Polyimide and Polybenzimidazole Derivatives for Gas Separation Applications

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Idaho National Laboratory

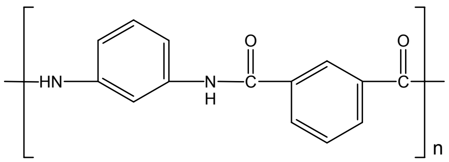
May, 2007

Carbon Capture and Sequestration Conference

CO_2 Separation Using Membranes

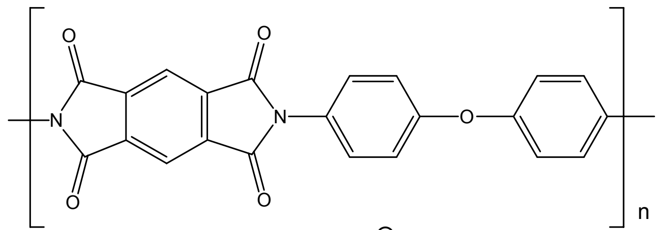
- **Purpose - Develop high-temperature membranes for efficient separation of CO_2 from methane and nitrogen containing streams**
- **Approach:**
  - Develop and test thin, dense film polymer membranes at temperatures of 100 to 400ºC to take advantage of enhanced gas diffusion
  - Develop polymer membranes that have tunable permeability at an optimum temperature range for separation
  - Functionality 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

High Performance Polymers: Alternatives for Carbon Separation and Sequestration at High Temperature



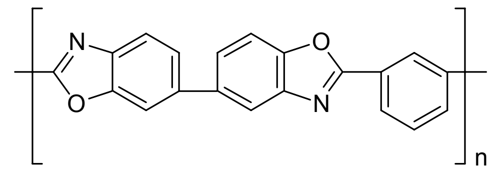
Nomex®

Polyamides
(Nylon, Nomex®)



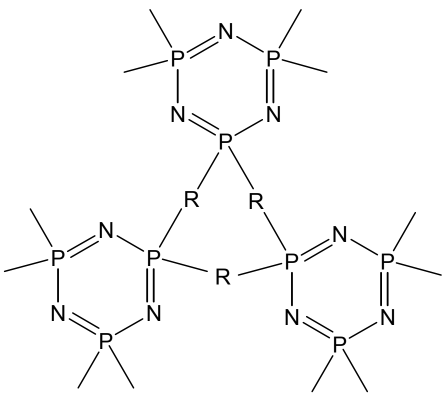
Kapton®

Polyimides
(Kapton®, VTEC)



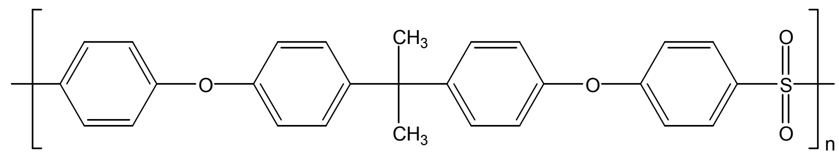
PBO

Polyazoles
(PBI, PBO)



Cyclomatrix

Phosphazenes
(Cyclomatrix derivatives)



Poly (ether sulfone)

Polysulfones
(Polyphenylsulfone)

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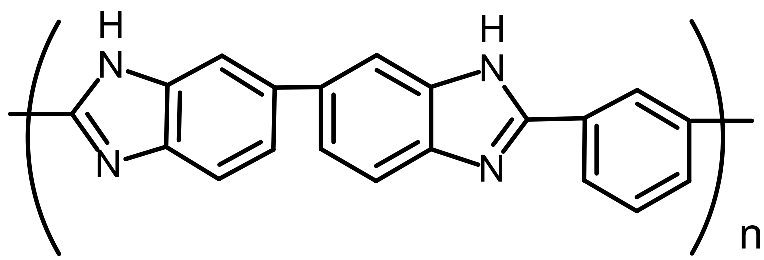
Soluble N-Substituted Polybenzimidazoles by Post-Polymerization Modification

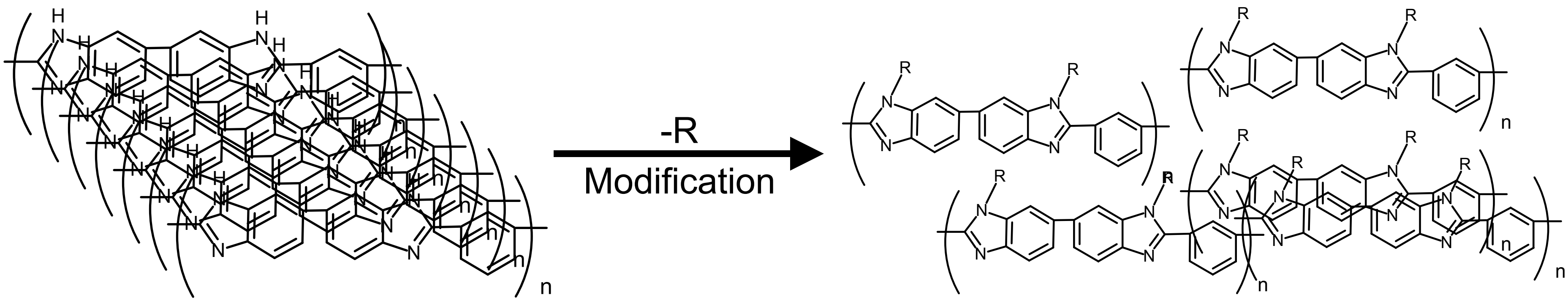
Polybenzimidazole (PBI)
Commercial product trademark – Celazole®

- **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.

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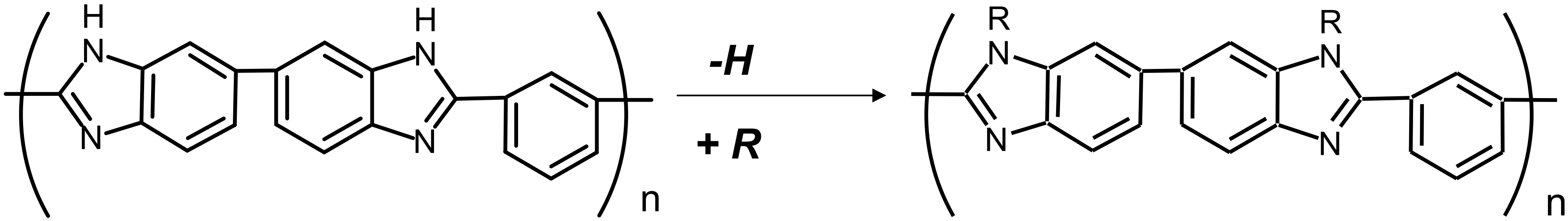
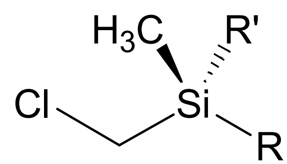
Post-Polymerization Polymer Modification
*General Reaction**



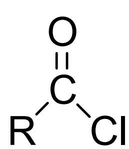
Two different classes of N-substituents (-R) were developed.
[More than 40 N-substituted PBI compounds were synthesized.]

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

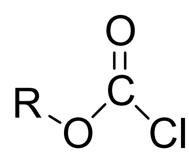


R,R' = alkyl, aromatic

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



(**1**)



(**2**)

R−Br

(**3**)

R = alkyl, aromatic

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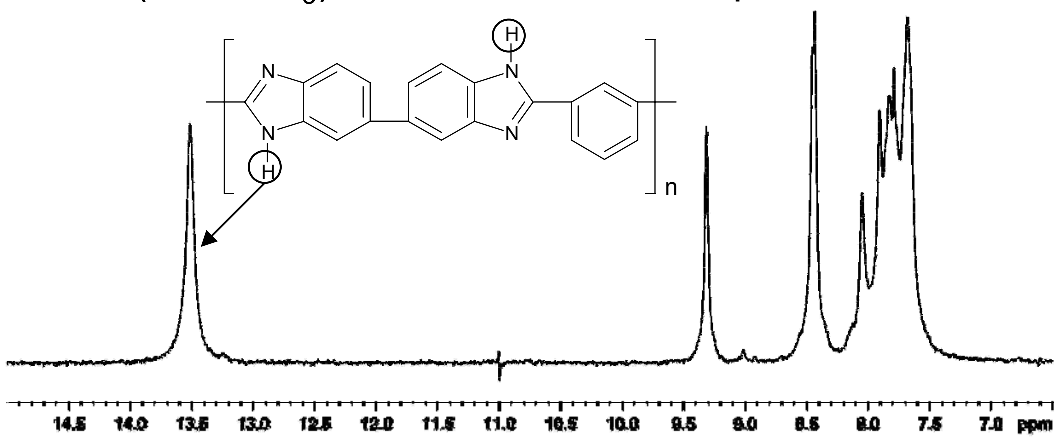
<u>*U.S. Patent Application No. 10/862,921</u>
<u>*U.S. Patent Application No. 10/969,456</u>

N-Substituted PBI vs. Parent PBI

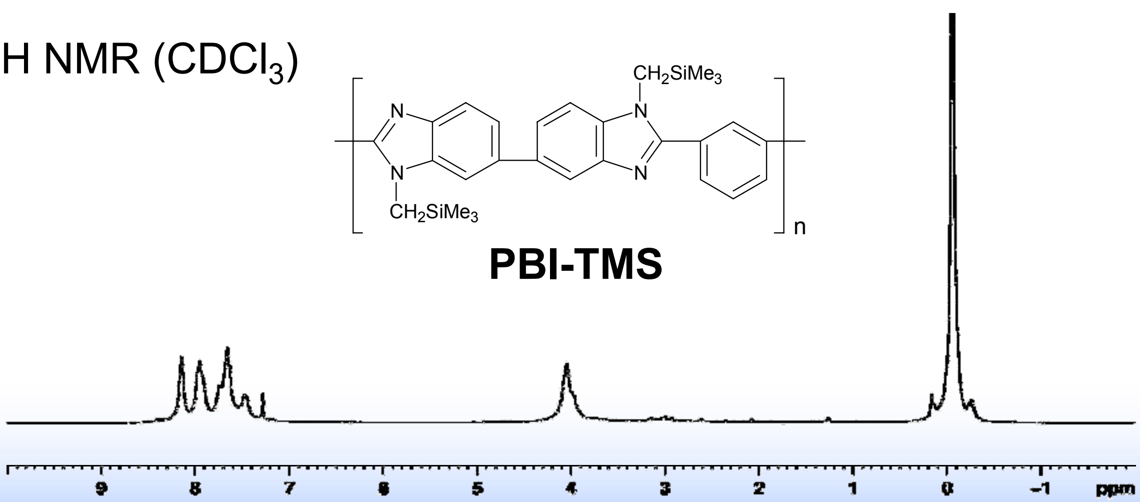
The dominate intermolecular interaction for the Parent PBI is hydrogen bonding.

^{1}H NMR (DMAc-d_9): Benzimidazole N-H protons are at 13.7 ppm



N-Substituted PBI does not exhibit this bonding, and formation of stable films is difficult without other additives or plasticizers that remain after solvent removal.

^{1}H NMR ($CDCl_3$)



Substituted PBI - Summary of Accomplishments

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 soluble in common solvents (i.e. THF, $CHCl_3$, Methanol)
- Adding ligands gave greater free volume (PALS)
- Some functionalized polymers form good films
- Membranes tested (at ambient and high T)
- Molecular weights determined

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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.

A change was needed !

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VTEC Polyimide (RBI, Inc.):

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 080-051 and PI 1388.

PI 080-051
Free-casted film at 25 °C

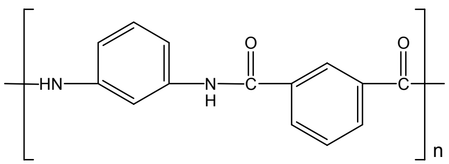
PI 080-051 Film after
heated at 250 °C (atm) for 24 hours

Other High Performance Polymers and Various Polymer Blends

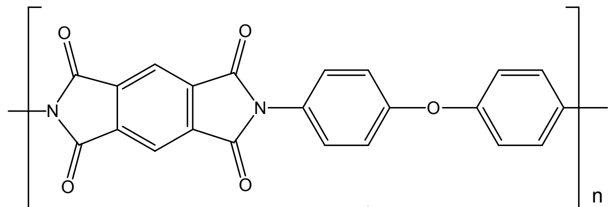
Nomex®

Kapton®
(from manufacturer)

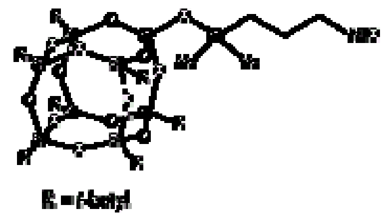
VTEC blended with POSS



Nomex®



Kapton®



POSS

- Successfully blended VTEC with other polymers.
- Successfully formed membrane films with the blends
- Tested films from manufacturers (Kapton®).
- Able to blend POSS (Polyhedral oligomeric silylsesquioxane) with VTEC polyimides and formed films with the blends.

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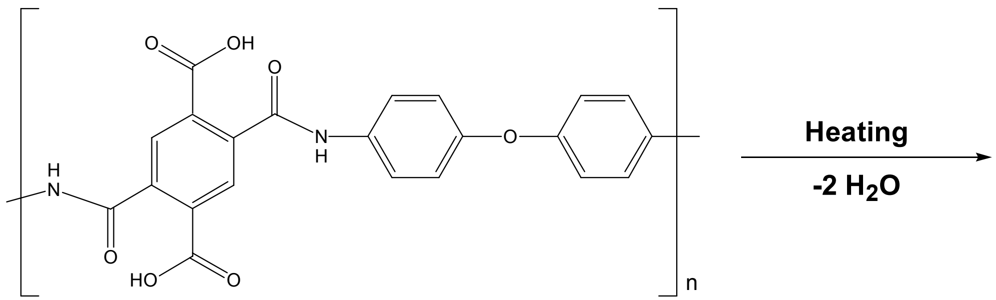
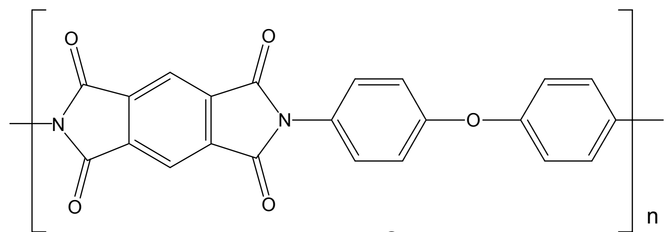
Polyimides

The polymer is the polyamic acid (pre-polymer) before heat treatment



Polyamic acid (Pre-polymer) to Kapton®



Kapton®

After the heat treatment regimen, the polyimide (Kapton®) polymers result

VTEC Polyimides

^1H NMR used to verify that the VTEC polymers have carboxylic acid groups (pre-polymer), therefore heat processing is needed.

Polymer Films	TGA Weight Loss under Nitrogen Before heat treatment; Onset of Decomposition	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 80-051	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)

- **High thermal decomposition temperatures (>500°C)**
- **Very small dimensional changes when heating to 400°C**

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Pure Gas Data Collected at 30° C for VTEC Polyimides

Polymer	Permeability (barrers)[a]						Selectivity α	
	H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2	CO_2/CH_4
VTEC PI 1388 No Heat Treatment	1.50	b	b	b	0.08	0.15	10.0	1.9
VTEC PI 80-051 No Heat Treatment	3.68	b	b	b	0.59	0.43	8.6	0.7
VTEC PI 851 No Heat Treatment	4.36	b	b	b	0.25	0.48	9.1	1.9
VTEC PI 1388 Heat cycled to 250° C	3.30	b	b	b	0.10	0.3	11.0	3.0
VTEC PI 80-051 Heat cycled to 250° C	7.59	b	b	b	0.27	0.68	11.2	2.5
VTEC PI 851 Heat cycled to 250° C	3.01	b	b	b	0.53	0.32	9.4	0.6

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

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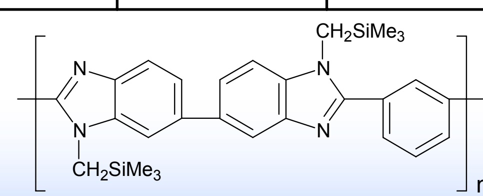
Pure Gas Data Collected at 30° C[a]

Polymer	Permeability (barrers)[b]						Selectivity α	
	H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2	CO_2/CH_4
VTEC PI 80-051	3.56	0.20	0.06	0.19	0.03	0.48	7.4	16.0
VTEC PI 1388	3.97	0.06	0.04	0.17	0.05	0.53	7.5	10.6
PBI Performance Products - PBI	2.82	c	c	c	0.37	0.58	5.0	1.6
DuPont – Kapton®-HN	1.6	c	c	c	0.04	0.28	5.7	7.0
VTEC blend - PI 80-051/ ~20 wt% PBI	3.45	0.05	0.02	0.17	0.02	0.61	5.7	30.5
VTEC blend - PI 80-051/ ~20 wt% PBI-TMS	5.37	0.15	0.08	0.39	0.05	1.50	3.6	28.0
VTEC blend - PI 1388/ ~20 wt% PBI-TMS	4.91	0.15	0.07	0.32	0.04	1.16	4.2	33.0
VTEC blend - PI 1388/ ~17 wt% POSS	6.5	c	c	c	0.8	2.1	3.1	2.6

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



PBI-TMS

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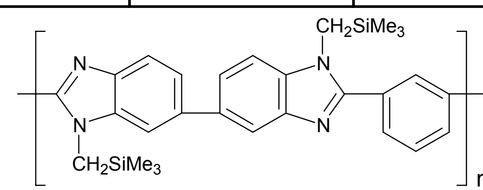
Mixed Gas Data Collected at 250° C.[a]

Polymer	Permeability (barrers)[b]						Selectivity α	
	H_2	Ar	N_2	O_2	CH_4	CO_2	H_2/CO_2	CO_2/CH_4
VTEC PI 80-051	83.0	3.1	c	c	2.3	9.3	8.9	4.0
VTEC PI 851	55.4	2.8	c	c	1.8	5.6	9.9	3.1
PBI Performance Products – PBI	48.7	1.7	c	c	1.3	4.9	9.9	3.8
DuPont – Kapton®-HN	17.9	2.5	c	c	1.9	5.0	3.6	2.6
VTEC blend PI 1388/ ~20 wt% PBI	30.5	1.1	c	c	0.8	4.0	7.6	5.0
VTEC blend PI 1388/ ~20 wt% PBI-TMS	63.7	7.0	c	c	4.1	12.4	5.1	3.0
VTEC blend PI 80-051/ ~20 wt% PBI-TMS	39.0	2.6	c	c	2.1	8.1	4.8	3.9

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



PBI-TMS

Preliminary Data – High Temperature Membrane Treatment - Pure Gas

- **Membrane Treatment Procedure**
  - Cast Membrane and allow solvent to evaporate
  - Drive water out of film
  - Heat to 475°C for approx. 1 hour
  - Test membrane at 30°C

Polymer	H_2	Ar	N_2	O_2	CH_4	CO_2	CO_2/CH_4	H_2/CO_2
VTEC	3.72	0.133	0.057	0.24	0.007	0.63	90	5.9
VTEC	3.71	0.039	0.034	0.23	0.009	0.62	70	6.0
VTEC	5.64	0.148	0.09	0.522	0.05	2.44	48	2.3

Permeabilities measured in barrers: [(10-10)((cm3 (STP) x cm)/(cm2 x sec x cmHg))]

Preliminary Data – High Temperature Membrane Treatment – Mixed Gas

- VTEC Membrane Treatment Procedure
  - Cast Membrane and allow solvent to evaporate
  - Drive water out of film
  - Heat to 475°C for approx. 1 hour
  - Test membrane at elevated temperatures

Temp (°C)	CO_2	CH_4	H_2	CO_2/CH_4
150	12.93	0.87	57.94	14.87
200	16.32	2.32	76.32	7.03

Permeabilities measured in barrers: [(10-10)((cm3 (STP) x cm)/(cm2 x sec x cmHg))]

Summary

- Increased PBI solubility in common solvents and increased PBI free volume.
- The N-substituted PBI polymers give better gas permeabilities, however H_2/CO_2 separation factors are not enhanced compared with the parent PBI.
- VTEC polyimides are very good candidates for high temperature gas separation.
- Developed film casting methodologies for many different high performance polymers and their blends.
- Preliminary gas testing of the VTEC polymers and VTEC/PBI blends show:
  - H_2/CO_2 separation factor (alpha) between 5-10, even at 250°C.
  - CO_2/CH_4 separation factor (alpha) of 28-33 at 30°C with VTEC/PBI and VTEC/PBI-TMS blends.
- Overall, the data obtained from these tests provide alternative high performance polymers for the DOE - Fossil Energy Carbon Sequestration effort.

Project Roles – PBI Portion

- **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

Los Alamos

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PALL Pall Corporation

INL Idaho National Laboratory

Acknowledgements

This work was supported by:

Department of Energy's National Energy Technology Laboratory Fossil Energy Program (DOE-NETL-FE) through Contract DE-AC07-05ID14517

National Science Foundation's Internal Research and Development (IR/D) Program

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