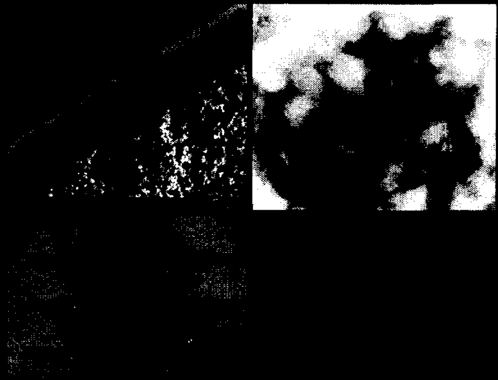
# 탄소-실리카막을 이용한 기체분리

이 영 무 교수
(한양대)



*Presented at the Membrane Workshop, The Membrane Society of Korea, March 26, 2004*

# Carbon-Silica Membrane for Gas Separation

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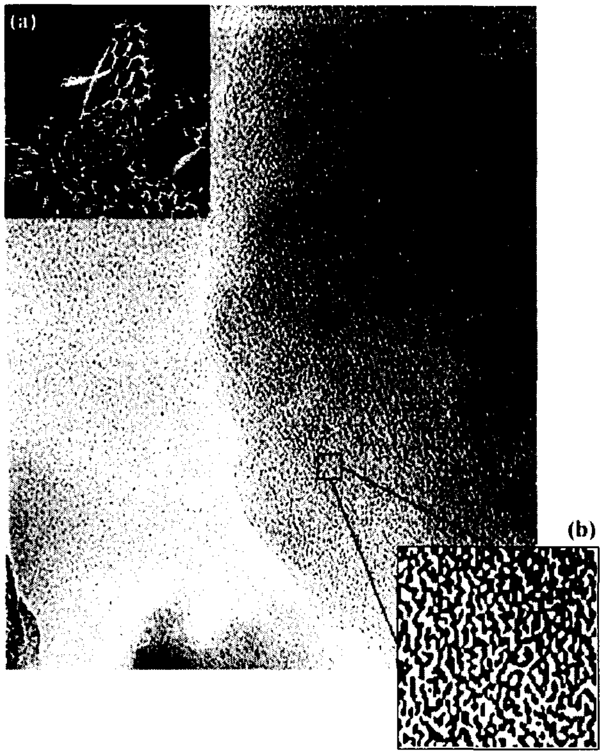
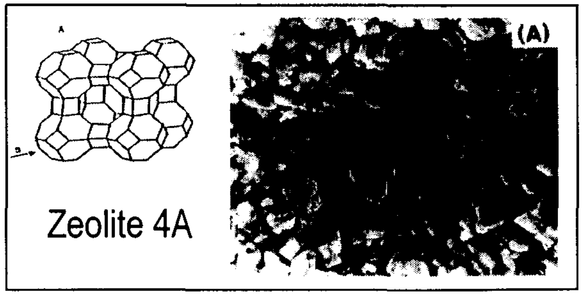
# Structure of Carbon Membrane



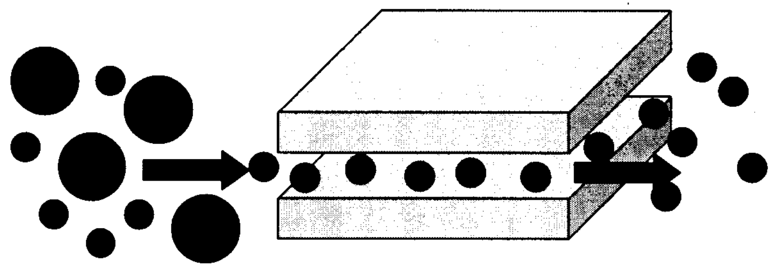

Carbon materials obtained from organic polymers are usually amorphous structure.

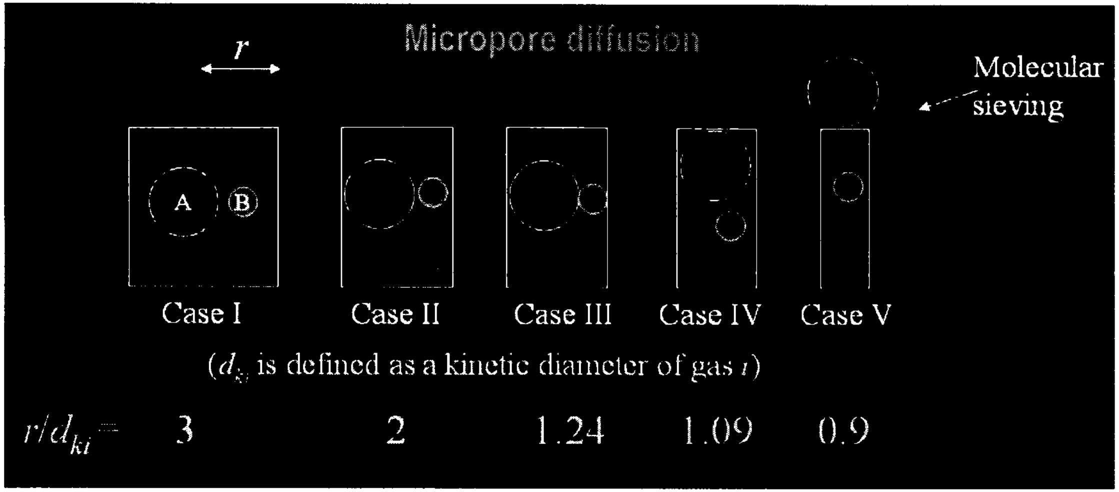
The structure of carbon materials is not nearly as well defined as that of zeolite. Carbon are amorphous materials with comparatively wide pore size distribution as compared to the crystalline zeolites with monodisperse ultramicropore and micropore dimensions.



# Selective Phenomena in Carbon Membranes

- Knudsen diffusion
  : Pore size relative to permeant molecules, separation distance between penetrants.
- Selective condensation
  : Pore sizes > 30 angstroms in diameter
- Selective adsorption
  : Pore size, physicochemical interactions between permeants and pore surfaces.
- Molecular sieving
  : <u>Pore radius (in the range of 2.5 to 5.5 Å)</u>



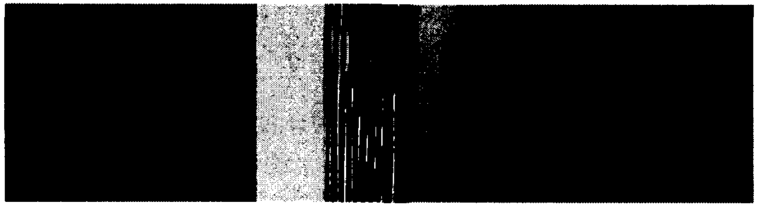



***Molecular sieving*** *will control transport if the order of magnitude of the pore size is 2 to 3 times the molecular diameter.*

# Factors Determining Carbon Membrane Performance

1. **Type of polymeric precursors**
2. **Membrane geometries**

Dip-coating Spin-coating



Thin unsupported films | Coated hollow tube (ceramic tube) | Coated round disk (porous steal disk)

3. **Pyrolysis conditions**

**Pyrolysis temperature (500 – 1000 °C)**
: Temp ↑, selectivity ↑ (permeability ↓)

**Heating rate**
: Heating rate ↓, selectivity ↑ (permeability ↓)

**Pyrolysis atmosphere**
: He, $N_2$, Ar or vacuum
: Oxidization step (optional)

| Heat treatment Temperature (°C) | Average d-spacing (Å) |
|---|---|
| 600 | 4.4-4.2 |
| 800 | 4.0-3.7 |
| 1000 | 3.7-3.5 |

*5.2-5.0: usual glassy polymer

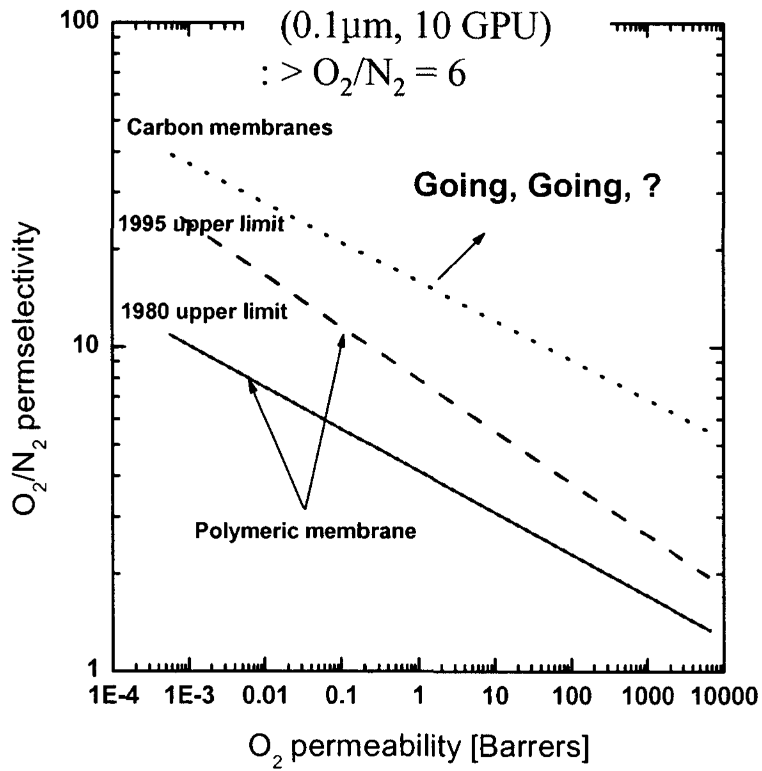
# Polymeric Precursors

- Polyvinylidene chloride-acrylate terpolymer latex
- Polyfurfuryl alcohol
- Polyacrylonitrile
- 6F-polyimide copolymer
- Kapton-like polyimide (cured polyamic acid)
- Cellulose and cellulose derivatives
- BPDA-pp'ODA polyimide
- Phenolic resin
- PAN/PMMA copolymer
- Phenol formaldehyde resin
- Polyacrylonitrile mixed with other polymers
- Siloxane-containing copolyimides
- Polyimide/SMM blend polymers
- Polyimide/$SiO_2$ composite polymers

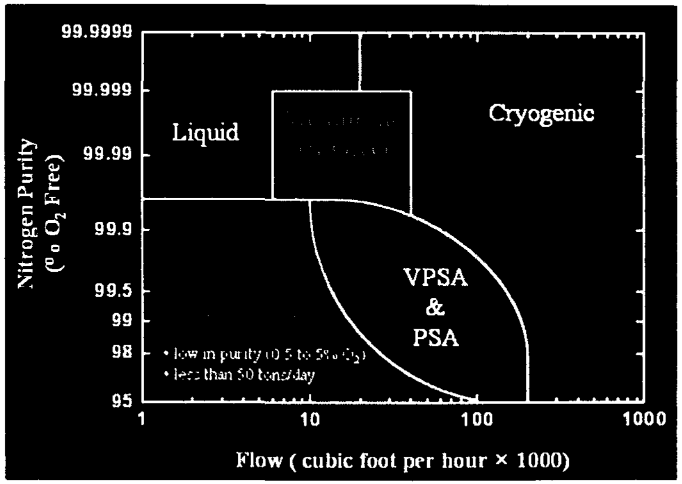
This work

# Limitation & Breakthrough

Commercial standard
: > 1 Barrer
(0.1μm, 10 GPU)
: > $O_2/N_2 = 6$

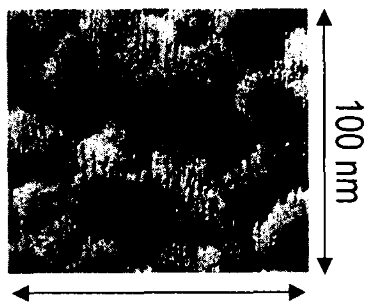



**Technology Map of the Air Separations Market**

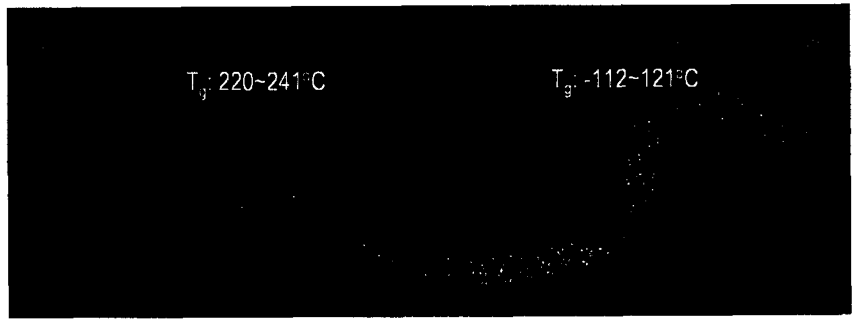



New membrane materials are needed!!

# Properties of Poly(imide siloxane) (PIS)




Surface topology
of poly(imide siloxane)



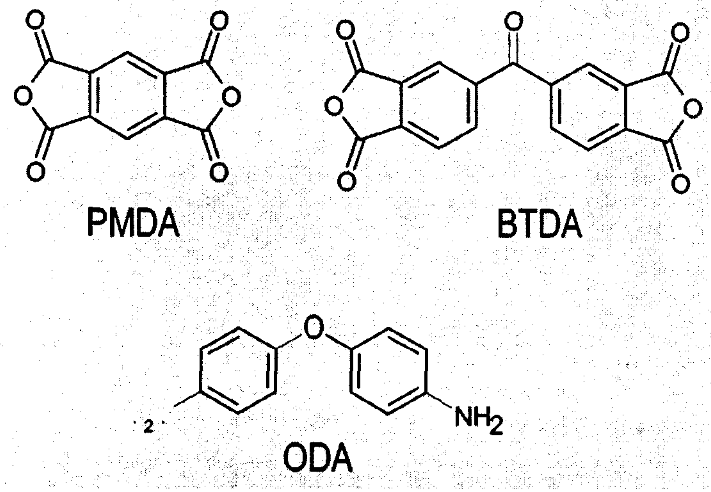

- Low dielectric constant
- High glass transition
- Low moisture absorption
- Good thermal stability (300 – 400 °C)
- Good polymer/metal adhesion compared to other polyimides
- Unique surface properties
- Microphase separated structures

Important packaging applications in the micro-electronic industry
Dielectric films
Stop barrier films

# Polymer Design

**Dianhydride**:
Pyromellitic dianhydride (PMDA)
Benzophenonetetracarboxylic dianhydride (BTDA)

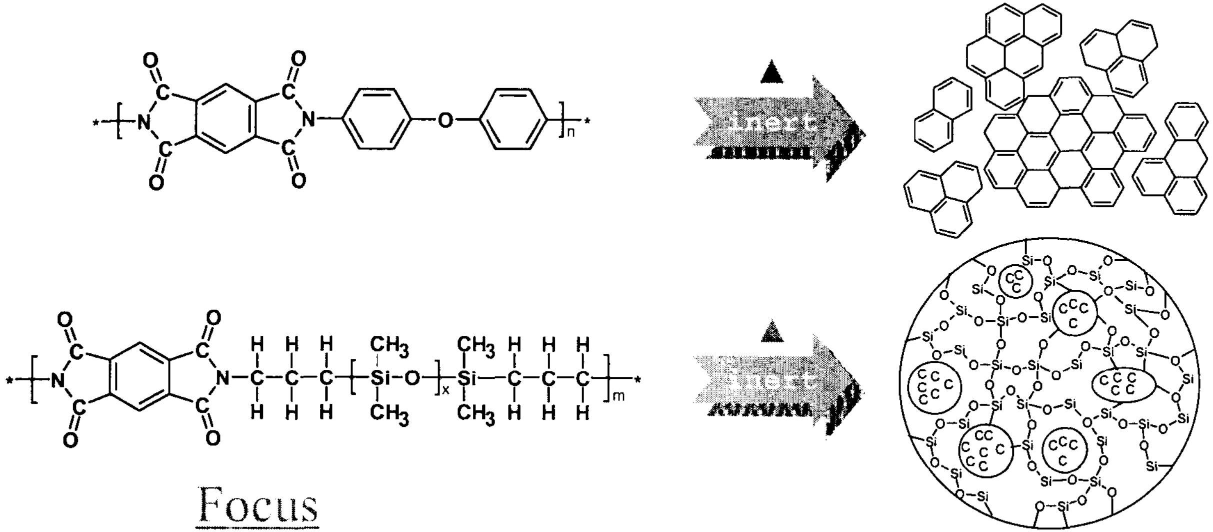
**Diamine:**
Oxydianiline (ODA)
Aminopropyl poly(dimethyl siloxane) (PMDS)
($M_n$ = 900 and 1600)



PMDA BTDA ODA

| | | | | | |
|---|---|---|---|---|---|
| Class I | PMDA+ODA+PDMS(9) | Siloxane content | PIS9 I (6%) | PIS9 II (27%) | PIS9 III (46%) |
| Class II | BTDA+ODA+PDMS | Siloxane domain size | R-PIS (34%) | B-PIS (34%) | |
| Class III | PMDA+ODA+PDMS(16) | Siloxane chain length | PIS16 I (6%) | PIS16 II (27%) | PIS16 III (46%) |

# Pyrolytic Carbon Membrane Containing Silica




Focus

: Effect of siloxane content or domain size

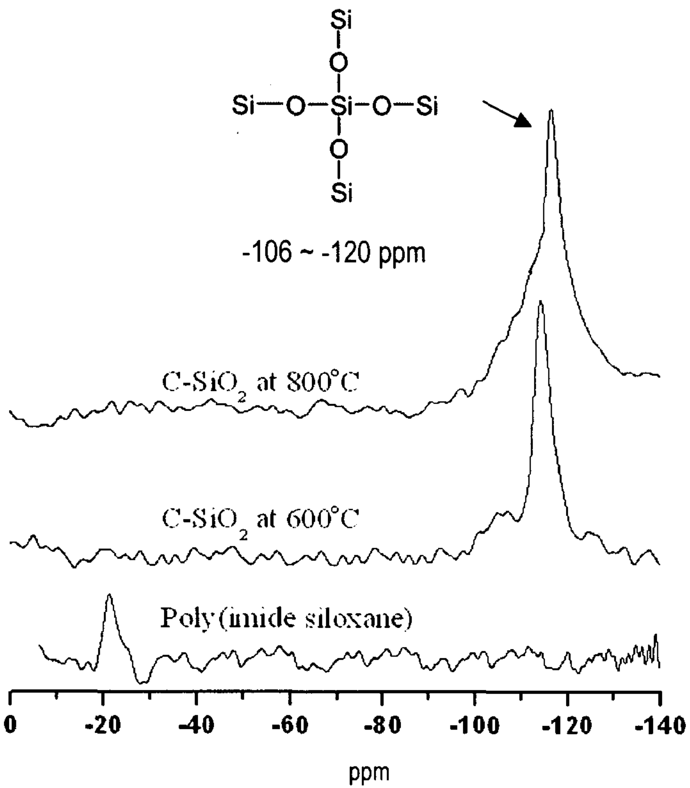
: Effect of siloxane chain length


Reference

1. H.B.Park, I.Y.Suh, Y.M.Lee, *Chem. Mater.* 2002 (14) 3034
2. H.B.Park and Y.M.Lee, *J. Membr. Sci.* 2003 (213) 263
3. H.B.Park and Y.M.Lee, *Membr. J.*(Korea) 2002 (12) 107

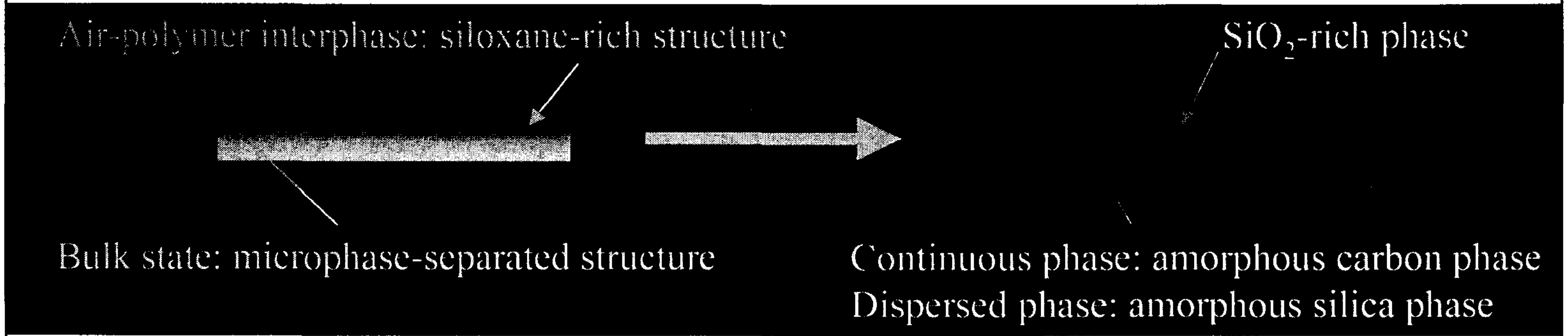
# Silica Formation in Bulk State

**Solid state $^{29}$Si-NMR**




**TEM image**

# Unique Surface Properties of Poly(imide siloxane)




- **Polysiloxanes** are generally used as a surface modifier through *blending* or *copolymerization* with other Polymers, because of the free rotatability and polarizability of the Si-O bond.

- The **–Si-O-Si- chain** is able to align itself accordingly, resulting in a rich *in-depth distribution of the surface in copolymers and blends.*

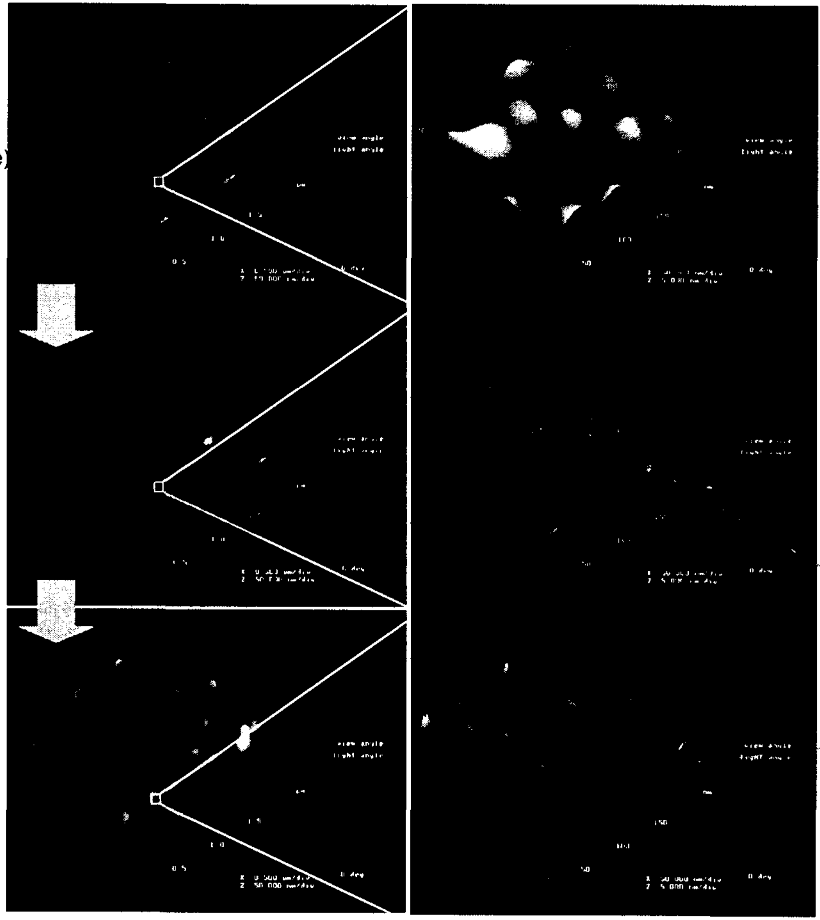
- **Air-polymer surfaces** of siloxane-containing copolymers as well as their blends with other polymers are *substantially enriched in the lower-surface-energy siloxane.*

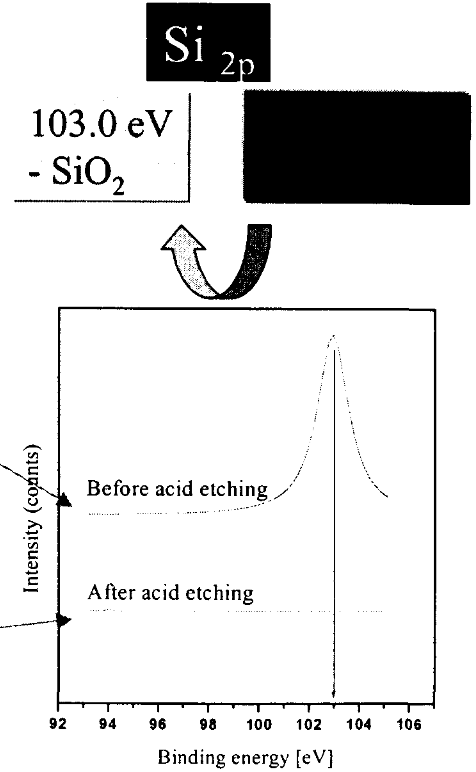
# Silica Formation on Top Surface

Poly(imide siloxane)

Surface of C-$SiO_2$ membrane *before acid etching*

Surface of C-$SiO_2$ membrane *after acid etching*





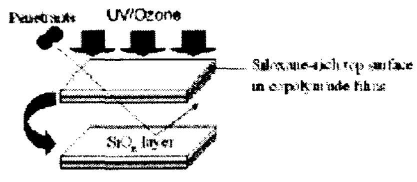
# Other Applications

**Ho Bum Park, Doo Won Han, and Young Moo Lee***

*Chem. Mater.*

Effect of a UV/Ozone Treatment on Siloxane-Containing Copolyimides: Surface Modification and Gas Transport Characteristics

UV/ozone treatment converts the surfaces of copolyimide films having a siloxane-rich top surface (air–polymer side) into silica layers, which is mainly affected by factors such as UV-exposure time and polymer composition (siloxane content).




Conversion of siloxane-containing copolyimide films into silica-layered copolyimide films by UV/ozone treatment

*Chem. Mater.* 15, 2003, 2346

## Effect of a UV/Ozone Treatment on Siloxane-Containing Copolyimides: Surface Modification and Gas Transport Characteristics

Ho Bum Park, Doo Won Han, and Young Moo Lee*

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*Received January 3, 2003. Revised Manuscript Received April 9, 2003*

We have prepared poly(imide siloxane) (PIS) films having various siloxane contents using a two-step polymerization technique and subjected them to a UV/ozone treatment using UV excitation in the range $\lambda$ = 185~254 nm to form an $SiO_x$ layer on the surface of the PIS films. From electron spectroscopy chemical analysis (ESCA), we have confirmed that the PDMS surface layer in the PIS films converts into silica as the UV/ozone treatment time increases. Solid-state $^{29}Si$ NMR provides evidence that the PDMS and silica coexist in the bulk. Gas permeation experiments on non-UV/ozone-treated and on UV/ozone treated PIS films were carried out using helium (He), oxygen ($O_2$), nitrogen ($N_2$), and carbon dioxide ($CO_2$) penetrants. For PIS films having a high siloxane content (i.e., a volume fraction of 0.457), the UV/ozone treatment decreased the gas permeabilities, but increased the selectivity of several gas pairs owing to the formation of a dense silica layer, which increased with increasing treatment time.

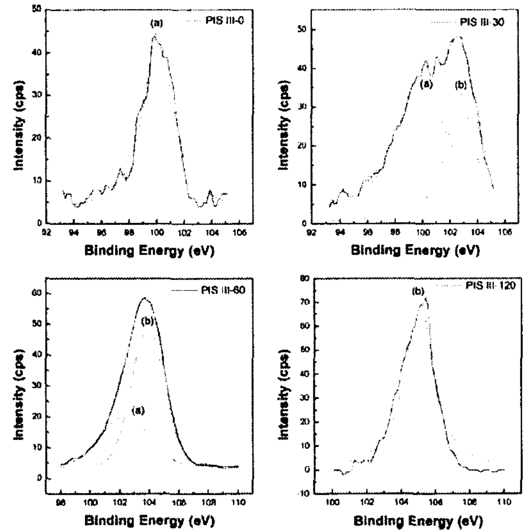



Figure 5. ESCA spectra of non-UV/ozone-treated and UV/ozone-treated PIS films: (a) = main PDMS peak; (b) = main silica peak.

# Class I: Gas Permeation Data

## Class I: Poly(imide siloxane) (Effect of Siloxane Content)

**Table. Gas Permeation Results for C−$SiO_2$ Membranes at 25 °C**

| pre-cursor | pyrolysis temp (°C) | permeability (Barrer)[a] | | | | selectivity to $N_2$ | | |
|---|---|---|---|---|---|---|---|---|
| | | He | $O_2$ | $CO_2$ | $N_2$ | $O_2/N_2$ | $CO_2/N_2$ | $He/N_2$ |
| PIS I | 600 | 315 | 7.6 | 21 | 0.33 | 23 | 62 | 955 |
| | 800 | 442 | 27 | 89 | 1.47 | 18.4 | 61 | 304 |
| | 1000 | 121 | 4.5 | 12 | 0.19 | 24 | 64 | 643 |
| PIS II | 600 | 1258 | 30 | 84 | 1.35 | 22.2 | 62 | 1033 |
| | 800 | 1393 | 68 | 204 | 3.68 | 18.5 | 56 | 341 |
| | 1000 | 133 | 2 | 7.4 | 0.10 | 20 | 74 | 1330 |
| PIS III | 600 | 610 | 111 | 386 | 18 | 6.2 | 21 | 34 |
| | 800 | 981 | 168 | 765 | 16.8 | 10 | 46 | 58 |
| | 1000 | 207 | 9.5 | 36 | 0.63 | 15 | 57 | 56 |

[a] 1 Barrer = $10^{-10}$ $cm^3(STP) \cdot cm/cm^2 \cdot s \cdot cmHg$.

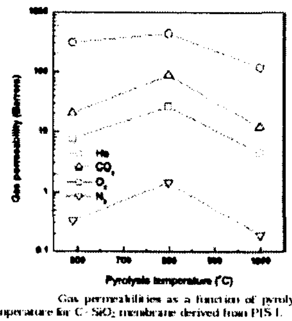
H.B.Park, I.Y.Suh, Y.M.Lee. *Chem.Mater.* Vol.14,No.7, 2002,3043

Increase of siloxane content → permeability *up*
selectivity *down*

Pyrolysis temperature effect → maximum permeability at 800 °C

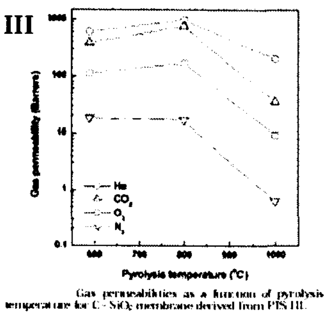
→ Why?

**PIS I**



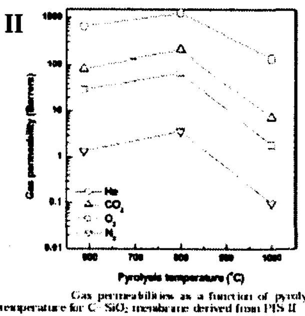
Gas permeabilities as a function of pyrolysis temperature for C−$SiO_2$ membrane derived from PIS I.

**PIS III**

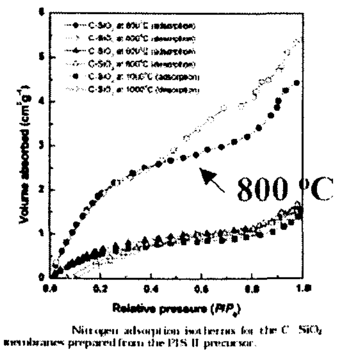


Gas permeabilities as a function of pyrolysis temperature for C−$SiO_2$ membrane derived from PIS III.

**PIS II**



Gas permeabilities as a function of pyrolysis temperature for C−$SiO_2$ membrane derived from PIS II.

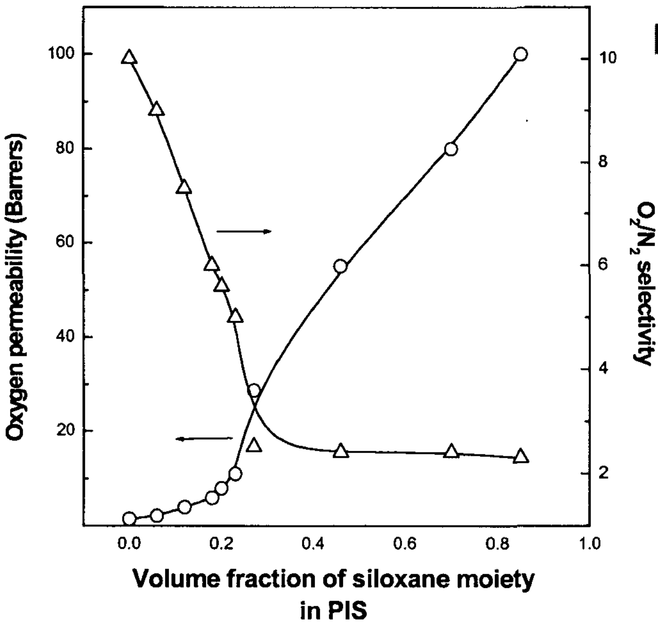


Nitrogen adsorption isotherms for the C−$SiO_2$ membranes prepared from the PIS II precursor.

**BET N2 Sorption**

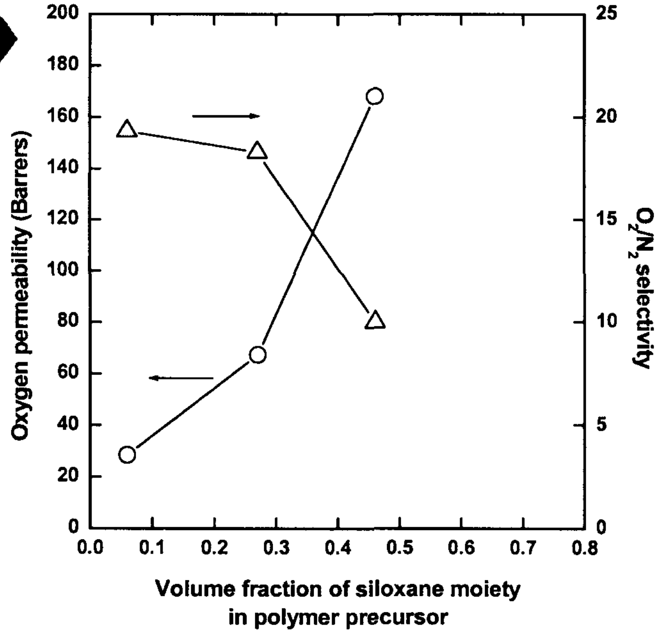
# Effect of Siloxane Content in PIS on Permeability and Selectivity of Carbon-Silica

**Precursor**
**: Poly(imide siloxane)**




Pyrolysis

**Carbon-Silica Membrane**




All C-$SiO_2$ membranes were prepared at pyrolysis temperature of 800 °C

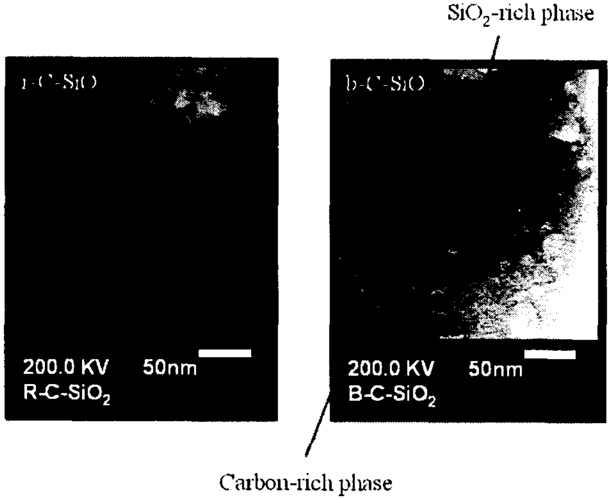
# Class II: Siloxane Domain Size

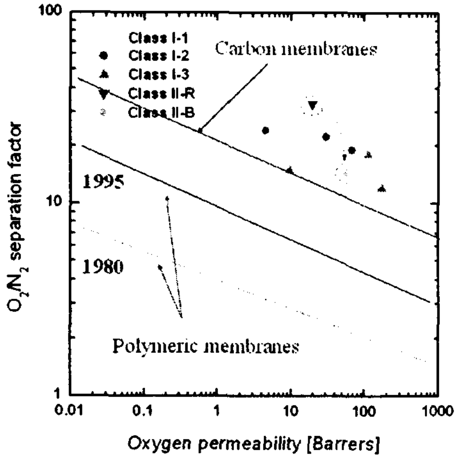
Gas permeabilities of precursors and their pyrolytic C–$SiO_2$ membranes at 25 °C (class II)

| Sample code | Permeability (Barrer[a]) | | | | Selectivity | | |
|---|---|---|---|---|---|---|---|
| | He | $CO_2$ | $O_2$ | $N_2$ | $He/N_2$ | $CO_2/N_2$ | $O_2/N_2$ |
| *b*-PIS | 9.70 | 3.29 | 0.94 | 0.22 | 44.1 | 15.0 | 4.3 |
| *r*-PIS | 6.75 | 0.93 | 0.27 | 0.06 | 112.5 | 15.5 | 4.5 |
| *b*-C–$SiO_2$ | 1449 | 155 | 55.8 | 3.9 | 371.5 | 39.7 | 14.3 |
| *r*-C–$SiO_2$ | 1107 | 26 | 19.3 | 0.6 | 1845.0 | 43.3 | 32.1 |

*H.B. Park, Y.M. Lee / Journal of Membrane Science 213 (2003) 263–272*

[a] 1 Barrer = $10^{-10}$ $cm^3(STP)cm/cm^2\,s\,cmHg$.




At the same composition, domain size of *random* PIS > domain size of *block* PIS

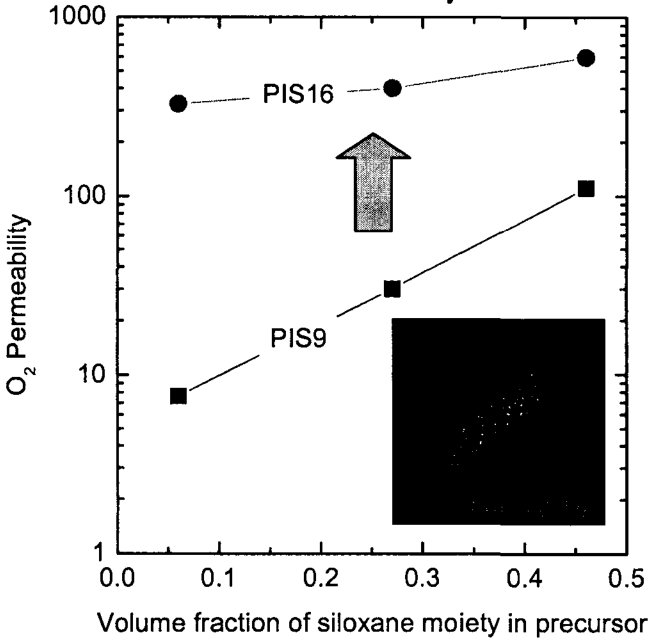
Gas permeability: random PIS < block PIS

Gas selectivity: random PIS > block PIS

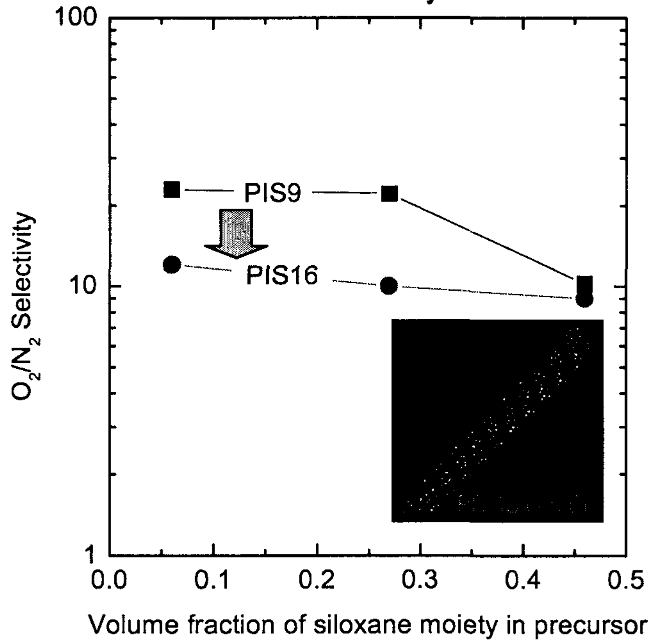
# Class III: Gas Permeation Data

## Class III: Poly(imide siloxane) (Effect of Siloxane Chain Length)

Permeability




Selectivity




All C-$SiO_2$ membranes were prepared at pyrolysis temperature of 600 °C

PIS 9 ($M_n$ of PDMS = 900), PIS 16 ($M_n$ of PDMS = 1600)

# Contribution to Diffusion Selectivity

(Effect of Siloxane Chain Length)
Comparison data: Class I and Class II

| | Diffusivity ($cm^2$/sec) | | Diffusion selectivity |
|---|---|---|---|
| | $D(O_2)$ | $N(O_2)$ | $D(O_2)/N(O_2)$ |
| PIS I(9) | $1.38\times10^{-9}$ | $1.40\times10^{-10}$ | 9.9 |
| PIS I(16) | $5.21\times10^{-8}$ | $5.46\times10^{-9}$ | 9.5 |
| PIS II(9) | $4.55\times10^{-9}$ | $5.00\times10^{-10}$ | 9.1 |
| PIS II(16) | $7.45\times10^{-8}$ | $1.47\times10^{-8}$ | 5.1 |
| PIS III(9) | $4.86\times10^{-8}$ | $9.20\times10^{-9}$ | 5.2 |
| PIS III(16) | $1.59\times10^{-7}$ | $3.82\times10^{-8}$ | 4.2 |

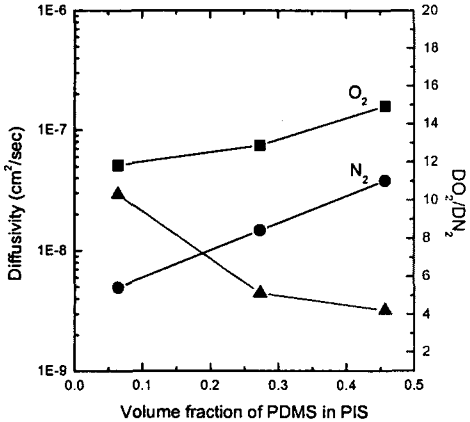
*Silica domain* derived from siloxane domain would act as *more permeable phase*.

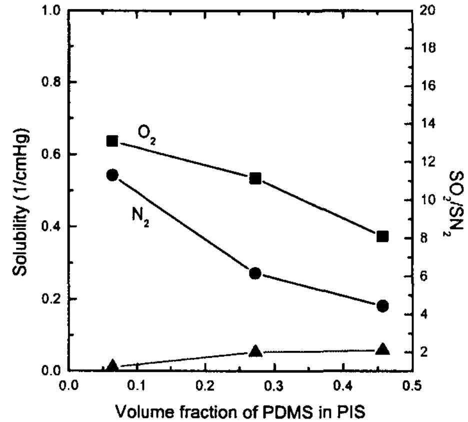
Diffusivity of C-$SiO_2$ membrane increased with siloxane content and chain length in poly(imide siloxane) while diffusion selectivity decreased.

**Siloxane content: I < II < III**
**Temperature: 25 °C**
**Diffusion coefficient (*D*) was calculated from time-lag experiment.**

# Contribution to Permselectivity

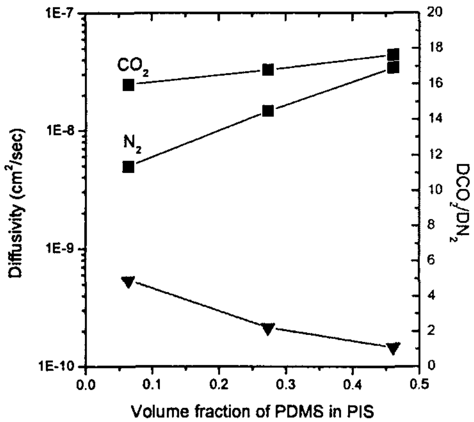
## $O_2/N_2$ separation

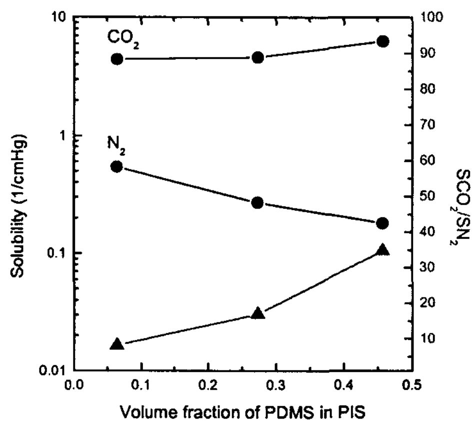



- Larger contribution of diffsivity selectivity

## $CO_2/N_2$ separation

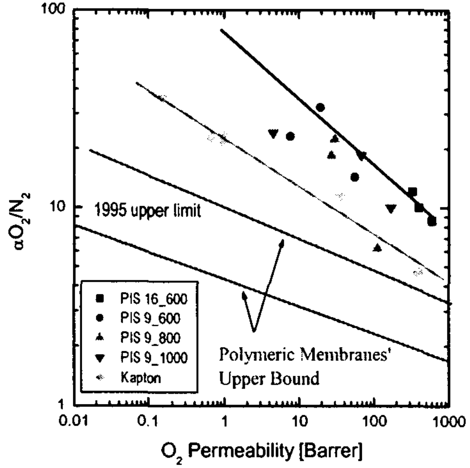


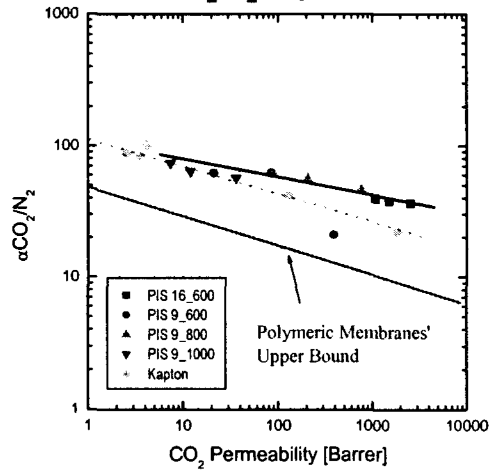

- Smaller contribution of diffsivity selectivity
- Relatively larger contribution of sorption selectivity

# Summary of C-$SiO_2$ Separation Performance

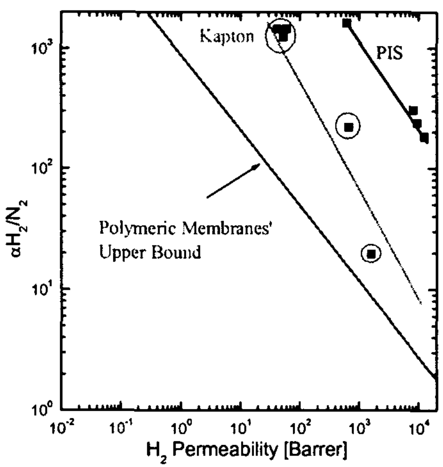
## $O_2/N_2$ separation



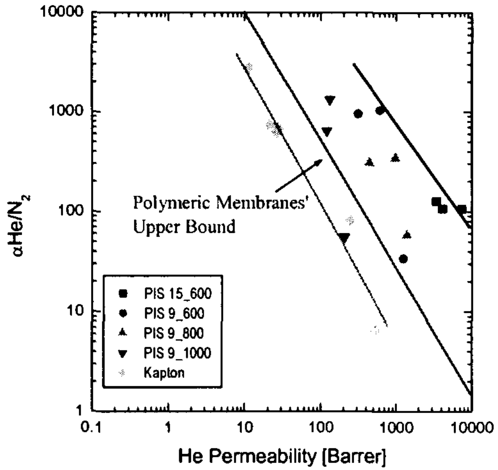

## $CO_2/N_2$ separation




## $H_2/N_2$ separation




## $He/N_2$ separation



# Mixed Gas Permeation Data I

Feed Composition
- For $O_2/N_2$ separation, $O_2 : N_2$ (21% : 79%)
- For $CO_2/N_2$ separation, $CO_2 : N_2$ (15% : 85%)

Operation Condition
- Feed pressure (5 atm), Operating temperature (30°C)

Pyrolysis temperature
- up to 800°C

| Precursor | Permeance (GPU)[a] | | Conc. of Enriched Gas (%) | | Selectivity | | | |
|---|---|---|---|---|---|---|---|---|
| | $O_2$ | $CO_2$ | $O_2$ | $CO_2$ | $O_2/N_2$ | | $CO_2/N_2$ | |
| | | | | | Single | Mixed | Single | Mixed |
| PIS I | 5.2 | 12.8 | 79.3 | 92.5 | 18.4 | 14.4 | 61.0 | 70.0 |
| PIS II | 12.3 | 29.4 | 77.5 | 91.8 | 18.5 | 13.0 | 56.0 | 63.4 |
| PIS III | 23.4 | 101.0 | 72.8 | 90.3 | 10.0 | 10.1 | 46.0 | 52.8 |

[a] 1 GPU = $10^{-6}$ $cm^3$ (STP) / $cm^2 \cdot sec \cdot cmHg$

# Mixed Gas Permeation Data II

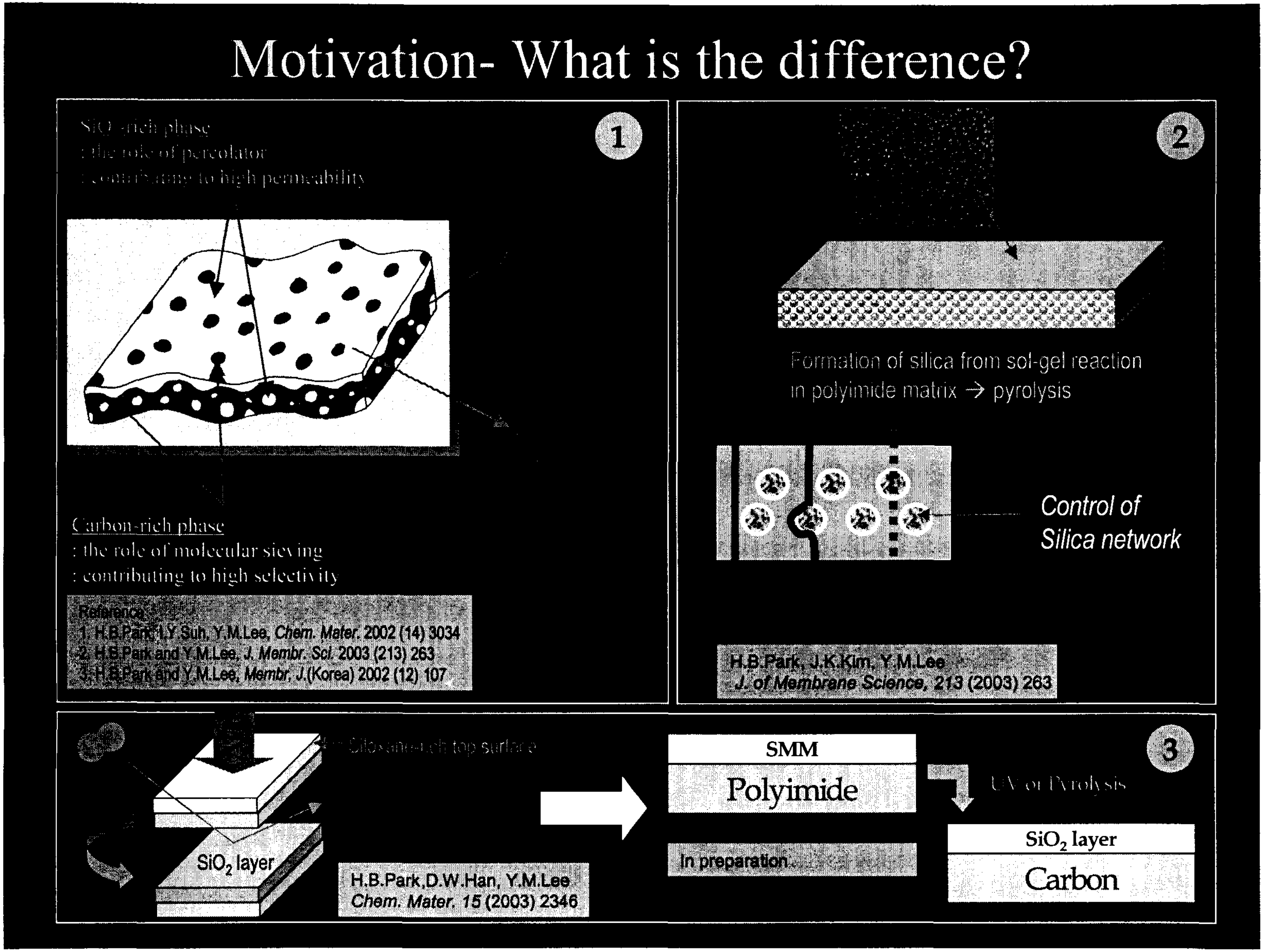
Feed Composition
- For $O_2/N_2$ separation, $O_2 : N_2$ (21% : 79%)
- For $CO_2/N_2$ separation, $CO_2 : N_2$ (15% : 85%)

Operation Condition
- Feed pressure (5 atm), Operating temperature (30°C)

Pyrolysis temperature
- up to 600°C

| Precursor | Permeance (GPU)[a] | | Conc. of Enriched Gas (%) | | Selectivity | | | |
|---|---|---|---|---|---|---|---|---|
| | $O_2$ | $CO_2$ | $O_2$ | $CO_2$ | $O_2/N_2$ | | $CO_2/N_2$ | |
| | | | | | Single | Mixed | Single | Mixed |
| PIS I-9 | 1.6 | 4 | 84.8 | 92.0 | 23 | 21 | 62 | 65 |
| PIS I-16 | 22 | 89 | 77.6 | 88.1 | 12 | 13 | 40 | 42 |
| PIS II-9 | 6 | 17 | 82.7 | 91.4 | 22 | 18 | 62 | 60 |
| PIS II-16 | 27 | 116 | 70.5 | 87.6 | 10 | 9 | 38 | 40 |
| PIS III-9 | 22 | 77 | 72.7 | 87.0 | 13 | 10 | 45 | 48 |
| PIS III-16 | 40 | 168 | 68.0 | 86.4 | 9 | 8 | 37 | 36 |

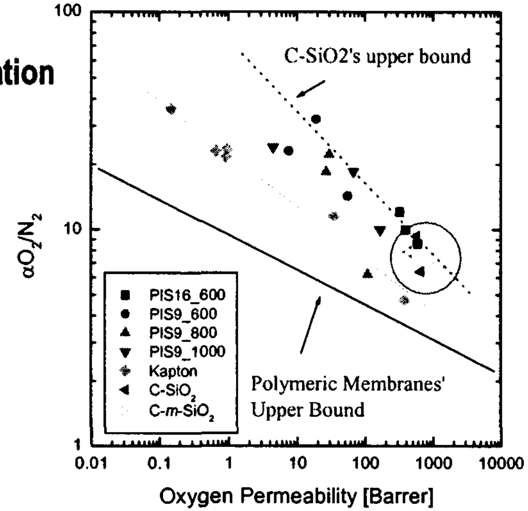
[a] 1 GPU = $10^{-6}$ $cm^3$ (STP) / $cm^2 \cdot sec \cdot cmHg$



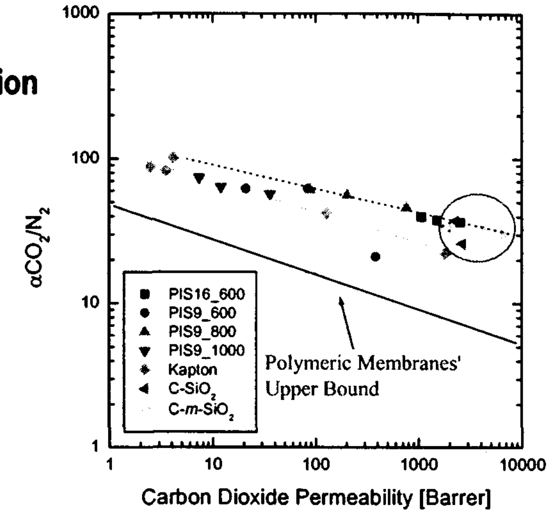
Motivation- What is the difference?
1
SiO -rich phase
: the role of percolator
: to high permeability
Carbon-rich phase
: the role of molecular sieving
: contributing to high selectivity
Reference
1. H.B.Park, I.Y.Suh, Y.M.Lee, Chem. Mater. 2002 (14) 3034
2. H.B.Park and Y.M.Lee, J. Membr. Sci. 2003 (213) 263
3. H.B.Park and Y.M.Lee, Membr. J.(Korea) 2002 (12) 107
2
Formation of silica from sol-gel reaction
in polyimide matrix → pyrolysis
Control of
Silica network
H.B.Park, J.K.Kim, Y.M.Lee
J. of Membrane Science, 213 (2003) 263
3
top surface
$SiO_2$ layer
H.B.Park, D.W.Han, Y.M.Lee
Chem. Mater. 15 (2003) 2346
SMM
Polyimide
In preparation...
UV or Pyrolysis
$SiO_2$ layer
Carbon

# Summary of C/$SiO_2$ & C/*m*-$SiO_2$ Membrane

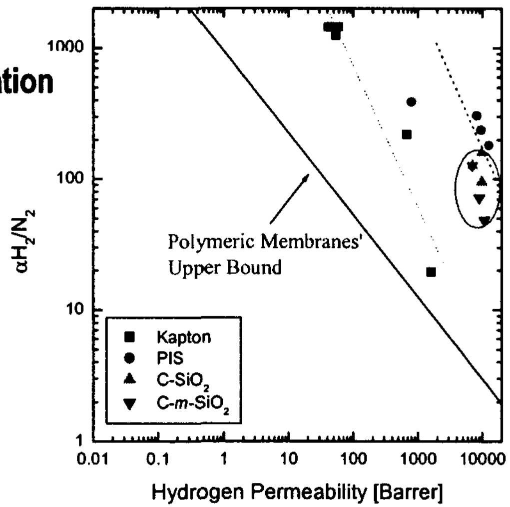
## $O_2/N_2$ separation




## $CO_2/N_2$ separation




## $H_2/N_2$ separation




## He/$N_2$ separation