New Soluble N-Substituted Polybenzimidazoles by Post-Polymerization Modification

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

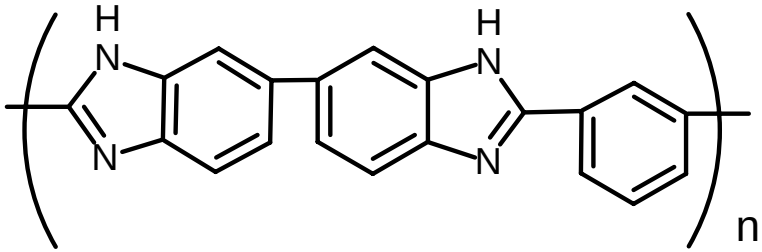
- **Purpose — Develop high-temperature membranes for more efficient separation of CO_2 from methane and nitrogen streams**
  - **Develop and test thin, dense film polymer membranes at temperatures of 100 to 400ºC to take advantage of enhanced gas diffusion**
  - **Develop polymer membranes that have 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 Vivek Khare)
  - 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***, Thomas A. Luther, Christopher J. Orme, Michael G. Jones, Alan K. Wertsching, and Eric S. Peterson)
  - Synthetic polymer chemistry expertise
  - Membrane formation and testing expertise

Polybenzimidazole (PBI)

- **History**
  - **H.A. Vogel and C.S. Marvel* (*J. Poly. Sci.*, 1961)**
  - **U.S. Patent Literature – various from Celanese**
    - **Commercial product trademark – Celazole®**
- **Polybenzimidazole (PBI)**
  - **Thermally stable (Tg ~ 450°C)**
  - **Chemically resistant**
  - **Not easily processed**

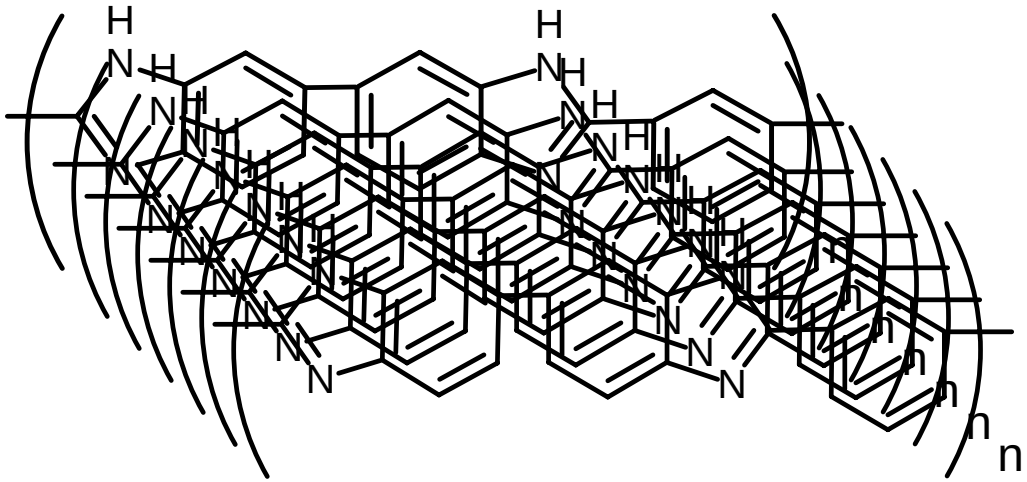


PBI

Key Elements for Success

- 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 to be a membrane

INL Synthetic Strategy

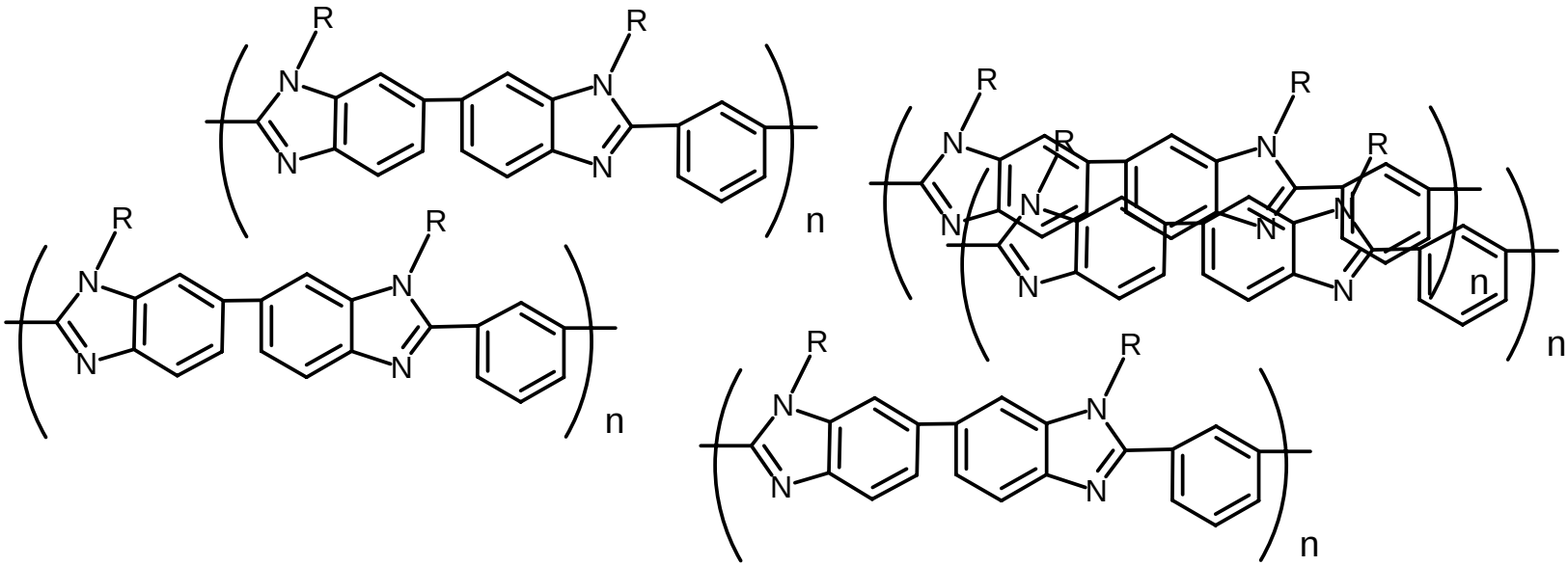


Pi-Pi interactions provide very stable molecular stacking properties and highly crystalline behavior

INL Approach: Larger substituent groups break up stacking and crystallinity

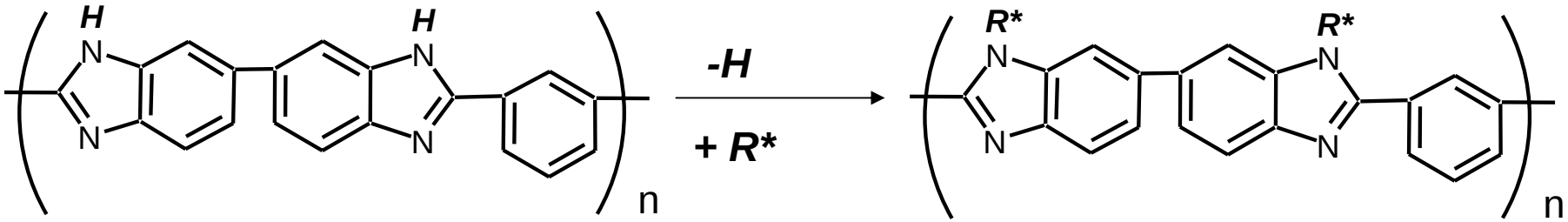
Molecular stacking increases crystallinity, high T_g, and low free

Post-polymerization Polymer Modification



Molecular stacking is decreased - the structure is opened up

Post-polymerization Polymer Modification General Reaction

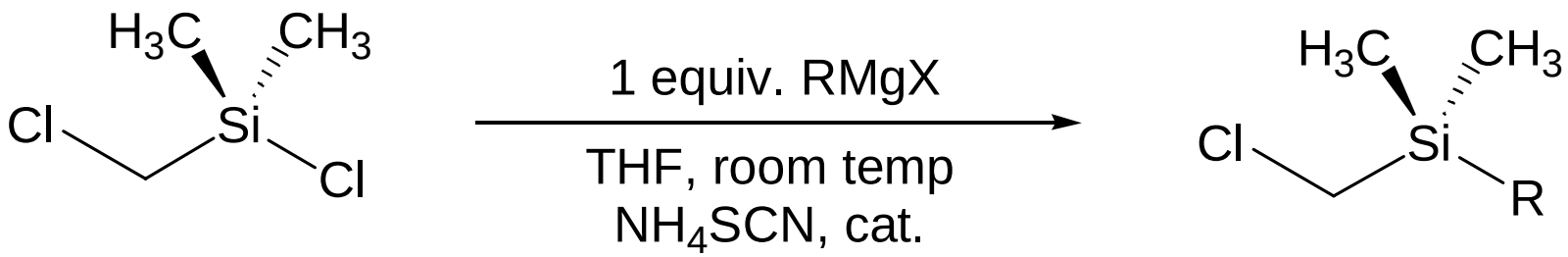


***R* =** (Methyl)Me_2SiCH_2- **(1)**, (Phenyl)Me_2SiCH_2- **(2)**, (Vinyl)Me_2SiCH_2- **(3)**, (Allyl)Me_2SiCH_2- **(4)**, (Hexyl)Me_2SiCH_2- **(5)**, (Decyl)Me_2SiCH_2- **(6)**

Modification of already formed polymer utilizing already known methods, but unique pendant groups

1-4 (chloromethyl)silanes can be obtained commercially.

Catalytic Reaction* for Hexyl (5) and Decyl (6)



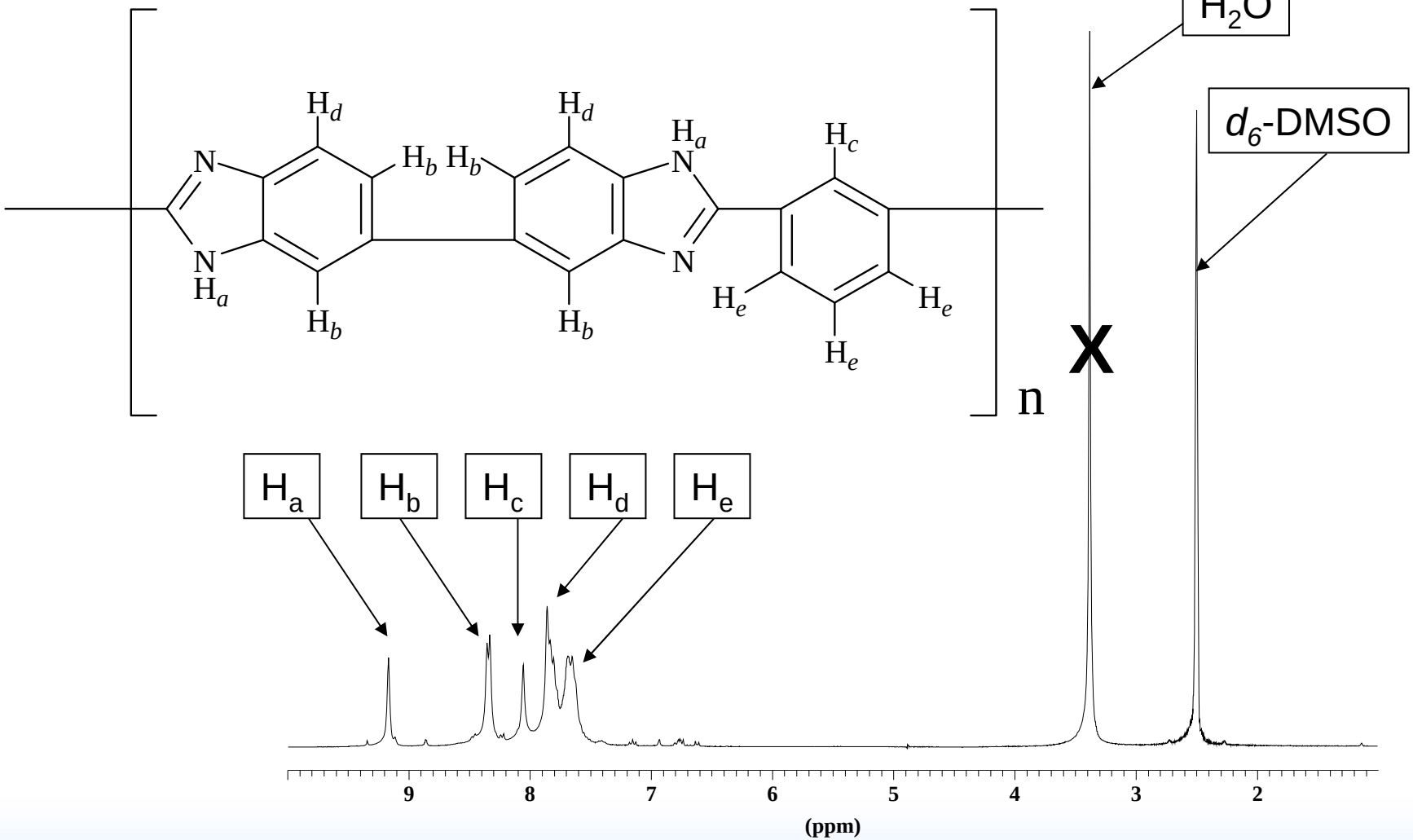
R = hexyl **(5)**, decyl **(6)**

Gives good yields under mild conditions

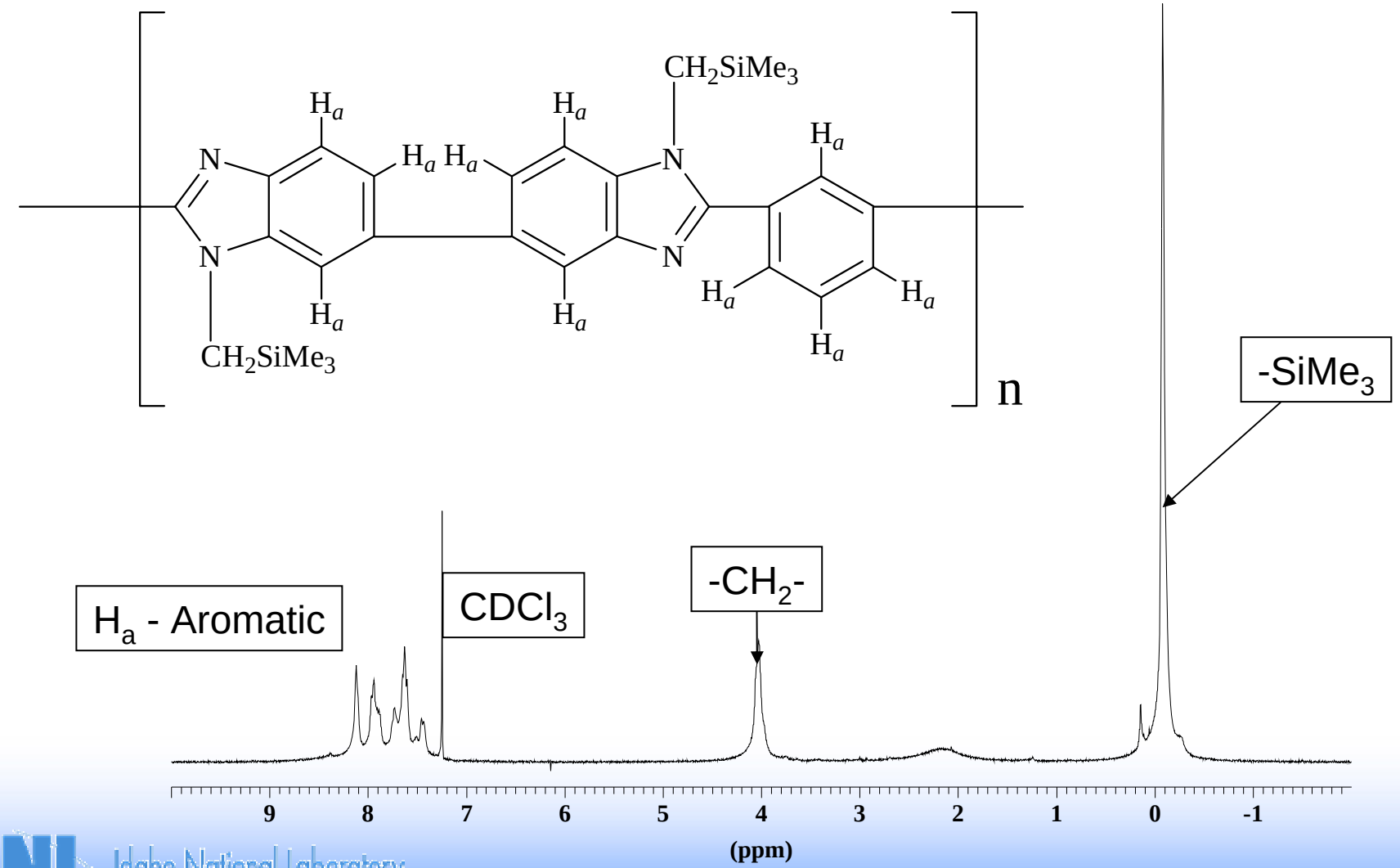
Hexyl (5) – 0.125 mmHg/ 44°C, 80% yield
Decyl (6) – 0.125 mmHg/ 60-63°C, 78% yield

*****Lennon, P. J.; Mack, D. P.; Thompson, Q. E. *Organometallics*, **1989**, *8*, 1121.

^{1}H NMR of Parent PBI (Celazole®) in d_6-DMSO



^{1}H NMR of (Methyl)Me_2SiCH_2-(PBI) (1) in $CDCl_3$



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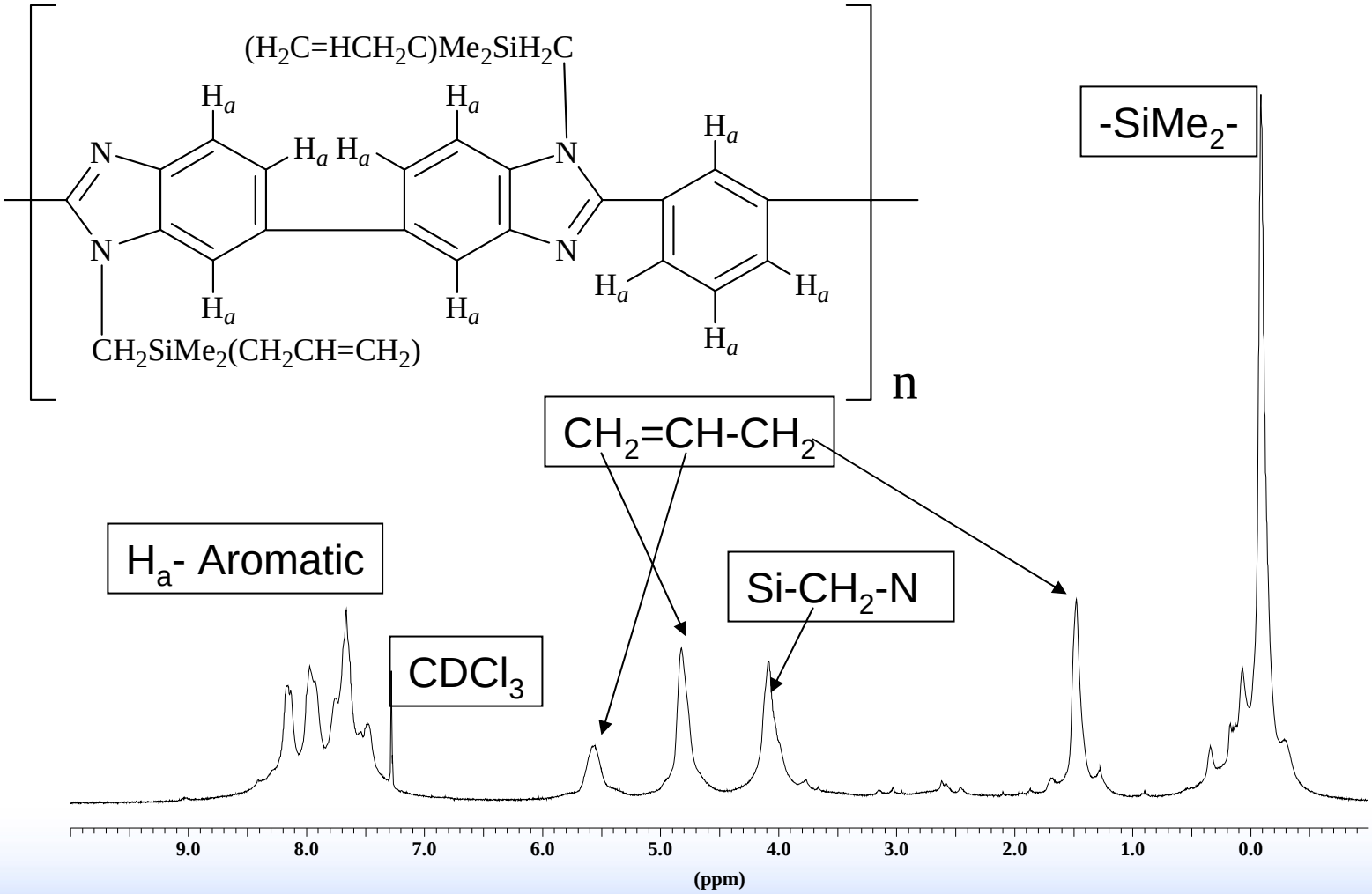
^{1}H NMR of (Allyl)Me_2SiCH_2-(PBI) (4) in $CDCl_3$



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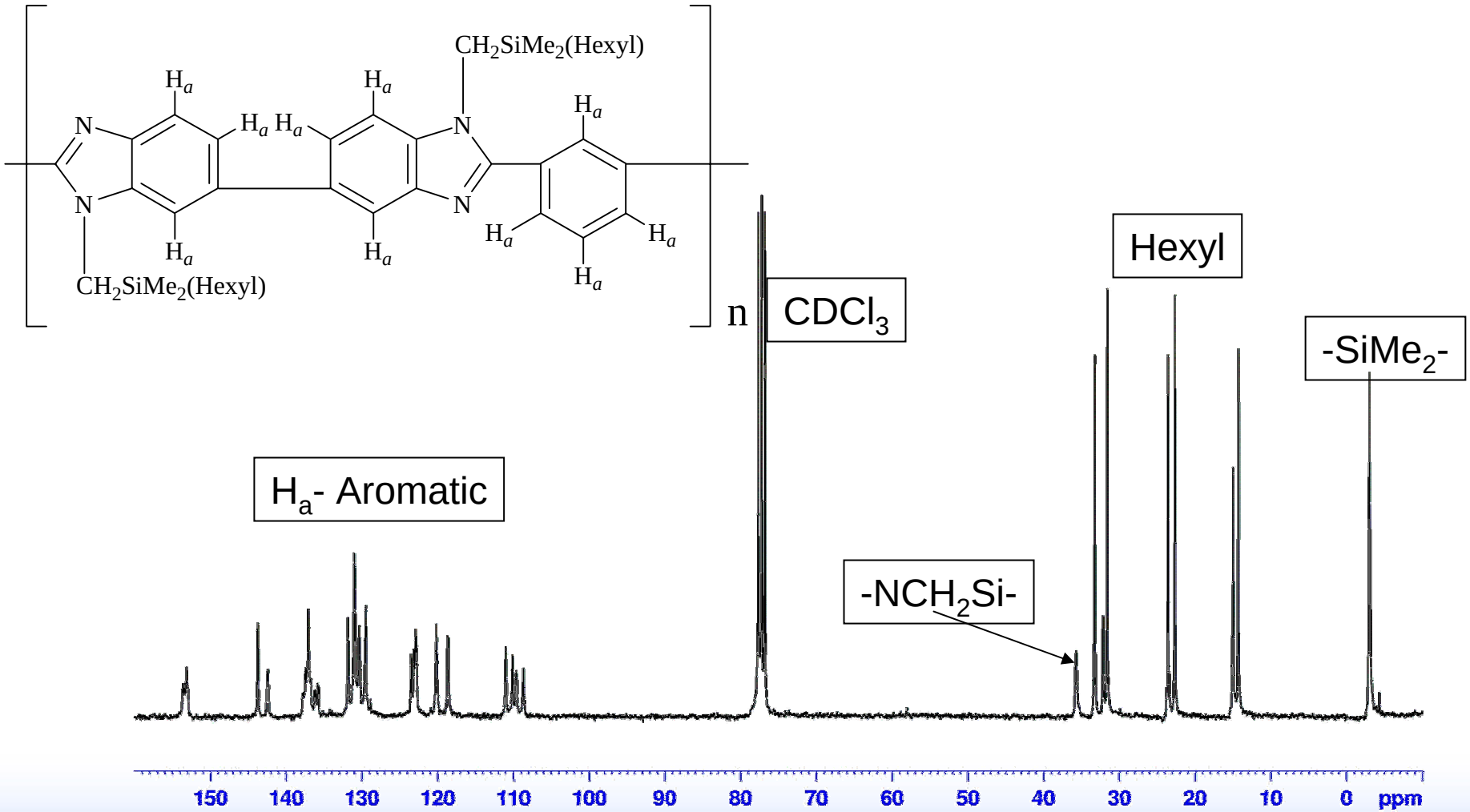
^{13}C NMR of (Hexyl)Me_2SiCH_2-(PBI) (5) in $CDCl_3$



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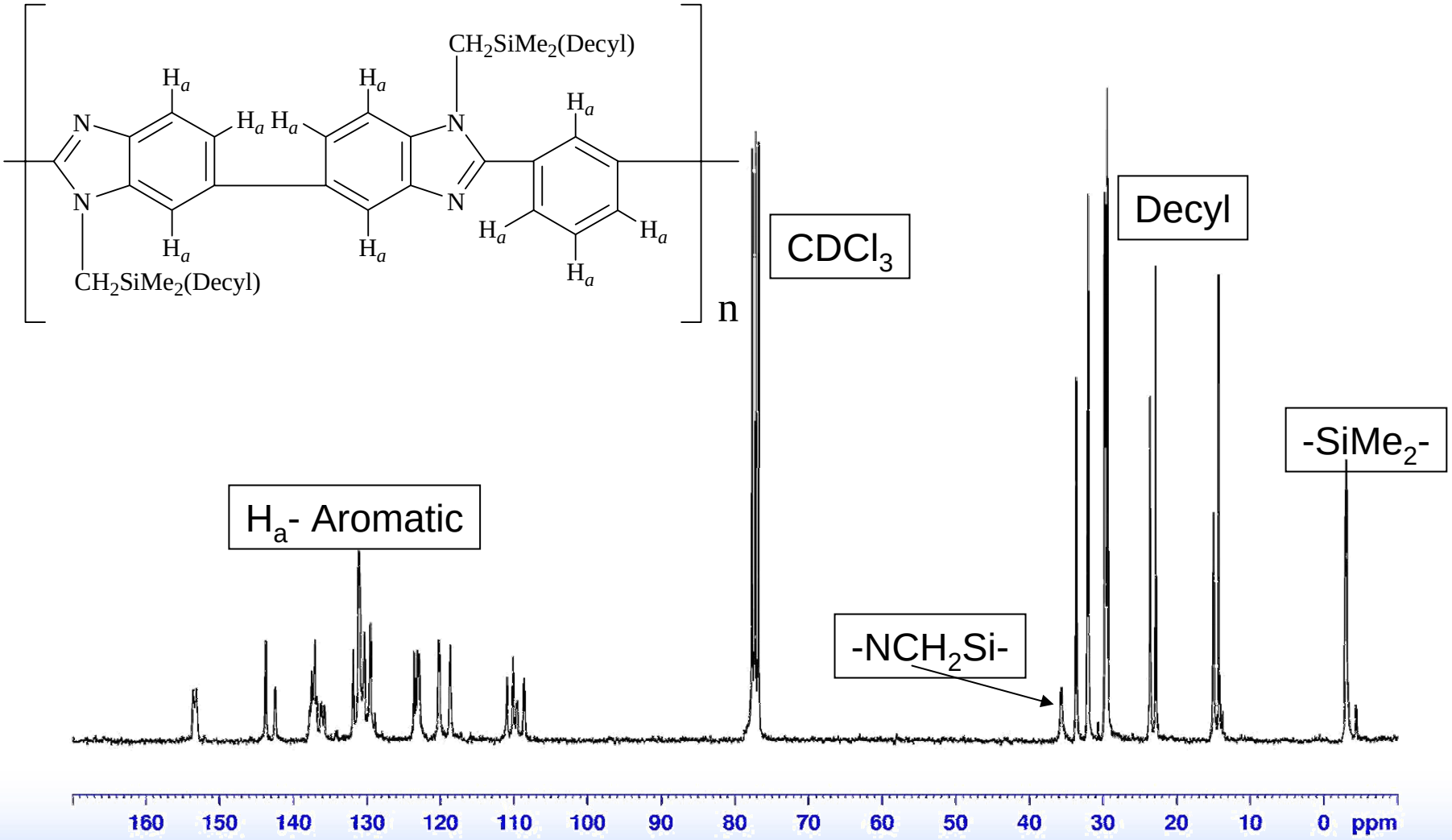
^{13}C NMR of (Decyl)Me_2SiCH_2-(PBI) (6) in $CDCl_3$



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Solvent Solubility of Some Polybenzimidazoles

	Solubility - Grams / mL of Solvent				
Polymer	**THF**	**$CHCl_3$**	**CH_2Cl_2**	**DMAc**	**NMP**
Parent PBI[a] (Celazole®)	Not Soluble	Not Soluble	Not Soluble	Partially soluble	Partially soluble
(Methyl)Me_2SiCH_2-(PBI) **(1)**	0.2-0.25	0.2-0.25[b]	0.01-0.05	Soluble	Soluble
(Vinyl)Me_2SiCH_2-(PBI) **(3)**	0.2-0.25	0.2-0.25[b]	Swells Slightly Soluble	Soluble	Soluble
(Allyl)Me_2SiCH_2-(PBI) **(4)**	0.2-0.25	0.2-0.25[b]	Swells Slightly Soluble	Soluble	Soluble

[a]From C.S. Mavel, *et al*: DMSO - Soluble; DMF - Partially soluble; Formic acid - 0.05-0.06g/mL
[b]Elevated temperature and constant stirring (~50°C).

"Batch Mode" LLS Molecular Weight Determinations and Yield

Polymer	"Batch Mode" – Mw (g/mol)[a]	Yield %
Parent PBI (Celazole®)	8,000-10,000[b]	**N/A**
(Methyl)Me_2SiCH_2- **(1)**	10,000-15,000	**50**
(Phenyl)Me_2SiCH_2- **(2)**	*c*	**15**
(Vinyl)Me_2SiCH_2- **(3)**	10,000-15,000	**50**
(Allyl)Me_2SiCH_2- **(4)**	45,000-55,000	**50**
(Hexyl)Me_2SiCH_2- **(5)**	45,000-55,000	**50**
(Decyl)Me_2SiCH_2- **(6)**	65,000-90,000	**50**

[a]Solvent - THF (Tetrahydrofuran)
[b]Solvent - DMAc (N,N-Dimethylacetamide)
[c]not determined.

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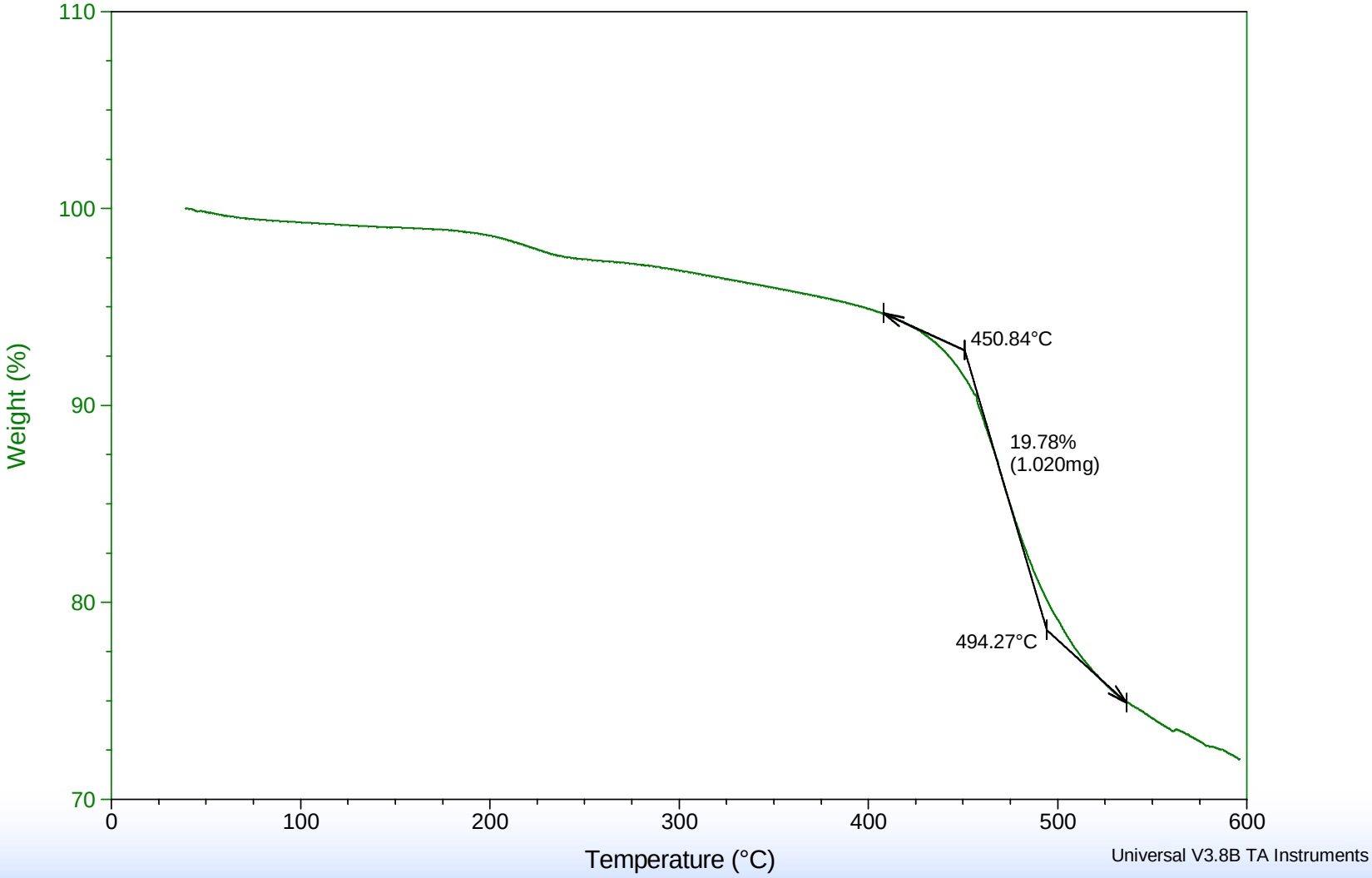
TGA Results of Selected PBI Polymers

Polymer	Initial Weight Loss under N_2
Parent PBI (Celazole®)	512 ºC
(Methyl)Me_2SiCH_2-PBI **(1)**	448 ºC
(Phenyl)Me_2SiCH_2-PBI **(2)**	430 ºC
(Vinyl)Me_2SiCH_2-PBI **(3)**	464 ºC
(Allyl)Me_2SiCH_2-PBI **(4)**	451 ºC

TGA of (Allyl)Me_2SiCH_2-(PBI) (4)



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Polybenzimidazole Pure Gas Permeabilities (in barrers)[a]

Polymer	H_2	Ar	N_2	O_2	CH_4	CO_2
Parent PBI (Celazole®)@ 30ºC	4.6	0.18	0.12	0.29	0.13	0.85
Parent PBI (Celazole®)@ 55ºC	5.7	0.07	0.09	0.31	0.11	0.25
Allyl-PBI **(4)**@ 30ºC	1.6	0.4	0.2	0.4	0.7	2.5
PBI-Hexyl **(5)**@ 30ºC	20.6	8.0	8.9	9.9	12.8	18.3

[a]Permeabilities in barrers, $\left((10^{-10})\frac{cm^3(STP)\times cm}{cm^3\times sec\times cmHg}\right)$.

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Summary

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
- Added ligands that give greater free volume
- Polymer is freely soluble in common solvents (ie. THF, $CHCl_3$)
- Onset Decomposition = ~450 °C
- Measured Mw ‘s
- Some of the functionalized polymers form good films

Acknowledgements

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