not tested

Summary

- We are able to obtain high performance polymers from companies, like PBI Performance Products, Inc. and RBI/VTEC.

- VTEC polyimides are very good candidates for high temperature gas separation. We are currently testing these polymers and their blends with POSS. Preliminary gas testing of the VTEC polymers and VTEC/PBI blends show a H_2/CO_2 separation factor (alpha) between 5-10.

- We have been able to cast films of many different high performance polymers and their blends. We are in the process of gas testing the polymers.

- Overall, the data obtained from these tests will give alternative high performance polymers for the carbon sequestration effort.

Acknowledgements

The work was supported by the United States Department of Energy's National Energy Technology Laboratory through Contract DE-AC07-05ID14517 and the Internal Research and Development (IR/D) Program at the National Science Foundation.