Cornell University

Environmentally Benign Development of Standard Resists in Supercritical Carbon Dioxide Using CO_2 Compatible Salts

ERC Teleseminar
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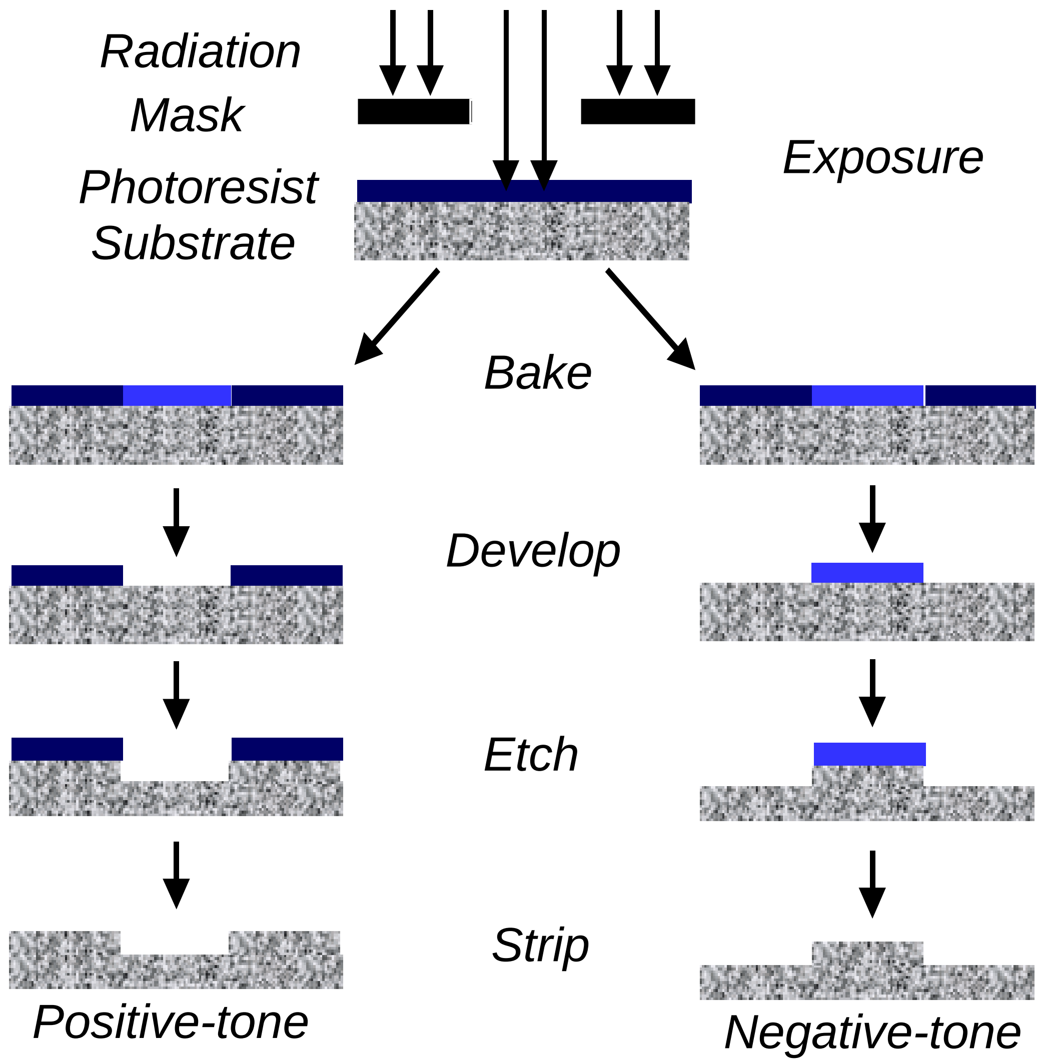
Outline of the experimental work

- Background
  - Lithography (Key problems)
  - Supercritical CO_2 (Basics, Advantages)
  - Previous work using $scCO_2$ (fluorinated resists, molecular glasses, additives)
- Fluorinated Quaternary Ammonium Salts (QAS) as supercritical CO_2 compatible additives
  - Design and Synthesis of QAS
  - Dissolution test of standard EUV/DUV resists
  - EB-patterning and development in QAS/$scCO_2$ solution
- Conclusions (experimental results)
- Computational Simulations (G. Toepperwein)

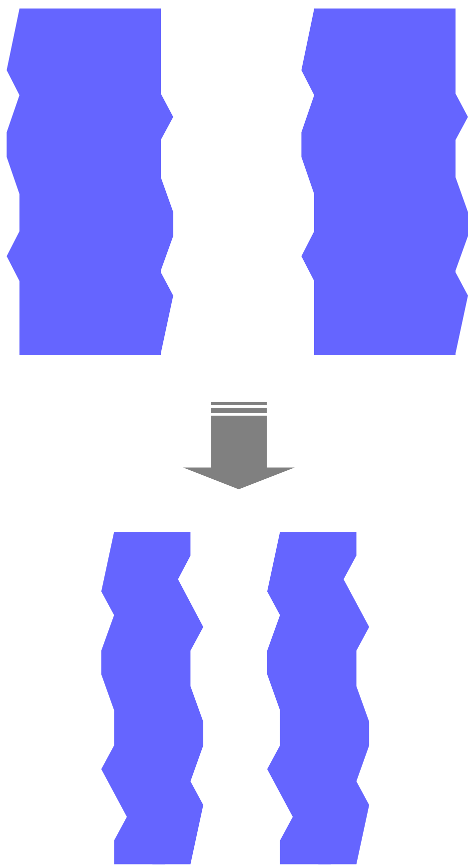
Photolithographic Process



Next Generation Lithography: Key Problems

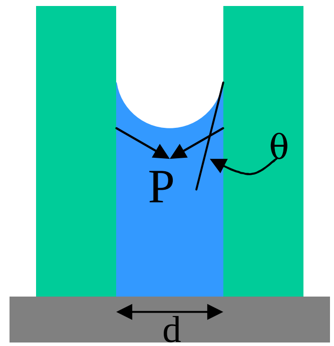
Pattern Variations

< 3nm for 32nm node



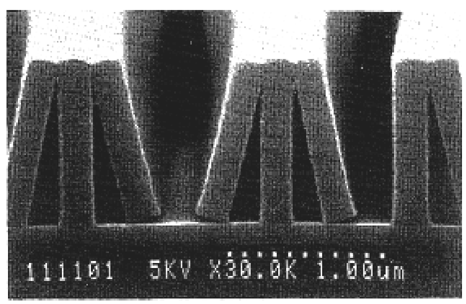
Pattern Collapse

Reduce surface tension



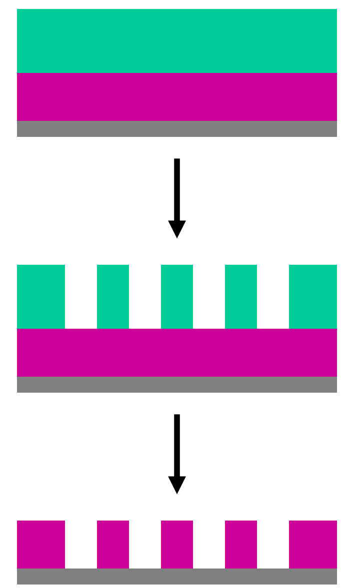
$$P = \frac{\sigma}{R} = \frac{2\sigma\cos\theta}{d}$$

@ 50nm L/S, aspect ratios >2:1 collapse w/water



Non-polar Materials

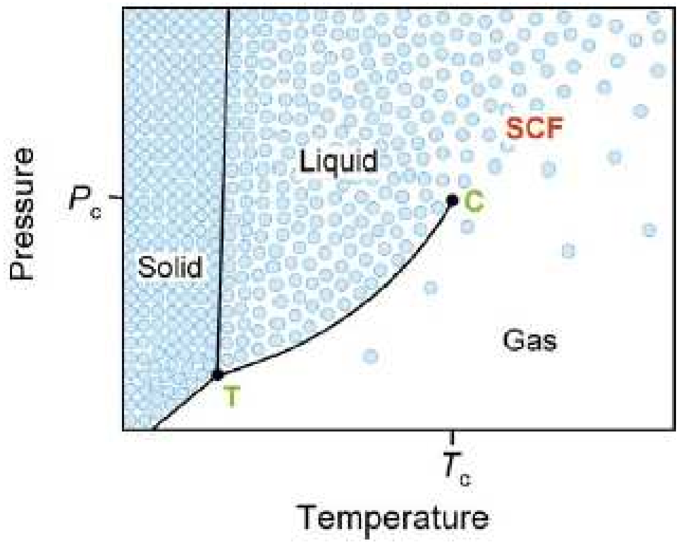
Low-k applications



Lack of appropriate non-polar developers → Must use mulitple subtractive steps

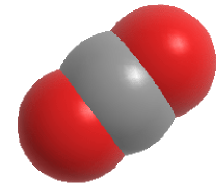
T. Tanaka et al., *JJAP* **1993**, 32, 6059.

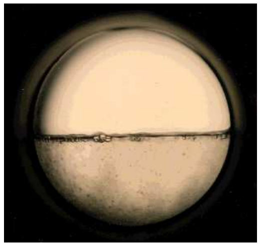
Supercritical CO_2 Basics



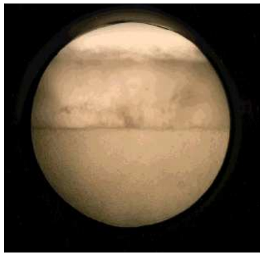
T_c = 31.1 ºC, P_c = 72.8 bar

- Environmentally safe
- Tunable solvent strength
- Low viscosity and surface tension
- Chemically stable
- Abundant and cheap





Below critical point – separate liquid and gas phases



Near critical point – meniscus begins to fade

Above critical point – no meniscus, homogeneous phase

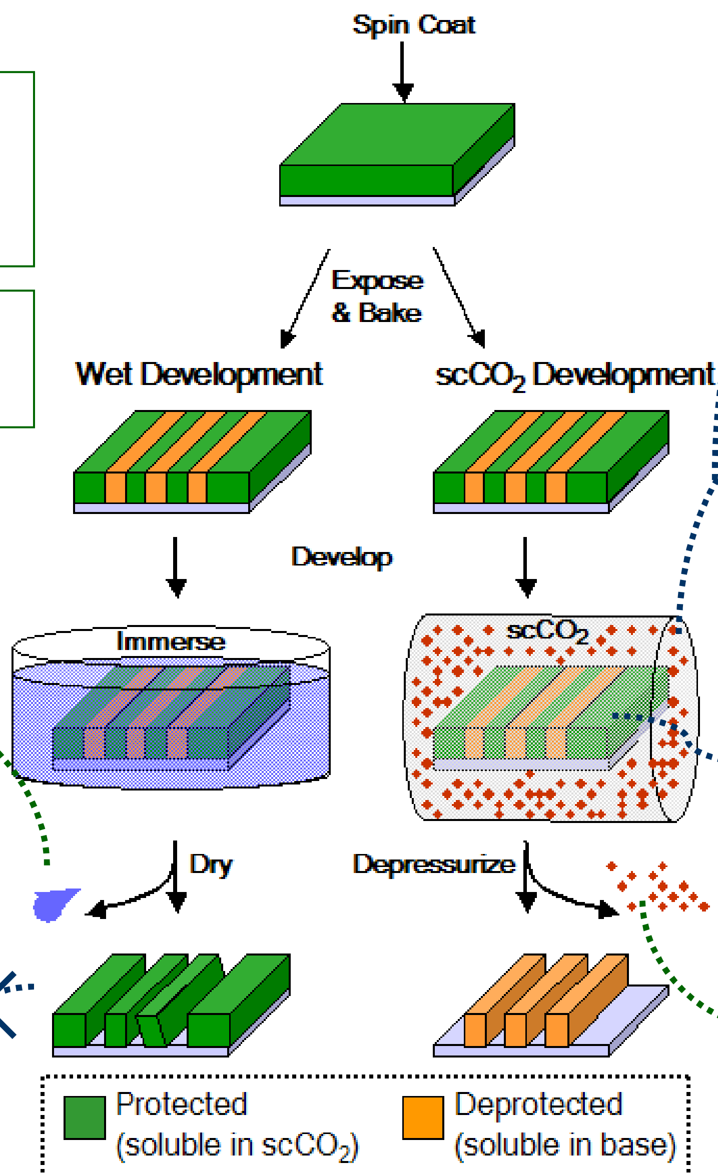
A. I. Cooper, *J. Mater. Chem.* **2000**, 10, 207-234.

Advantages of $scCO_2$ development

Elimination of organic solvents and ultra-pure water during processing

2 gram DRAM chip → 32 kg of water

Williams, et al., *Environ. Sci. Tech.*, **36**, 5504, (2002).



Liquid-like density, Tunable Solvating Power

Gas-like transport

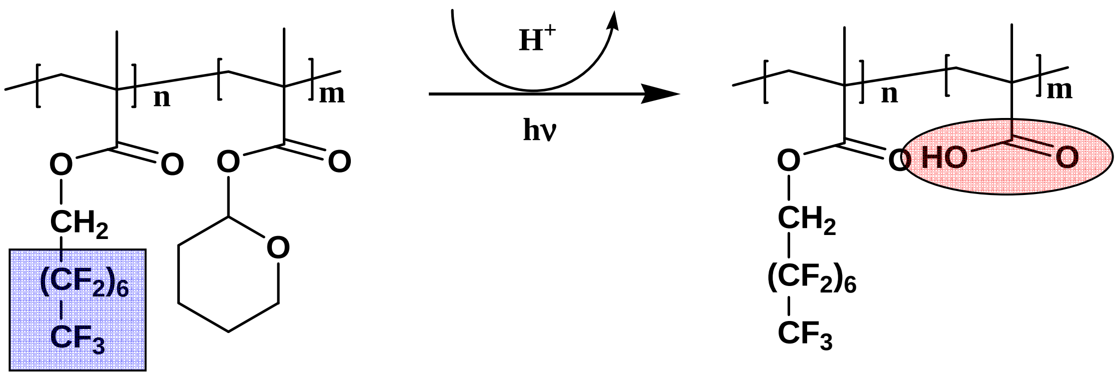
Penetrates crevices, no residue

Solvent is cleanly separated from resist residues via depressurization

No surface tension, eliminates pattern collapse

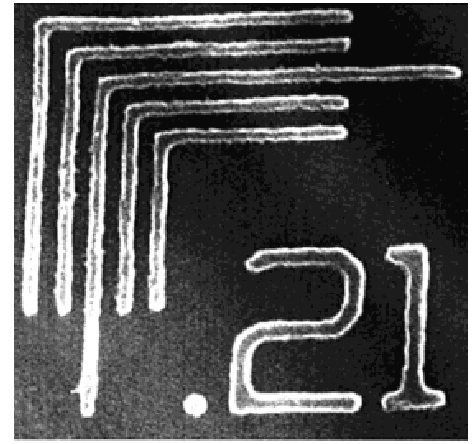
$scCO_2$ Soluble Photoresists

- **Fluoro polymers**



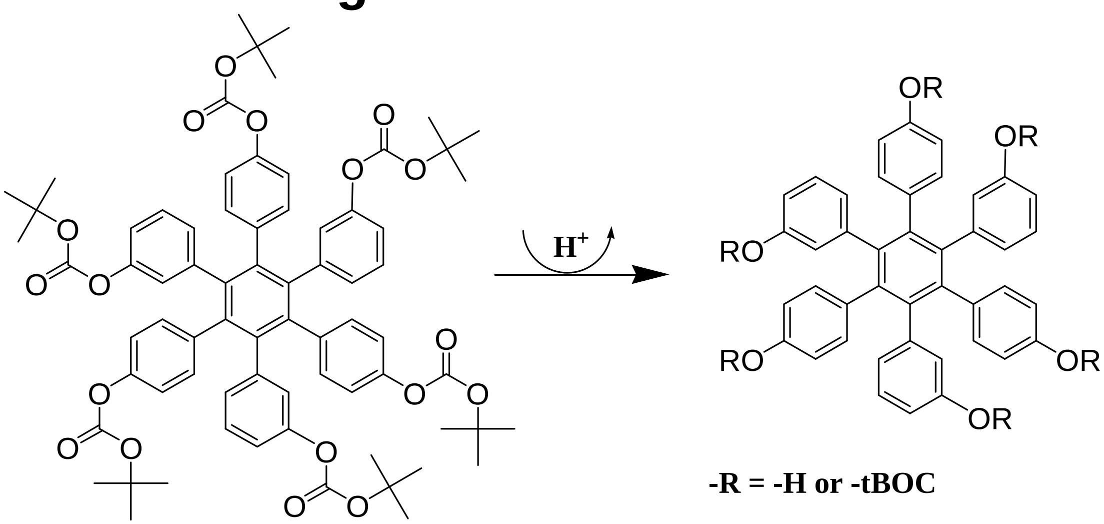
Soluble

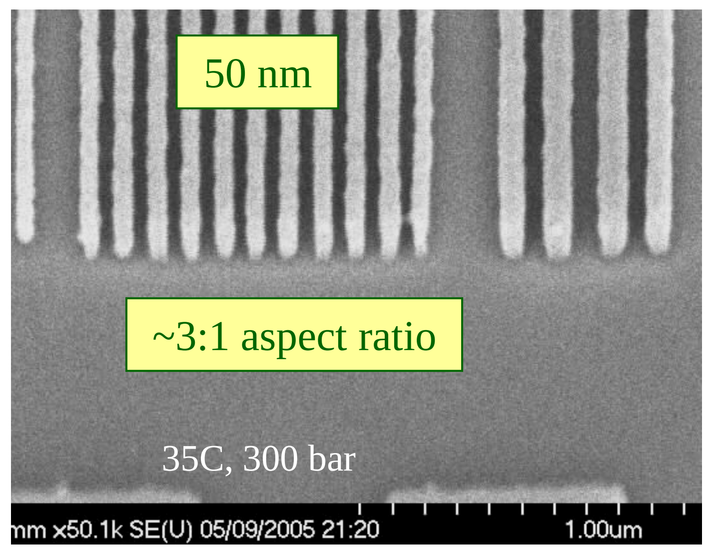
Insoluble



N. Sundararajan, C. K. Ober, et al., *Chem. Mater.* **2000**, 12, 41.

- **Molecular glasses**

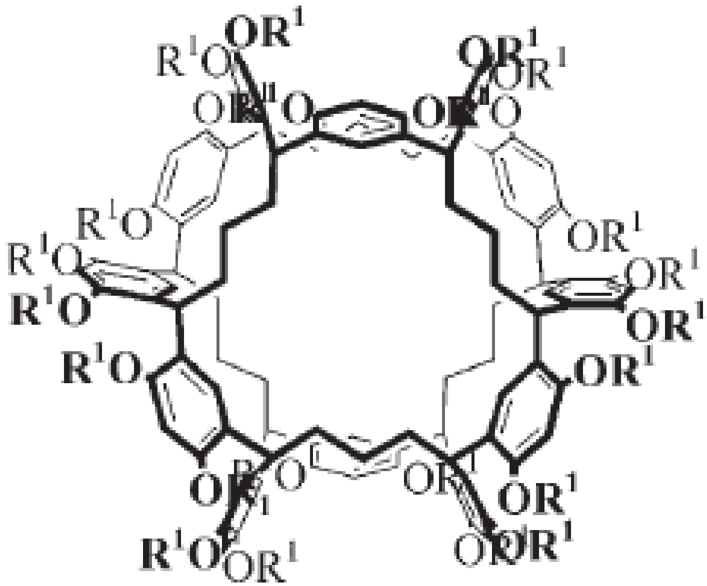




N. Felix, K. Tsuchiya, C. K. Ober, *Adv. Mater.* **2006**, 18, 442-446.

Recent result - $scCO_2$ development of "Noria-boc" -

Noria-boc : High molecular weight molecular glass



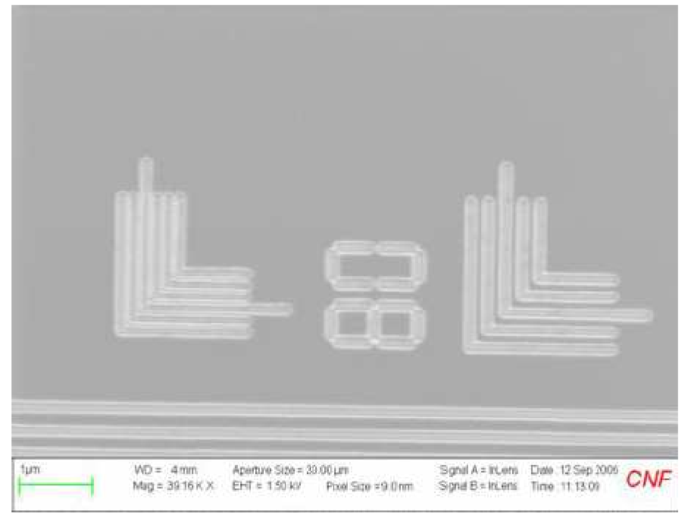
noria-Boc

R^1 = $-COOC(CH_3)_3$

$M_{w\ Noria\text{-}boc}$ = 4108.3 g/mol
$M_{w\ Noria}$ = 1705.9 g/mol

Noria-boc is insoluble in TMAH,
Noria is soluble in TMAH.

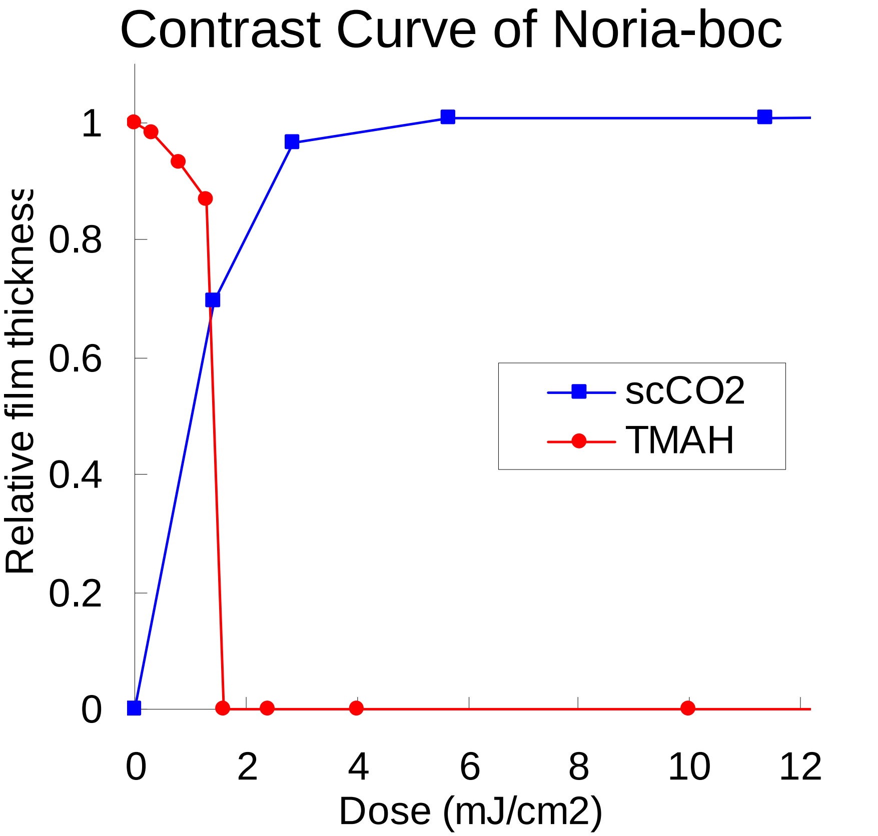
Collaboration with Prof. Nishikubo / Kudo group (Kanagawa University)



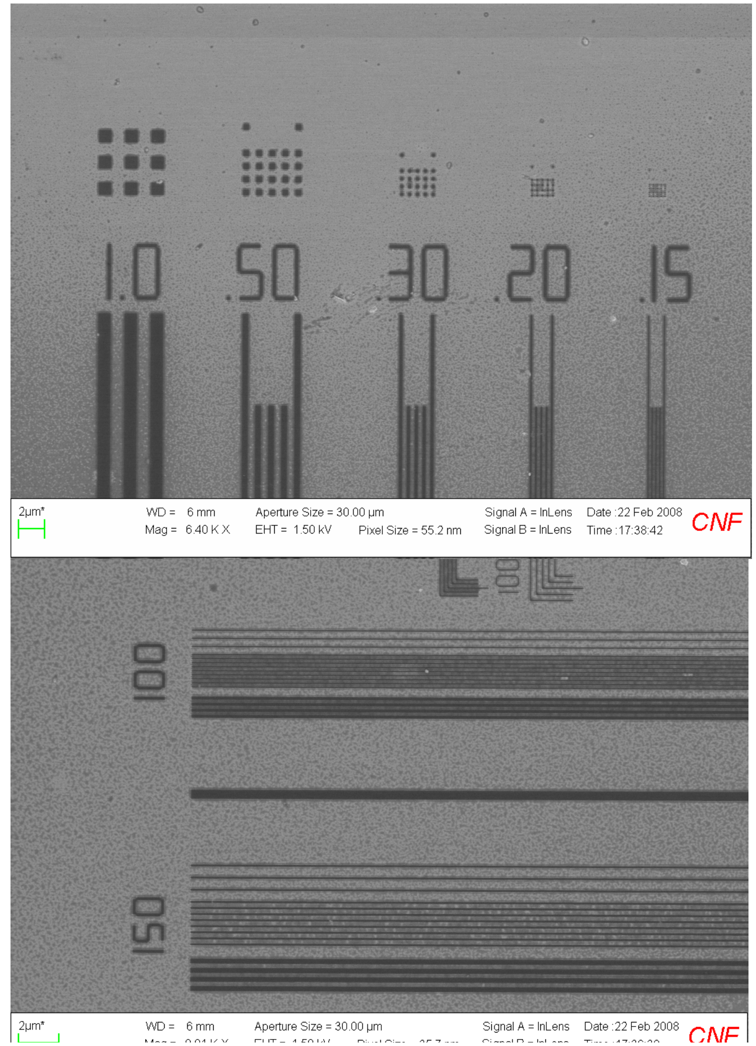
EB-patterned 'Noria-Boc' developed in 0.26 N TMAH (EB dose 76.8 μC/cm^2, PAB 115 ^{o}C 60 s, PEB 140 ^{o}C 150 s, development 60 s)

H. Kudo, T. Nishikubo, et al., *Angew. Chem. Int. Ed.* **2006**, 45, 7948.
C. K. Ober, T. Nishikubo, et al.,Proc. of SPIE, **2007**, 6519, 65194B

Recent result - $scCO_2$ development of “Noria-boc” -



$scCO_2$: development for 30 min at 50°C, 5000 psi.
TMAH: developemnt for 60 sec with 0.26 N TMAH.

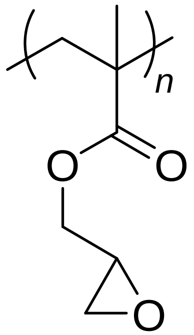


Noria-boc showed negative tone property in $scCO_2$.

Dose: 150 um/cm², development for 15 min at 50°C, 5000 psi, pure $scCO_2$ flow 30 min.

Additives for $scCO_2$ to develop conventional resists

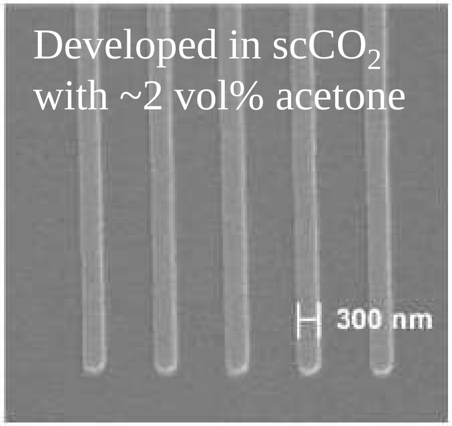
- **Co-solvents**



Addition of acetone as a co-solvent

↓

Non-fluorine polymer was dissolved in $scCO_2$.
- Increase solvent density
- Tune polarity of fluid



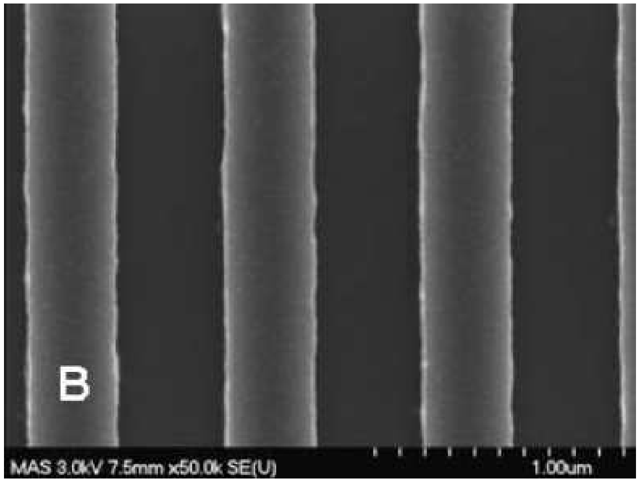
C. K. Ober, K. K. Gleason, et al., *JVST B.* **2004**, 22, 2473-8.

- **$scCO_2$ Compatible Salts**

Micell Integrated Systems developed a new additive for $scCO_2$.

$(R)_a(R')_bN^+X^-$

where a + b = 4, and R' is a partially fluorinated alkyl or aryl group, and X- is the counter anion

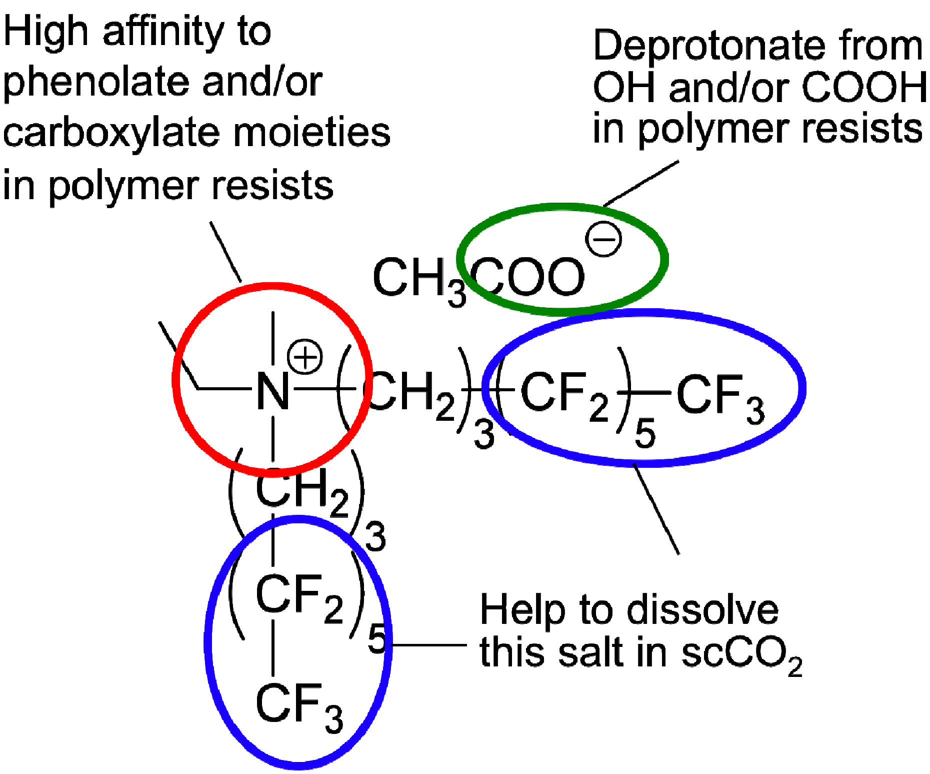


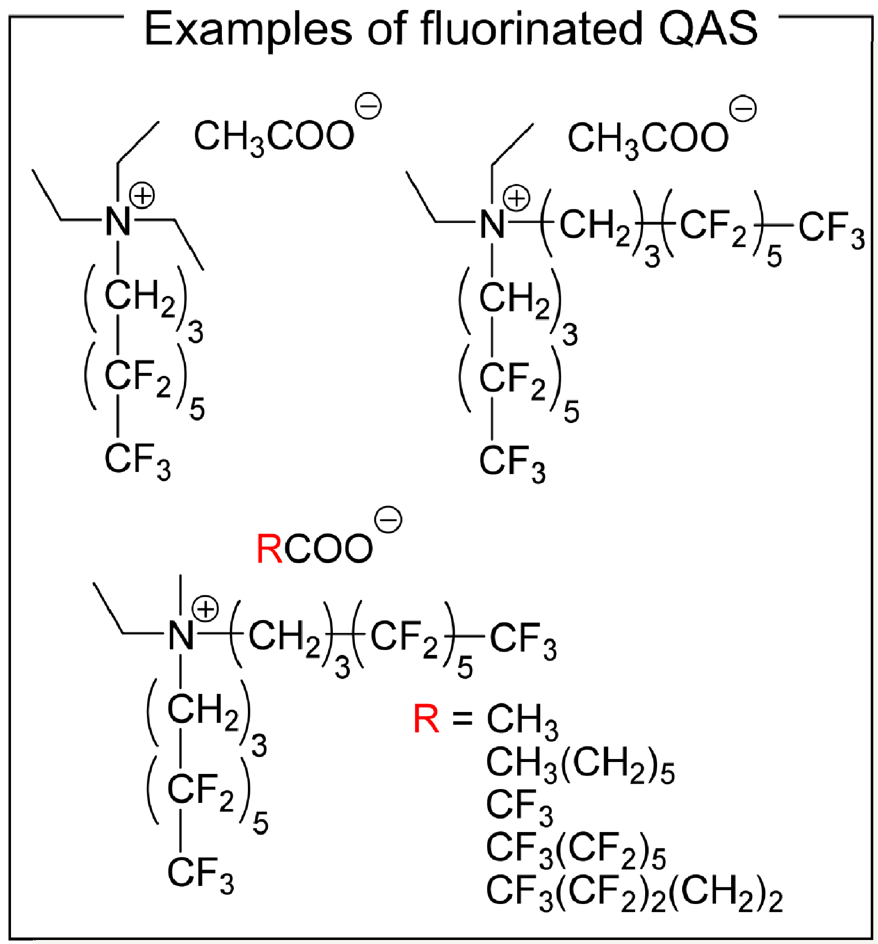
M. Wagner, et al., *Proc. of SPIE* **2006**, 6153, 61531I, *Proc. of SPIE* **2006**, 6153, 615345, *Proc. of SPIE* **2006**, 6153, 615346, *Proc. of SPIE* **2006**, 6153, 61533W, *Proc. of SPIE* **2007**, 6519, 651948.

Quaternary Ammonium Salts (QAS)

$scCO_2$ Compatible Additives:

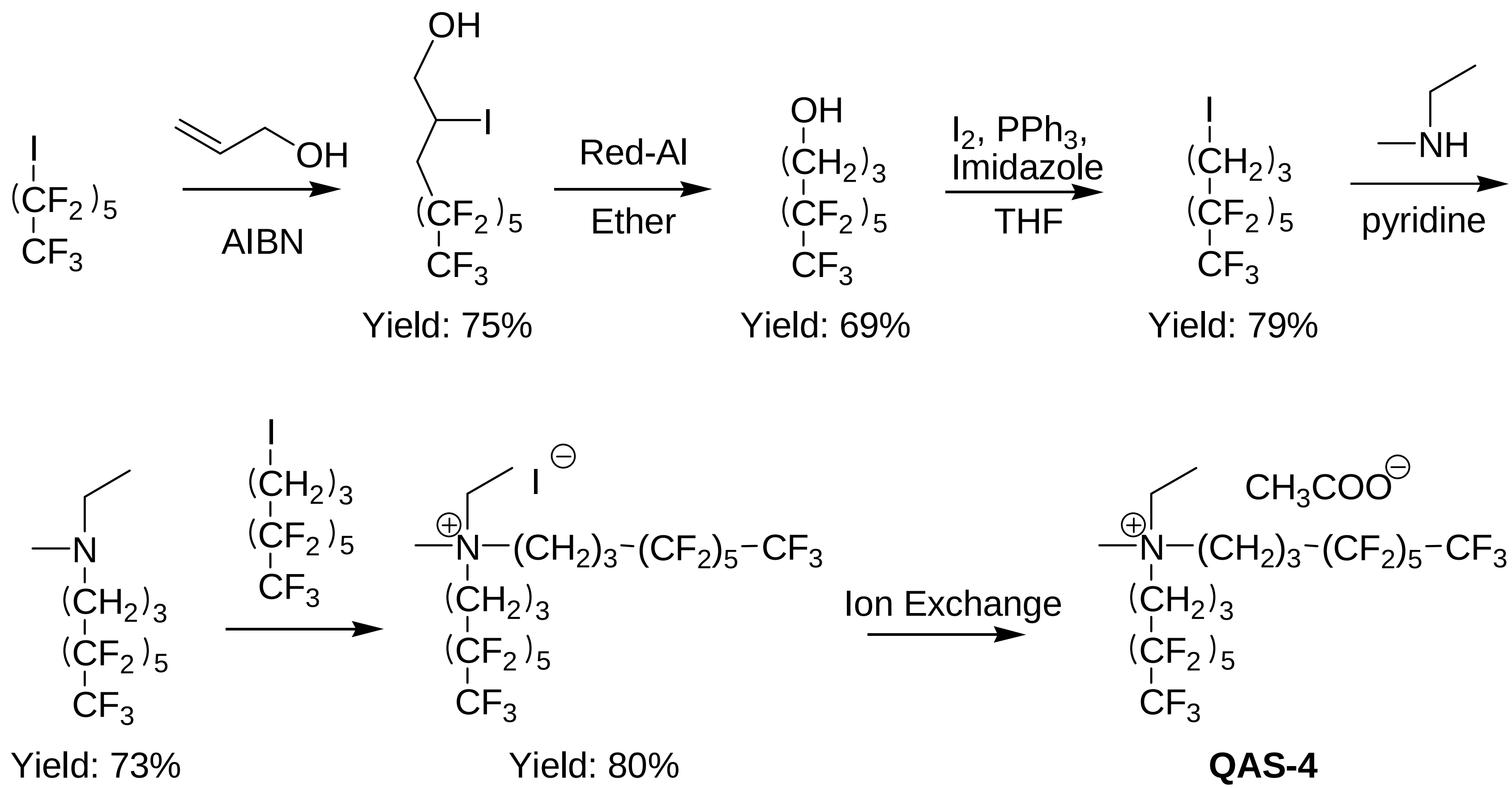
Fluorinated Quaternary Ammonium Salts (QAS)





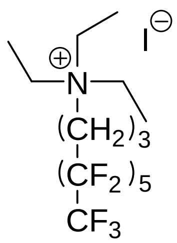
Some of the fluorinated ammonium salts form ***Micelle*** in $scCO_2$.

Synthesis of QAS

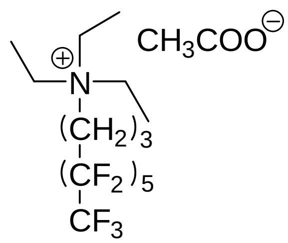


Other QAS were obtained by changing the amine and/or counter anions.

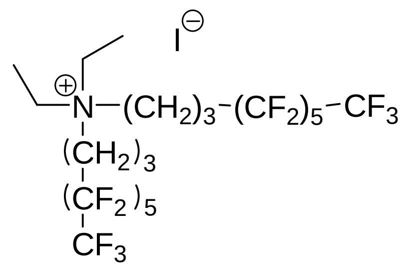
Series of QAS synthesized and tested as additives



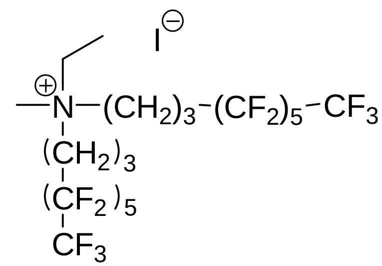
QAS-A



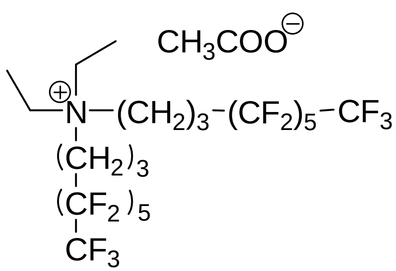
QAS-B



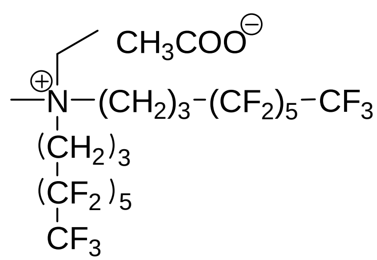
QAS-1



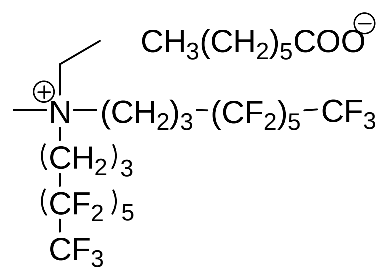
QAS-2



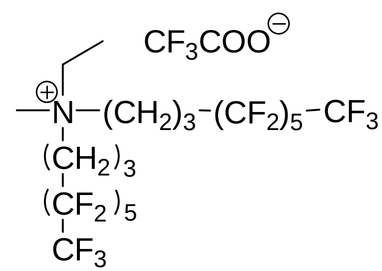
QAS-3



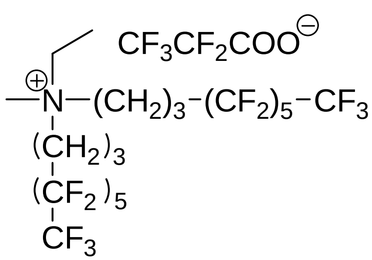
QAS-4



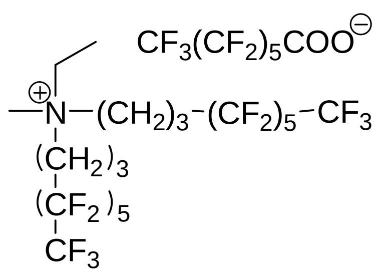
QAS-5



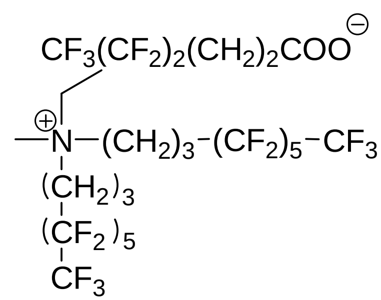
QAS-6



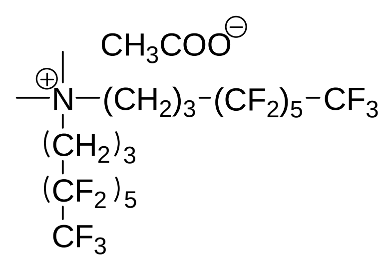
QAS-7



QAS-8

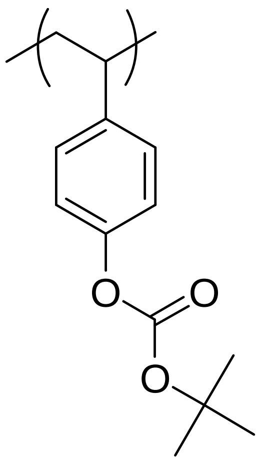


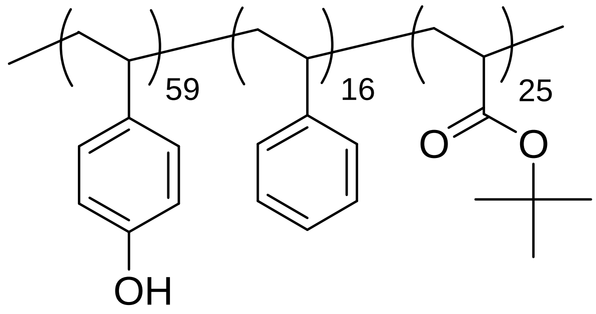
QAS-9



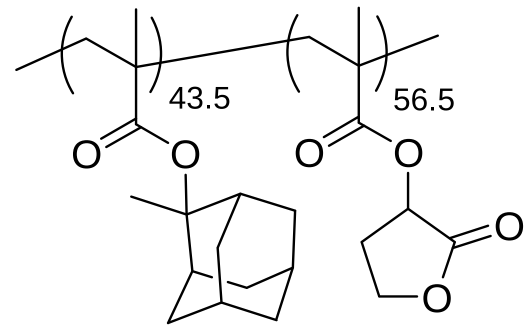
QAS-10

A series of standard EUV / DUV resists





'GIJ' from DuPont Electronic Polymers (**ESCAP**)



PMAMA-co-GBLMA from Mitsubishi Rayon America (**PMAMA-co-GBLMA**)

PBOCST

From TOK

EUV-P568 : Old EUV resist made from PHOST based polymer with t-Boc

EUVR-P3015 : Molecular glass resist

EUVR-P1123 : One of the latest EUV resist made from PHOST based polymer with bulky protecting group

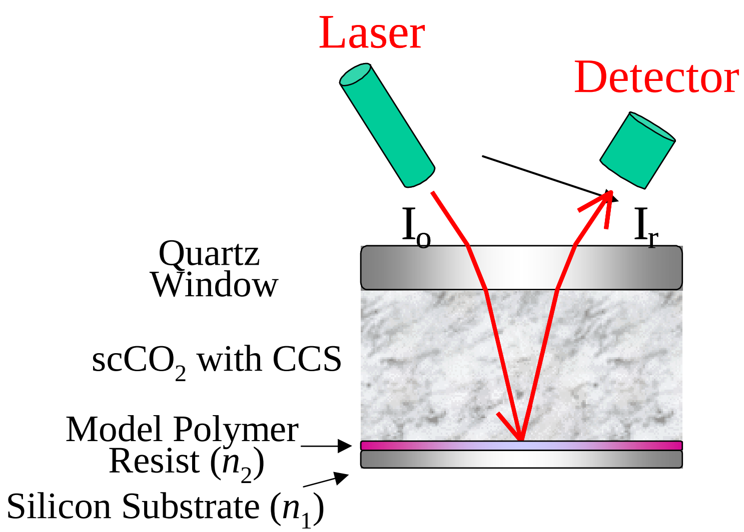
TARF-P6111 : ArF (193 nm) resist made from poly(methacrylate) backbones.

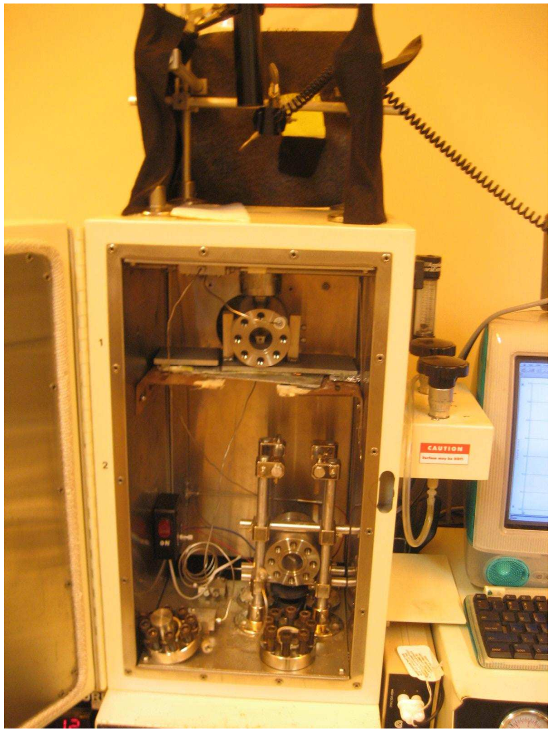
All of these resists are insoluble in $scCO_2$ at any temperatures and pressures.

Experimental Procedure

Steps involved in finding the appropriate QAS:

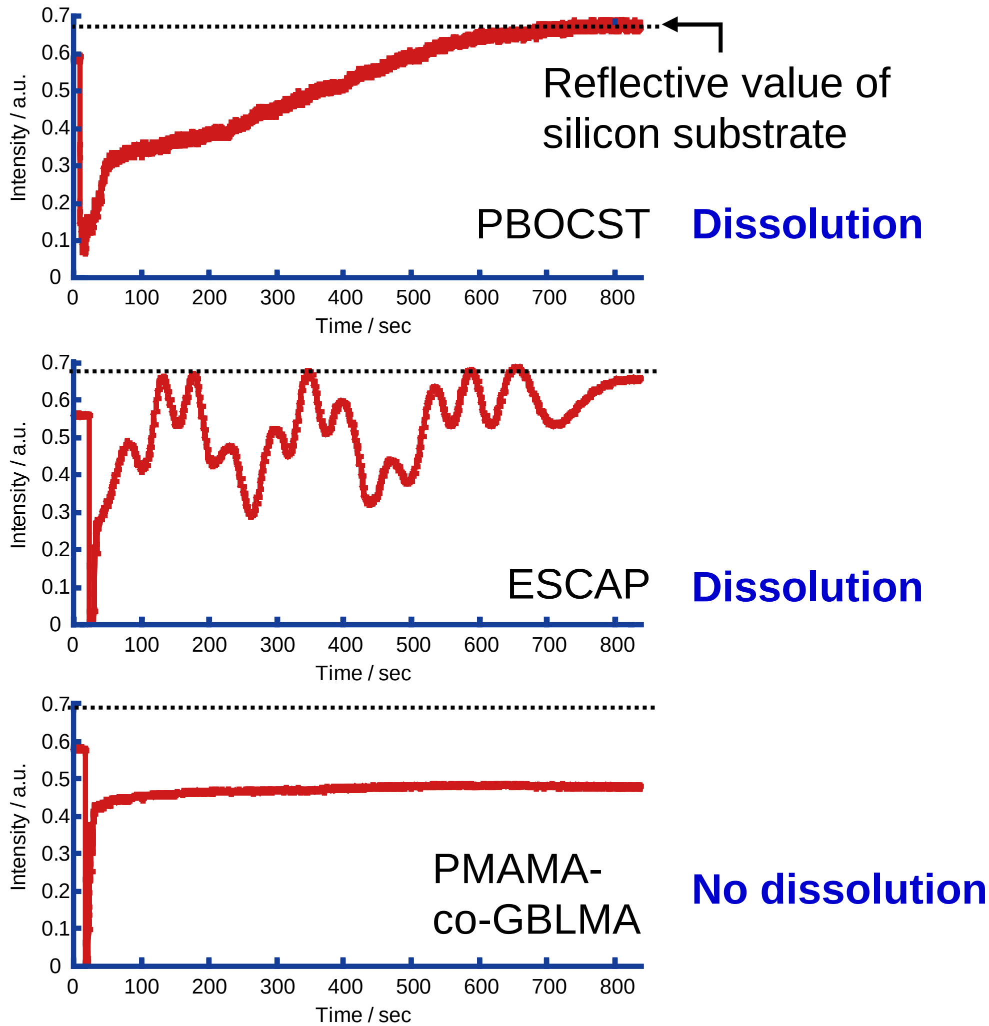
1) Synthesize and check the solubility of the salt in $scCO_2$. (50 ^{o}C and 5000 psi).
2) Check the effect of the salt on standard polymer resist. (Dissolution rate monitor)



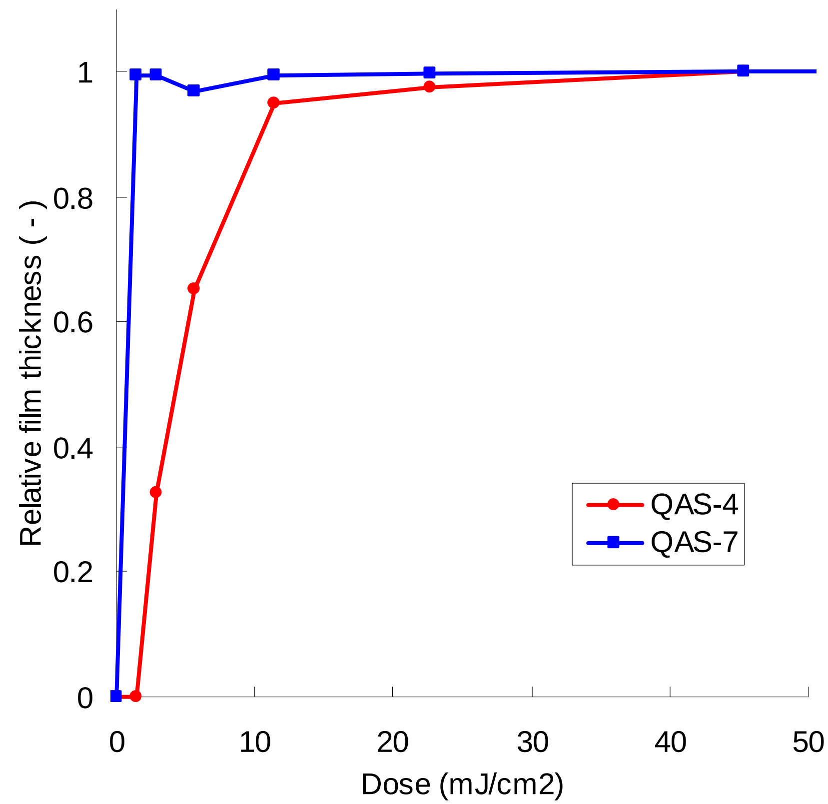


3) Measure the change in thickness by *profilometer*.
4) Development of EB-patterned Resists with appropriate QAS.

Dissolution monitoring and contrast curves

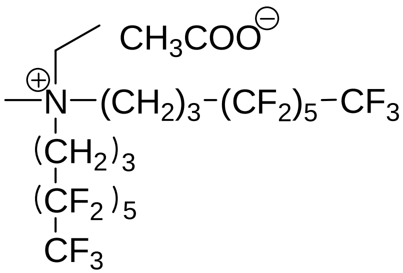
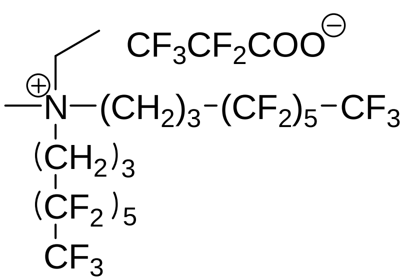


Dissolution rate monitor plots of unexposed films with QAS-4/$scCO_2$ solution (1.25 mM) at 50ºC and 5000 psi.



Contrast Curve of EUV-P568 (TOK) developed in $scCO_2$ with QAS-4 or QAS-7 (1.25 mM) at 50ºC, 5000 psi for 15 min.

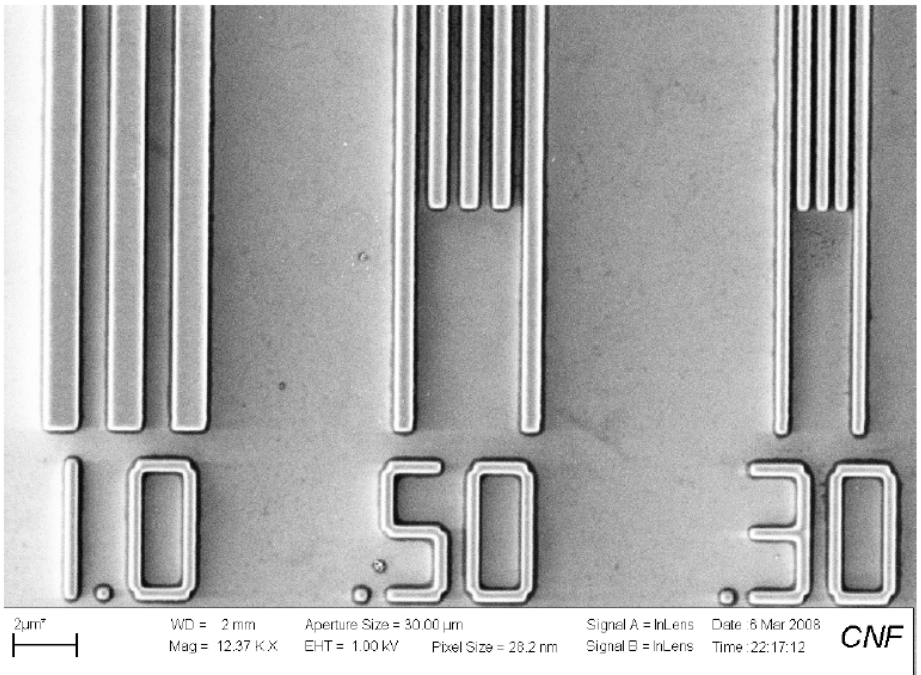
Dissolution Results of model resists with QAS

QAS	Resist	Unexposed	Exposed	note
 **QAS-4** (1.25 mM)	PBOCST	**Dissolution** (40 nm/min)	**Slow dissolution** (1-4 nm/min)	*Negative tone resist*
	ESCAP (Du Pont)	**Dissolution** (25 nm/min)	**No dissolution**	*Negative tone resist*
	PMAMA-co-GBLMA (Mitsubishi Rayon)	No dissolution	No dissolution	
	EUV-P568 (TOK)	**Dissolution** (15 nm/min)	**Slow dissolution** (1-2 nm/min)	*Negative tone resist*
 **QAS-7** (1.25 mM)	PBOCST	No dissolution	No dissolution	
	ESCAP (Du Pont)	No dissolution	No dissolution	
	PMAMA-co-GBLMA (Mitsubishi Rayon)	No dissolution	No dissolution	
	EUV-P568 (TOK)	**Dissolution** (45 nm/min)	**Slow dissolution** (<1 nm/min)	*Negative tone resist*

Exposed by UV lamp (254 nm, 24 mC/cm^2), developed in $scCO_2$ at 50^oC and 5000 psi.

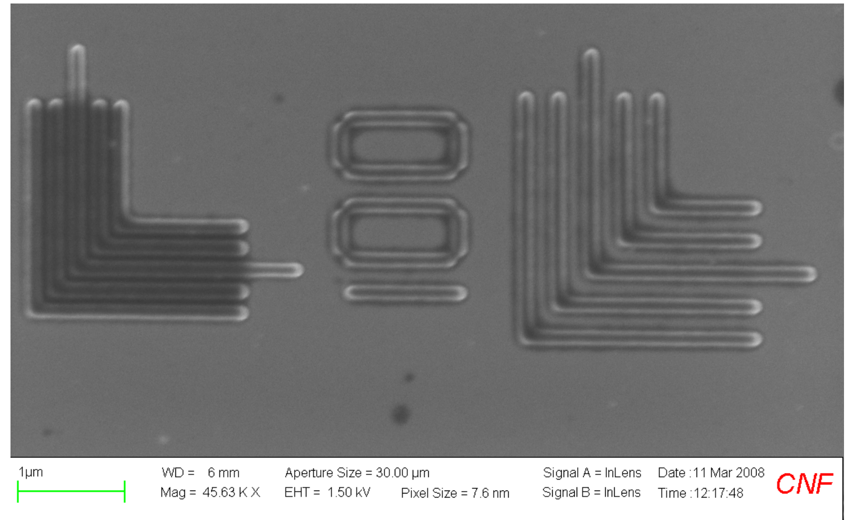
Electron Beam (EB)-Patterning

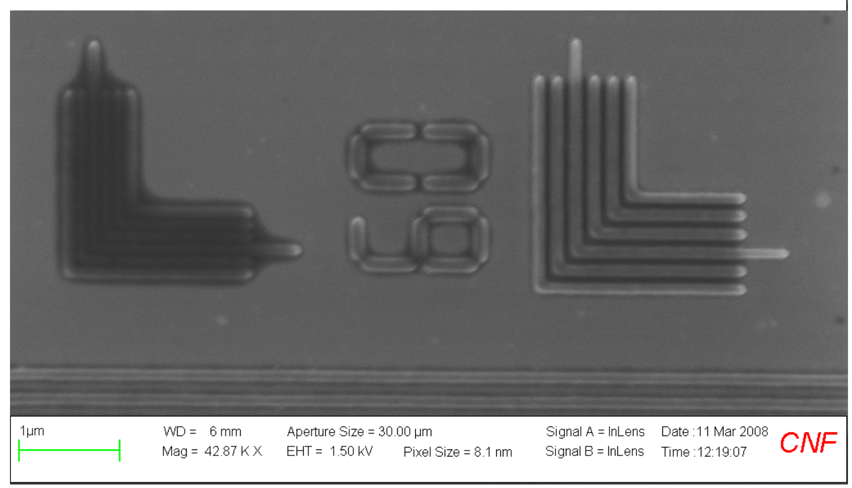
Development test of EB-patterned TOK resist (EUV-P568) with QAS-4 or QAS-7



Dose: 107 um/cm^2, QAS-4 (1.25 mM), dev. for 60 min at 50ºC, 5000 psi, flow 30 min

Pattern with sub-100 nm feature sizes were obtained.

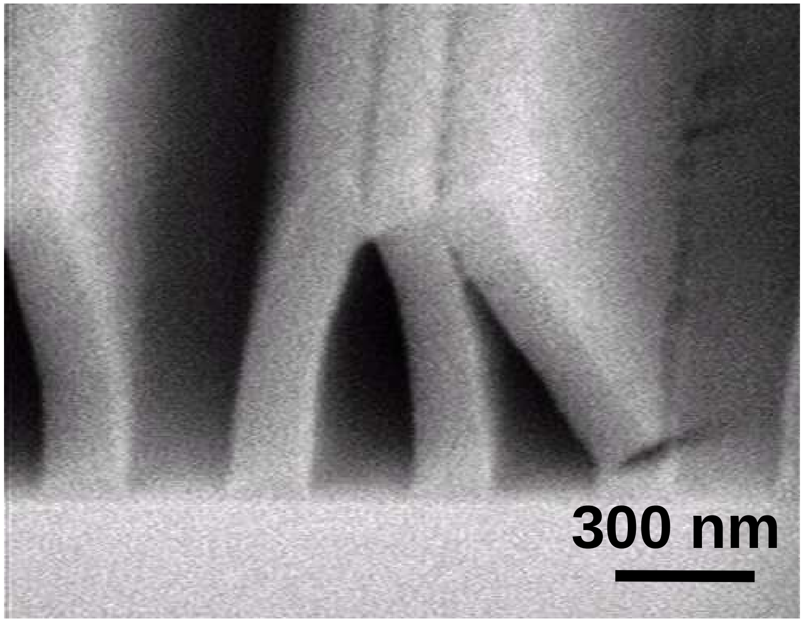




Dose: 20 um/cm^2, QAS-7 (1.25 mM), dev. for 60 min at 50ºC, 5000 psi, flow 30 min

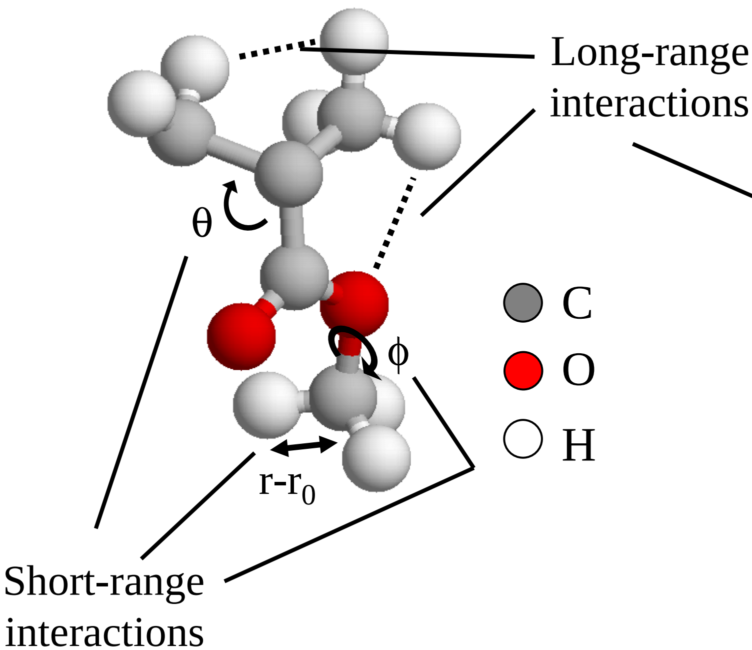
Simulation

- Rational design of QAS for $scCO_2$ development
  - Use molecular interaction to predict and control solubility outcomes
  - Connection to Experiement
- Methods
  - QAS solubility
  - Dissolution enchantment
  - QAS behavior
- Results



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

Model I



OPLS Model:

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

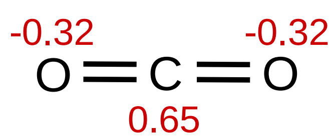
$$V_{LJ} = 4 \cdot \varepsilon \cdot \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

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

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

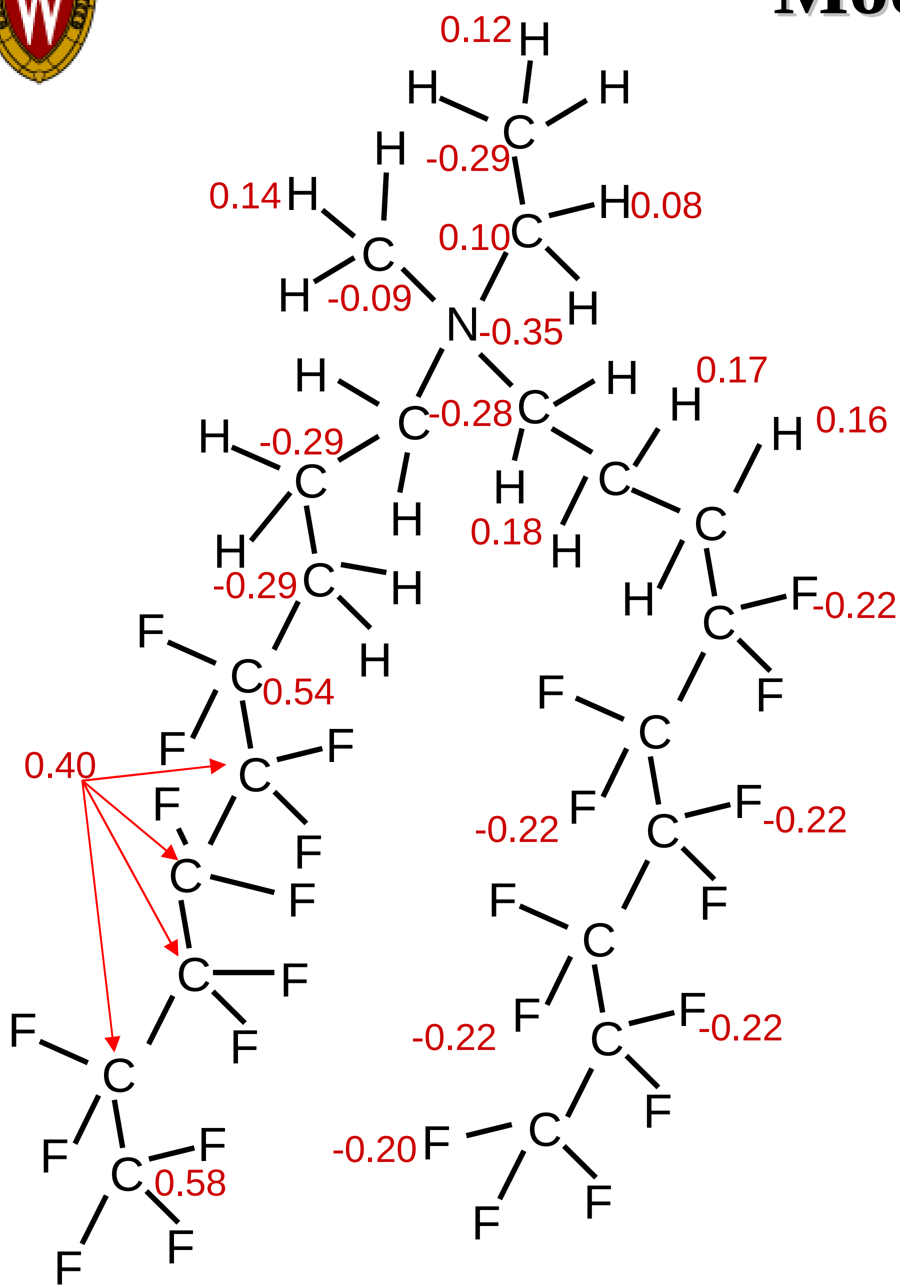
$$V_{ang} = \frac{1}{2} \cdot k_{ang} \cdot (\theta - \theta_0)^2$$

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



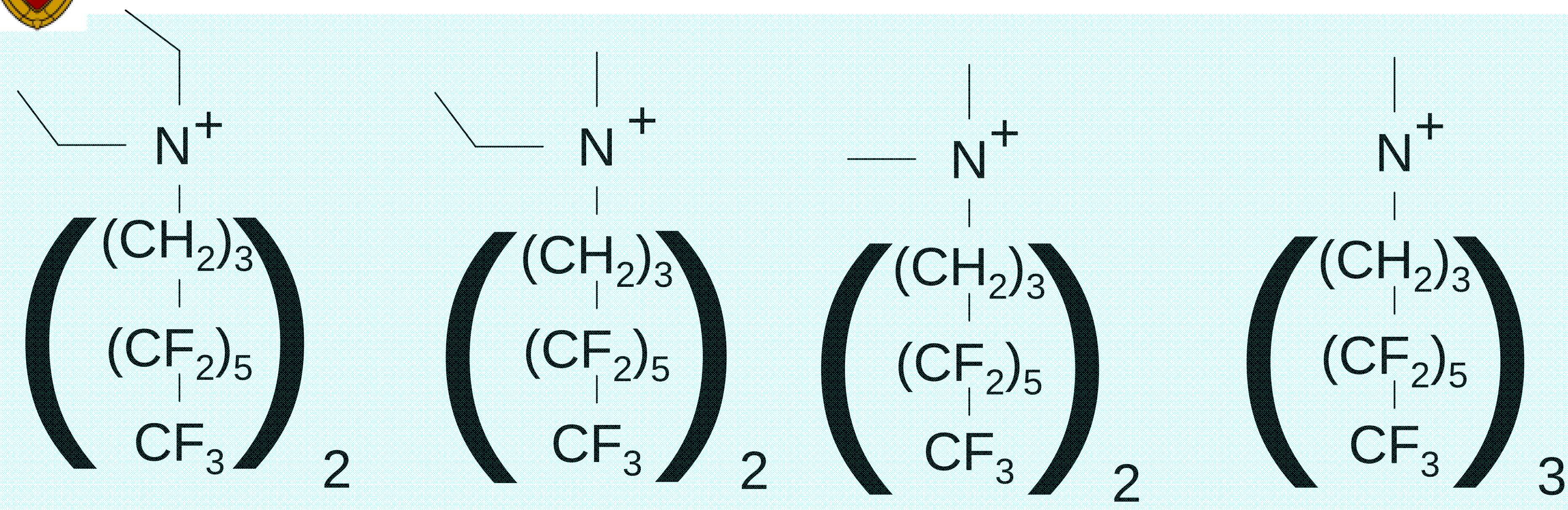
- OPLS force field employed for most parameters
- Process Conditions:
  T = 340K (~67°C)
  P = 345 bar

Model II



- We calculated charges (qi) using quantum mechanics
- Charge interactions vital to description of QAS
- When possible, polymer charges calculated on trimers, and middle polymer used

Salt Solubility



Diethyl | Ethyl-Methyl | Dimethyl | Monomethyl

Cations

Anions

$CF_3(CF_2)_{\mathbf{1}}COO^-$ $CF_3(CF_2)_{\mathbf{5}}COO^-$

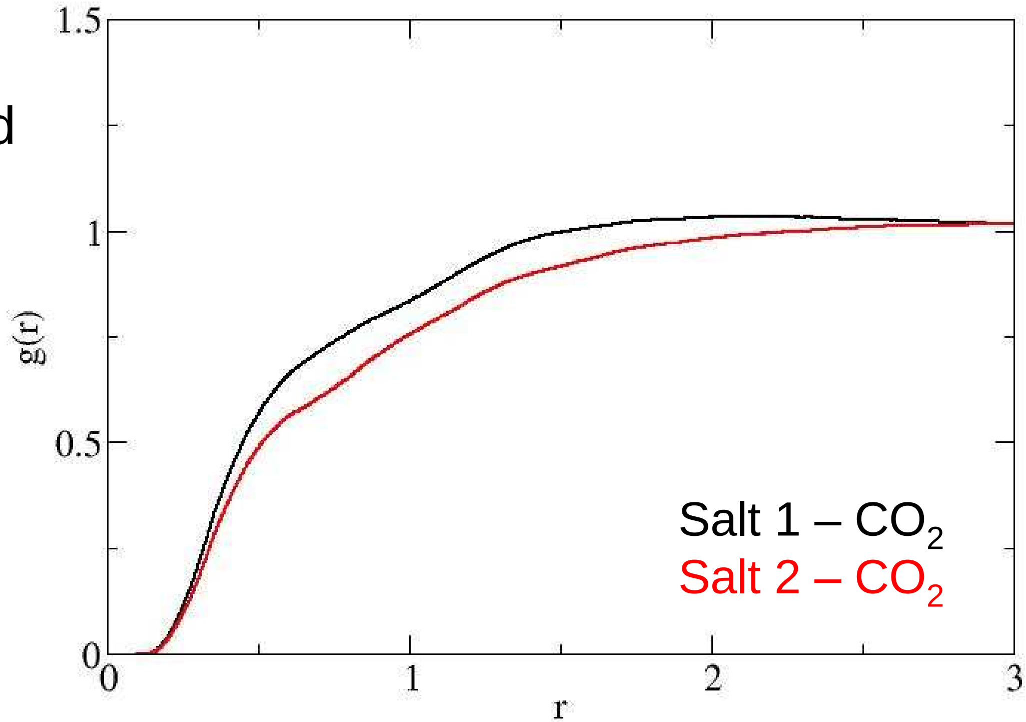
CH_3COO^- CF_3COO^- $CF_3(CF_2)_{\mathbf{2}}COO^-$

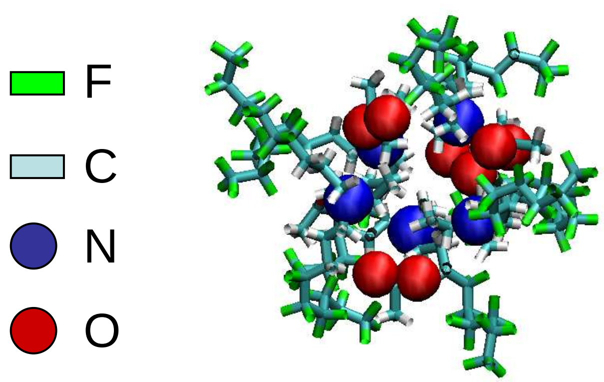
Salt Solubility

- g(r) is the local density as a function of distance from a fixed point

- Γ is the solubility enhancement factor
  - Γ > 0 → miscible
  - Γ < 0 → immiscible

- Screened possible salts by $scCO_2$ solubility





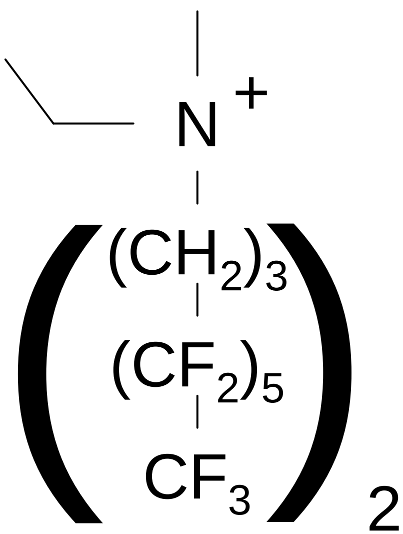
$$\Gamma_{i,j}(R) = \rho \int_0^R 4\pi r^2 \left(g(r)_{i,j} - 1\right) dr$$

$$\bar{v}_1^{\infty} = \frac{1}{\rho}\left[1 + x_2\left(\Gamma_{22}(\infty) - \Gamma_{12}(\infty)\right)\right]$$

Salt Solubility – Cation Choice

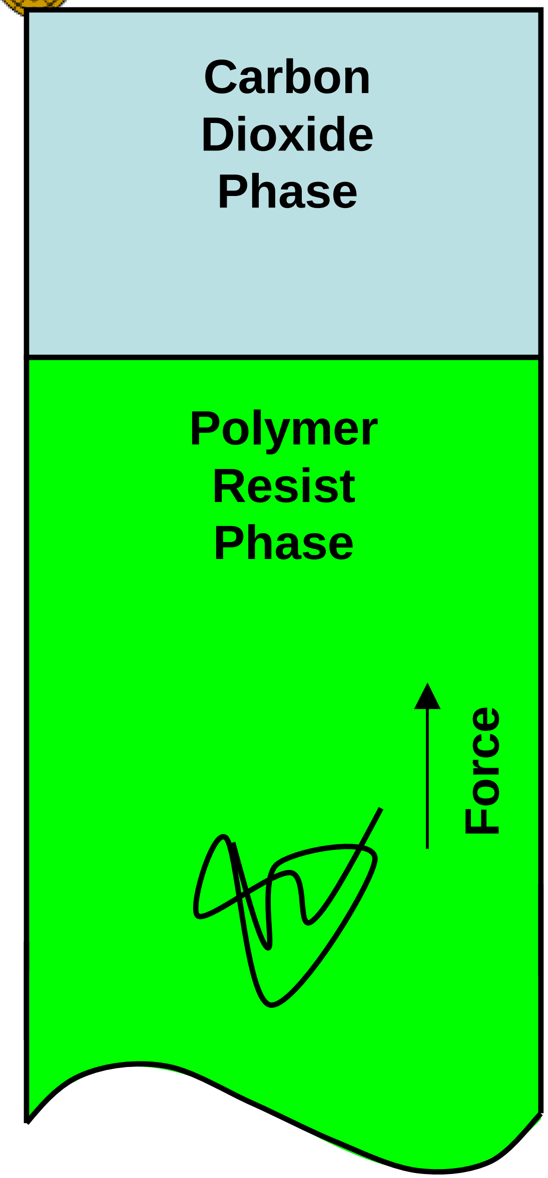
System	Γ	Partial Molar Vol [cm³/mol]
C1 – A1	-1.44	24.15
C1 – A2	-0.391	23.53
C1 – A3	0.957	19.32
C2 – A1	0.83	18.49
C2 – A2	0.14	21.44
C2 – A4	2.08	12.68
C2 – A5	13.57	9.74
C3 – A1	11.52	15.06
C4 – A1	-3.60	24.31

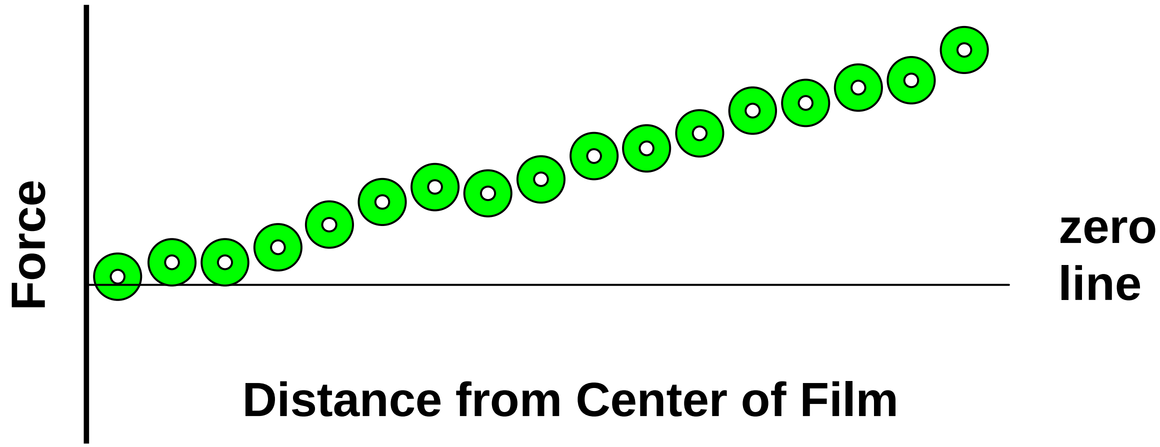
- Eliminate unpromising salts
- Identified “best” cation



Ethyl-Methyl

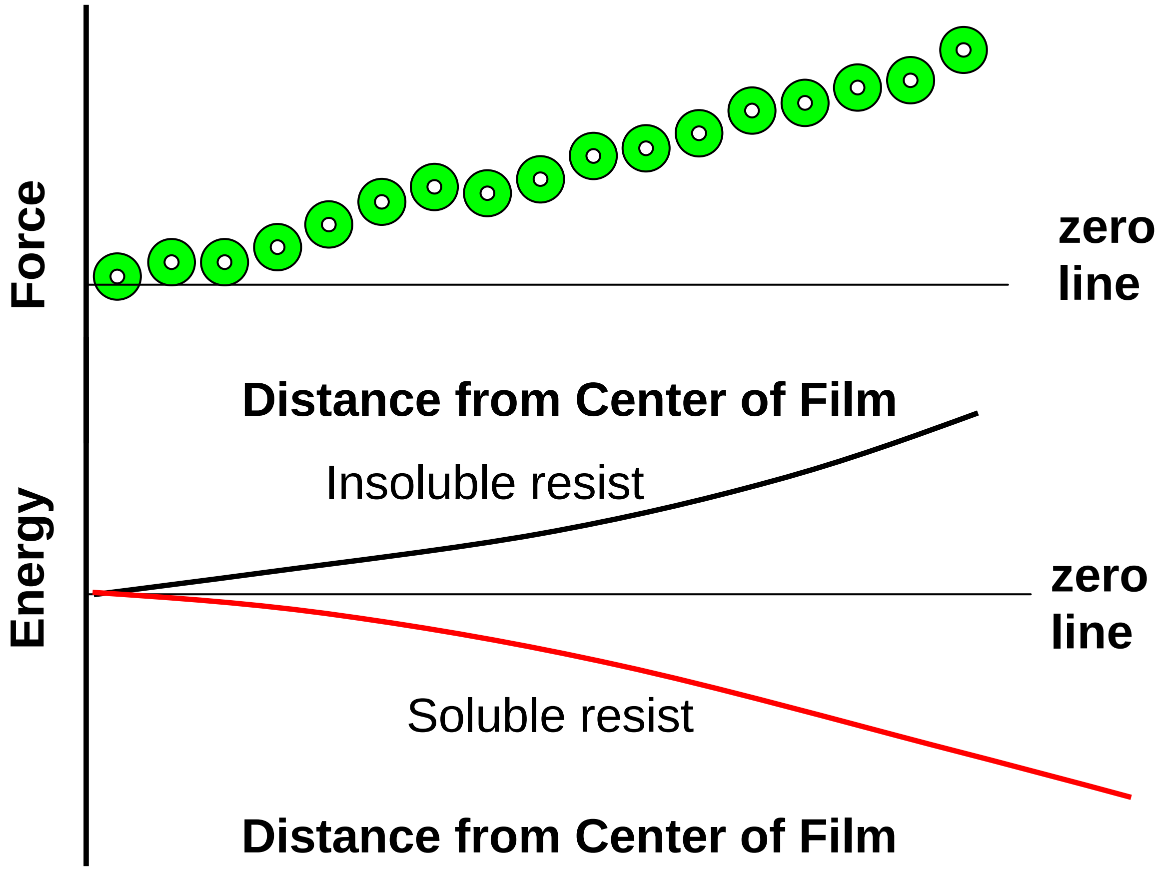
Thin Film Methods I



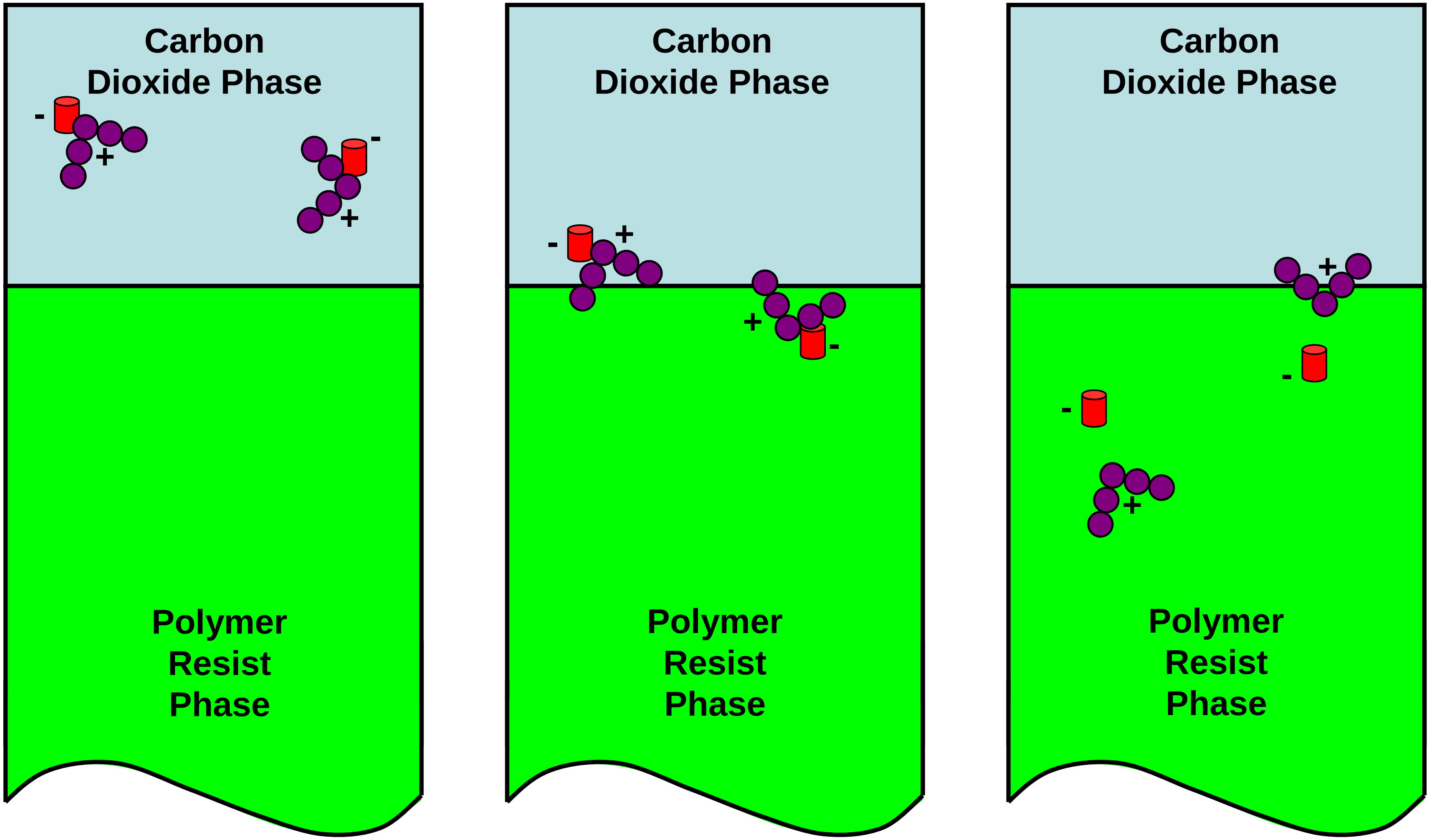


Thin Film Methods II

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



Classes of Salt Behavior



Non-Interacting

Surface Aggregation

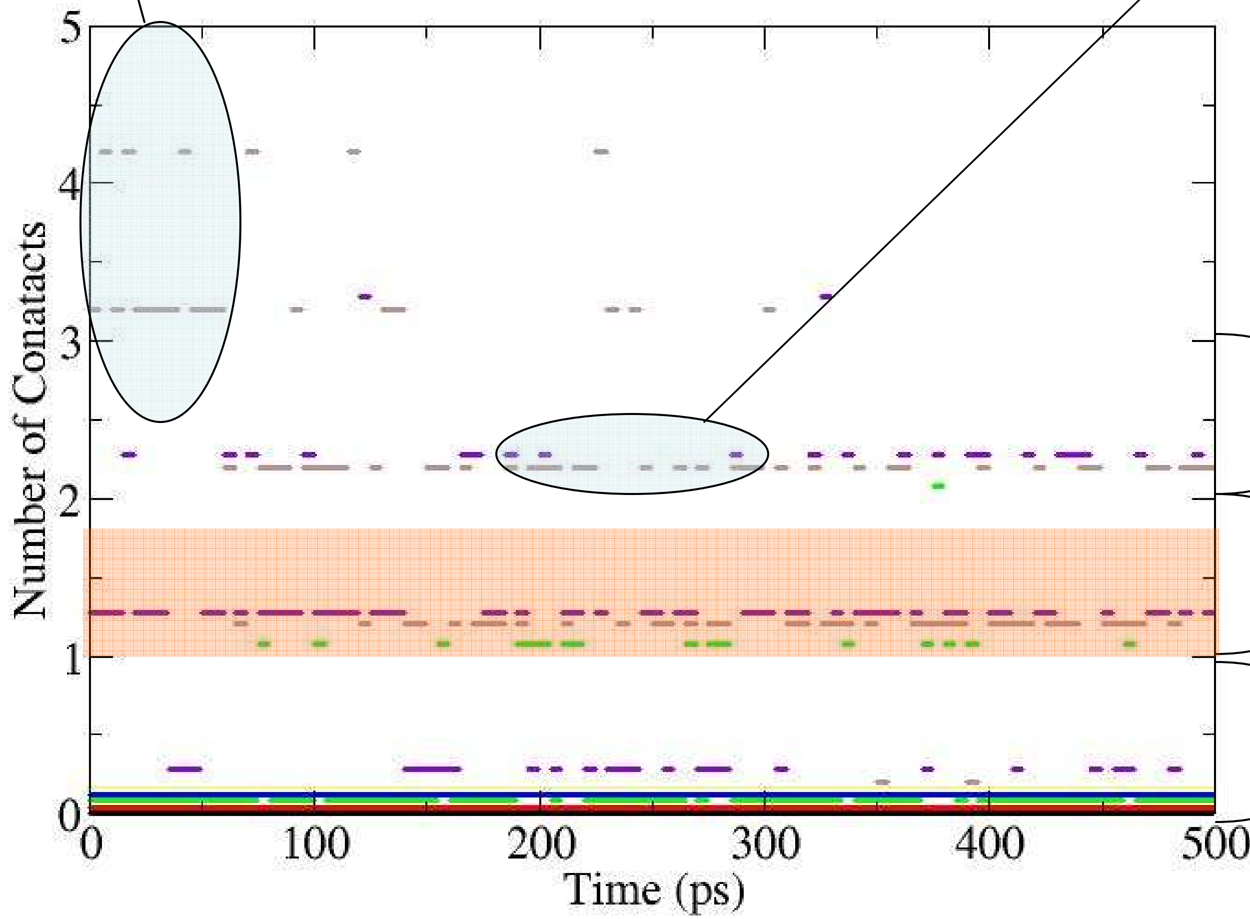
Penetration & Dissolution

Contact Analysis Method

We can see how the number of contacts a given species evolves over time.

Length of lines indicates how long-lived a configuration with that number of contacts lasts.

Each colored line represents a different particular bead or group



Lines are shifted up from integer values so we can see each one clearly.

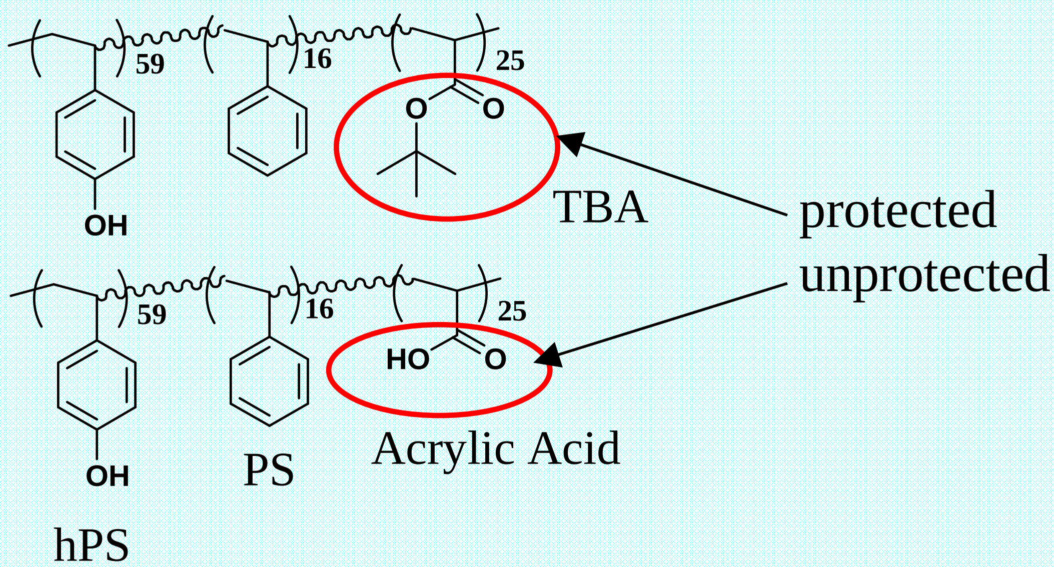
2 Contacts

1 Contact

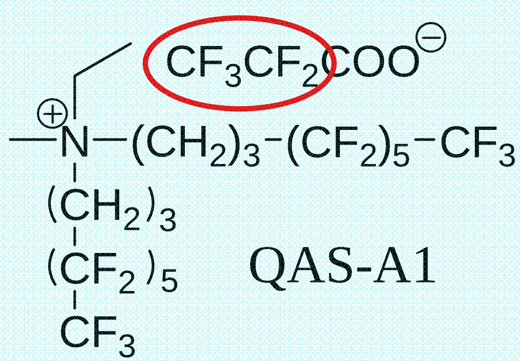
0 Contacts

Systems of Interest – Polymer Resists

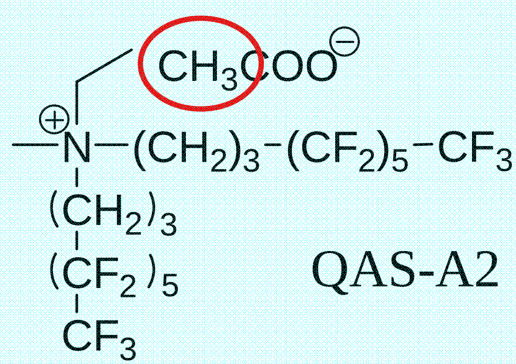
ESCAP



QAS-A: for ESCAP

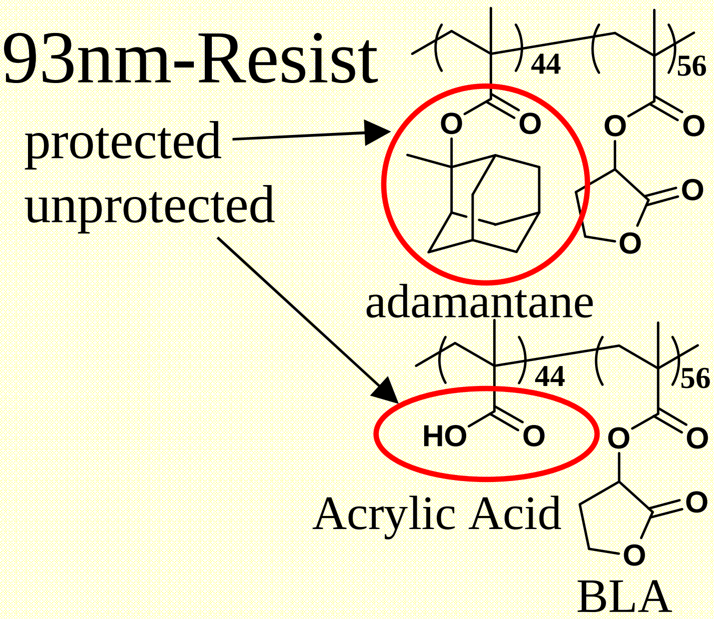


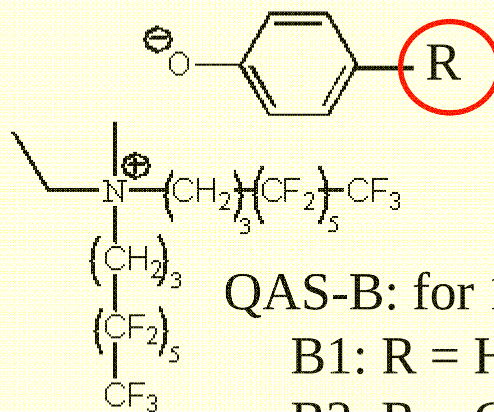
QAS-A1



QAS-A2

193nm-Resist





QAS-B: for 193nm-resist

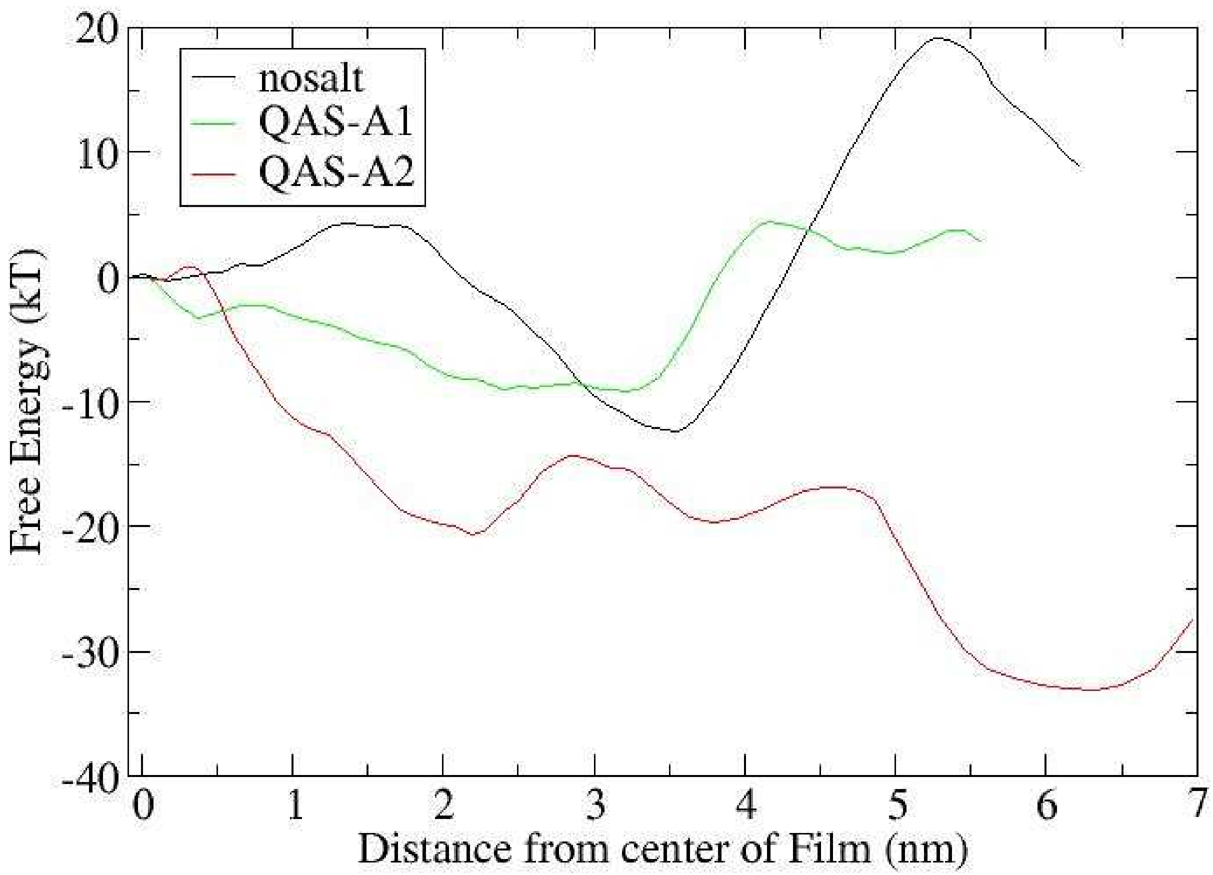
B1: R = H

B2: R = CH_3

B3: R = CF_3

B4: R = NO_2

ESCAP Results



Simulation Results:

No salt – no dissolution

QAS-A1 – no dissolution

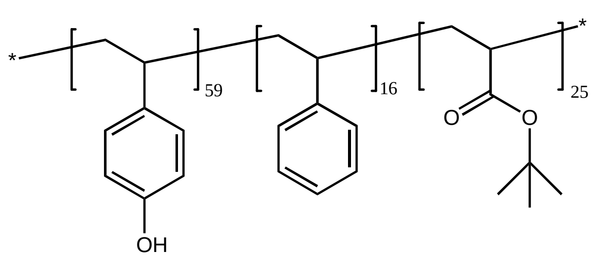
QAS-A2 – dissolution

Experimental Results:

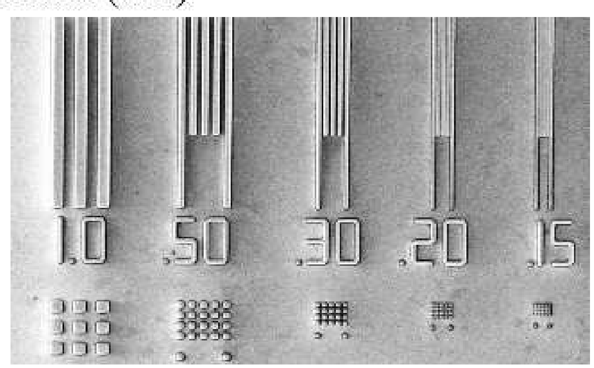
No salt – 0 nm/sec

QAS-A1 – 0 nm/sec

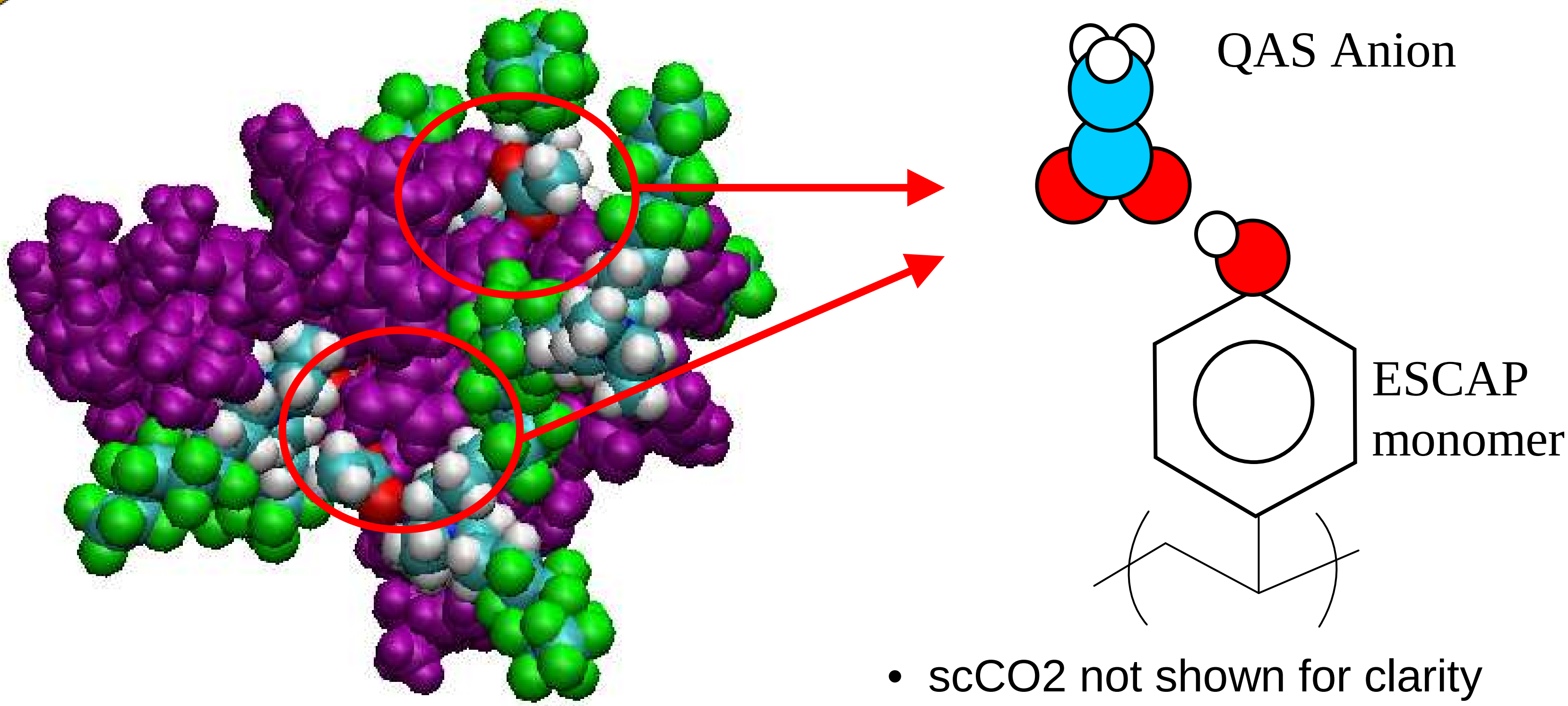
QAS-A2 – 20 nm/sec



hPS **PS** **TBA**



ESCAP Results



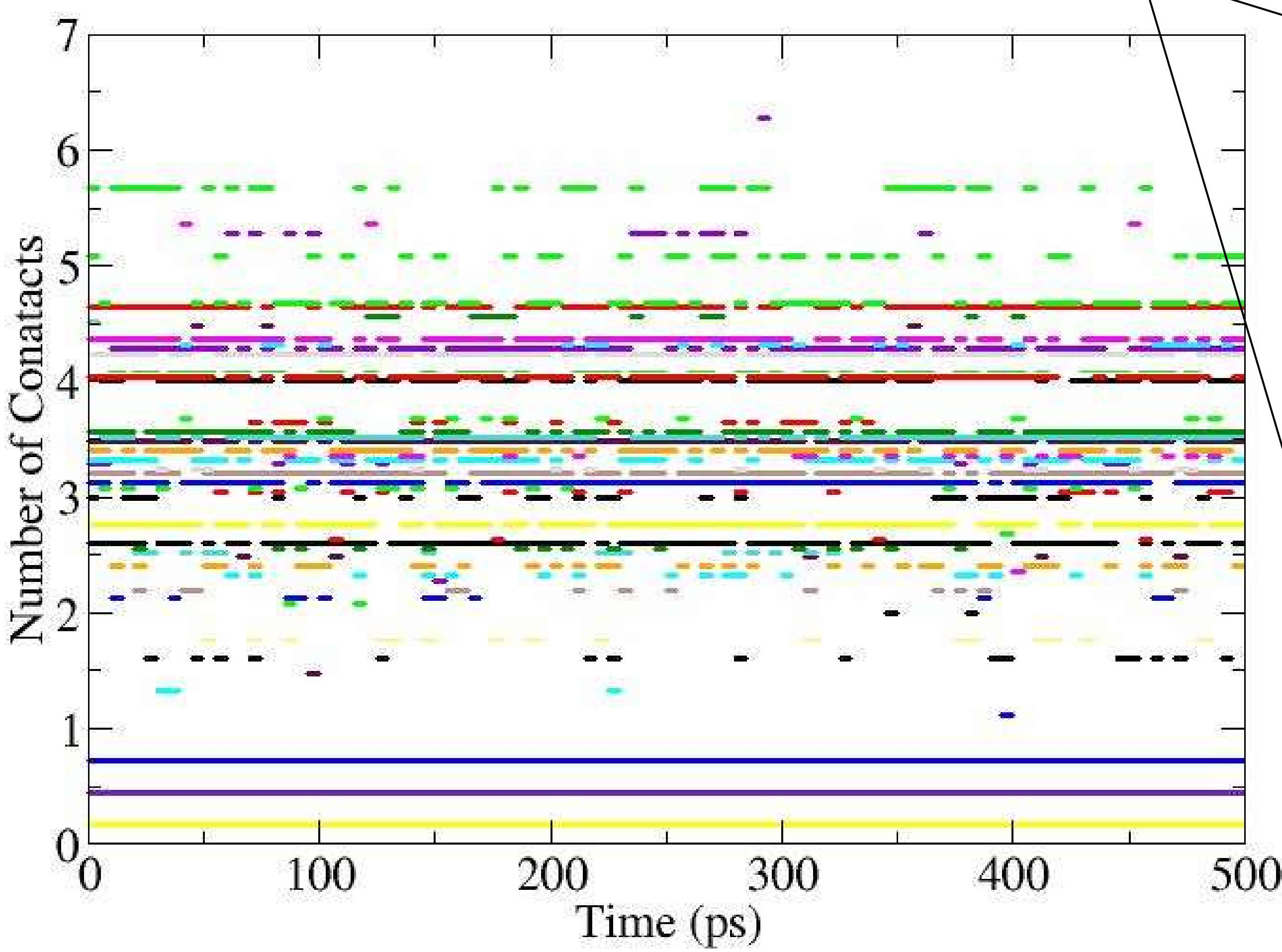
- The –OH group of ESCAP associates with the anions.

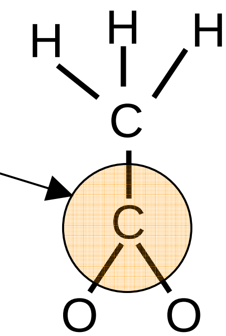
- $scCO_2$ not shown for clarity
- **Purple** – ESCAP
- **Green** – Fluorine (QAS-A2)
- **Cyan** – Carbon (QAS-A2)
- **Red** – Oxygen (QAS-A2)
- **White** – Hydrogen (QAS-A2)

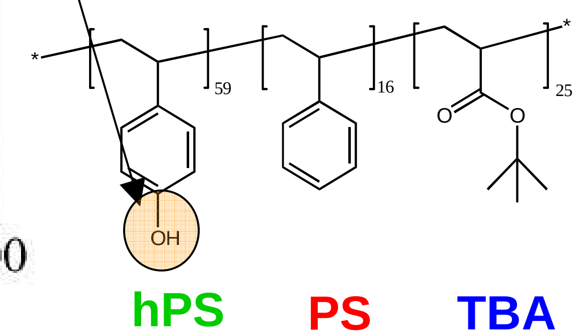
Contact Analysis – ESCAP (hPS)

QAS-A2 Anion

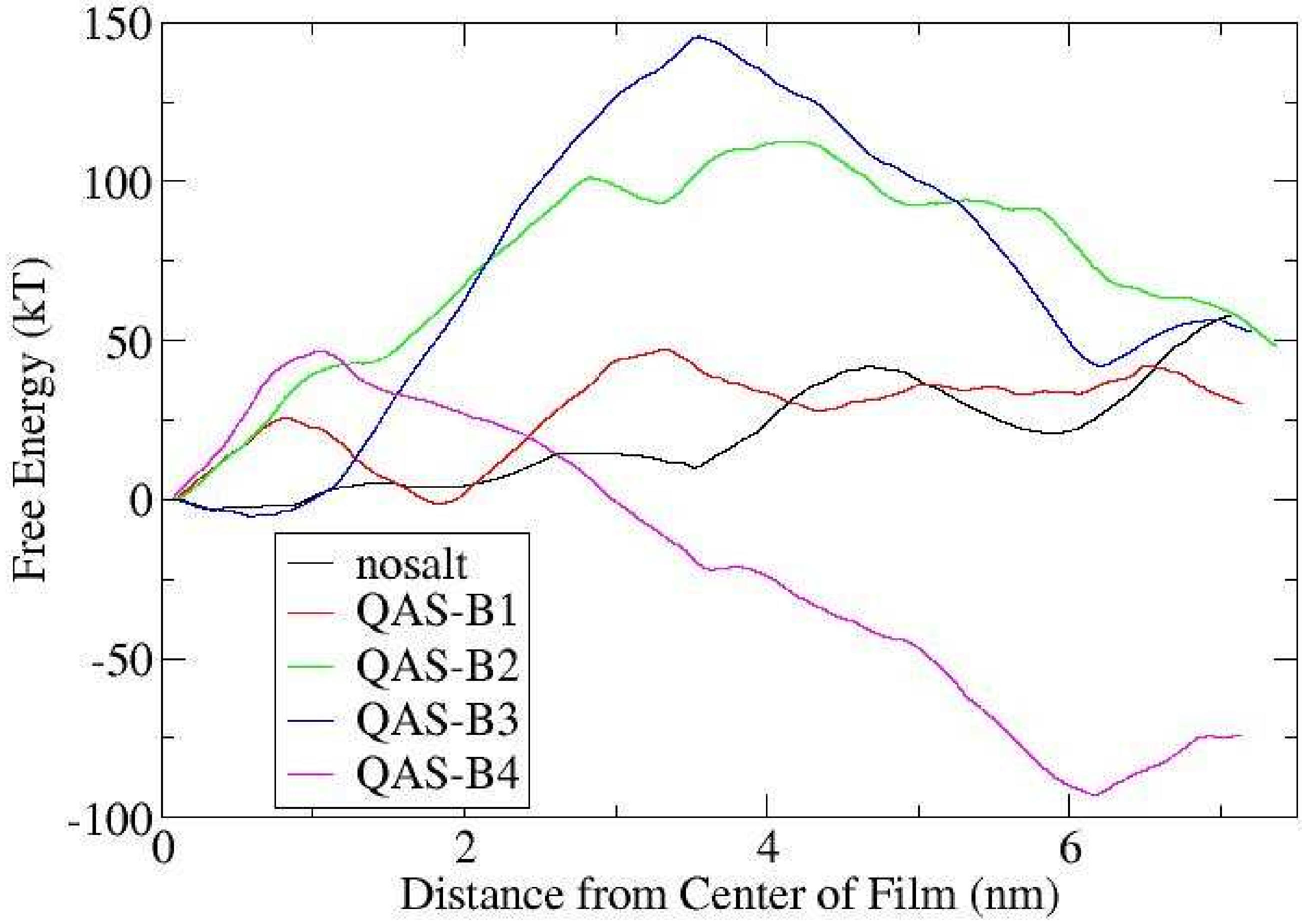
Number of hPS contacts by each QAS-A2 anion





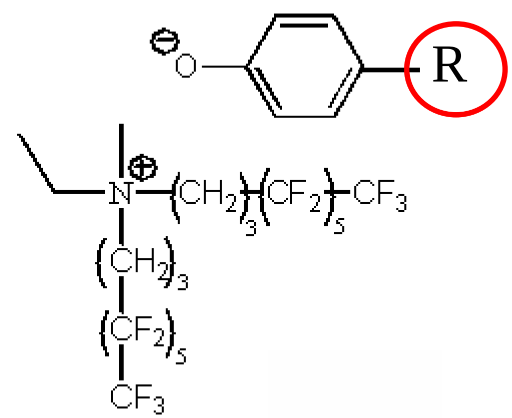


193nm-Resist Results



Simulation Results:
No salt – no dissolution
QAS-B1 – no dissolution
QAS-B2 – no dissolution
QAS-B3 – no dissolution
QAS-B4 – Dissolution

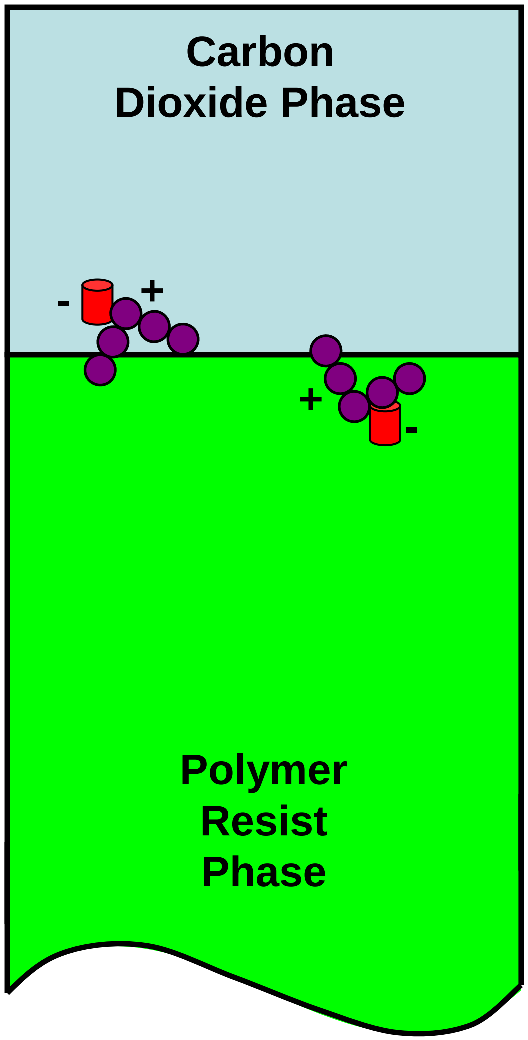
Experimental Results:
No salt – 0 nm/sec
QAS-B1 – 0 nm/sec
QAS-B2 – unknown
QAS-B3 – unknown
QAS-B4 – unknown



We predict addition of QAS-B4 to allow resist to dissolve in $scCO_2$

B1: R = H
B2: R = CH_3
B3: R = CF_3
B4: R = NO_2

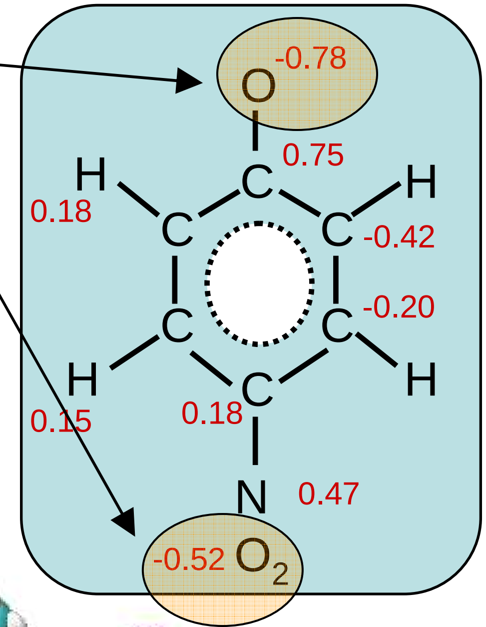
QAS-B4

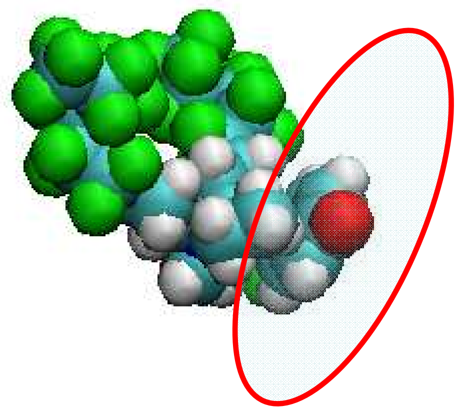


Surface Aggregation

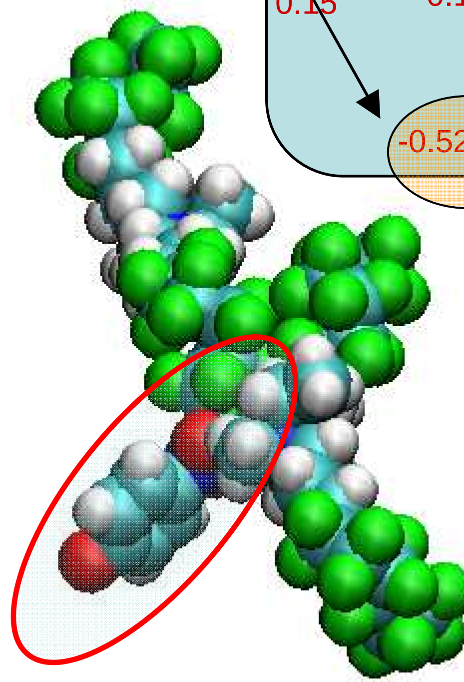
- QAS-B4 charge delocalized
- QAS-B4 anion interacts with resist
- Surface aggregating salts with solubility enhancement.

QAS-B4





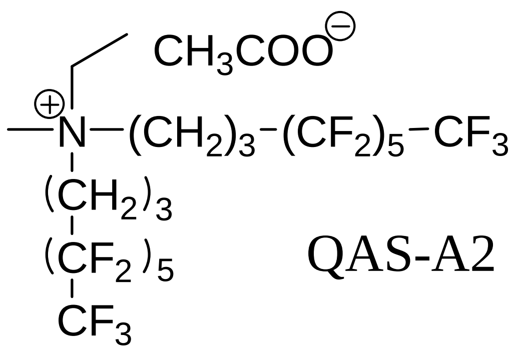
Other QAS-B



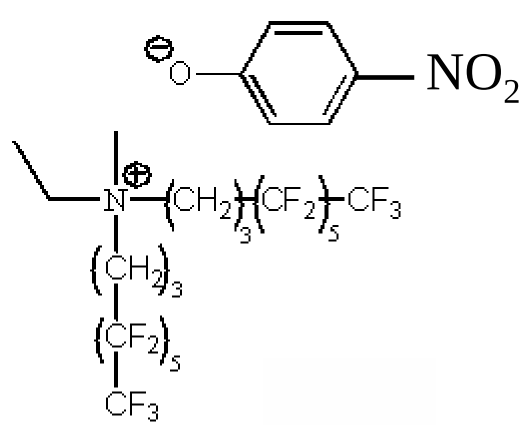
QAS-B4

Conclusions

- ESCAP (model)
  - Simulation: Only soluble in QAS-A2
  - Experimental: Confirmed
- 193nm-resist (model)
  - Only soluble in QAS-B4
  - Simulations guiding experiment



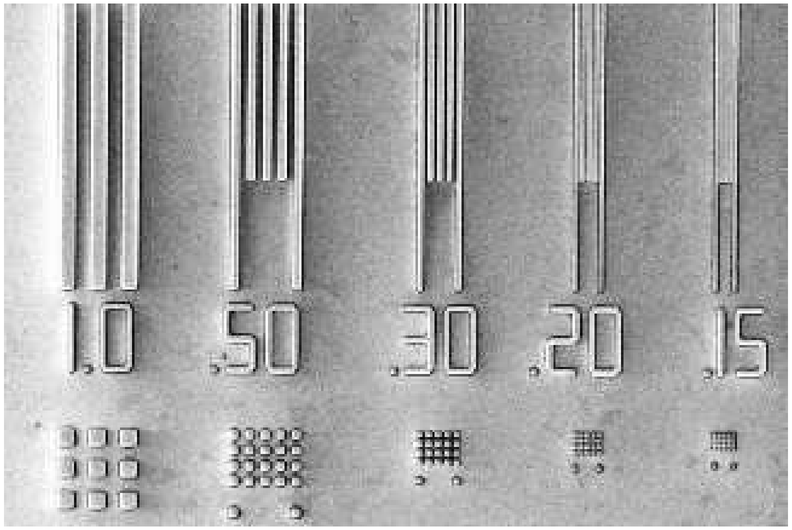
QAS-A2



- Methods of investigation
  - Dissolution rate measurement
  - Contrast curves
  - Computation simulations

Conclusions

- Use of $scCO_2$ use as a solvent improves LER and eliminates pattern collapse.
- Conventional and EUV polymer resists can be realized with fluorinated quaternary ammonium salts (QAS) as additives to $scCO_2$.
- QAS design
  - Amount of fluorination and choice of anion important.
  - Asymmetric architectures are favorable



Negative tone patterns with sub-100 nm features can be achieved.

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