Polymers with "Goldilocks" Cavities Tuned for Fast, Selective Transport of Small Molecules and Ions

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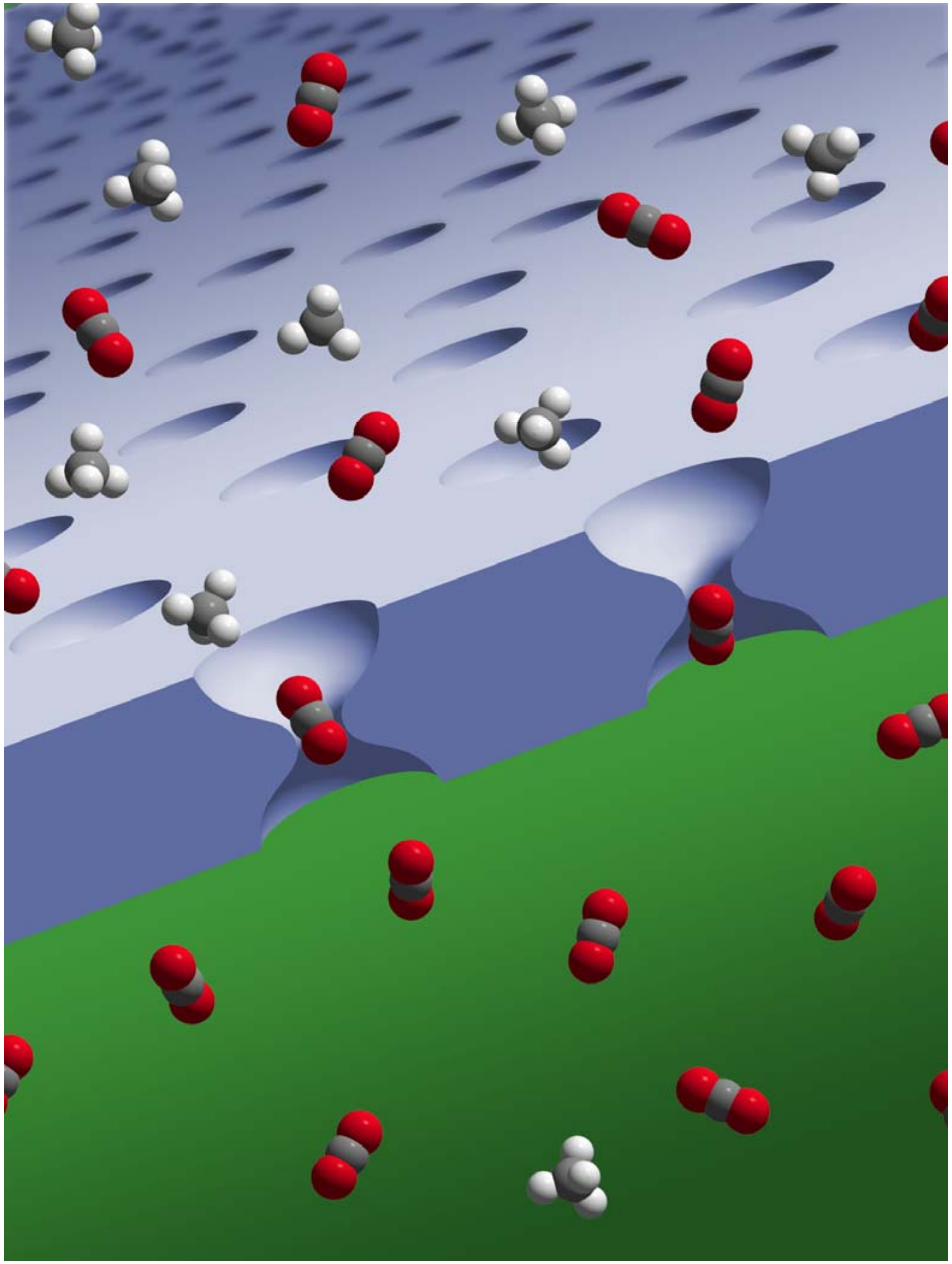


“Hourglass” shaped Membrane

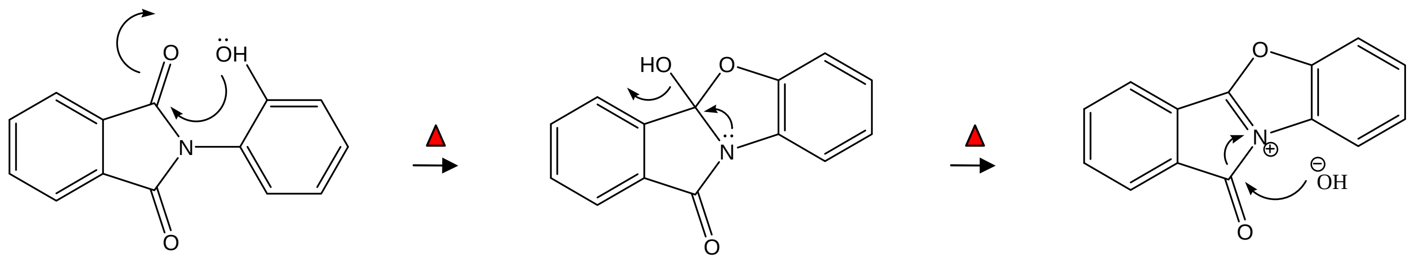
Science 318, 254 (2007)

Candidate Polymers

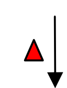
- *Polybenzimidazoles*
- *Polyquinoxalines*
- *Polybenzothiazoles*
- *Polybenzoxazoles*

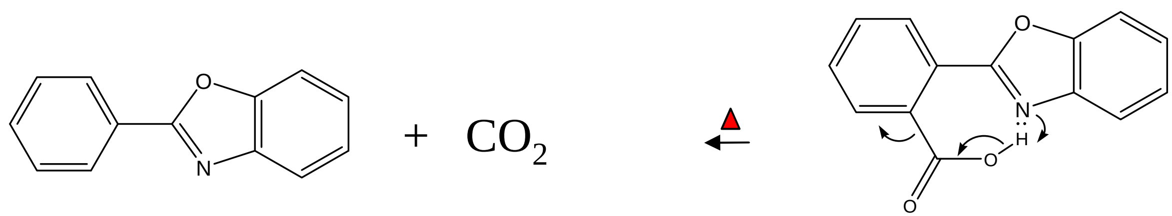
- High temperature durability (~600 ^{o}C at air atmosphere)
- High chemical stability (soluble in strong acids)
- High mechanical property
- Flat, rigid rod structure for good gas selectivity
- Strong interchain interaction due to charge transfer complex
- **Low gas permeability** **and** **difficult membrane fabrication**
- **Not enough gas permeation data**

Thermal Conversion Mechanism Of PIOFG



- Temperature: 350 – 500 ^{o}C
- Atmosphere: vacuum or inert
- State: Film, fiber, and powder (solid state)





1. *Vysokomol. Soyed.* B9 (1967) 873
2. *Polymer* 40 (1999) 3463

Prerequisites for New Polymer Designs

For high permeability,

> fast diffusion and large solubility – large free volume elements
> analog of microporous inorganic materials

For high selectivity,

> narrow cavity size distribution
> analog of amorphous carbon molecular sieve

For excellent thermal and chemical stability,

> analog of semi-rigid or rigid-rod aromatic polymers

For slow physical aging

> strong interchain interaction, or crosslinking structure

Polymer Membranes for Gas Separation

$$P = D \cdot S \quad \textbf{(1)}$$

Solution-diffusion mechanism

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B}\right) \cdot \left(\frac{S_A}{S_B}\right) \quad \textbf{(2)}$$

- ***Diffusion-selective***

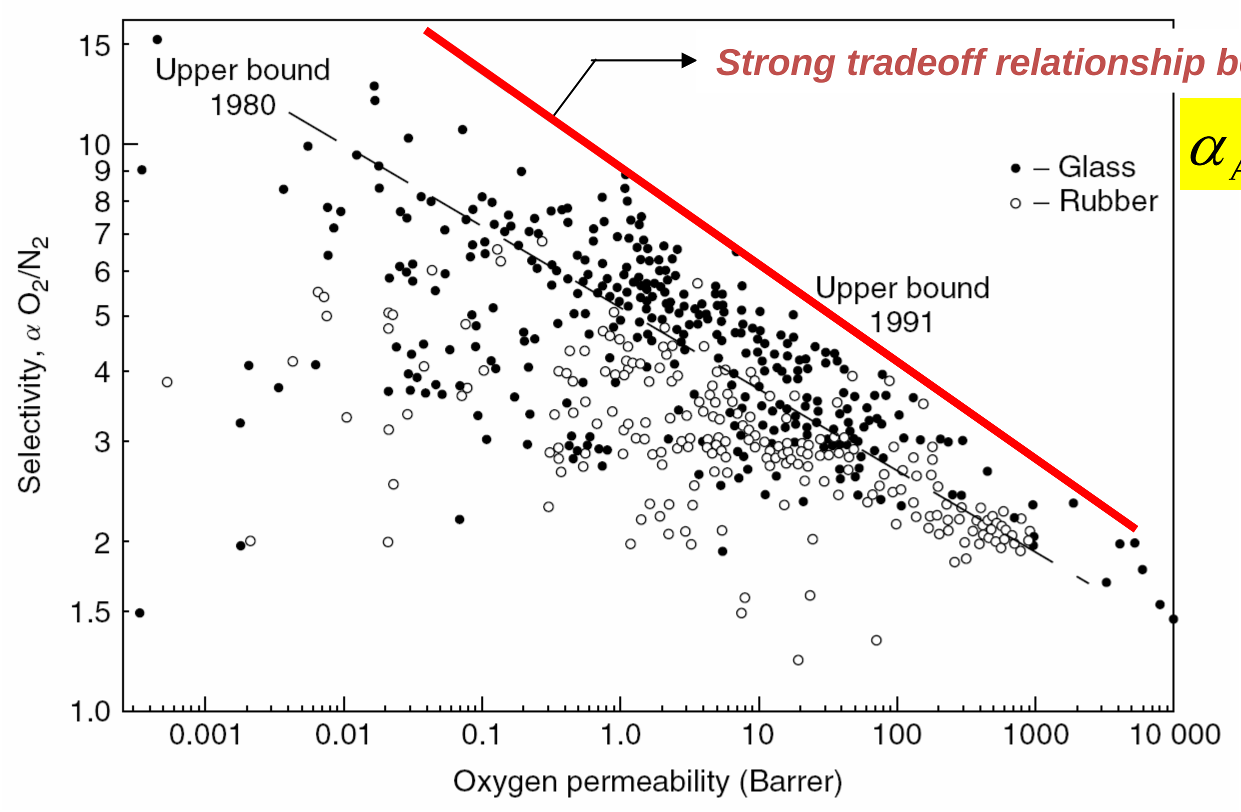
  - O_2/N_2, H_2/N_2, H_2/CH_4, etc
  - Glassy polymers (rigid & stiff chain)

- ***Sorption-selective***

  - $C_{>3+}/H_2$, CO_2/H_2, Vapor/permanent gas, etc
  - Rubbery polymers

Current Limitation of Polymeric Membranes for Gas Separation

Robeson, L.M., J. Membr. Sci. 62, 165 (1991)



Strong tradeoff relationship between P and α

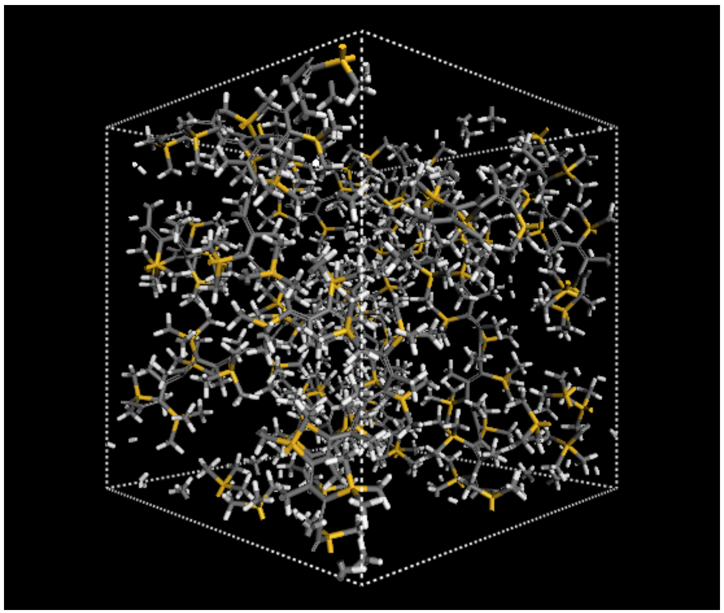
$$\alpha_{AB} = k^{-1/n} P_A^{1/n}$$

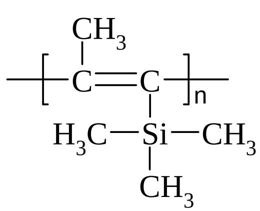
***Usually, glassy polymer membranes** show high selectivity,*

but low permeability...

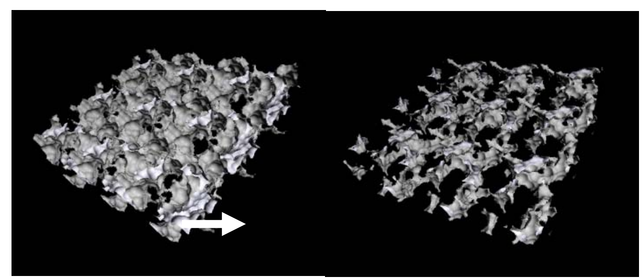
The Most Permeable Glassy Polymer (PTMSP)

PTMSP





- *High glass transition temperature*
- *High free volume*
- *Ultrahigh gas permeability*
- *Low selectivity for small gases*
- *Fast physical aging*



Bulk density = 0.75 gcm^{-3} → aging → Bulk density = 0.95 gcm^{-3}

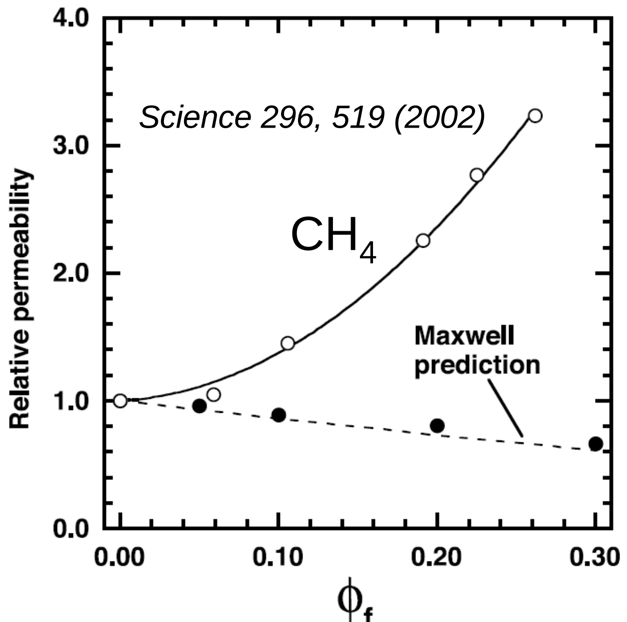
O_2 permeability: 6000 Barrer
O_2/N_2: 1.8

O_2 permeability: 1820 Barrer
O_2/N_2: 1.9

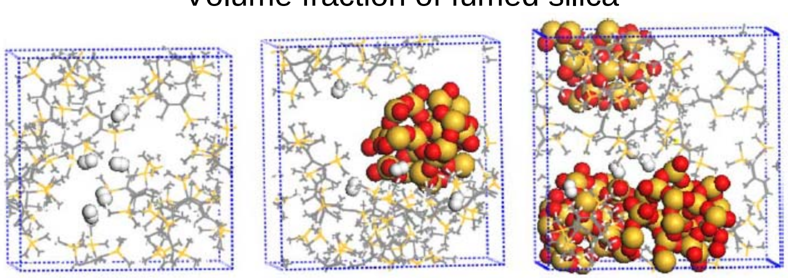
L. Starannikova, V. Khodzhaeva, Yu. Yampolskii, J. Membr. Sci, 244, 183 (2004)

Way to Improve Gas Permeability in Glassy Polymer Membranes

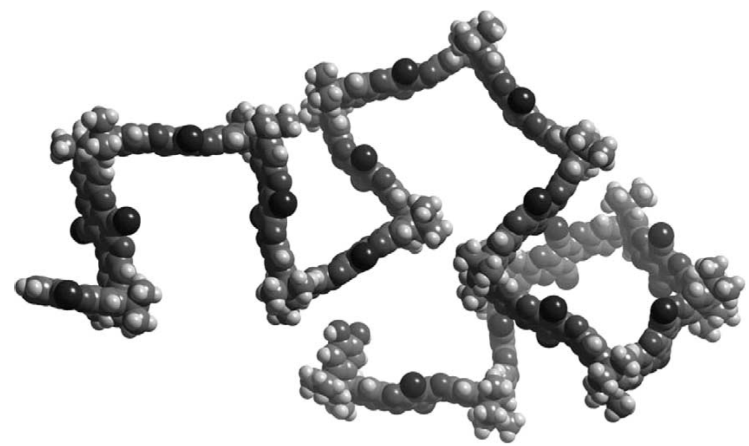
(1) **Nanocomposite**



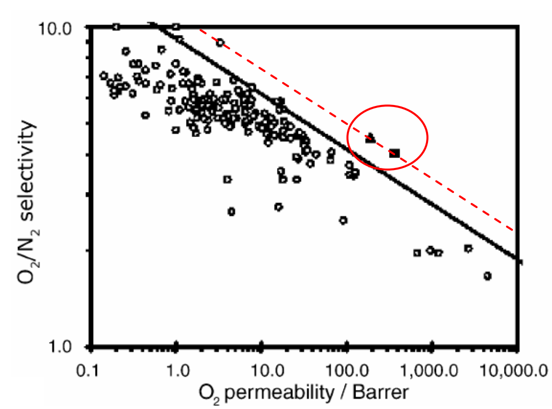
Volume fraction of fumed silica



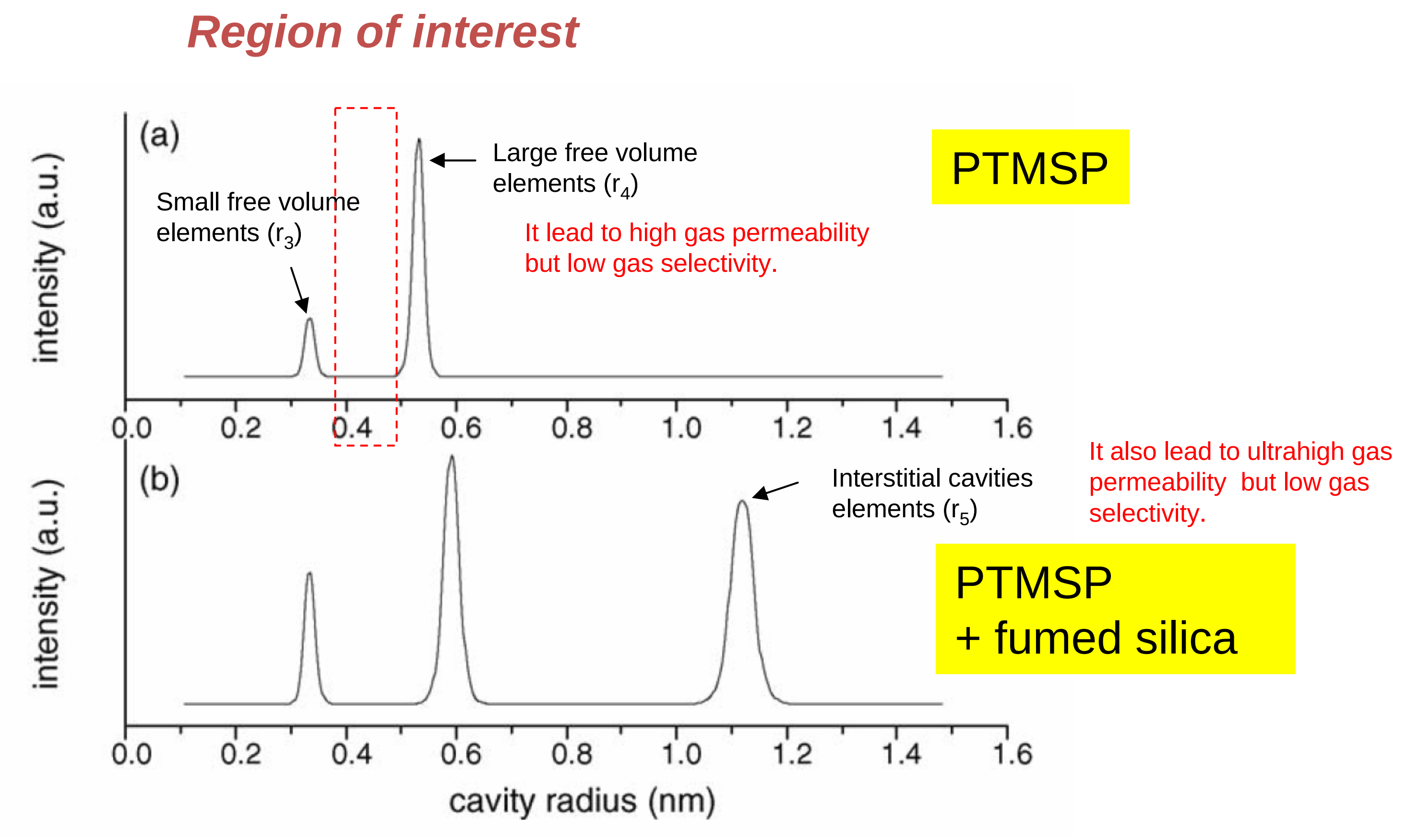
(2) **Polymer with intrinsic microporosity**



J. Membr. Sci. 251, 263 (2005)

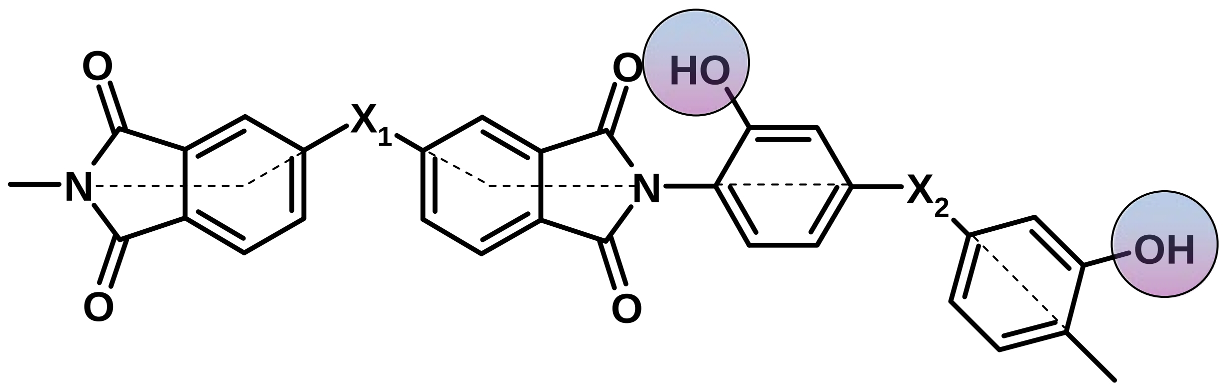


Free Volume Elements for Fast Molecular Transport



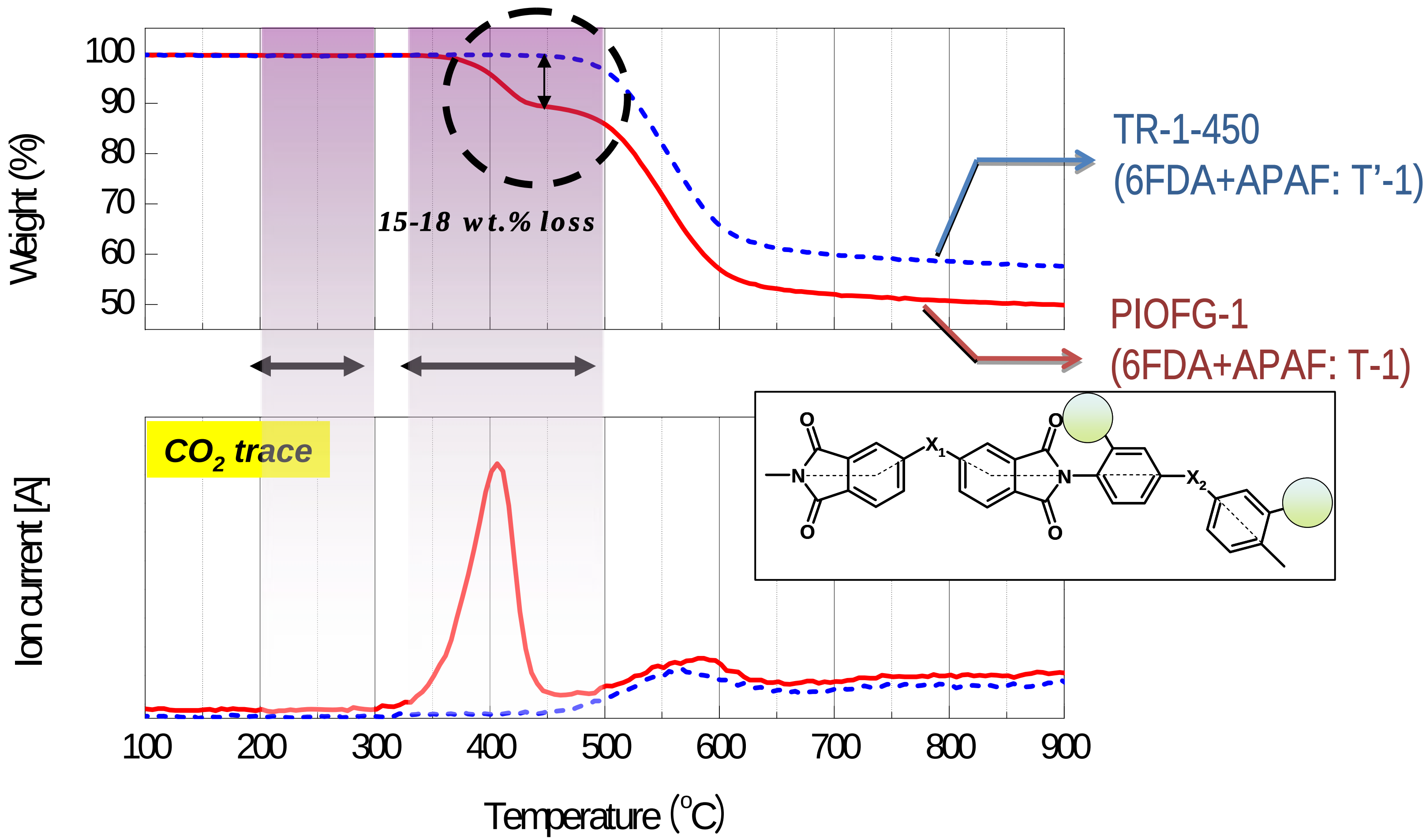
J. Membr. Sci. 278, 83 (2006)

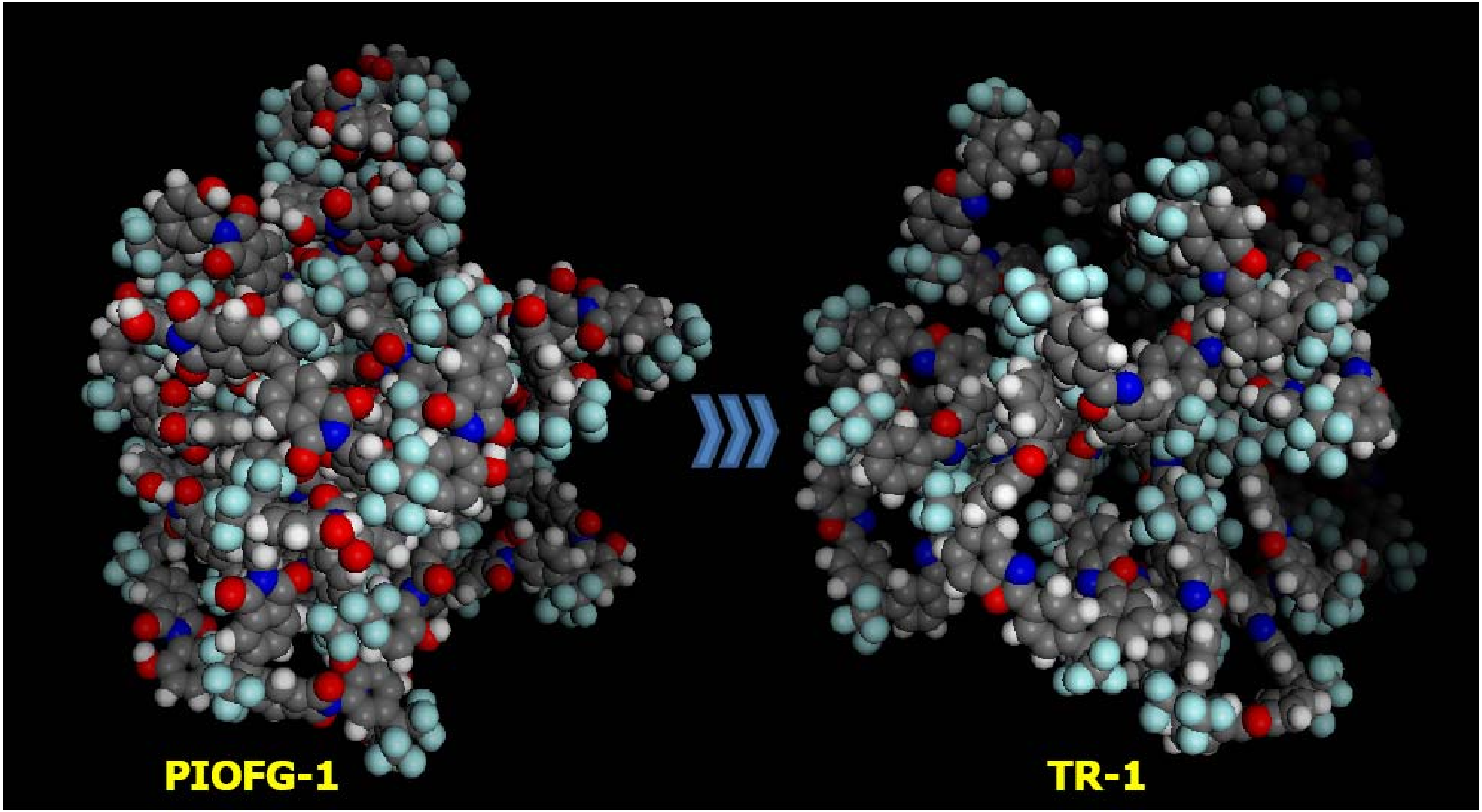
Polyimides with Ortho - Positioned Functional Groups (PIOFG)



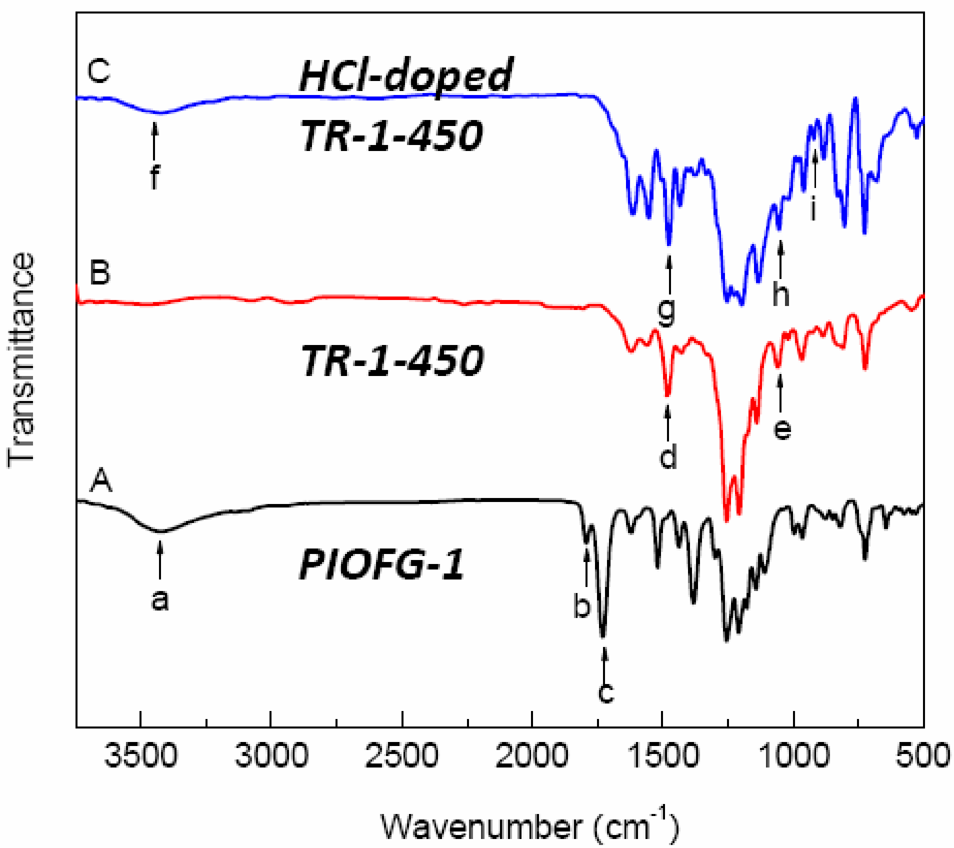
- Soluble
- High glass transition temperature (>350 ^{o}C)
- Thermally stable polymers for photoresist
- Non-linear optical (NLO) applications

Thermal Conversion Process of PIOFG at High Temperature

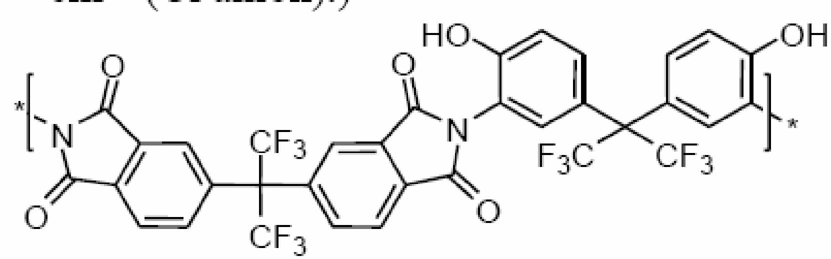



PIOFG-1
TR-1

Spectroscopic Evidence for Thermal Conversion of PIOFG



FT-IR spectra of: (A) T-1, (B) T′-1, and (C) HCl-doped T′-1 samples (10 M HCl aqueous solution). (Key: ***a.*** = 3,400 cm^{-1} (HO-phenylene), ***b*** = 1,788 cm^{-1} (symmetric C=O stretching vibration), ***c*** = 1,720 cm^{-1} (asymmetric C=O stretching vibration), ***d***(= *g*) and ***e***(= *h*) = 1,480 and 1,058 cm^{-1}, respectively, (**stretching vibration of benzoxazole ring**), *f* = 3,450 cm^{-1}(water), and *i* = 920 cm^{-1} (Cl anion).)



PIOFG-1

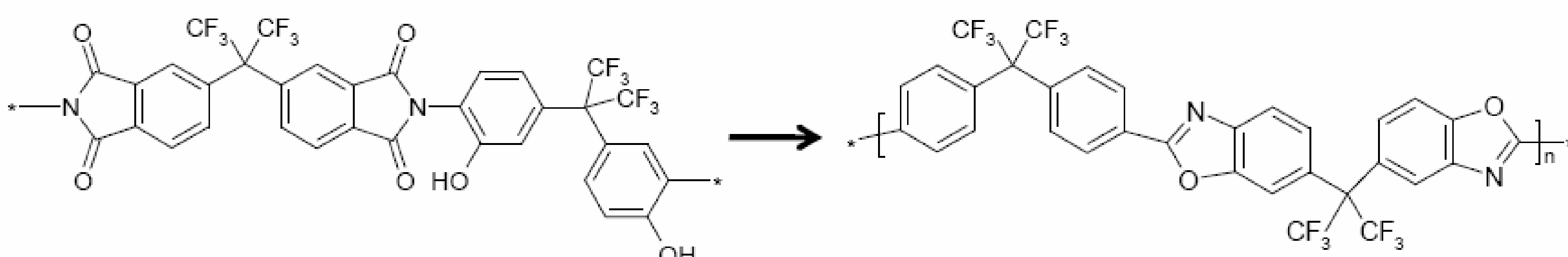
Elemental Analysis

[Table S2] Elemental analysis data of PIOFG-1 and TR-1-450

Polymer	Formula	C (wt%)	H (wt%)	N (wt%)	O (wt%)	F (wt%)
PIOFG-1	$[C_{34}H_{14}F_{12}N_2O_6]_n$	53.2±0.08 (52.7)*	1.87±0.06 (1.82)*	3.62±0.01 (3.62)*	11.3±0.22 (11.3)*	30.0±0.08 (29.4)*
TR-1-350	-	54.1±0.16	2.07±0.00	3.87±0.01	9.34±0.18	30.6±0.02
TR-1-400	-	55.2±0.01	2.02±0.01	4.05±0.00	7.23±0.03	31.5±0.04
TR-1-450	$[C_{32}H_{14}F_{12}N_2O_2]_n$	56.7±0.01 (55.9)*	1.93±0.02 (2.06)*	4.21±0.01 (4.08)*	4.89±0.12 (4.66)*	32.3±0.12 (33.2)*

*Calculated values

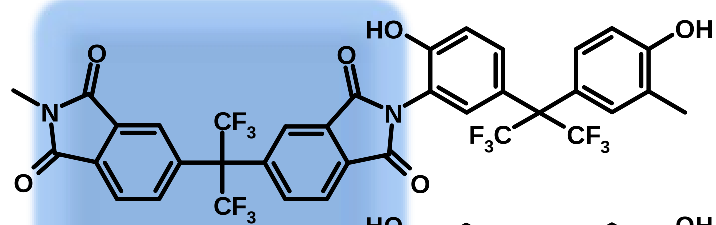
- Measured using ThermoFinnigan (Carlo Erba/Fison) EA1108
- Temperature: 1000 °C, (1060 °C for O)
- Catalyst: WO_3/Cu, (Nickel plated carbon, nickel wool, quartz turnings, soda lime, magnesium perchlorate anhydrone for O)
- Sample mass: 5 mg, (2 mg for O)
- Measured elements: C, H, N, O
- Standard material: BBOT (2,5-bis(5-tert-butyl-benzoxazole-2-yl) thiophene), (sulfanilamide for O)



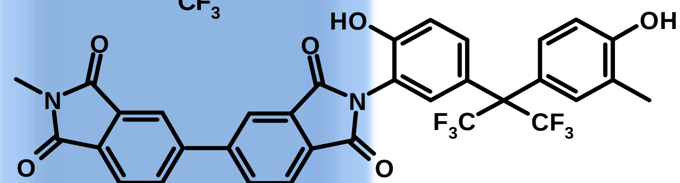
PIOFG-1 TR-1-450

Selected PIOFG Structures

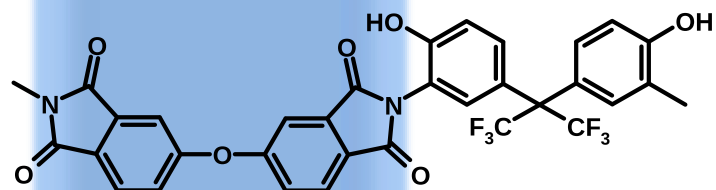
PIOFG-I



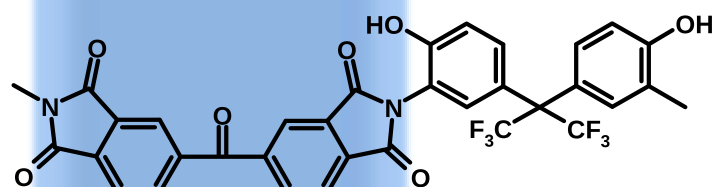
PIOFG-II



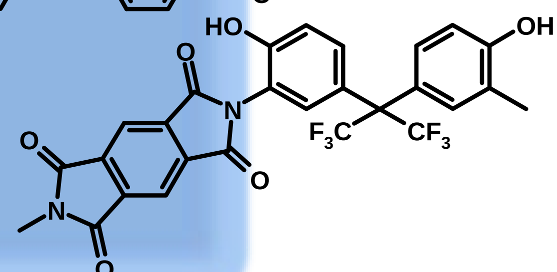
PIOFG-III



PIOFG-IV



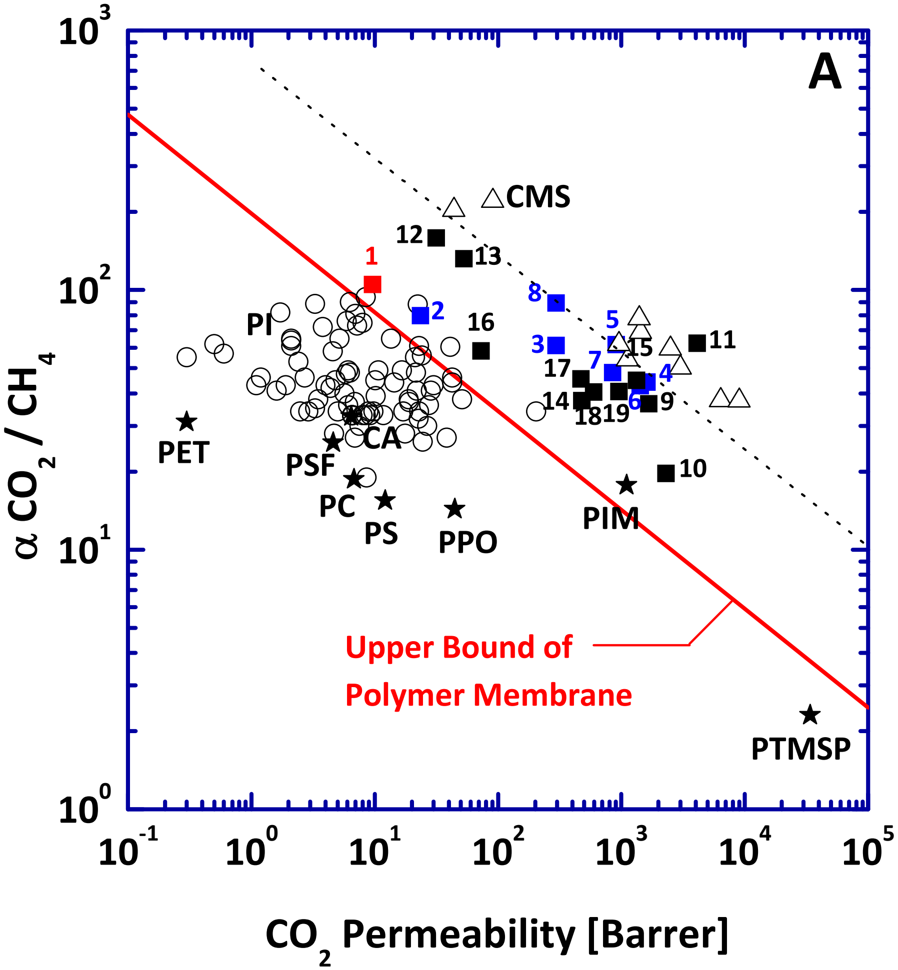
PIOFG-V



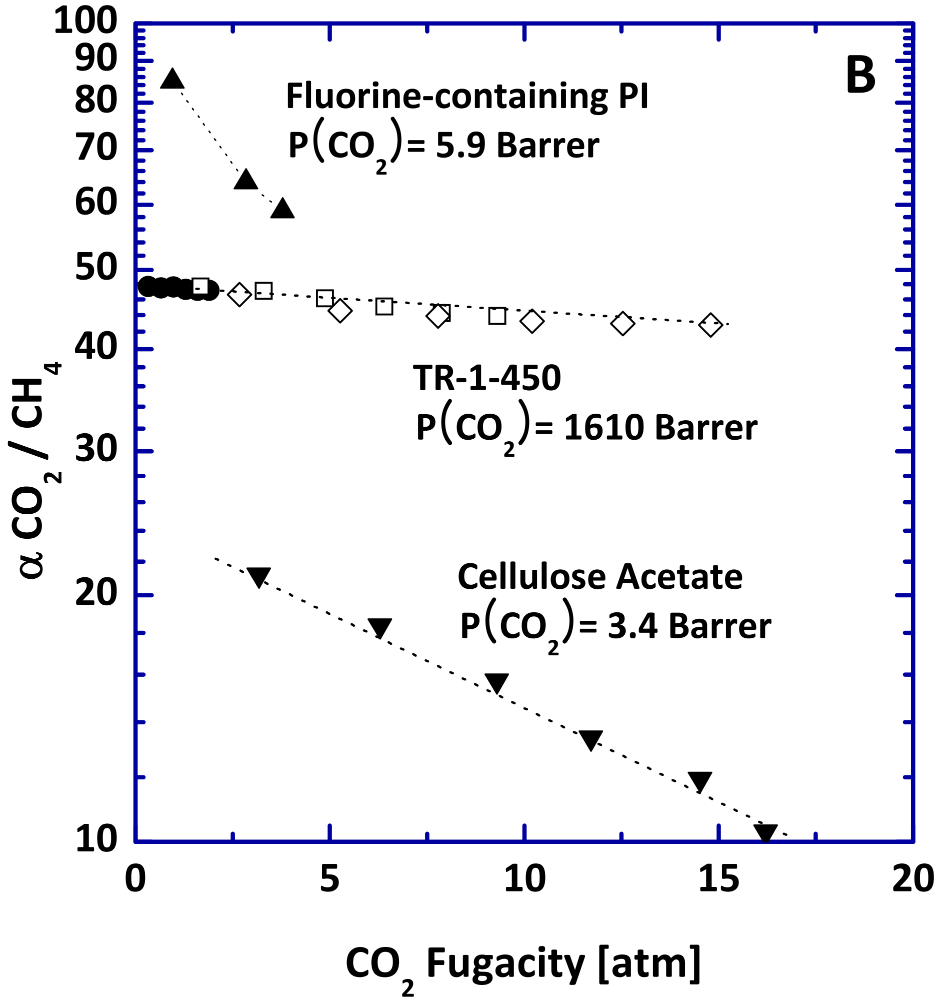
Physical Properties of PIOFG and TR Polymers

Sample code	*Density (g/cm³)*	*V (cm³/g)*	*V_w (cm³/g)*	*FFV*	*Increment in FFV (%)*	*d-spacing (nm)*
PIOFG-1	*1.503*	*0.665*	*0.430*	*0.159*	*65*	*0.548*
TR-1	*1.293*	*0.773*	*0.439*	*0.263*		*0.600*
PIOFG-2	*1.453*	*0.688*	*0.459*	*0.134*	*64*	*0.546*
TR-2	*1.271*	*0.787*	*0.473*	*0.219*		*0.606*
PIOFG-3	*1.469*	*0.681*	*0.455*	*0.131*	*57*	*0.503*
TR-3	*1.304*	*0.767*	*0.469*	*0.205*		*0.611*
PIOFG-4	*1.482*	*0.675*	*0.457*	*0.120*	*102*	*0.539*
TR-4	*1.240*	*0.806*	*0.470*	*0.243*		*0.602*
PIOFG-5	*1.478*	*0.677*	*0.443*	*0.148*	*28*	*0.560*
TR-5	*1.362*	*0.734*	*0.457*	*0.190*		*0.698*

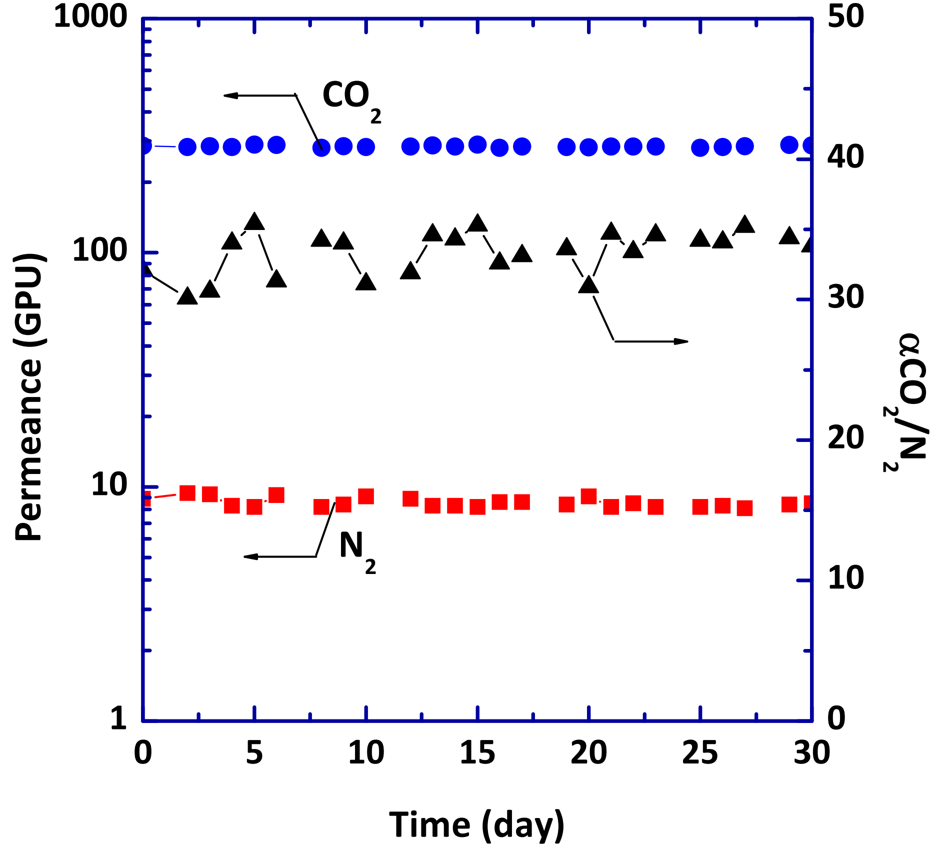
CO_2/CH_4 Separation



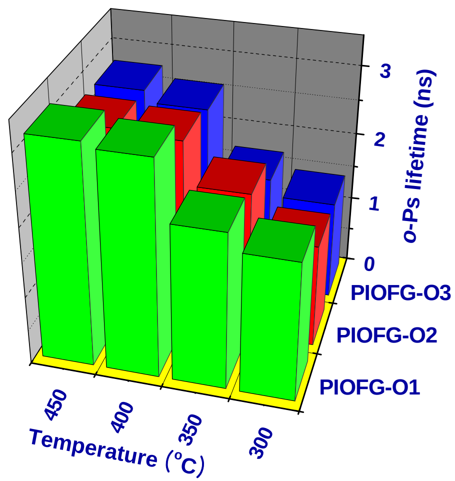
Anti - Plasticization Behavior of TR Polymer Membranes

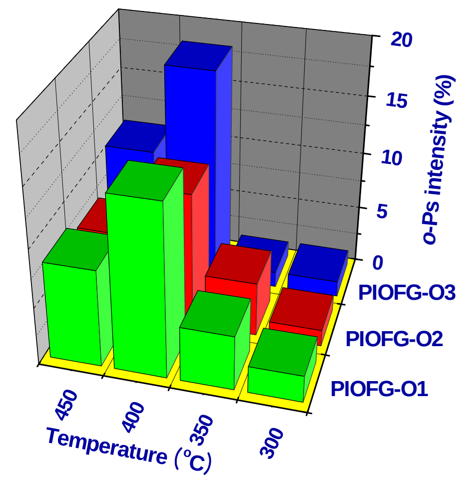


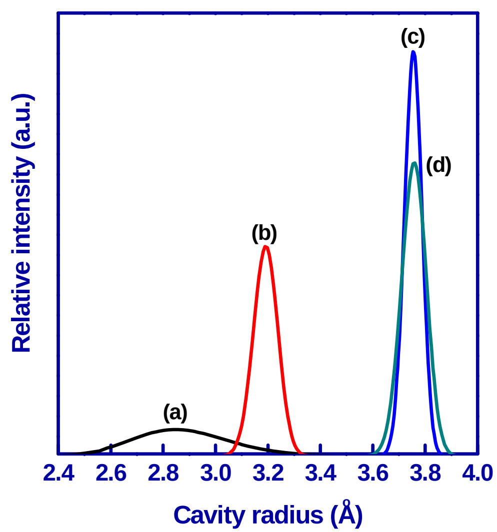
CO_2/N_2 Separation

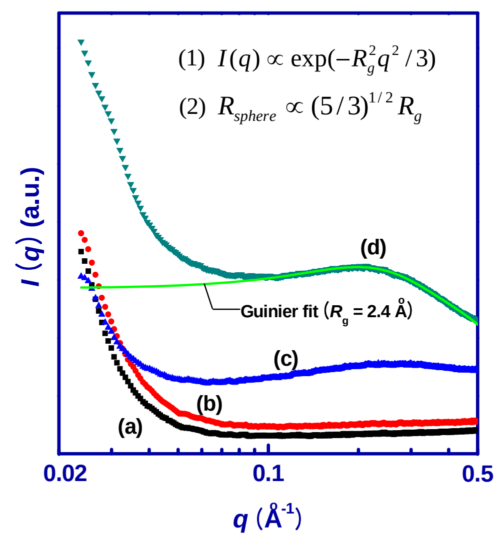


Cavity Size Distribution of PIOFG and TR Polymers

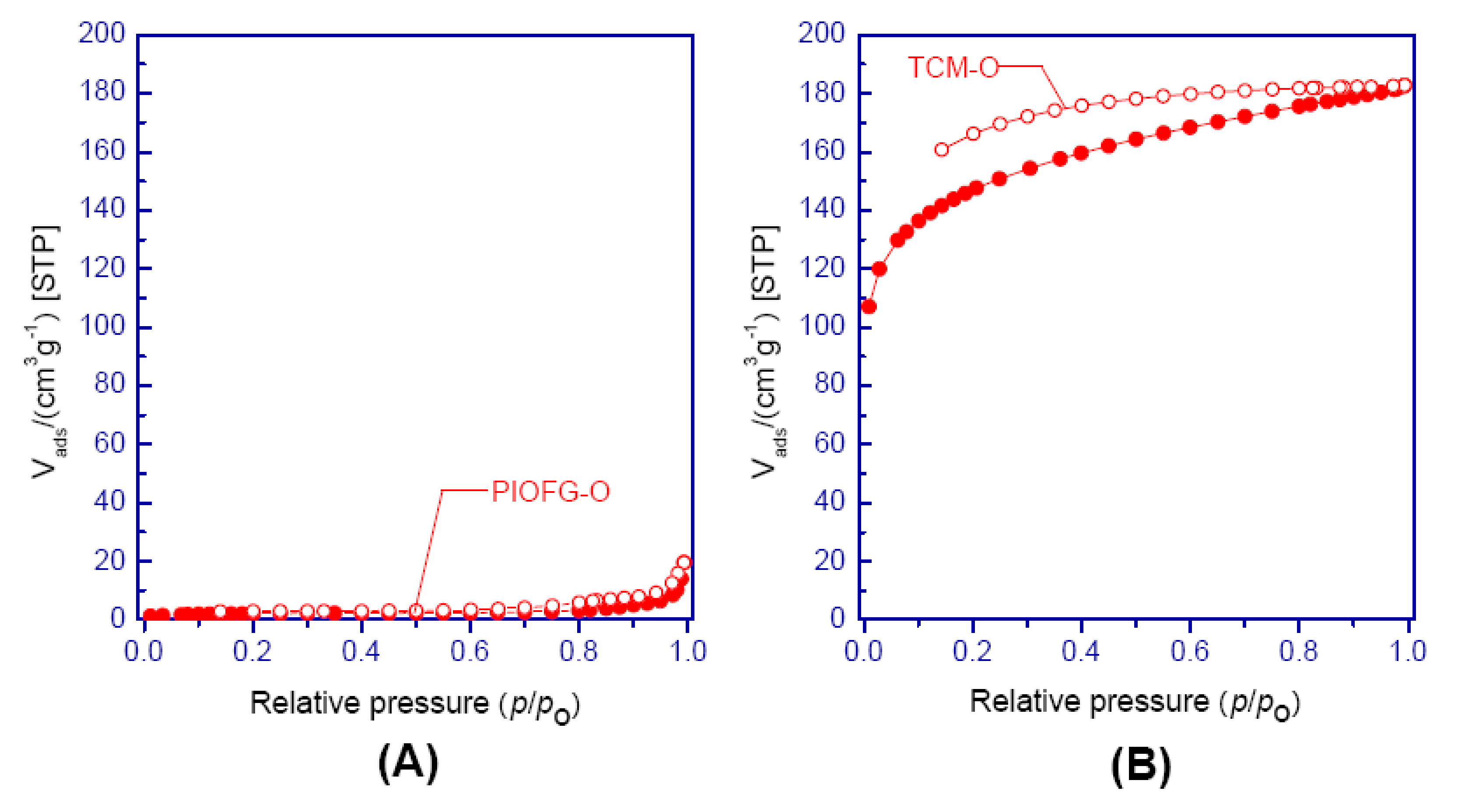






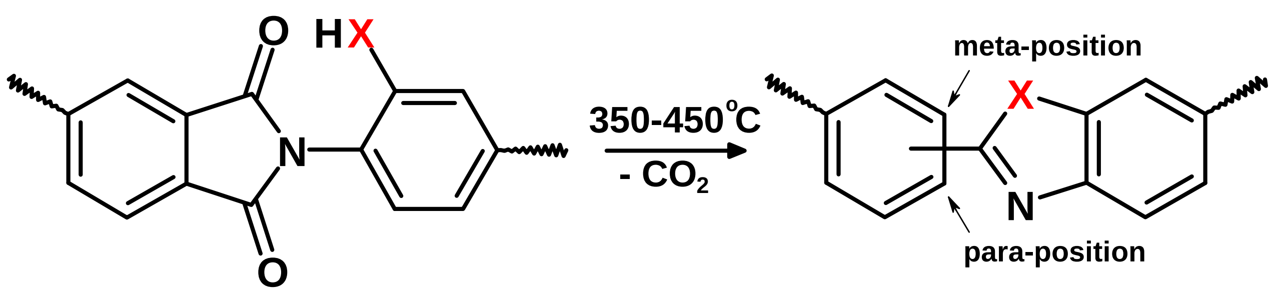


Microporous Character?

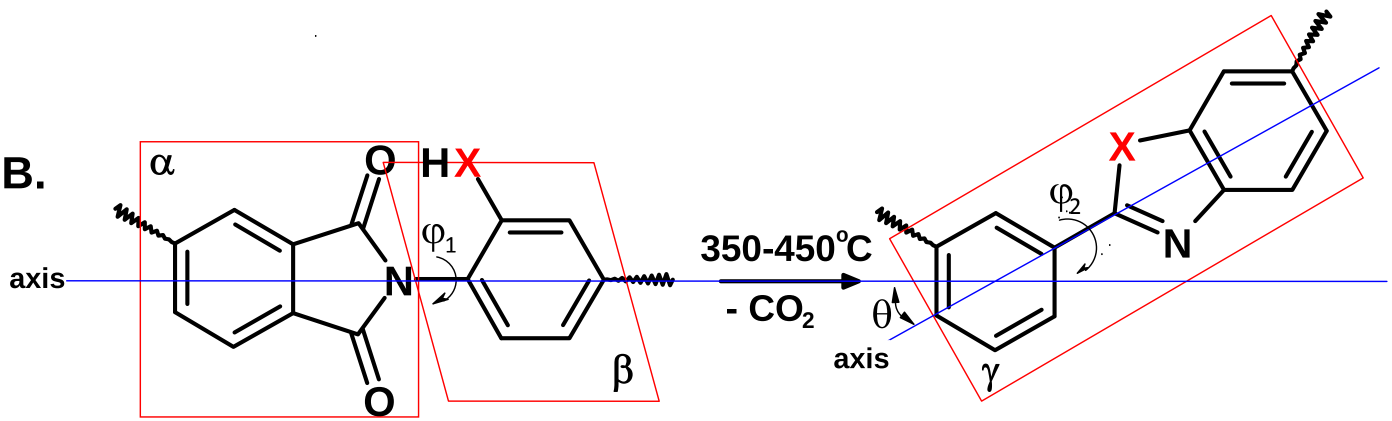


Chain Rearrangement of Interst

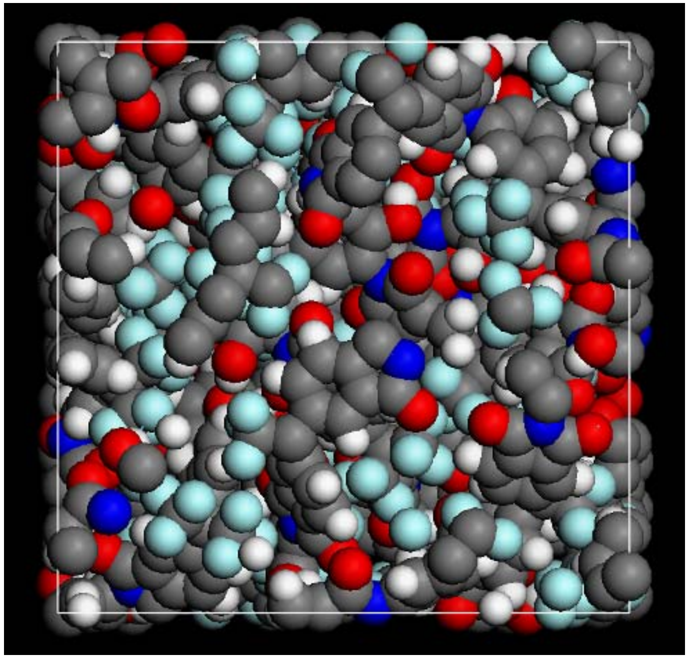
A.

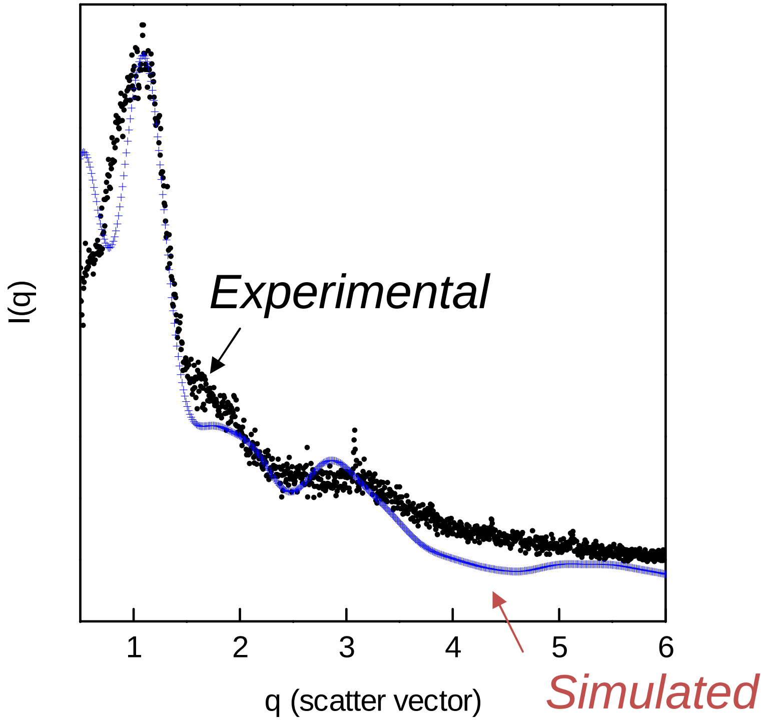


B.



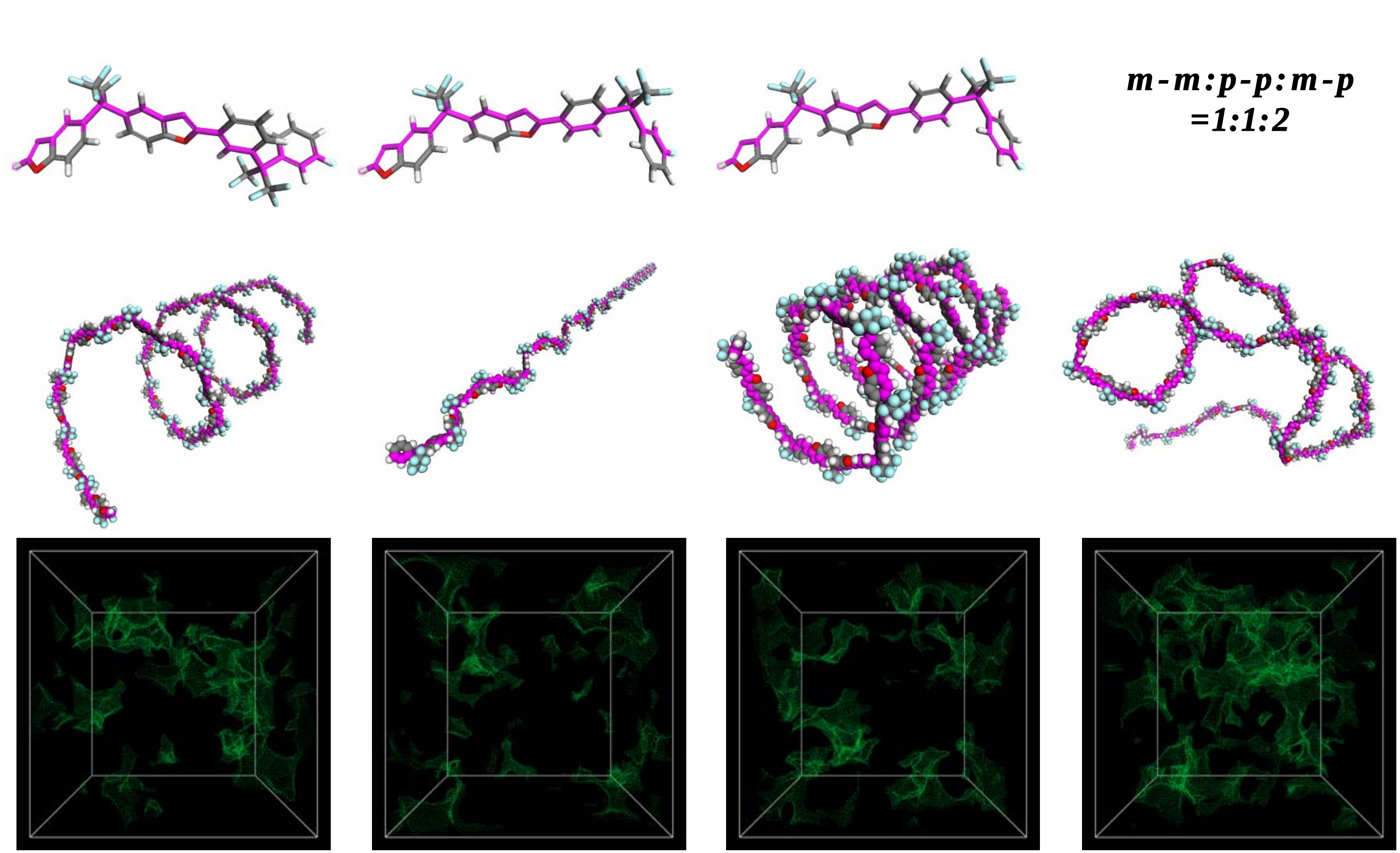
Simulated PIOFG - 1 Polymer Chain





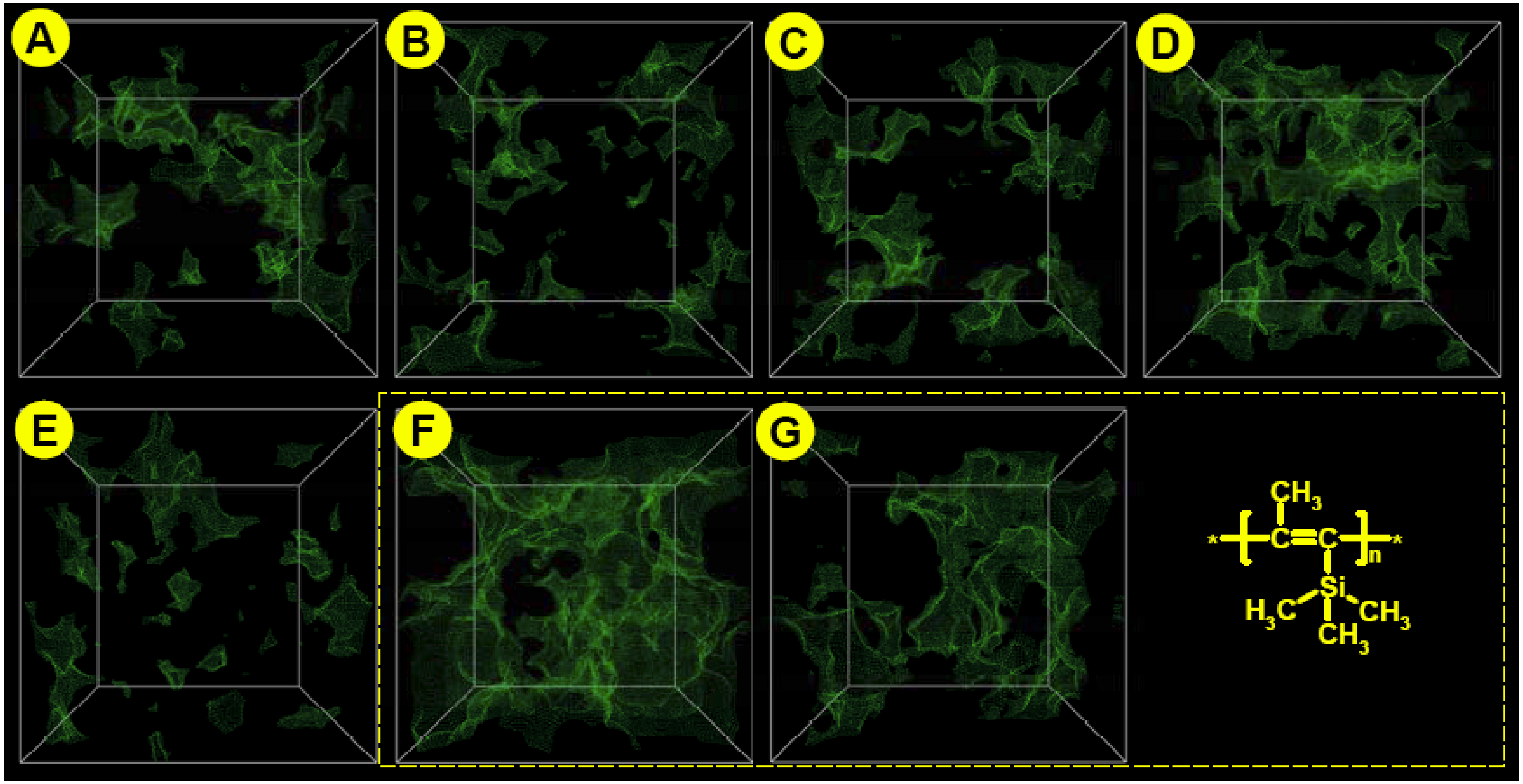
Effect of Regioisomerism on Final Polymer Structures

m-m linked PBO | ***m-p*** *(p-m)* linked PBO | ***p-p*** linked PBO | ***mixed*** PBO



Length: 30.736 Å, Angle: 90 °

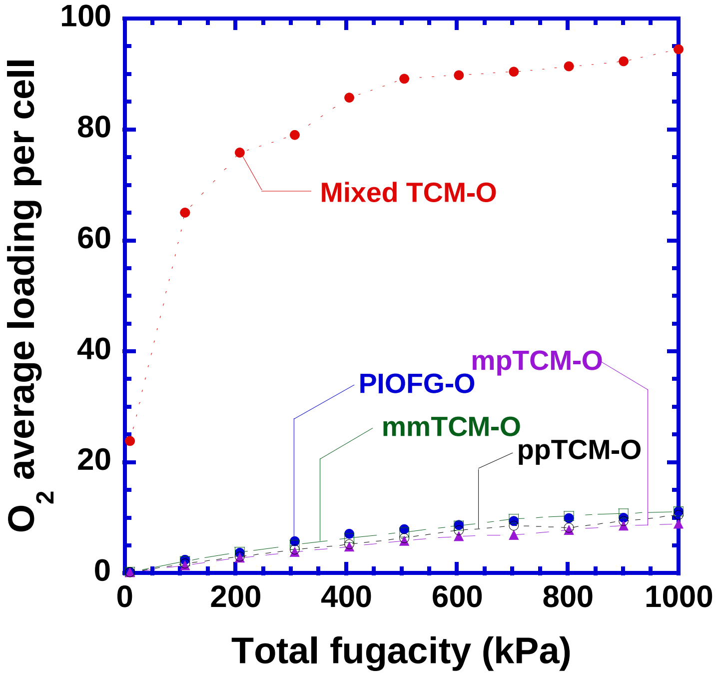
Effect of Packing Density on Different Chain Conformations

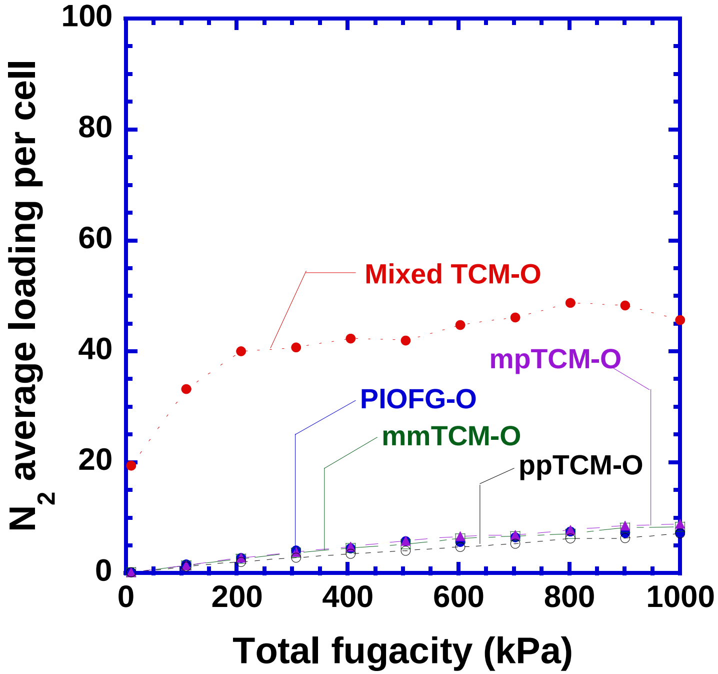


A: m-m TCM-O, B: m-p TCM-O, C: p-p TCM-O, D: mixed TCM-O

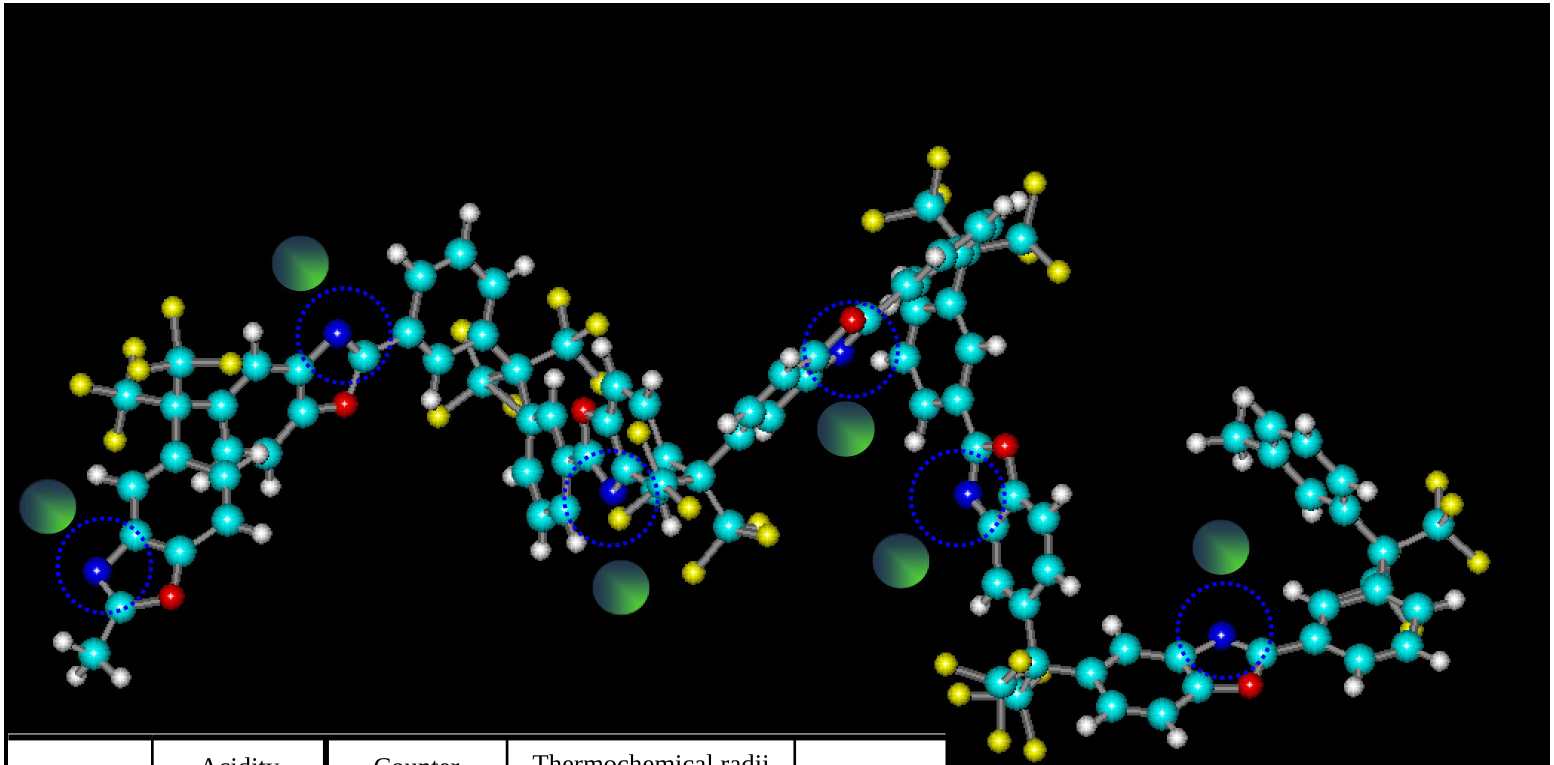
E: PIOFG-O (polyimide), F: pure PTMSP, G: aged PTMSP

Mixed Chain Conformation Increases the Amount of Sorption



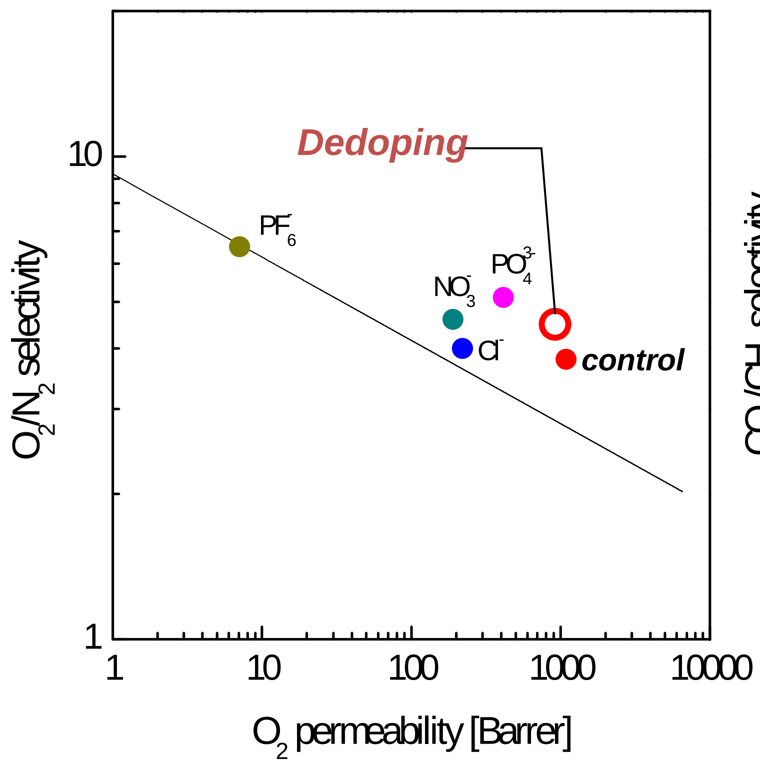


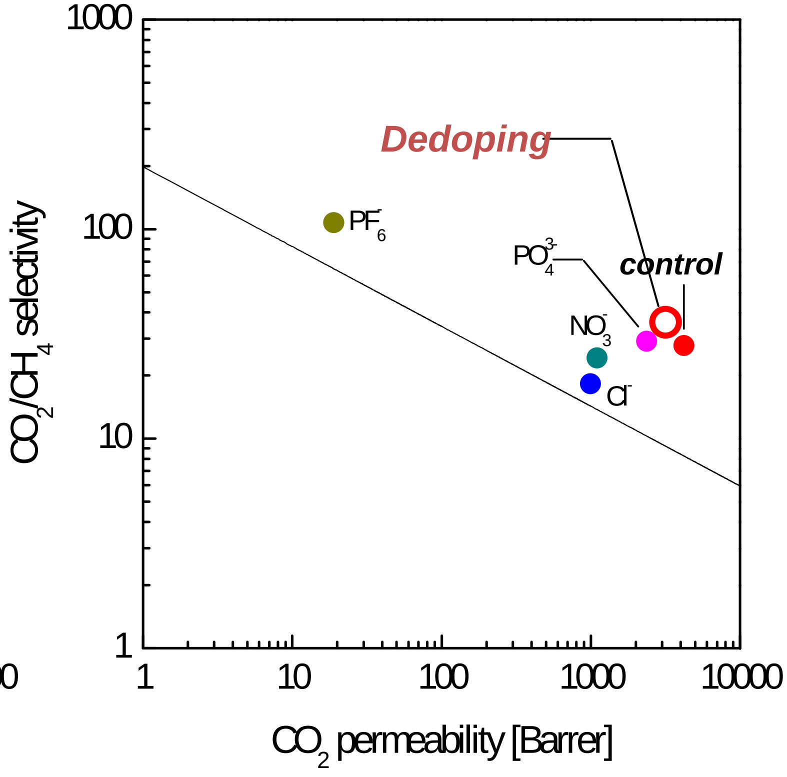
Control of Cavity Size By Dopants



Dopants	Acidity (pKa)	Counter anion	Thermochemical radii (nm)	Conc.
HCl	-7.00	Cl-	0.168	10 M
HNO_3	-1.30	NO_3-	0.200	10 M
H_3PO_4	2.15	H_2PO_4-	0.213	10 M
HPF_6	-1.60	PF_6-	0.242	10 M

Change in Gas Permeability by Dopants





Conclusions

- We showed aplastic, atypical free volume elements in dense, vitreous polymers can promote outstanding molecular and ionic transport along with enhanced separation performance.

  •The unusual cavity (free volume elements) evolution can be systematically tailored using a “molecular rearrangement concept” which takes place in the glassy, amorphous, confined polymers.

  •Free volume texture can be changed by controlling the degree of conversion, the flexibility of the original chain, and the insertion method of small dopant molecules.

  •The current approach overcomes the molecular separation limit of conventional organic polymers and demonstrates the expanded applicability of this family of polymers in physical and chemical separations.

Acknowledgements

CDRS
Carbon Dioxide Reduction
& Sequestration R&D Center

Brain Korea 21

Collaboration between University of Texas Austin and CSIRO

Mechanical properties of PIOFG, TR polymers and CMS films at 25 ^{o}C

Sample	Tensile strength (MPa)[g]	Elongation percent at break (%)[g]
PIOFG-1	83	3.1
TR-1-350	87	3.8
TR-1-400	95	3.5
TR-1-450	98	3.9
CMS-1[a]	42	0.4
CMS-2[b]	52	0.3
CMS-3[c]	34	0.6
PBO-1[d]	98	10
PBO-2[d]	99	11
PBO-3[d]	52	4
PBO-4[d]	77	8
PBO-5[e]	110	4.5
PBO-6[f]	89.6	10.9

[a] Carbon molecular sieve film derived from Kapton polyimide (carbonization temperature = 600 ^{o}C)
[b] Carbon molecular sieve film derived from Kapton polyimide (carbonization temperature = 800 ^{o}C)
[c] Carbon molecular sieve film derived from PIOFG-1 (carbonization temperature = 600 ^{o}C)
[d] Polybenzoxazole film (*S1*)
[e] Polybenzoxazole film (*S2*)
[f] Polybenzoxazole film (*S3*)
[g] Five specimens of each sample were tested. Standard deviation from the mean was within ±5%.

No Plasticization