Modeling of Environmentally Friendly Siloxane-Based Lithography Solvents

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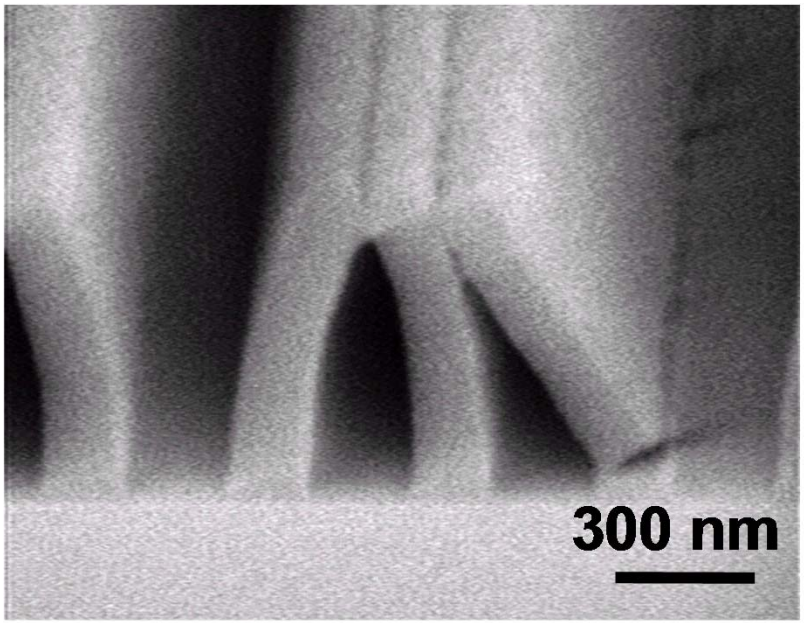
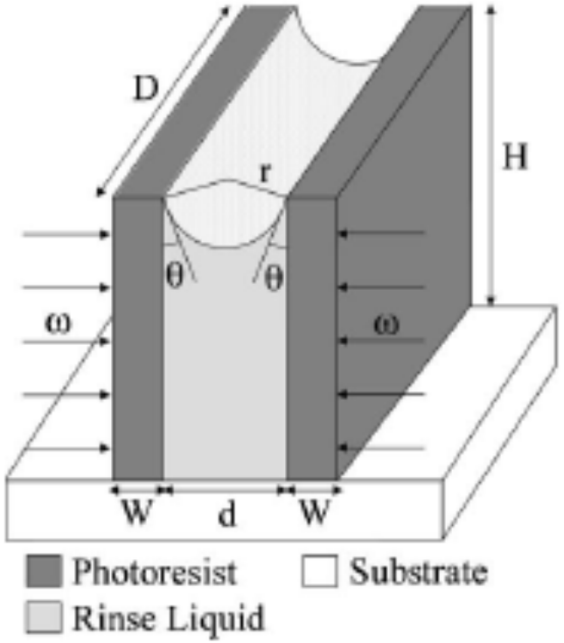
Motivation

- Drive to reduce device dimensions has many obstacles remaining in its path.
  - Pattern collapse due to finite size effects and increased capillary forces during rinse
  - LER due to acid diffusion
  - Environmental concerns



Stoykovich, Cao, Yoshimoto, Ocola, Nealey, *Advanced Materials* **15** 1180 (2003)

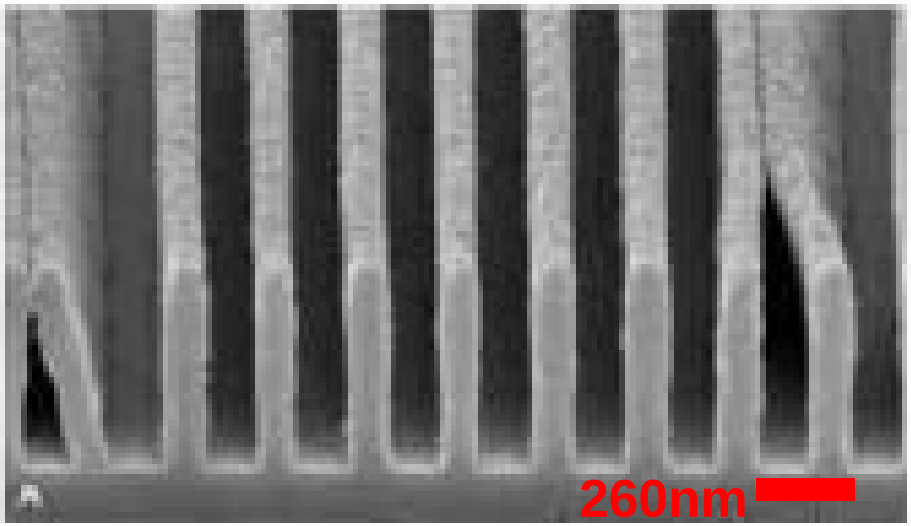


Yoshimoto Stoykovich Cao, de Pablo, Nealey; Journal of Applied Physics (2004)

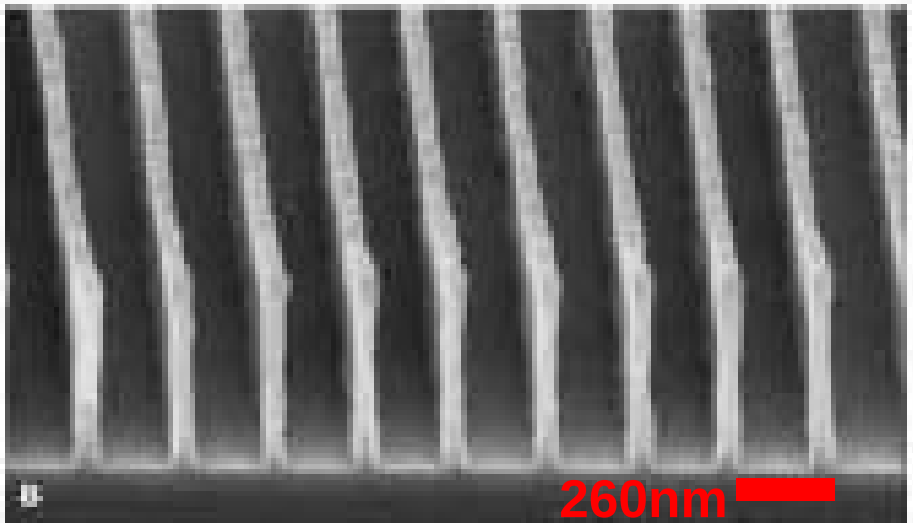
$scCO_2$ as a Solvent

- No surface tension
  - reduced capillary forces => abates pattern collapse
- Plasticizes polymeric photoresist
  - reduced LER
- Requires additives to enhance resist solubility or new resists

Developed with TMAH, 122nm lines.



Developed with QAS/$scCO_2$, 42nm lines.



Wagner, DeYoung, Harbinson; SPIE Vol.6153 (2006)
Zweber, Wagner, DeYoung, Carbonell; Langmuir (2009)
Goldfarb, de Pablo, Nealey, Simons, Moreau, Angelopoulos (2000)

Objectives

- Environmental goals
- Methodology
- Super-critical carbon dioxide
  - Use with traditional photoresists
  - Use with molecular glass photoresists
- Linear methyl siloxanes
  - Benefits
  - Model development
  - Model validation
  - Use with traditional photoresists
  - Exploration of dissolution mechanism
- Future Work

ESH Metrics and Impact

1. Reduction in the use or replacement of ESH-problematic materials

   100% reduction in the use of aqueous base TMAH developer

2. Reduction in emission of ESH-problematic material to environment

   Up to 100% reduction in VOCs and HAPs emission

3. Reduction in the use of natural resources (water and energy)

   Eliminate water usage

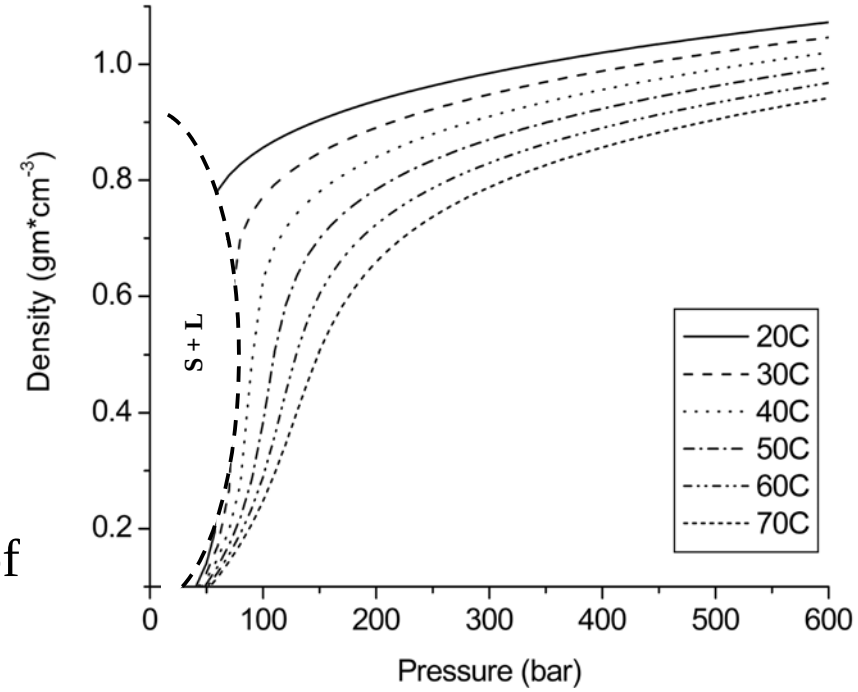
   Reduction in energy for water treatment and purification

4. Reduction in the use of chemicals

   Minimal use of organic solvents

Why a Non-Aqueous Developer Solvent?

- Environmentally friendly, zero VOC solvent
- Highly tunable solvating power
  - ρ(T,P)
  - Leaves no residue
  - Clean separations
- One-phase fluid
  - Zero surface tension
  - Transport, viscosity between that of liquid and gas
- Nonpolar, inert character

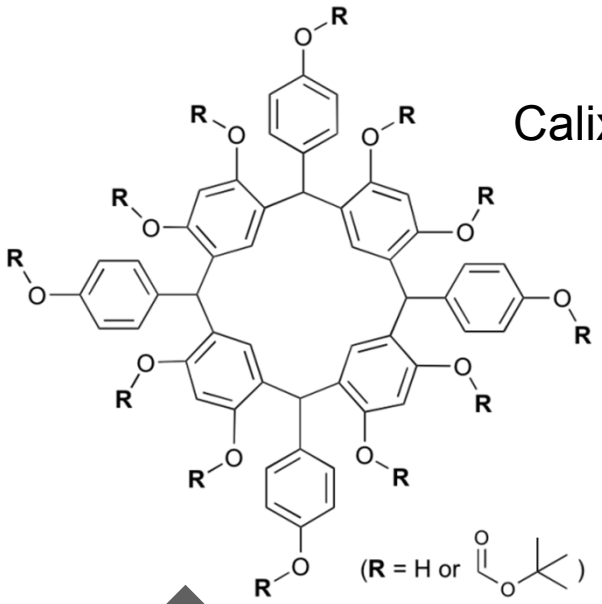


Potential to reduce LER and eliminate pattern collapse

Collaboration

Ober Group

- Synthesize photoresists
- Development process
- Provide experimental results



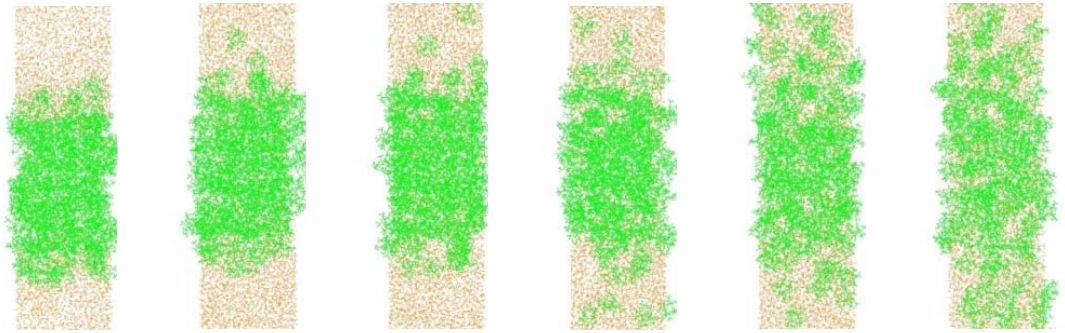
Calixerene

CHPB-boc

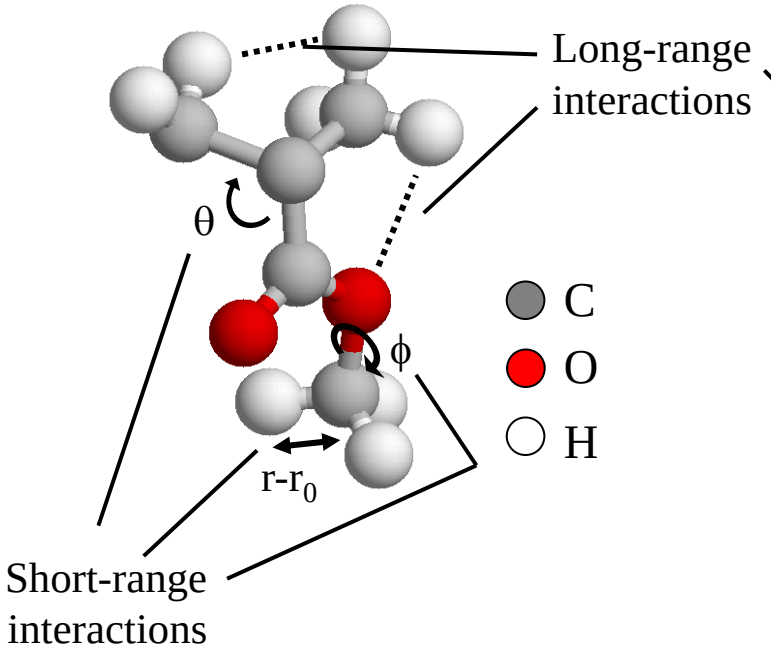
- Computer Simulations
- Pre-screening of possible photoresist structures
- Provide information on dissolution mechanism at a molecular level

de Pablo Group

Time (1ns-2ns between images)



Model



OPLS Model:

$$V_{tot} = \underbrace{V_{LJ} + V_{coul}}_{\text{Intermolecular}} + \underbrace{V_{bon} + V_{ang} + V_{tors}}_{\text{Intramolecular}}$$

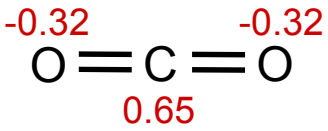
$$V_{LJ} = 4\cdot\varepsilon\cdot\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

$$V_{coul} = \frac{q_i\cdot q_j}{4\cdot\varepsilon_0\cdot\varepsilon\cdot r}$$

$$V_{bon} = \frac{1}{2}\cdot k_{bon}\cdot\left(r - r_0\right)^2$$

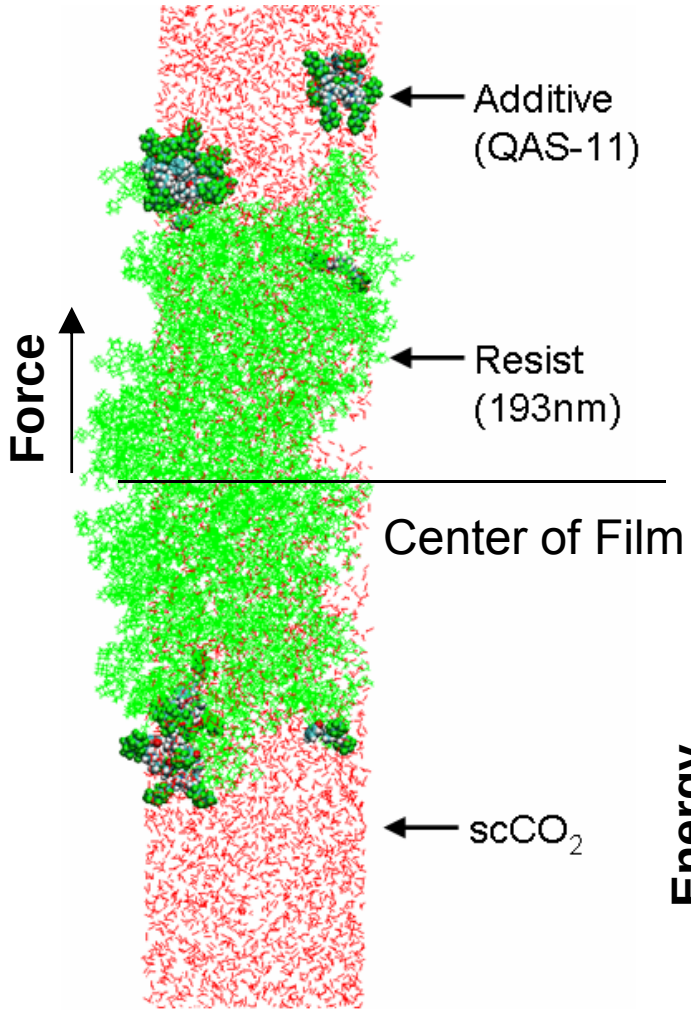
$$V_{ang} = \frac{1}{2}\cdot k_{ang}\cdot\left(\theta - \theta_0\right)^2$$

$$V_{tors} = \sum_n k_n\cdot\left(1 + \cos\left(n\cdot\phi - \phi_0\right)\right)$$



- OPLS force field employed for most parameters
- We calculated charges (q_i) using quantum mechanics

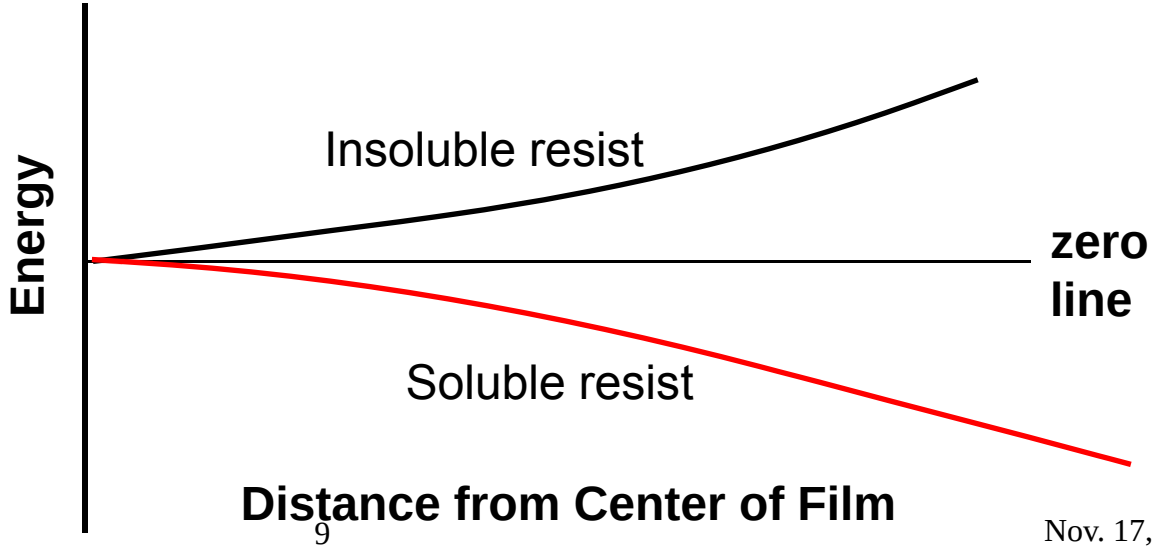
Film Energy Calculation



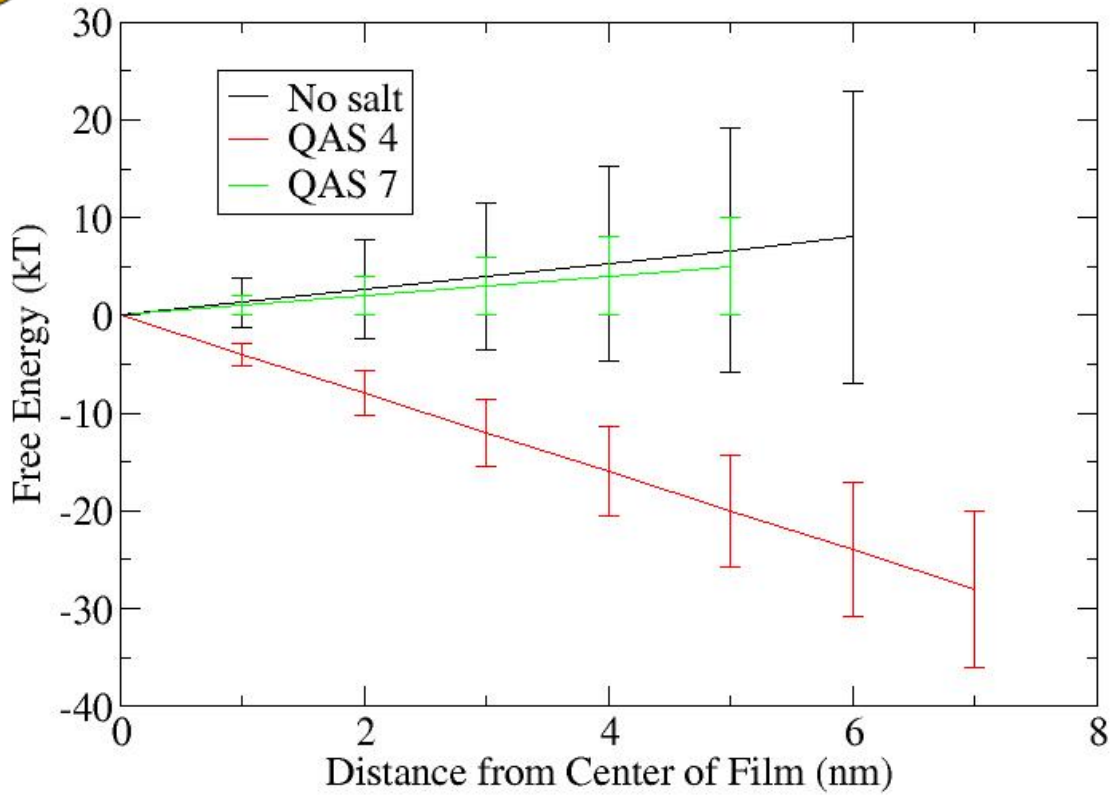
- Thin films of resist equilibrated in solvent via MD simulation
- Integrating the force on each chain as a function of position provide free energy

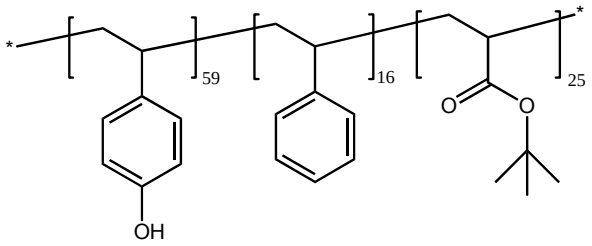
$$F(z) = \int_{z}^{z_\infty} \langle f(z') \rangle \, dz' + F(z_o)$$

- If the energy is lower at the surface than the center, the film is unstable

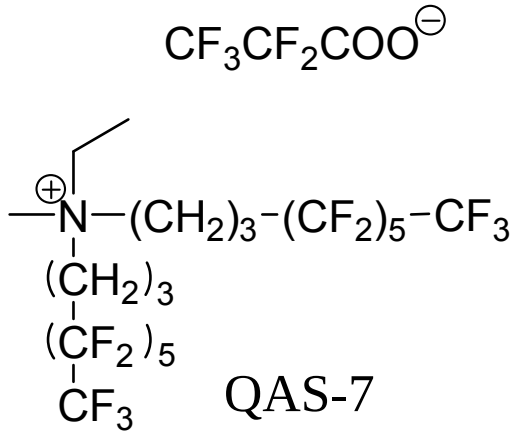


Sample Result: ESCAP Energy Curve

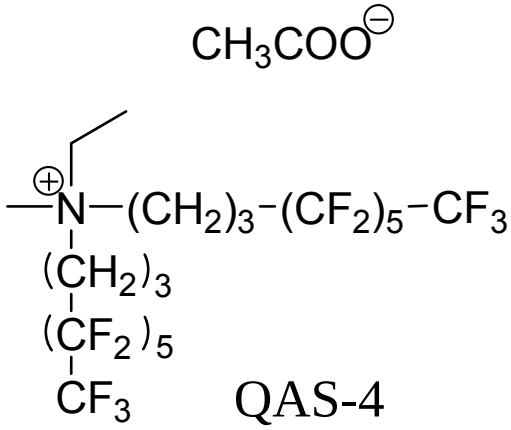




hPS PS TBA

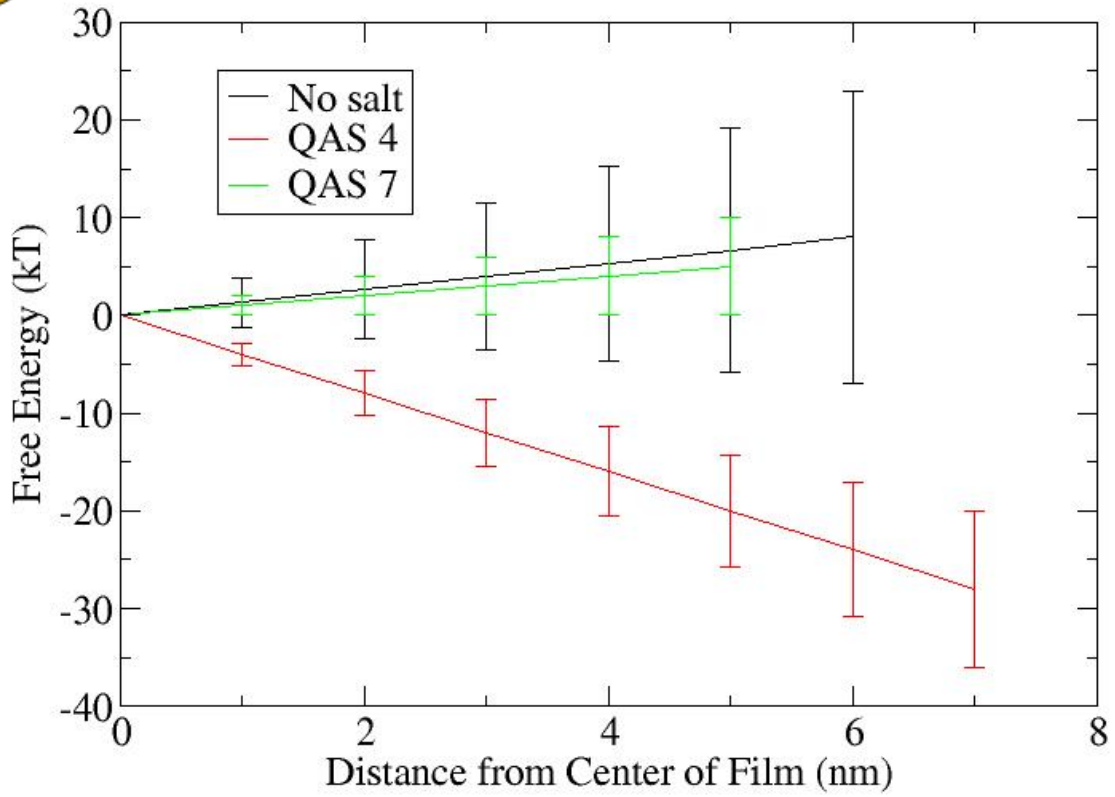


QAS-7



QAS-4

Sample Result: ESCAP Energy Curve

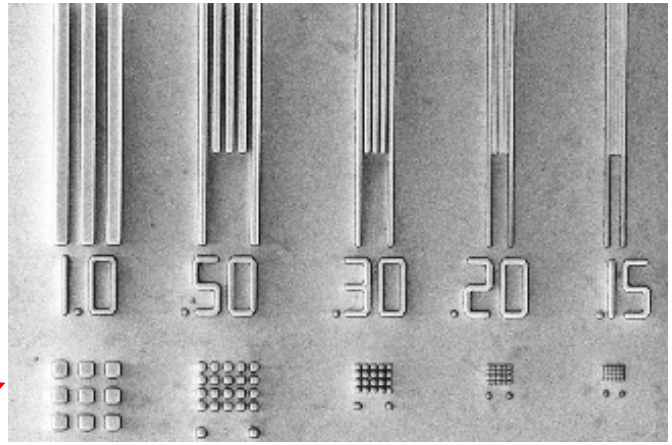


Experimental Results:

No salt – 0 nm/sec

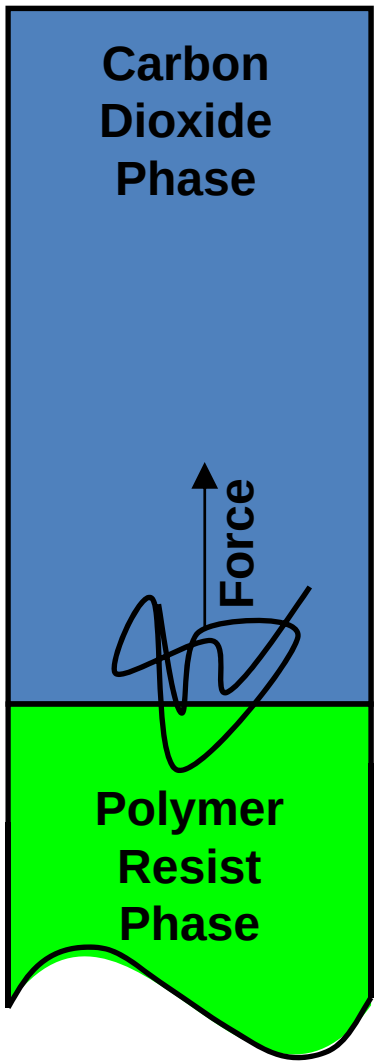
QAS-7 – 0 nm/sec

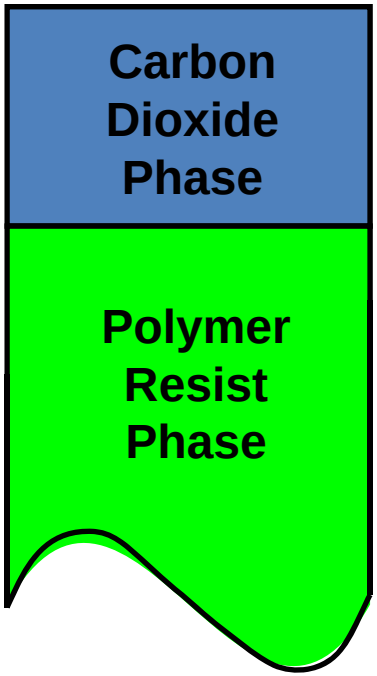
QAS-4 – 25 nm/sec



- Only addition of QAS4 to ESCAP results in reduced energy at surface of film (right of plot), indicating eventual dissolution
- Viability confirmed experimentally

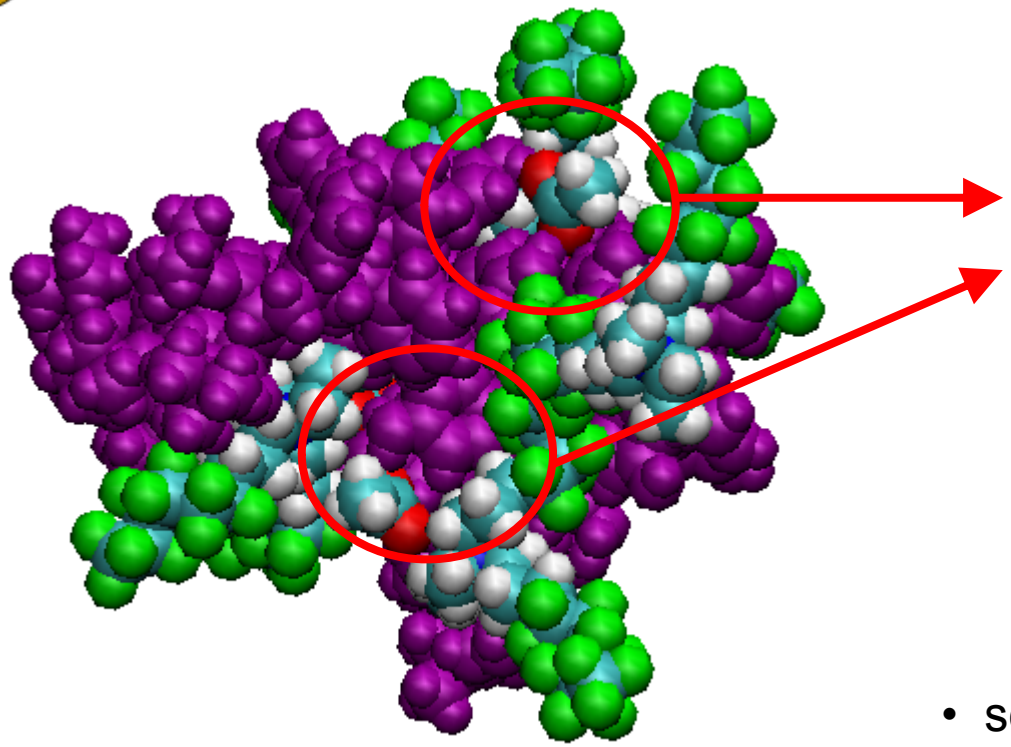
ESCAP Results

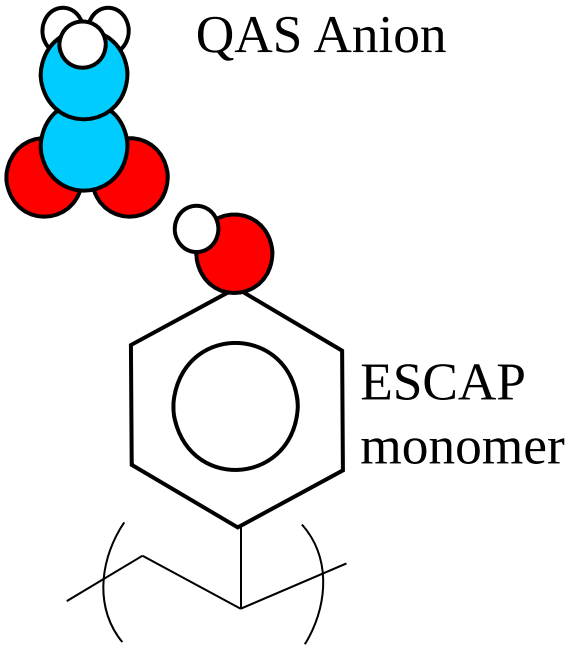




- scCO2 not shown for clarity
- **Green** – ESCAP resist
- **Blue** – QAS-4
- **Cyan** – Carbon (Extracted Chain)
- **Red** – Oxygen (Extracted Chain)
- **White** – Hydrogen (Extracted Chain)

ESCAP Results



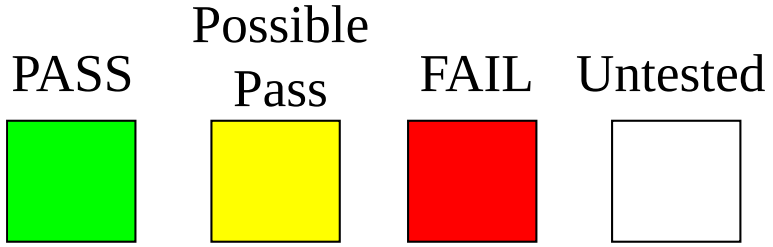


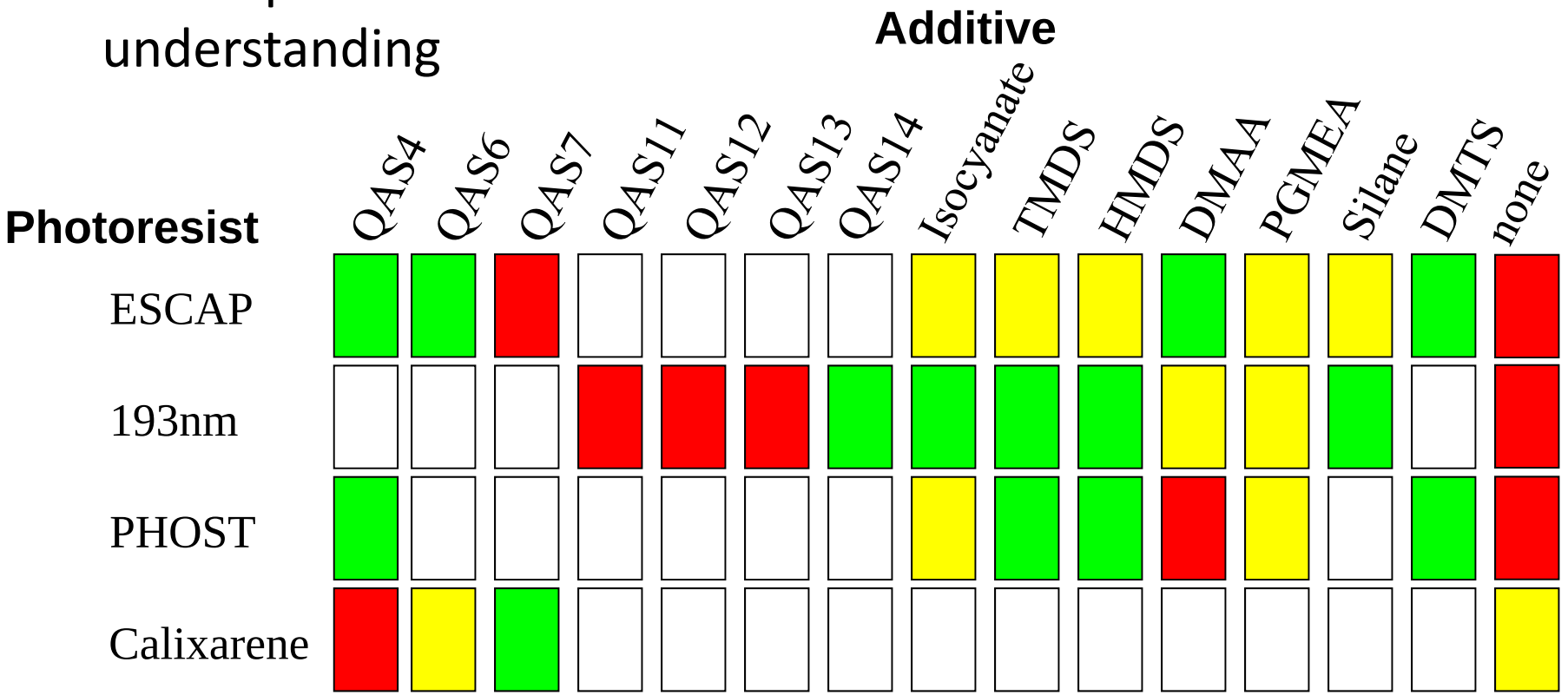
- The –OH group of ESCAP associates with the anions.
- Contacts last >500 ps.

- scCO2 not shown for clarity
- **Purple** – ESCAP
- **Green** – Fluorine (QAS-4)
- **Cyan** – Carbon (QAS-4)
- **Red** – Oxygen (QAS-4)
- **White** – Hydrogen (QAS-4)

Comprehensive Understanding

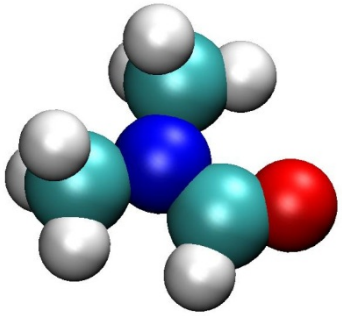
- Examined polymer resist dissolution enhancement for both protected and unprotected resist
- Develop mechanistic understanding



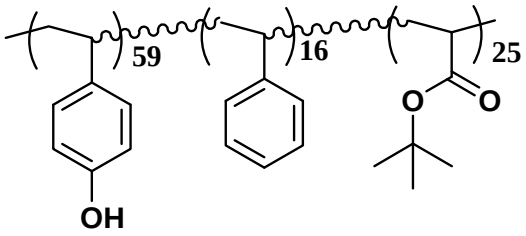


Additive Principles for DMAA

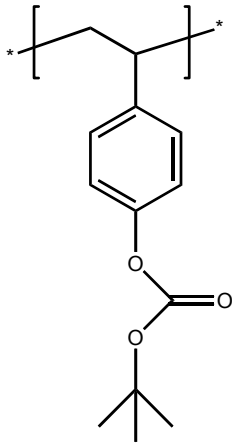
- QAS4 was effective due to hydrogen bonding; can we repeat this effect in a non-fluorinate additive?



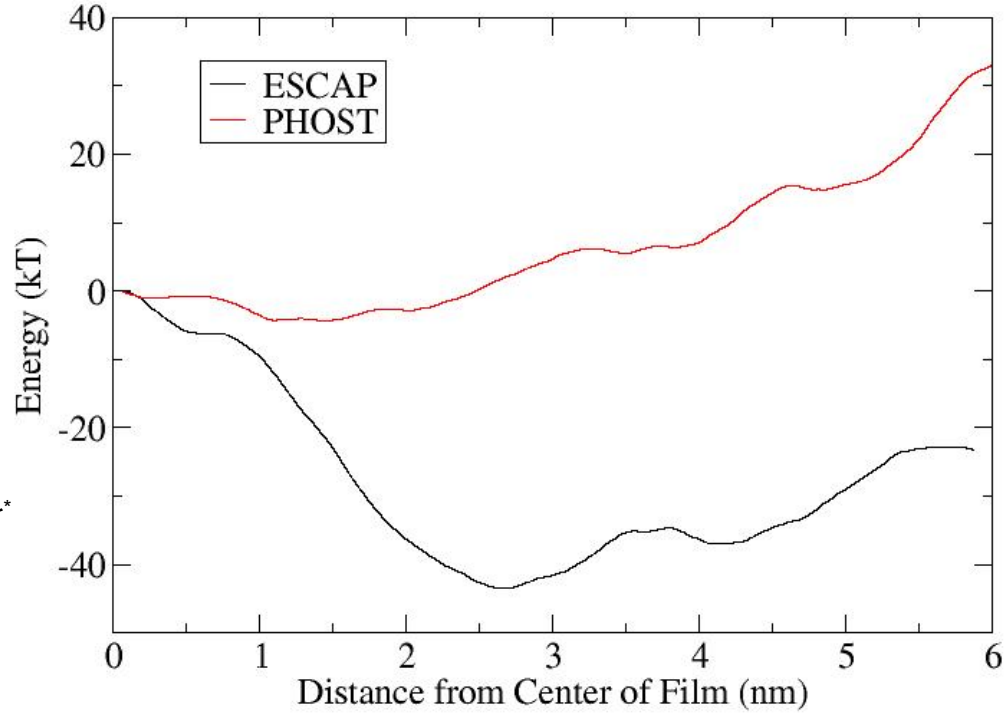
DMAA



ESCAP



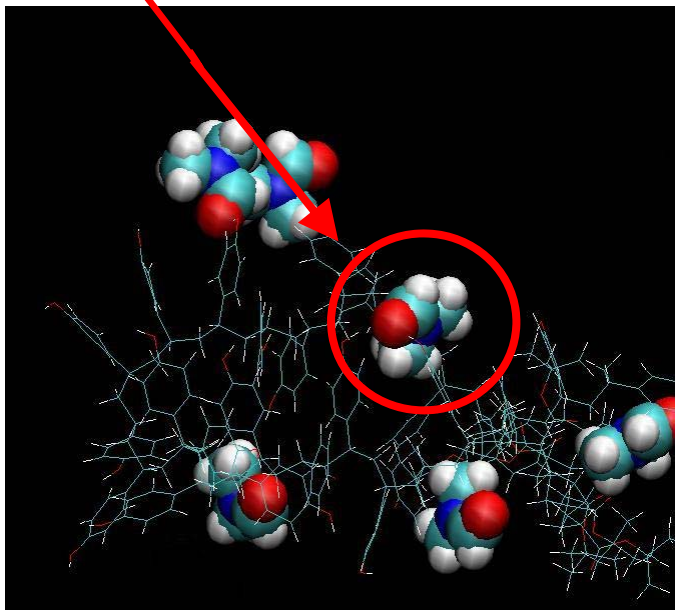
PHOST



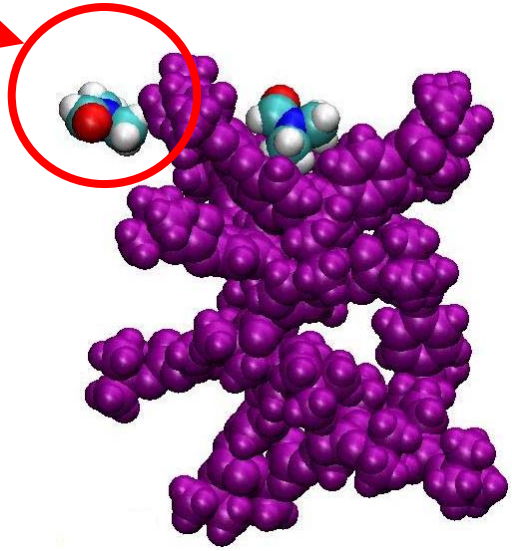
- DMAA enhances ESCAP solubility in $scCO_2$
- Unlike QAS4, does not aid PHOST development

DMAA Mechanism

- Additive was based on applying our understanding of QAS4 effectiveness on ESCAP
- DMAA demonstrates similar hydrogen bonding
- Ineffective with PHOST; obstructs terminal t-butyl group, instead exposing polar region, reducing $scCO_2$ solubility

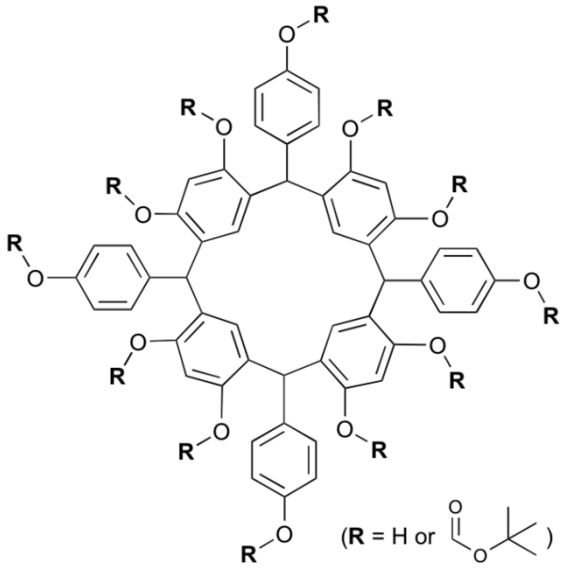


Can develop non-fluorinated additives, but they are more resist-specific



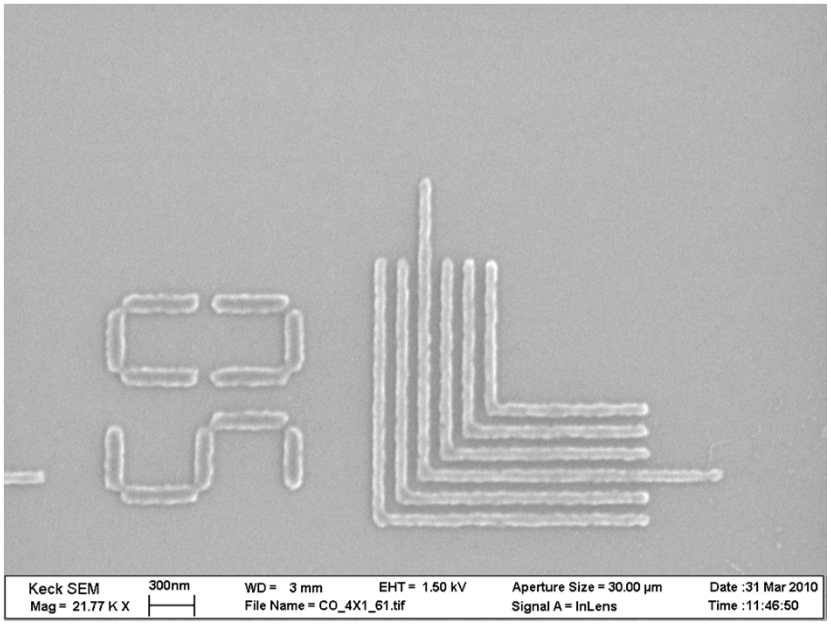
Molecular Glass Photoresist

- Low molecular weight materials capable of forming solid-like structures
- Improved LER
- More soluble than larger chemicals

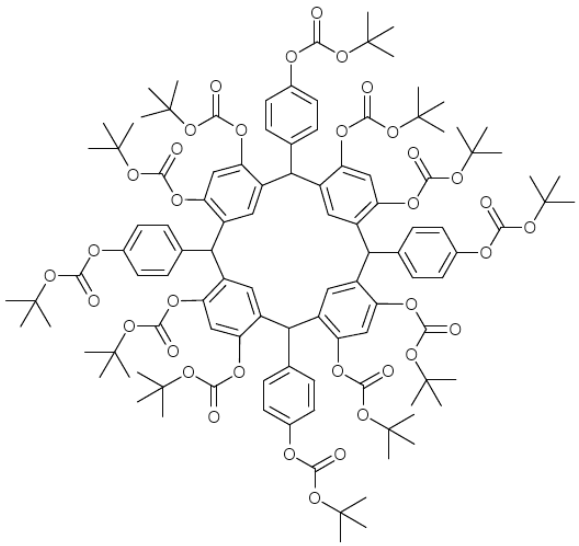


CHPB-boc

Calixarene

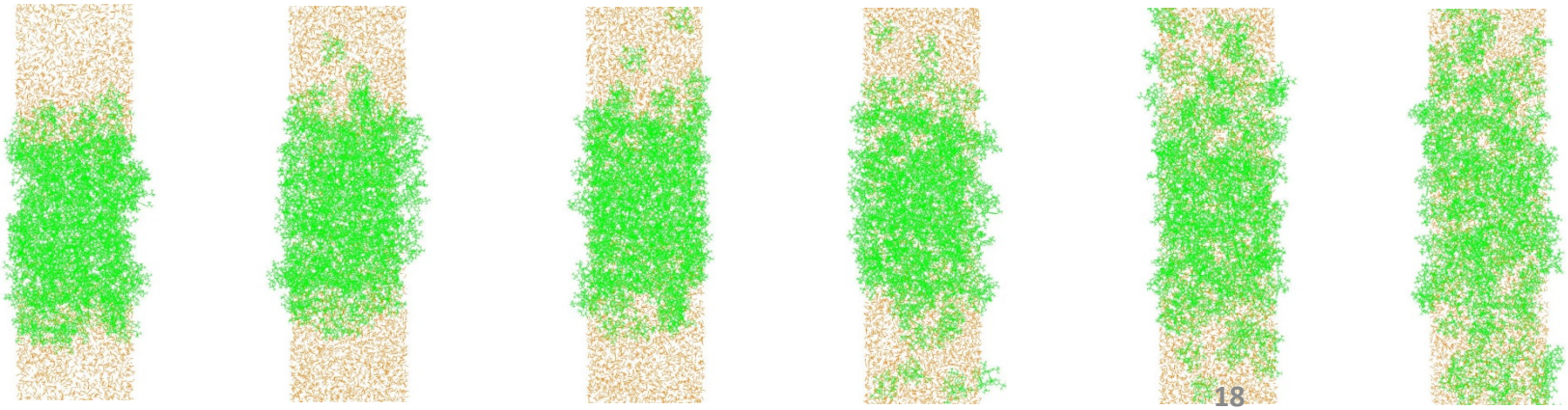


Predictive Power of Simulations: Calixarene



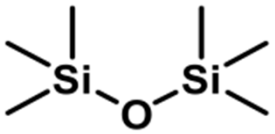
- Molecular glass photoresist capable of high-resolution patterns (low LER)
- We demonstrated potential of this via simulation before experiment
- Capable of dissolution in $scCO_2$ without any additive (first material to show this property, shown below)

Time (1-2 ns between images)

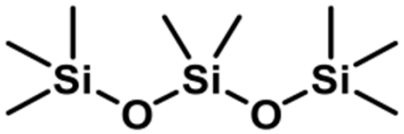


Silcon-Based Solvents

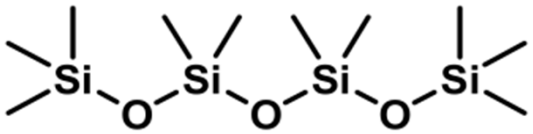
- Linear methyl siloxanes
- Low molecular weight
- Contain only silicon, carbon, hydrogen, and oxygen
- Non-polar solvent
- Solvent power can be enhanced by adding additives
- Low in toxicity, VOC exempt
- Non-ozone depleting
- Degrade to naturally occurring compounds
- Low surface tension



Hexamethyldisiloxane



Octamethyltrisiloxane

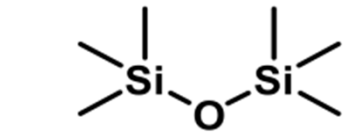


Decamethyltetrasiloxane

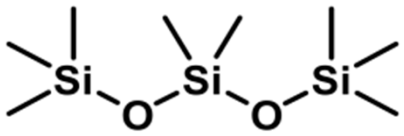
Objectives

- Generate the definitive molecular model for siloxane solvents
  - Complete parameterization of all bonds, charges, etc.
  - Reproduction of experimentally-obtained chemical properties (density, heat of vaporization, etc.)

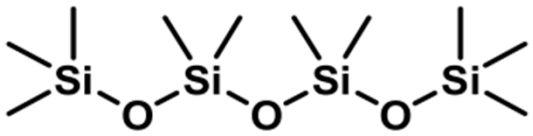
- Study behavior of traditional photoresists in siloxanes



Hexamethyldisiloxane



Octamethyltrisiloxane



Decamethyltetrasiloxane

Model

- Chose functional form consistent with generic formalism to enable transferability
- Parameters derived from quantum mechanical calculation and experimental analysis
- Modeled six elementary building blocks from which an arbitrary structure can be created

Model Formalism:

$$V_{Total} = \underbrace{V_{LJ} + V_{Coul}}_{\text{Intermolecular}} + \underbrace{V_{Bond} + V_{Ang} + V_{Tors}}_{\text{Intramolecular}}$$

$$V_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

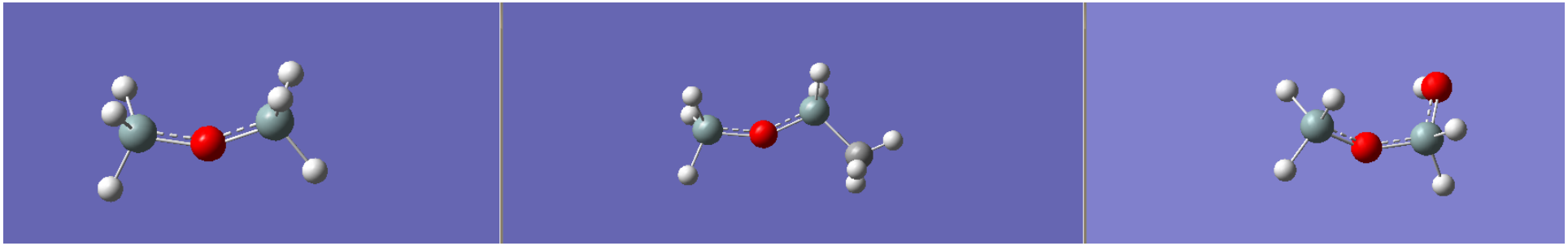
$$V_{Coul} = \frac{q_i q_j}{4\epsilon_0 \epsilon r}$$

$$V_{Bond} = \frac{1}{2}k_{Bond}\left(r - r_0\right)^2$$

$$V_{Ang} = \frac{1}{2}k_{Ang}\left(\theta - \theta_0\right)^2$$

$$V_{Tors} = \sum_{n=0}^{5} c_n \cdot cos(\phi)^n$$

Sample elementary building blocks:

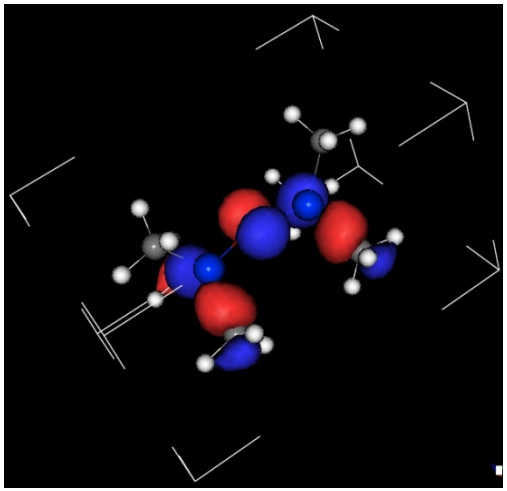


Si-O-Si-H **Si-O-Si-C** **Si-O-Si-O**

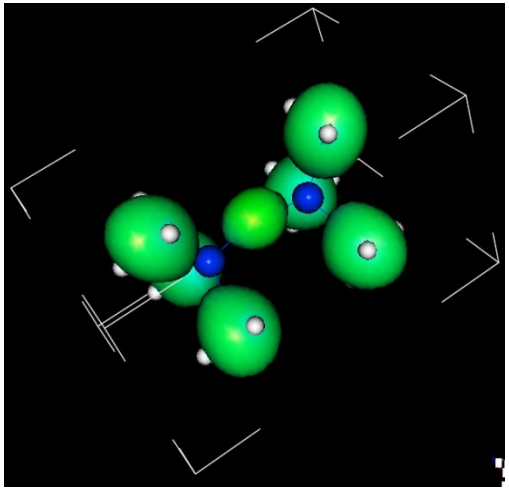
Quantum Mechanics

- Provides a detailed description of electron position as we probe different configurations
  - Can determine charges (q_i) directly
  - Map energy as a function torsion angle, etc.
  - rb3lyp model with 6-311+g(2d,p) basis set

HMD Siloxane

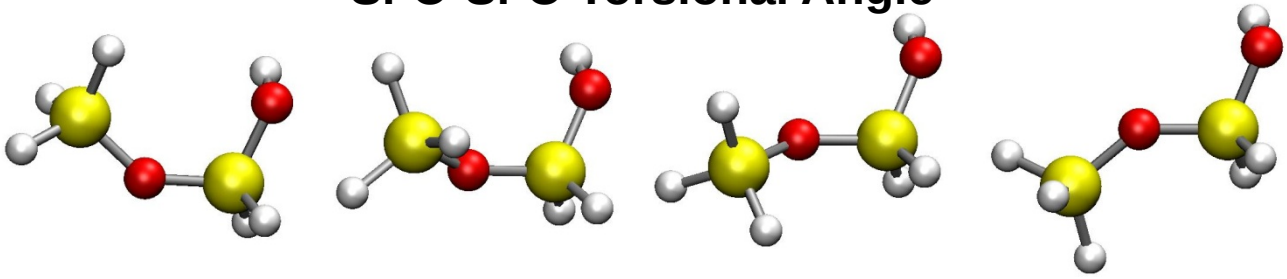


HOMO



LUMO

Si-O-Si-O Torsional Angle



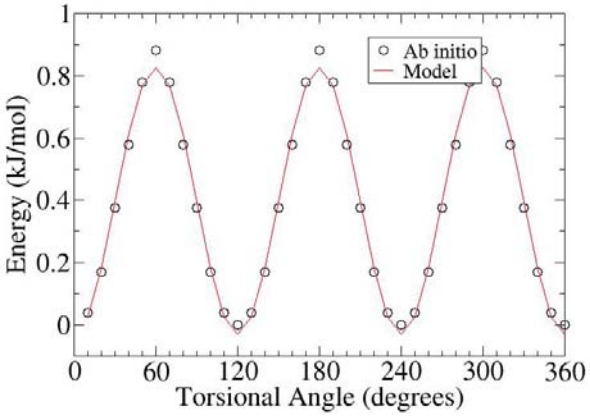
0° 60° 120° 180°

Potential Fitting – Torsional Sample

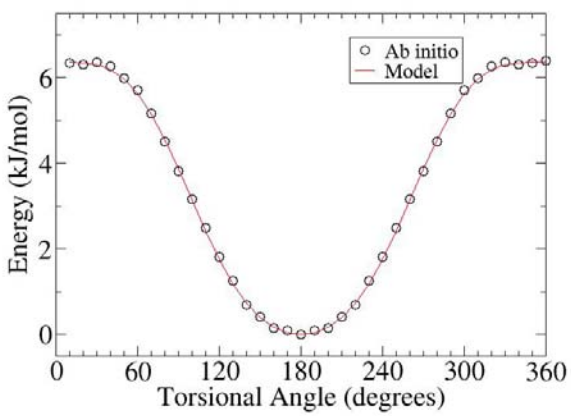
- Si-O-Si-C and Si-O-Si-O torsions most important parameters in determining shape of the solvents

- Torsional parameters fit to capture difference between quantum mechanical results and non-bonded interactions

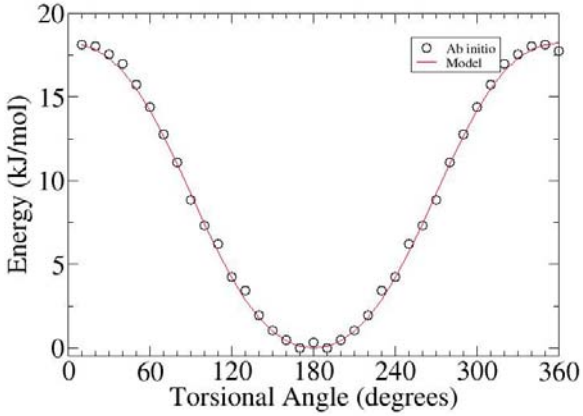
Si-O-Si-H



Si-O-Si-C

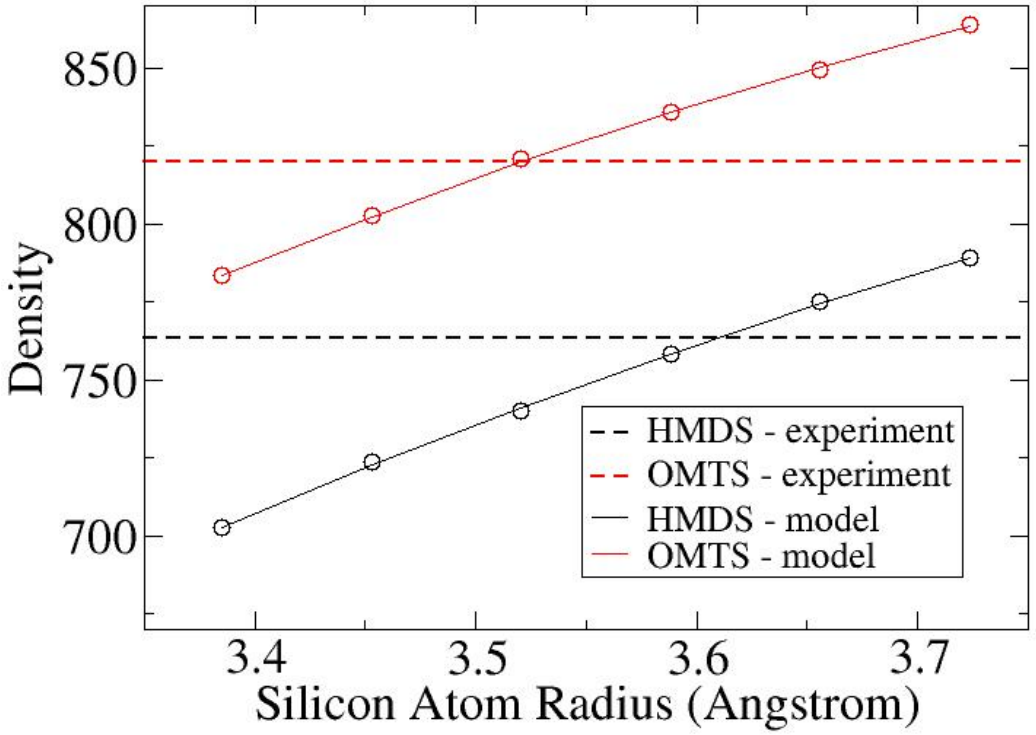


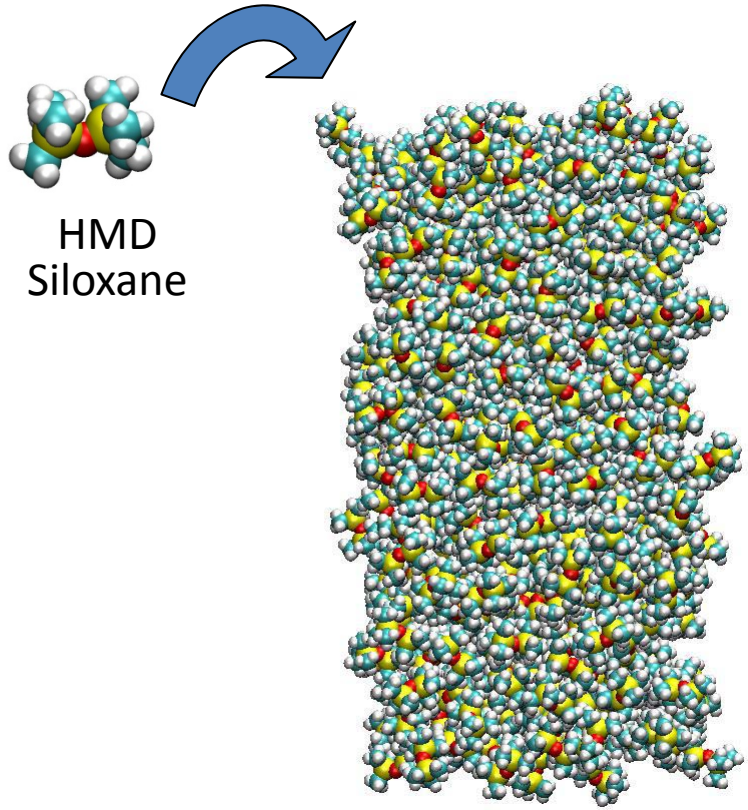
Si-O-Si-O



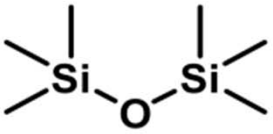
Intermolecular Interactions

- Having built a complete intramolecular model from quantum mechanics, we now tune intermolecular many-body interactions to match experiment

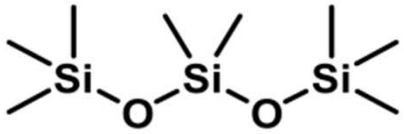




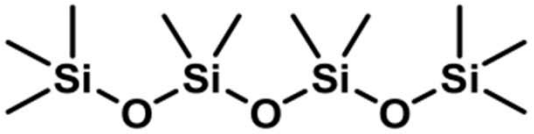
Model Verification



Hexamethyldisiloxane



Octamethyltrisiloxane



Decamethyltetrasiloxane

	HMD Siloxane		OMT Siloxane		DMT Siloxane	
	Experimental	Model	Experimental	Model	Experimental	Model
Heat of Vaporization (kcal/mol)	7.1	7.3	8.5	11.0	12.0	12.3
Specific Heat (cal/g*K)	0.46	0.50	0.29	0.48	0.41	0.53
Density (g/ml)	0.764	0.761	0.820	0.813	0.854	0.852
Dipole Moment (Debye)	Unknown	1.016	Unknown	1.203	Unknown	2.0553
Dielectric Constant	Unknown	1.339	Unknown	1.400	Unknown	1.875

- Good agreement with known properties

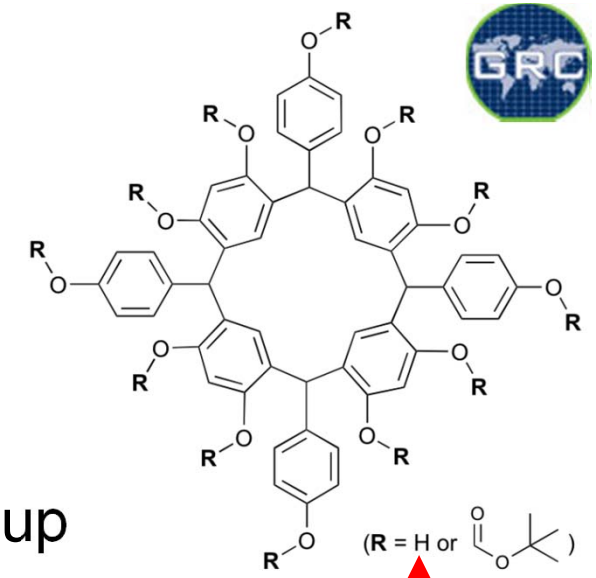
Energy Use

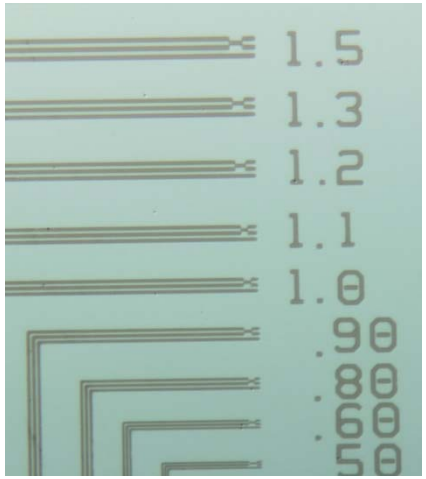
- Waste treatment is a major cost
  - Must separate solvent from dissolved polymer
- Siloxanes solvents require less heat to distill
  - Half the heat capactity
  - Order of magnitude lower heat of vaporization

Solvent	TMAH	HMD Siloxane
C_p	3.2 - 4.18 J/g K	1.83 J/g K
T_{boil}	383K	373K
ΔH_{vap}	>2260 J/g	296 J/g

Calixarene

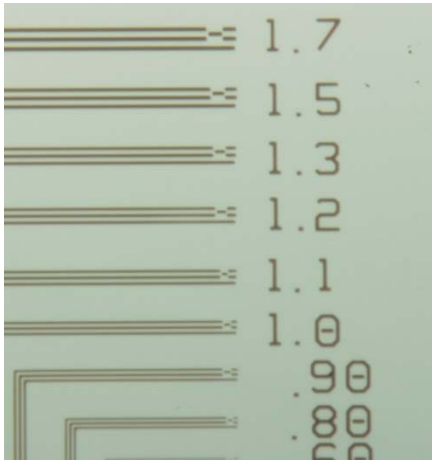
- Molecular glass resist
  - Inherently low LER
  - More soluble than polymers
- Selective dissolution proved by Ober group





HMD Siloxane
Dose:350 mJ/cm^2
PEB:90^{o}C, 30 sec

OMT Siloxane
Dose:250 mJ/cm^2
PEB:90^{o}C, 30 sec

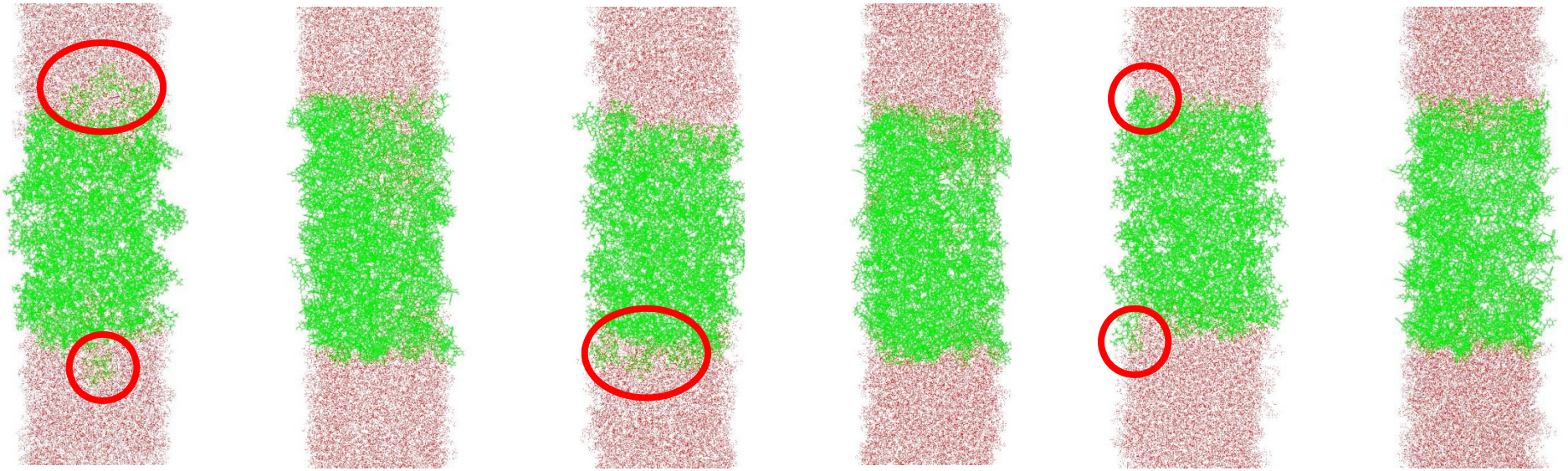


DMT Siloxane
Dose:300 mJ/cm^2
PEB:90^{o}C, 30 sec

Calixarene Results

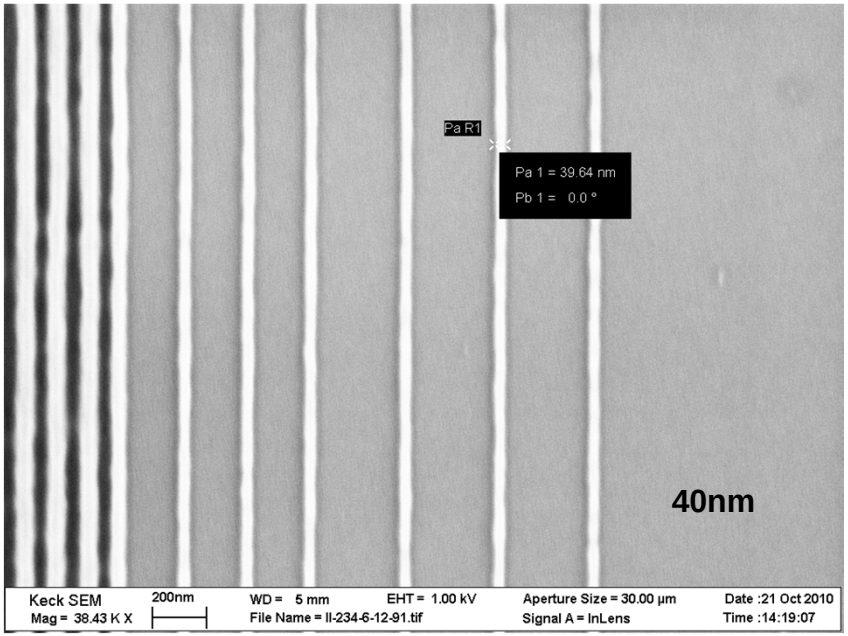
- Calixarene after 10ns in siloxane solvents:
  - Unexposed photoresist breaking away from surface
  - Exposed photoreist makes smooth interface
  - Negative tone resists
  - Excellent agreement with experiment

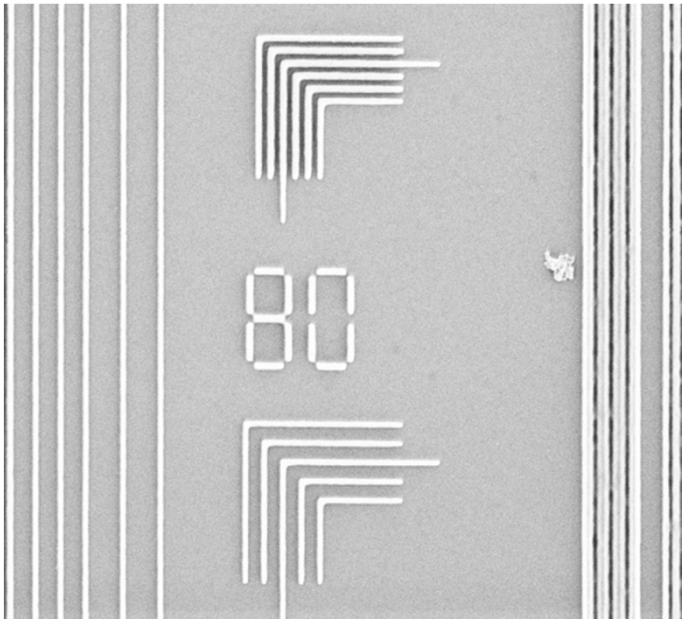
HMD Siloxane **OMT Siloxane** **DMT Siloxane**



unexposed **exposed** **unexposed** **exposed** **unexposed** **exposed**

Calixarene Patterning

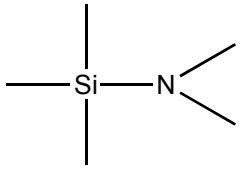




TOK photoresist
DMTS: HMDSO=1:20 at 40°C for 40 minutes
Resist film thickness ~350 nm

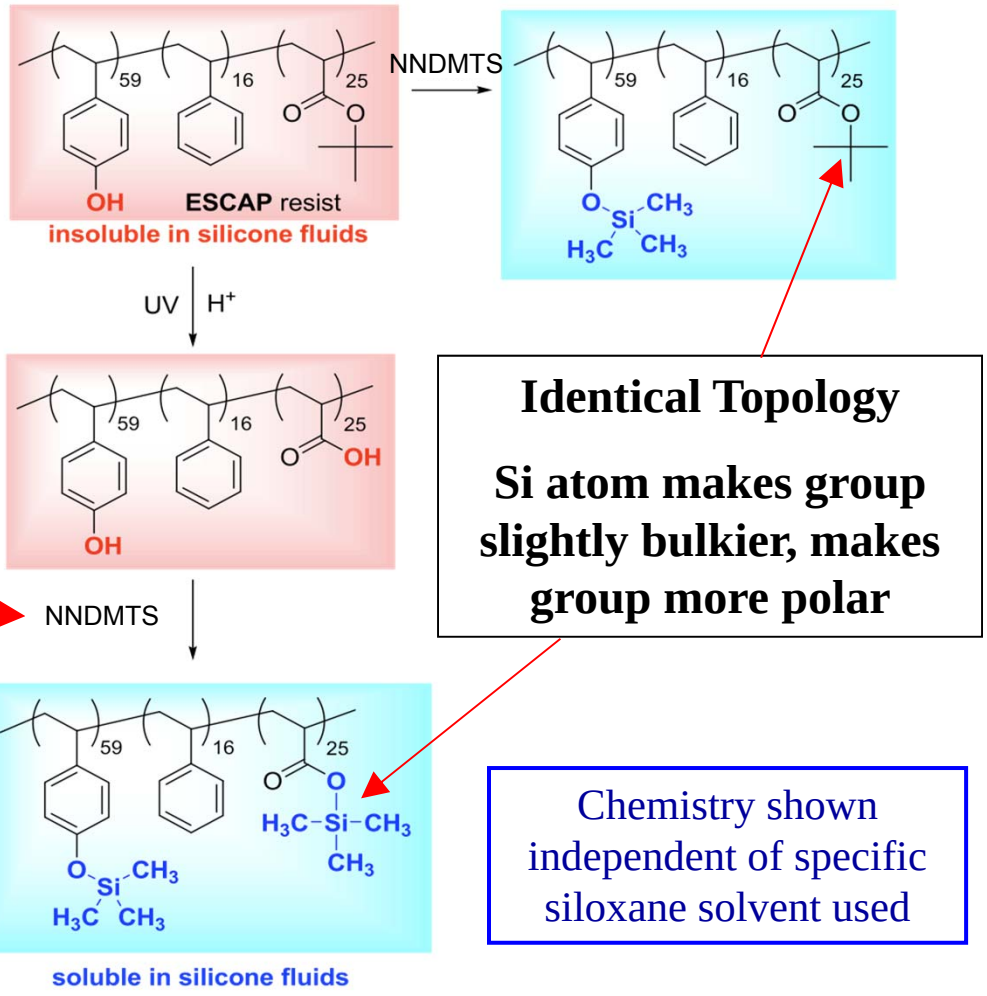
ESCAP

- ESCAP is our model EUV photoresist
  - Model previously developed and tested for $scCO_2$
- In experiment, chemically modified by NNDMTS:



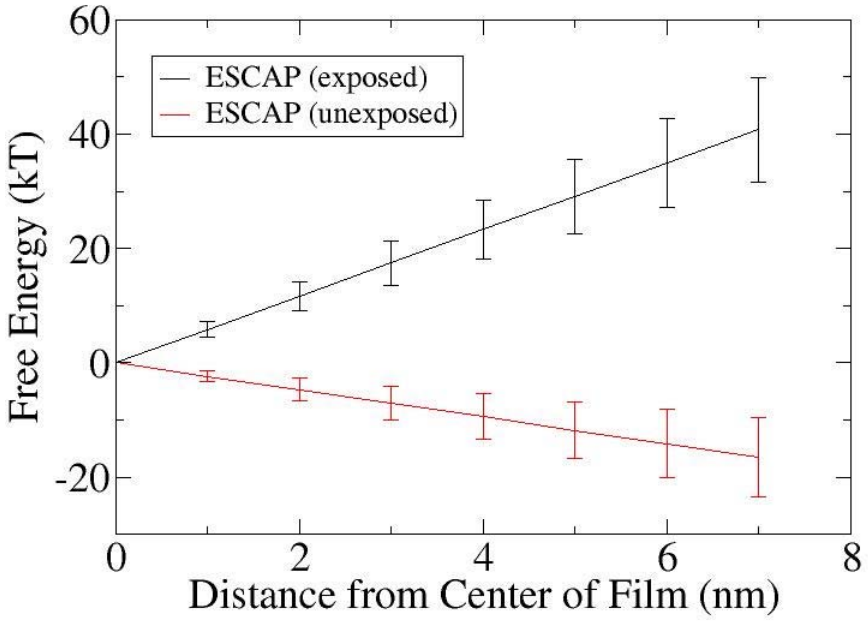
(N,N-Dimethyl)trimethyl silane

- Similarity between exposed and unexposed form makes ESCAP a serious test of model sensitivity

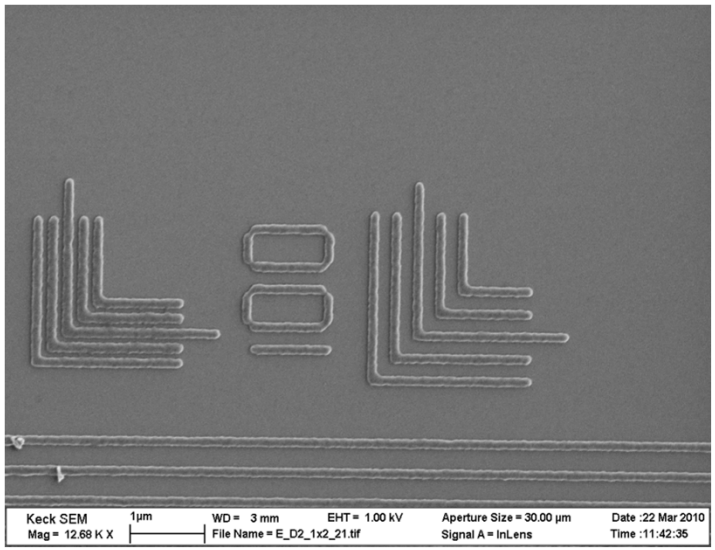


ESCAP Results

- Model predicts only unexposed films to be unstable:
  - Negative Tone
- Results from experimental collaborator corroborate result



Solvent: Hexamethyldisiloxane



Solvent: DMTS/Decamethyltetrasiloxane

e-beam dose = 20 µC/cm^2

Photoresist:ESCAP

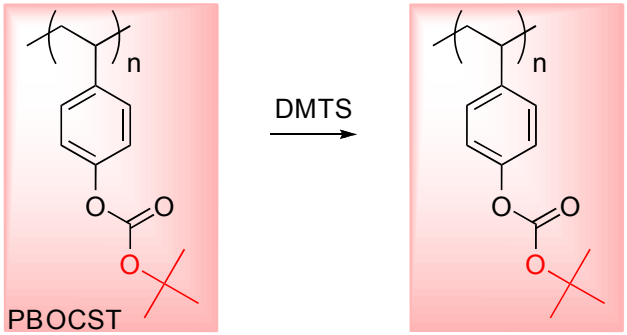
Chemical modifier: NNDMTS

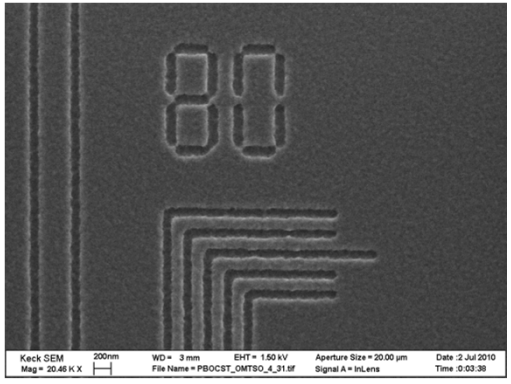
Solvent: Decamethyltetrasiloxane

Dose = 20 µC/cm^2

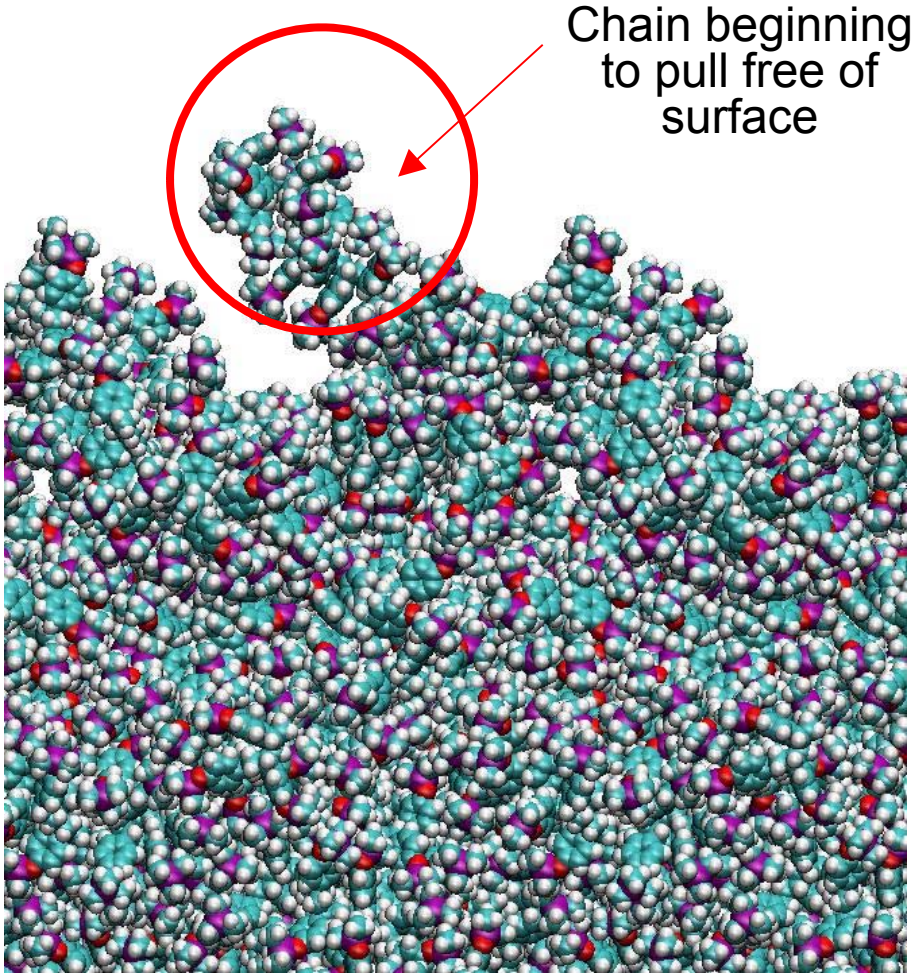
PEB: 115 ^{o}C, 60 sec

PHOST Results



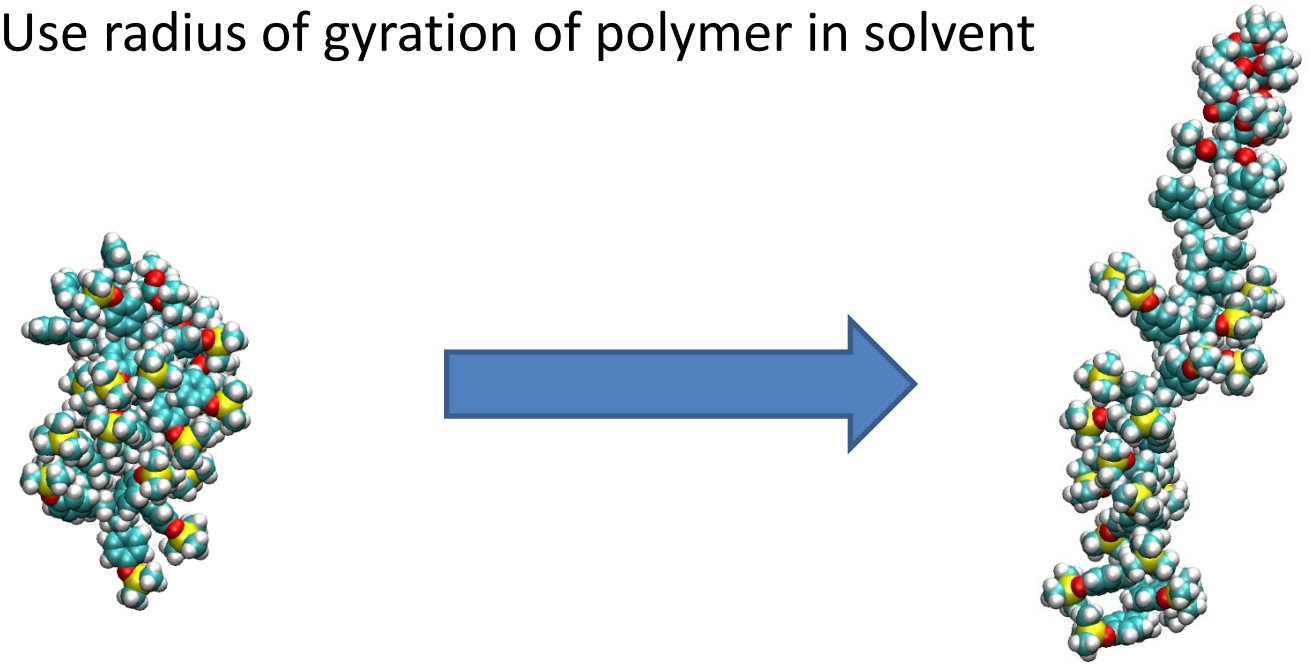


Solvent: DMTS/Octamethyltrisiloxane
e-beam dose = 100μC/cm^2



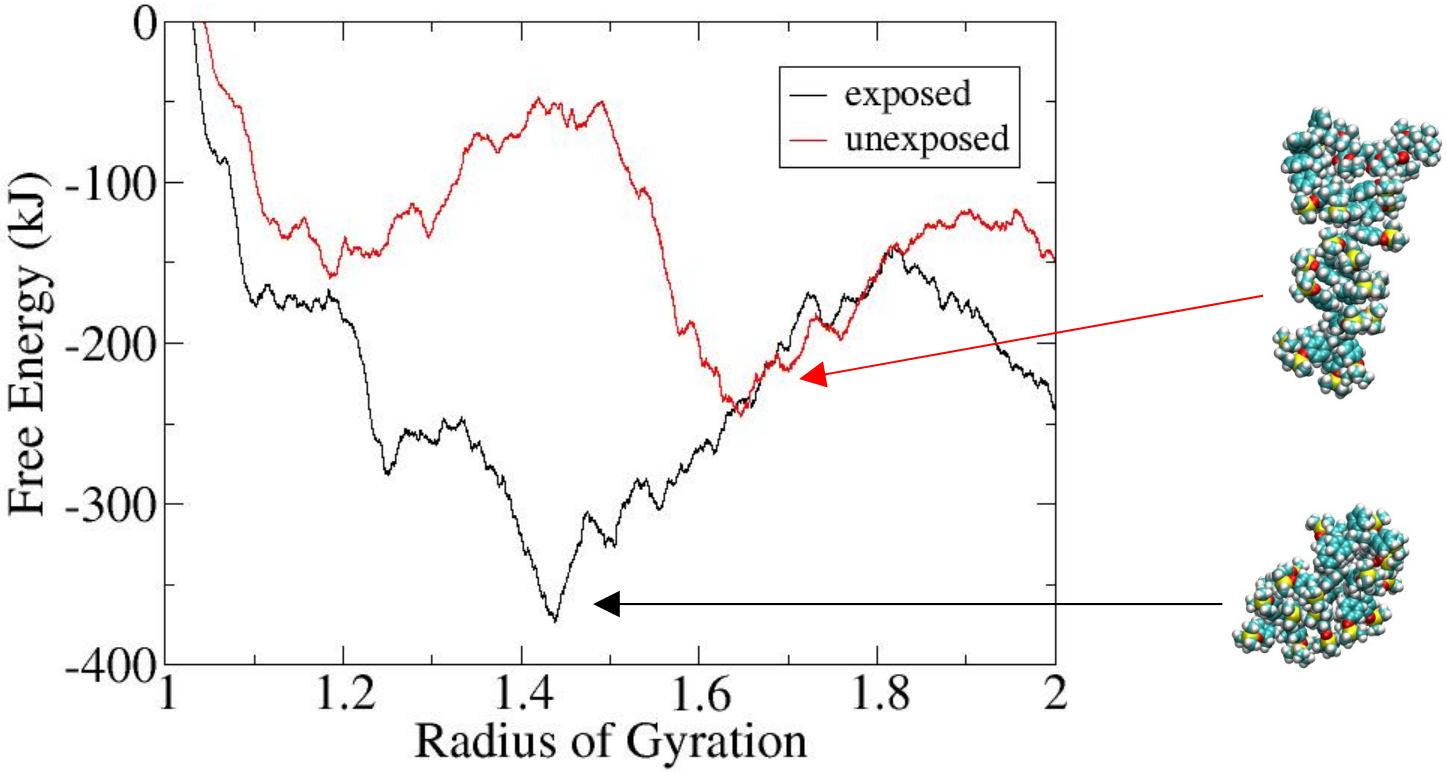
ESCAP in Solution

- What is the mechanism for ESCAP dissolution?
  - Need to understand structure of polymer in solvent and film
- Steered MD
  - Forces system to go through a range of configurations
  - Provides estimate of free energy
  - Use radius of gyration of polymer in solvent



Stretching Movie

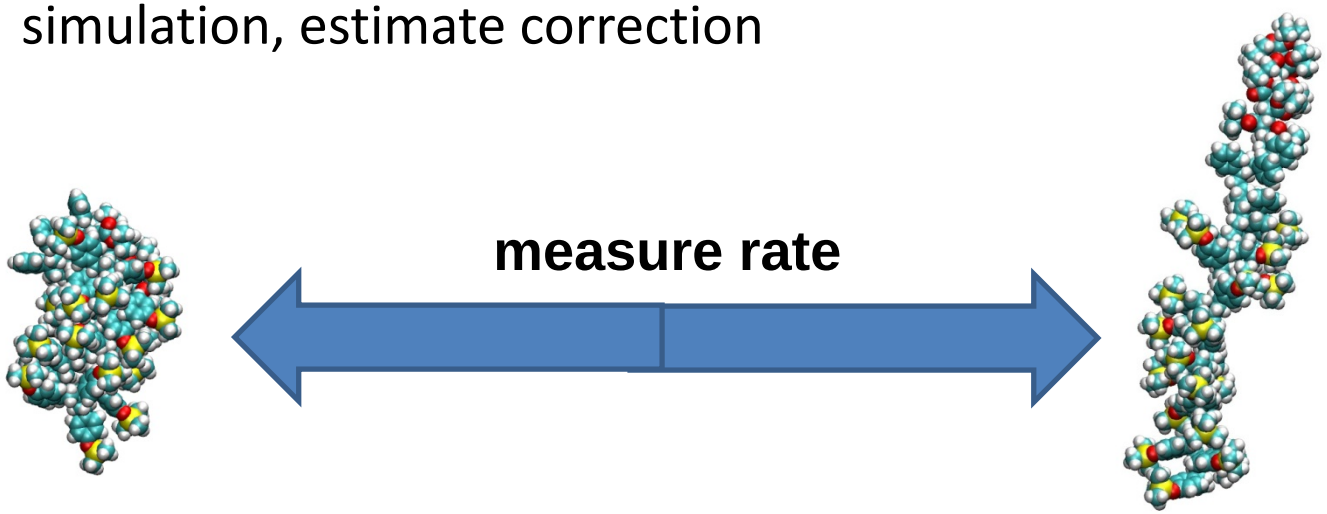
Stretching Result Curve



- Exposed: prefers to extend modified region while coiling
  - HMD Siloxane is borderline poor solvent
- Unexposed: prefers extended form, has meta-stable coil
  - HMD Siloxane is a good solvent, but dissolution requires exposed film surface to have correct confirmation

Flux Tempered Meta-Dynamics

- Steered MD accuracy depends on pulling rate
  - Too time consuming to get high accuracy
  - Need to refine free energy estimate with different method
- Flux Tempered Meta Dynamics (in progress)
  - Use initial estimate obtained by Steered MD
  - Bias sampling to negate current free energy estimate
  - Measure time to sample all configurations during long simulation, estimate correction



Conclusion

- Alternative solvents are promising
  - Environmentally benign
  - Help abate pattern collapse
  - Generic solutions possible
- Molecular simulation aids development
  - Screen without synthesizing
  - Develop mechanistic understanding
- Siloxane Solvents
  - Non-toxic
  - Energy efficient
  - Effective
  - Still exploring mechanistic understanding

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