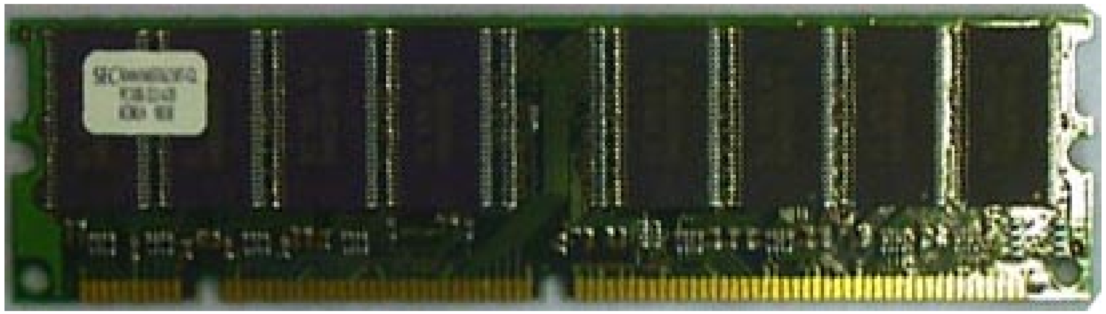
Part III. Functional Polymers for Semiconductor Applications

Outline of Part

Photoresist for Semiconductor Applications

- Introduction of photolithography
- Photoresist Materials for Exposure at 193 nm Wavelength
- Chemically Amplified Resists for F2 Excimer laser Lithography

Photoresist Materials for Exposure at 193 nm Wavelength



128 Mbyte SDRAM

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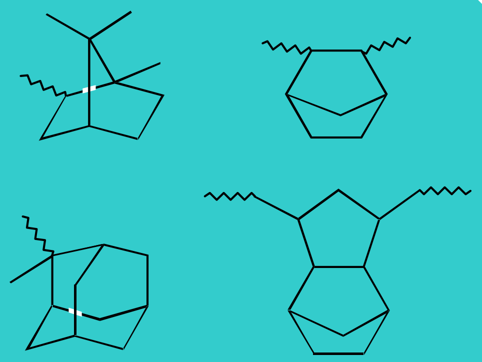
Kongju National University

Prof. Jin-Heong Yim

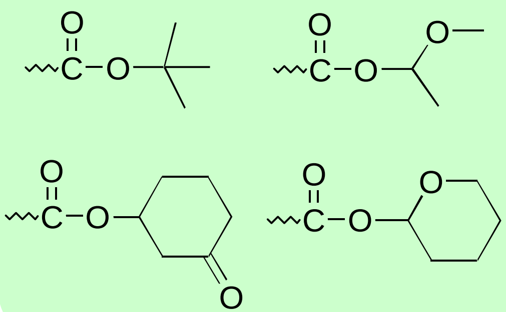
Design of Chemically Amplified Resist

Dry-Etching Resistance — **Adhesion** — **Solubility Change**



~OH ~OR

~COOH ~COOR



Requirements of 193-nm Photoresists

1. **Transparency at 193 nm** (Transmittance > 0.6 / μm)

2. **Good Dry-Etching Resistance**

   - Pattern formation with high aspect ratio (~ Novolac resist)

3. **High Thermal Stability**

   - Stable to temperature in process environments(T_d > 150°C, T_g > 100°C)

4. **Good Adhesion to Substrate**

5. **High Sensitivity**

   - Dose < 20 mJ/cm^2

6. **Compatibility with Conventional Developer (0.262 N TMAH)**

Target Point

Synthesis of photoresists materials that have

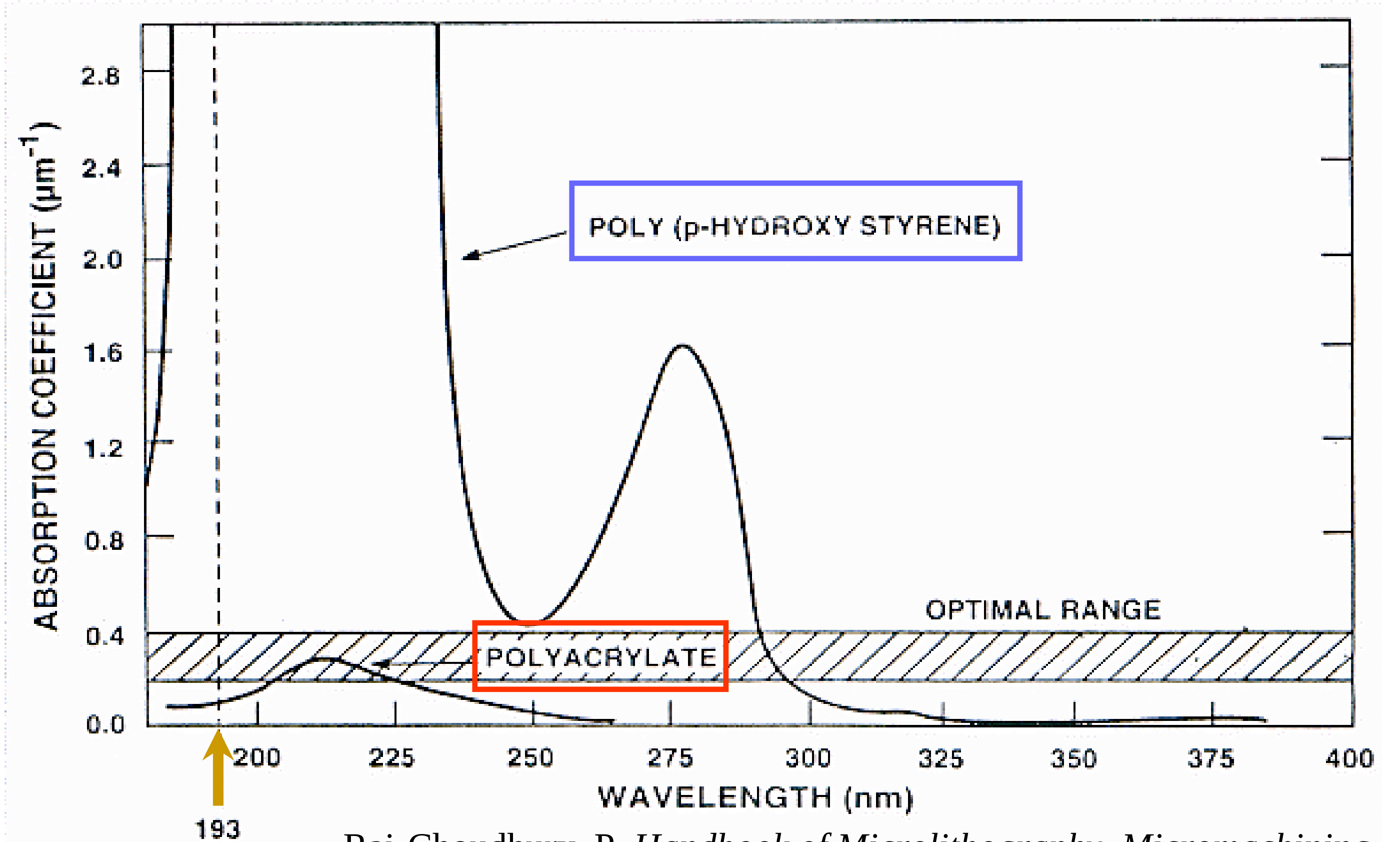
- Good mechanical and thermal properties
- High transparency at 193 nm wavelength
- Good etch resistance
- Capability of resolving sub-0.25μm feature size

193 nm Resist Materials

Challenges :

Conventional resists are unsuitable for 193 nm imaging due to their opacity at this wavelength.

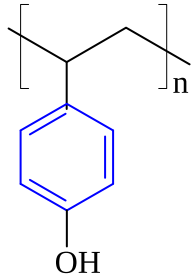
Comparison of Absorption Spectra (PHS vs. PMMA)



Rai-Choudhury, P. *Handbook of Microlithography, Micromachining, and Microfabrication*, Vol.1, SPIE Engineering Press,1997

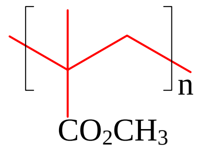
PHS

(Poly(hydroxystyrene))



PMMA

(Poly(methylmethacrylate))



193 nm Resist Materials

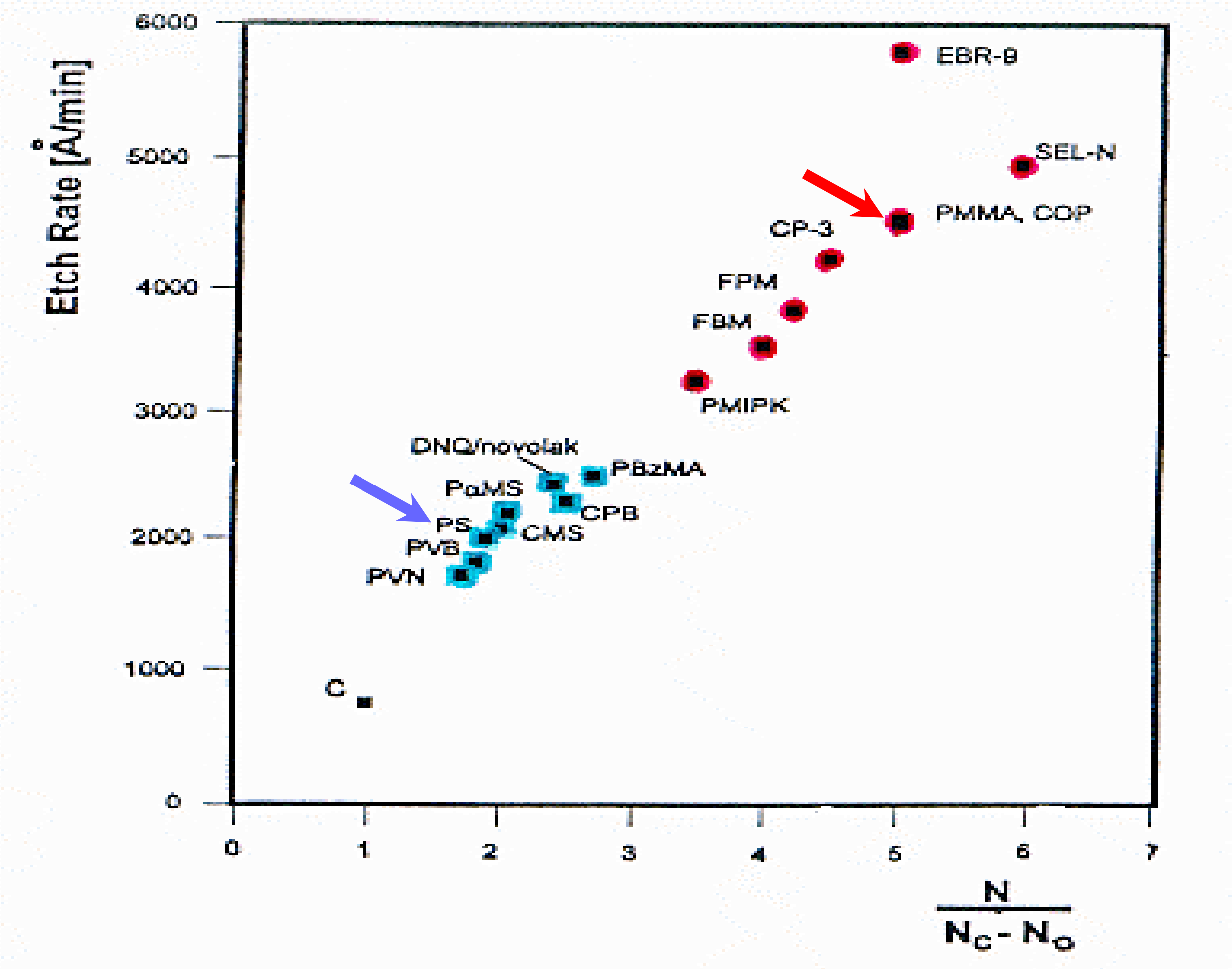
Challenges :

Etch resistance has been empirically linked to a high carbon/hydrogen ratio, but aromatics are precluded because of their absorption at this wavelength.

$$\text{Etch Rate} \propto \frac{N_{total}}{N_{carbon} - N_{oxygen}}$$

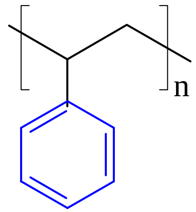
Gokan, H.; Esho, S.; Ohnishi, Y. *J. Electrochem. Soc.* **1983**, *130*, 143

Dry Etch Resistance of Organic Materials



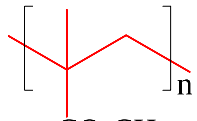
PS

(Polystyrene)



PMMA

(Poly(methylmethacrylate))



Ohnishi *et.al. J.Electrochem. Soc.: Solid-State Sci. Technol.*, 130, 143 (1983)

How Do it can be Achieve ?

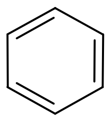
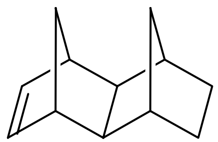
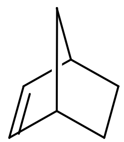
“Optical Transparency”

&

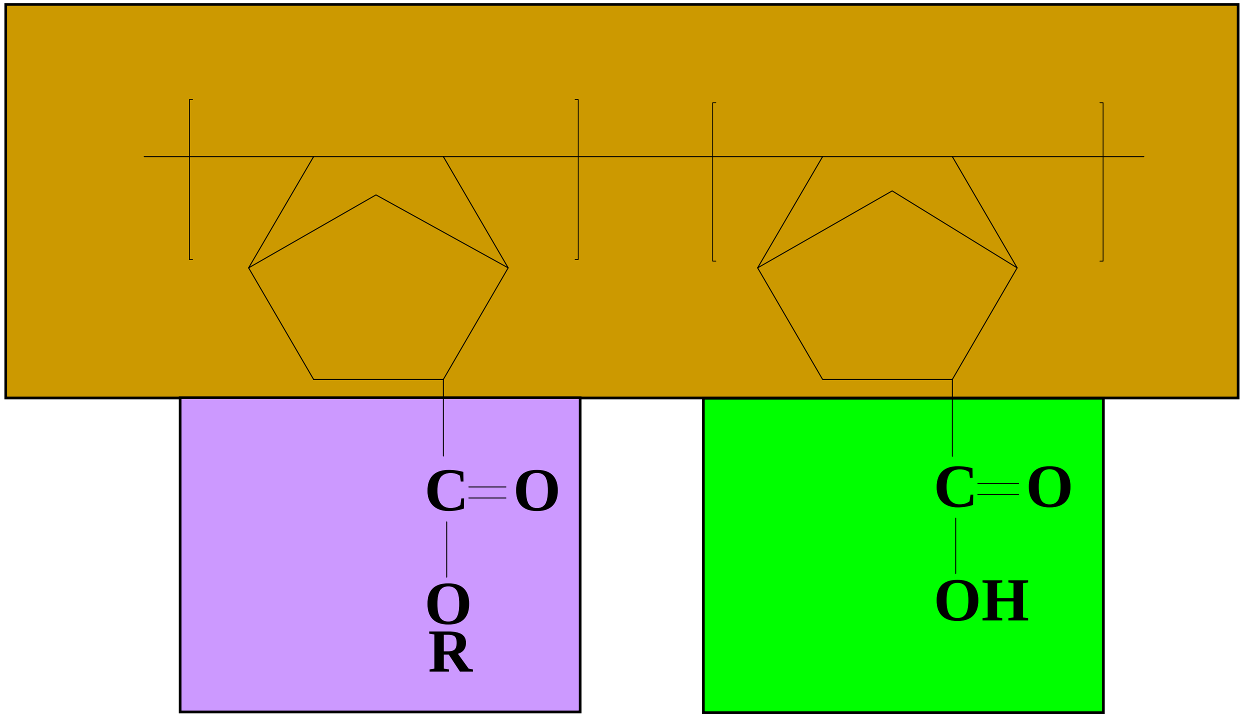
“Etch Resistance”

The Need for Polymers with High C:H Ratios

- **Etch rate is inversely proportional to the carbon to hydrogen ratio of the polymer.**
- **This observation leads to polymers containing aromatic or cyclic structures.**

Structure:				$CH_3(CH_2)_nCH_3$
Formula:	C_6H_6	$C_{12}H_{16}$	C_7H_{10}	C_nH_{2n+2}
C/H:	1	0.75	0.7	0.25

Typical Design Example

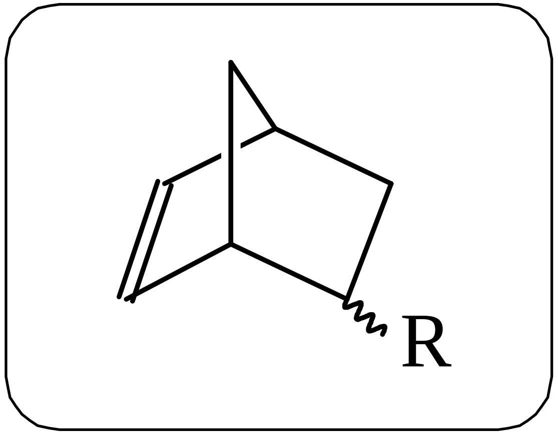


Tethering Function, Etch Resistance, Mechanical & Thermal Properties

Acid Lability

Base Solubility

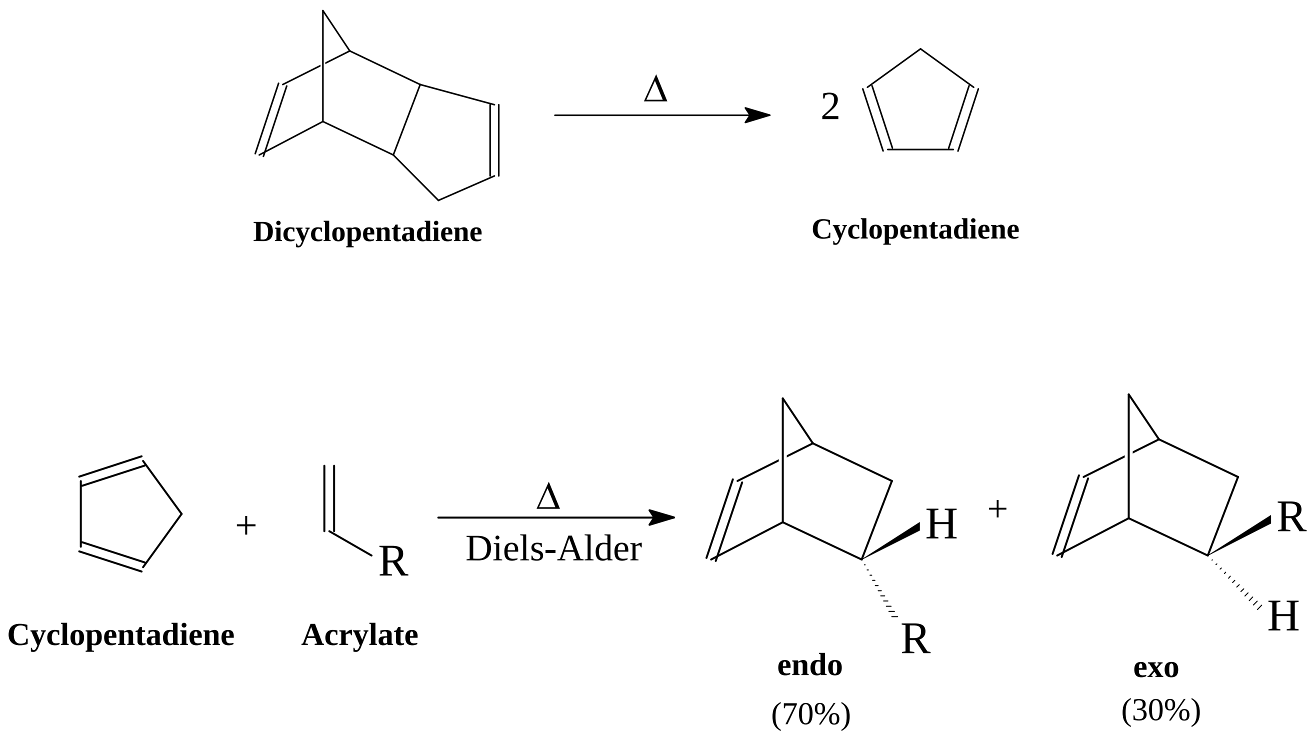
How About Alicyclic Compounds ?



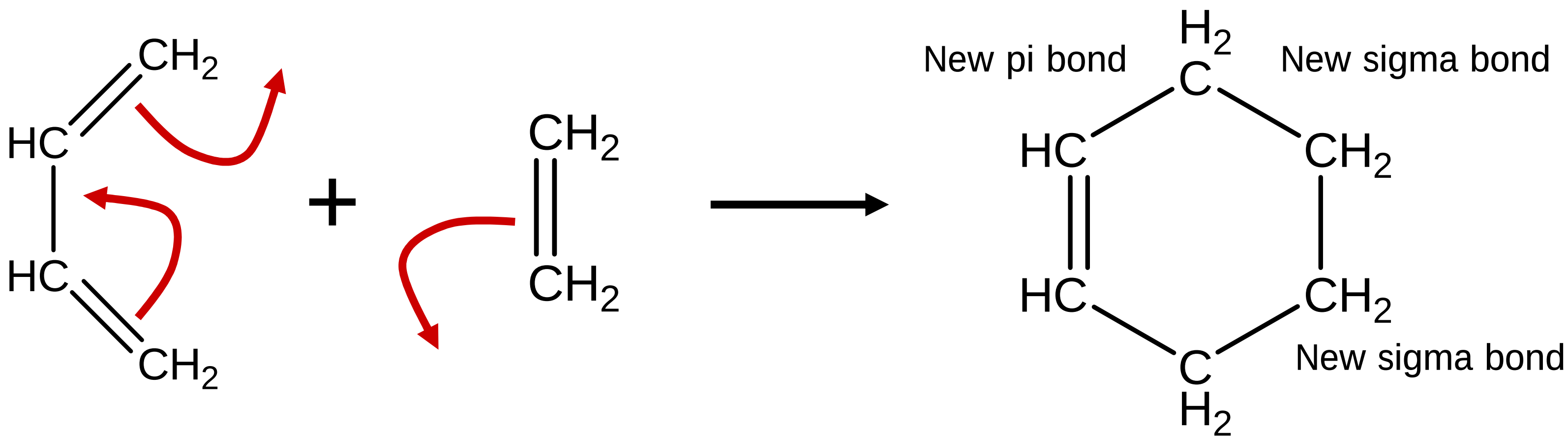
* No aromatic groups ➡ High transparency at 193 nm

* High Carbon/Hydrogen ratio ➡ Good etch resistance

Monomer Synthesis



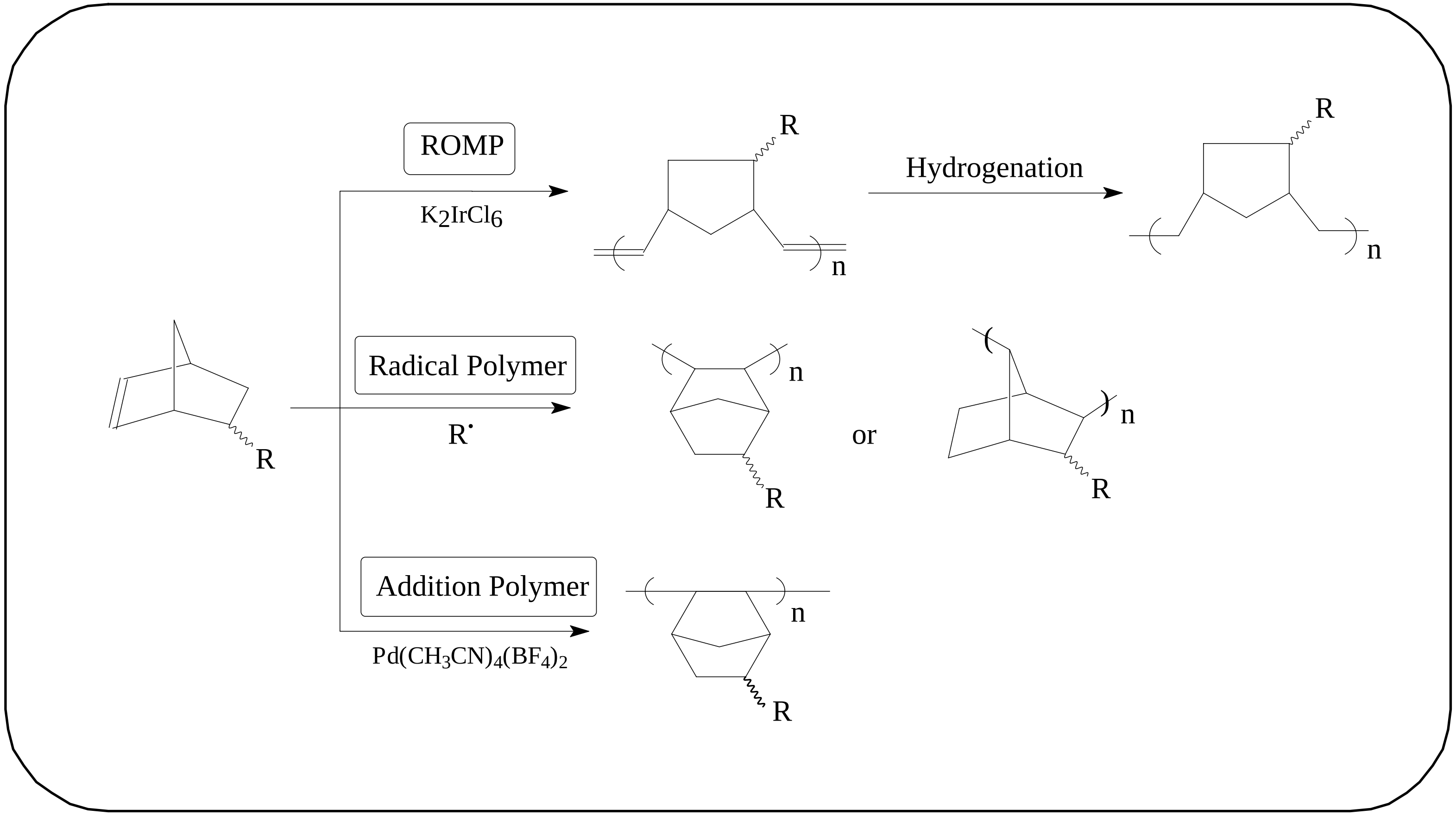
Diels-Alder Reaction



1,3-butadiene ethylene cyclohexene

3개의 pi 결합이 2개의 sigma 결합과 1개의 pi 결합으로 전환되었다!!!

Pathways to Polymerization



Addition Polymerization

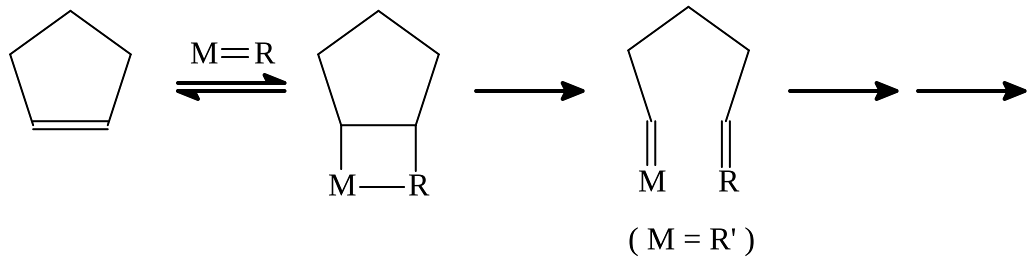
* Advantages

- High Thermal Stability
- Excellent Storage Stability

* Disadvantages

- Metal Contamination
- Low Yield

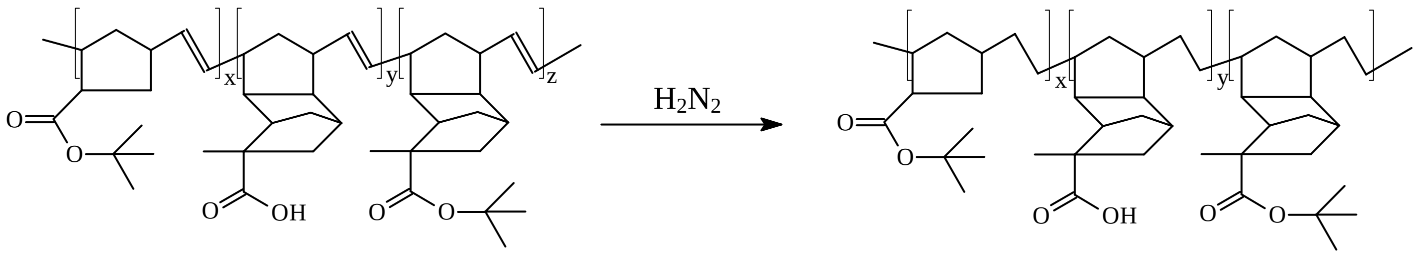
ROMP (Ring Opening Metathesis Polymerization)



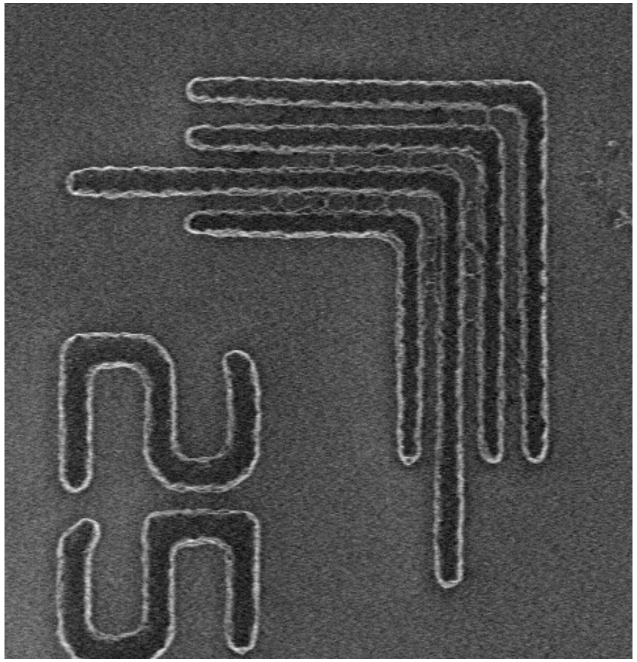
* Chain Polymerization Mechanism

* Driving Force is Release of Ring Strain

*** Example ***



Lithographic Performance of ROMP Polymers



* Advantages

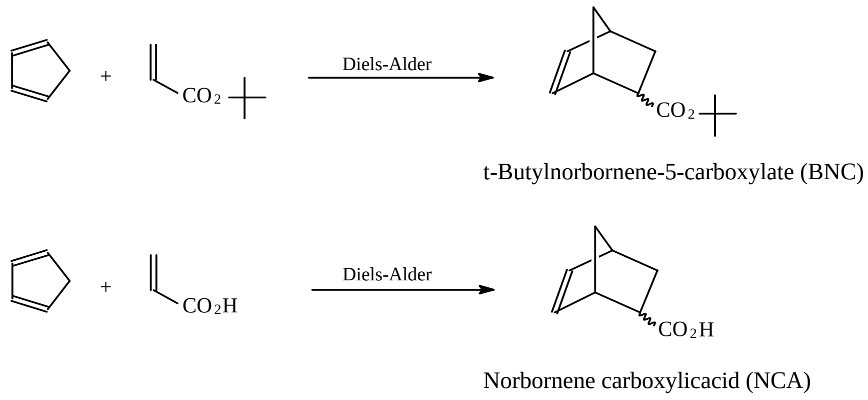
- Good transparency at 193nm
- High yield and controllable MW

* Disadvantages

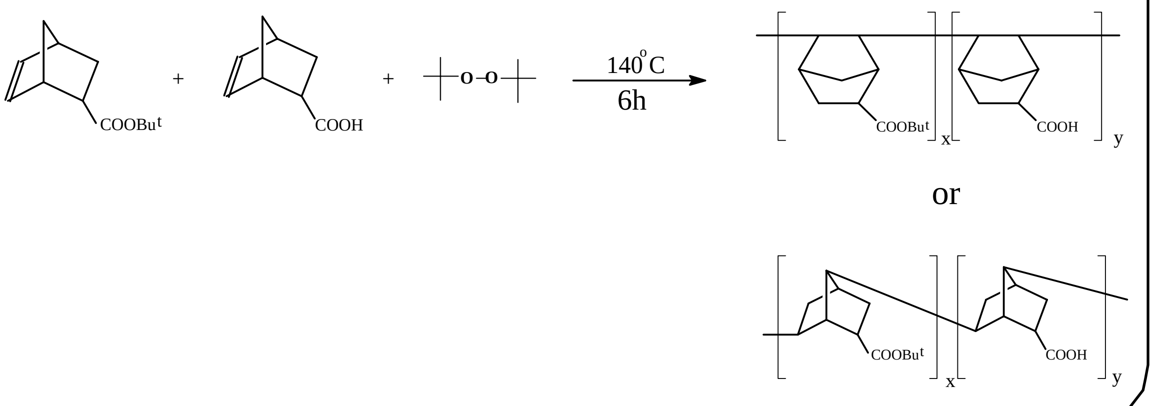
- Synthetic cost
- Phase separation with common PAGs
- Very dilute developer concentration
- Adhesion problem limit resolution

Radical Copolymerization

Monomer preparation :

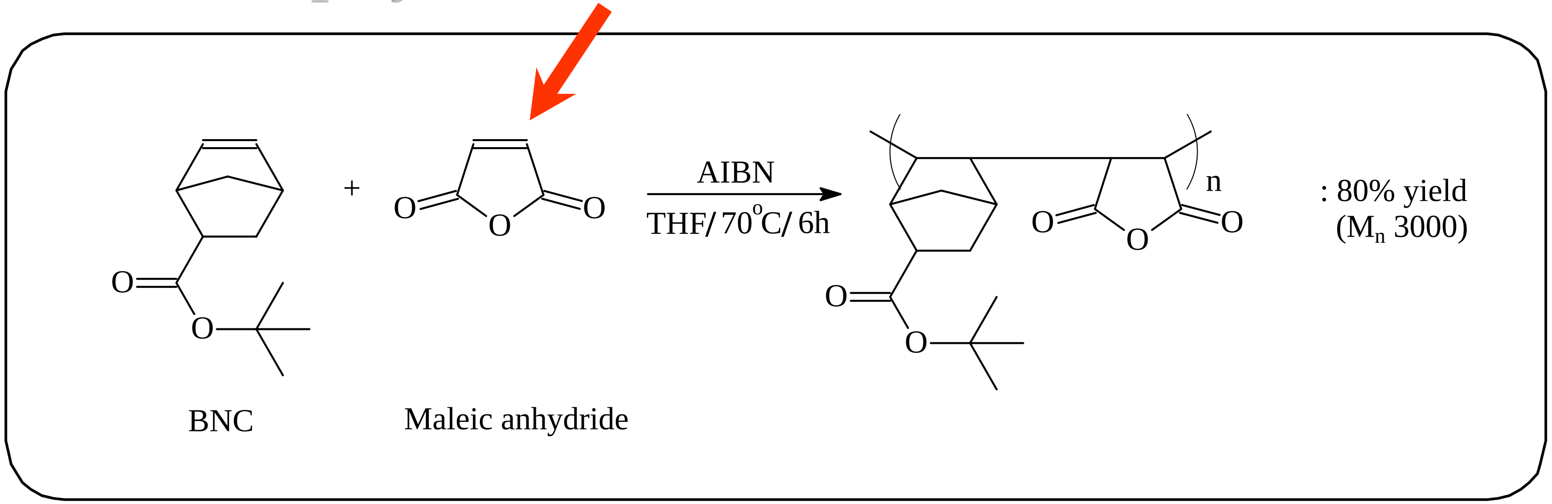


Polymerization :

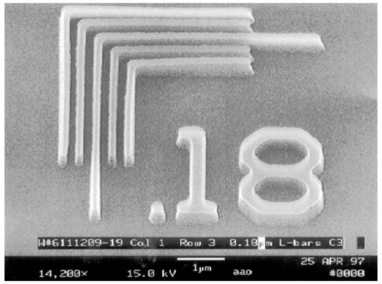


Improving Adhesion

BNC-MA copolymer



- Increasing polarity with MA to improve adhesion

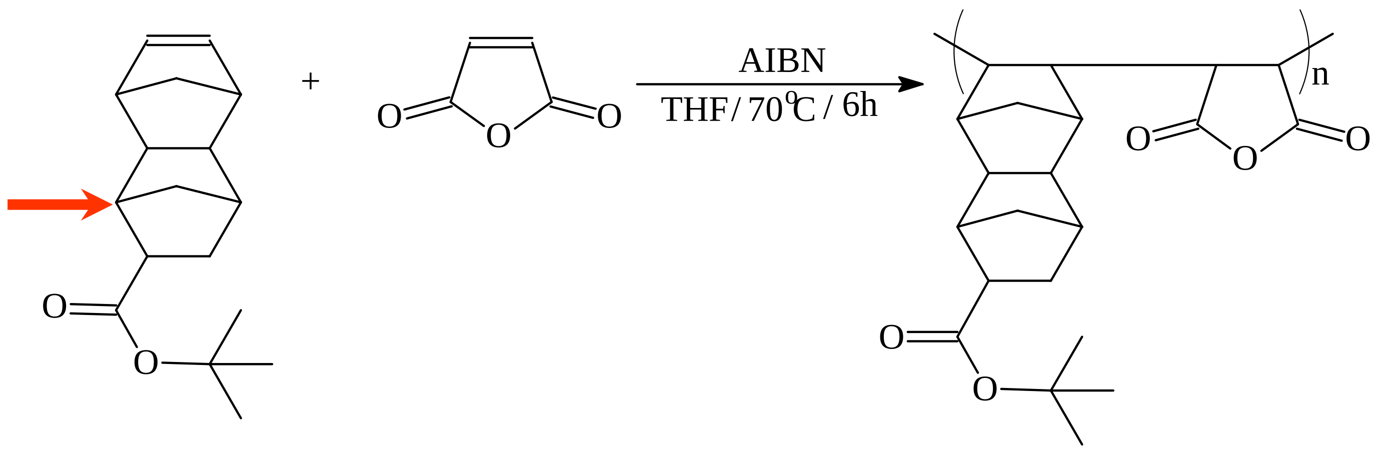


<Problem>

- Poor etch resistance

Improving Etch Resistance

DBNC-MA copolymer



: 40% yield
(M_n 3000)

DBNC

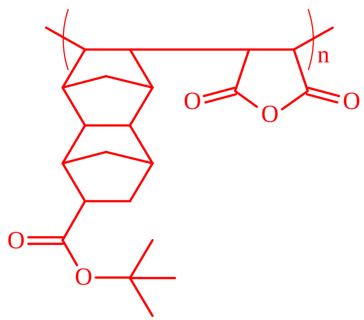
Maleic anhydride

- Enhancing etch resistance

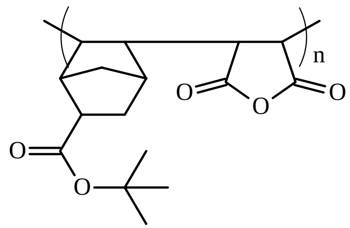
Result (etch data)

	DBNC-*alt*-MA copolymer	BNC-*alt*-MA copolymer	APEX-E
Rate (A/min)	453	633	603
Relative Rate	0.76	1.05	1.00

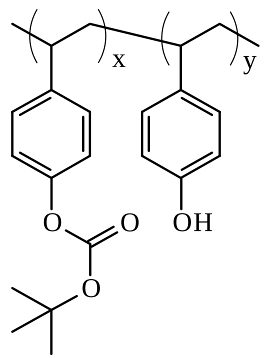
DBNC-*alt*-MA



BNC-*alt*-MA



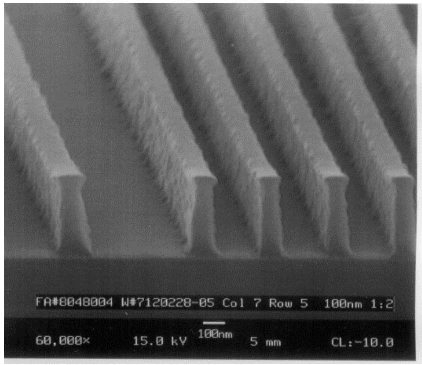
APEX-E



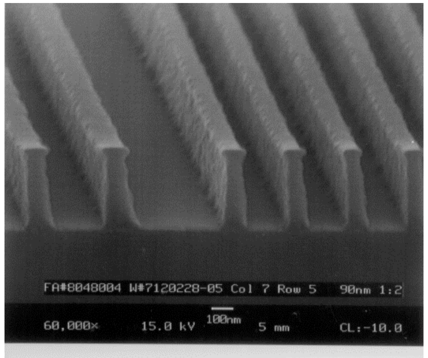
Takechi, S. Takahashi, M.; Kotachi, A.; Nozaki, K.;
Yano, E.; Hanyu, I.; *J. Photopolym. Sci. Technol.*, **1996**, 9(3), *475*.

Result (SEM)

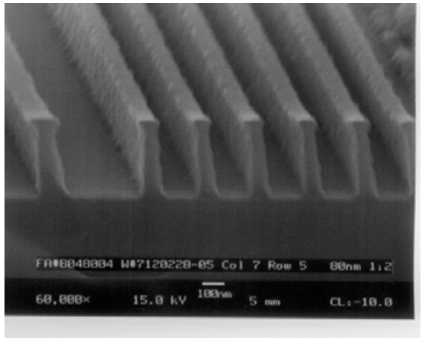
100nm Lines



90nm Lines



80nm Lines



!!!

Mid-Summary

1. <u>Addition Polymers</u>
   - thermal and storage stability
   - metal contamination and low yield
2. <u>ROMP Polymers</u>
   - excellent transparency and storage stability
   - capable of resolving 0.25μm features
   - require non-standard developer
3. <u>Radical Polymers</u>
   - alternating copolymers
   - capable of resolving 80 nm features
   - exhibit etch resistance higher than conventional resists

Chemically Amplified Resists for F_2 Excimer laser Lithography

- ✓ Resolution : < 70 nm
- ✓ Absorbance : < 2.0 /μm
- ✓ Sensitivity : < 30 mJ/cm^2

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157 nm Photoresist

Problem of the Transparency

- ✓ Solid state absorbance of photons in the 130 to 180 nm range (approximately 7 to 10 eV) is still dominated by valence band electronic transitions.
- ✓ Many "common" chemical bonds are sufficiently absorptive to lead to efficient exicitation of the polymer matrix.
- ✓ The 157 nm absorption is dominated by C(2p) electrons, whose absorption band edge is very close to 157 nm, and whose transition probability can be dramatically affected by the chemical bonding environment.

➡ C-F bonds are transparent at 157 nm !

Photon absorption Characteristics of several ground state electrons

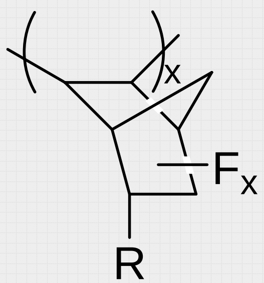
Electron	Chemical bond type	Binding energy (eV)	Band edge (nm)	157
C(1*s*)	Any	282–294	<4.4	
C(2*s*)	Any	12–25	<100	
C(2*p*)	Any	2–10	Varies	x
	C(2*p*)-F(2*p*)	10	<124	
	➡ C(2*p*)-H(1*s*)	7.5	<165	x
	C(2*p*)-O(2*p*)	7	<180	x
	C(2*p*) (benzene)	5.3	<240	x
	C(2*p*) (anthracene)	2.7	<450	x
	C(2*p*) (graphite)	2	<600	x
O(2*s*)	Any	23	<54	
F(2*s*)	Any	30	<41	
F(2*p*)	Any	10	<124	

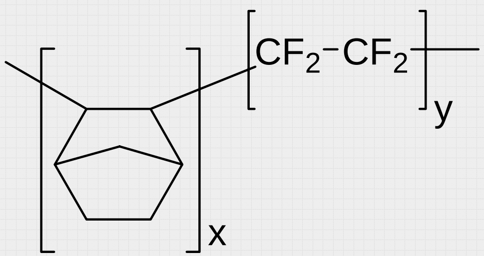
Absorption Coefficients at 157nm

Polymer	A (μm^{-1})	L(OD=0.4) (nm)
Si- O BACKBONE		
Poly(hydrosilsesquioxane)	0.06	6667
Poly(dimethylsiloxane)	1.61	248
Poly(phenylsiloxane)	2.68	149
CARBON BACKBONE		
Fluorocarbon, 100% fluorinated	0.70	571
Hydrofluorocarbon, 30% fluorinated	1.34	298
Partially esterified hyrofluorocarbon, 28%fluorinated	2.60	154
Poly(vinyl alcohol) (99.7%)	4.16	96
Fully esterified hydrocarbon, 31% fluorinated	4. 56	88
Ethyl cellulose	5.03	80
Poly(methylmethacrylate)	5.69	70
Polynorbornene	6.10	66
Polystyrene	6.20	64
Poly(vinyl phenol)	6.25	64
Poly(norbornylmethacrylate)	6.67	60
Poly(adamantylmethacrylate)	6.73	59
V1.0 acrylic terpolymer resin	8.20	49
Poly(chlorostyrene)	10.15	39
Poly(acrylic acid)	11.00	36

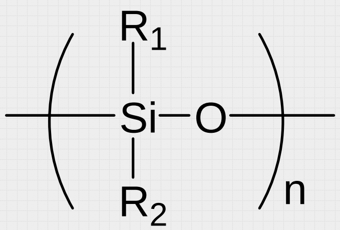
Backbone of the 157 nm Photoresist

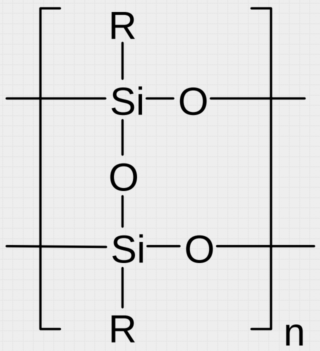
Hydrofluorocarbon





Functionalized Siloxane/Silsesquioxane





Problems of Materials

Hydrofluorocarbon Materials

- Difficulty with regard to aqueous base solubility
- Reduction of adhesion
- Difficulty of synthesis

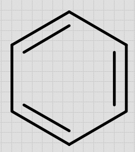
➡ Incorporation of fluorine into a resist must be done only in limited fashion

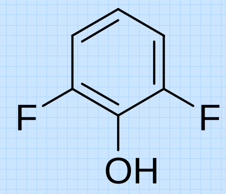
Siloxane/ Silsesquioxane Materials

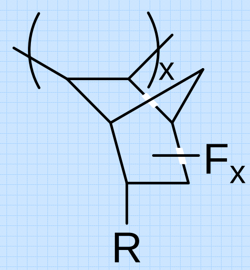
- Low T_g of siloxane
- Solubility of silsesquioxane

Etch Resistance

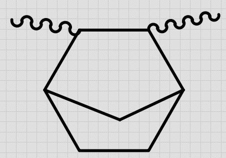
Aromatic compound

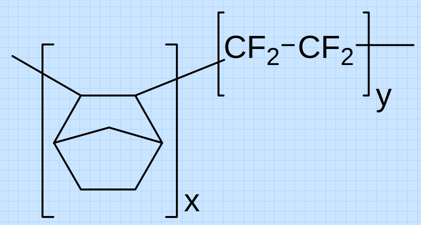




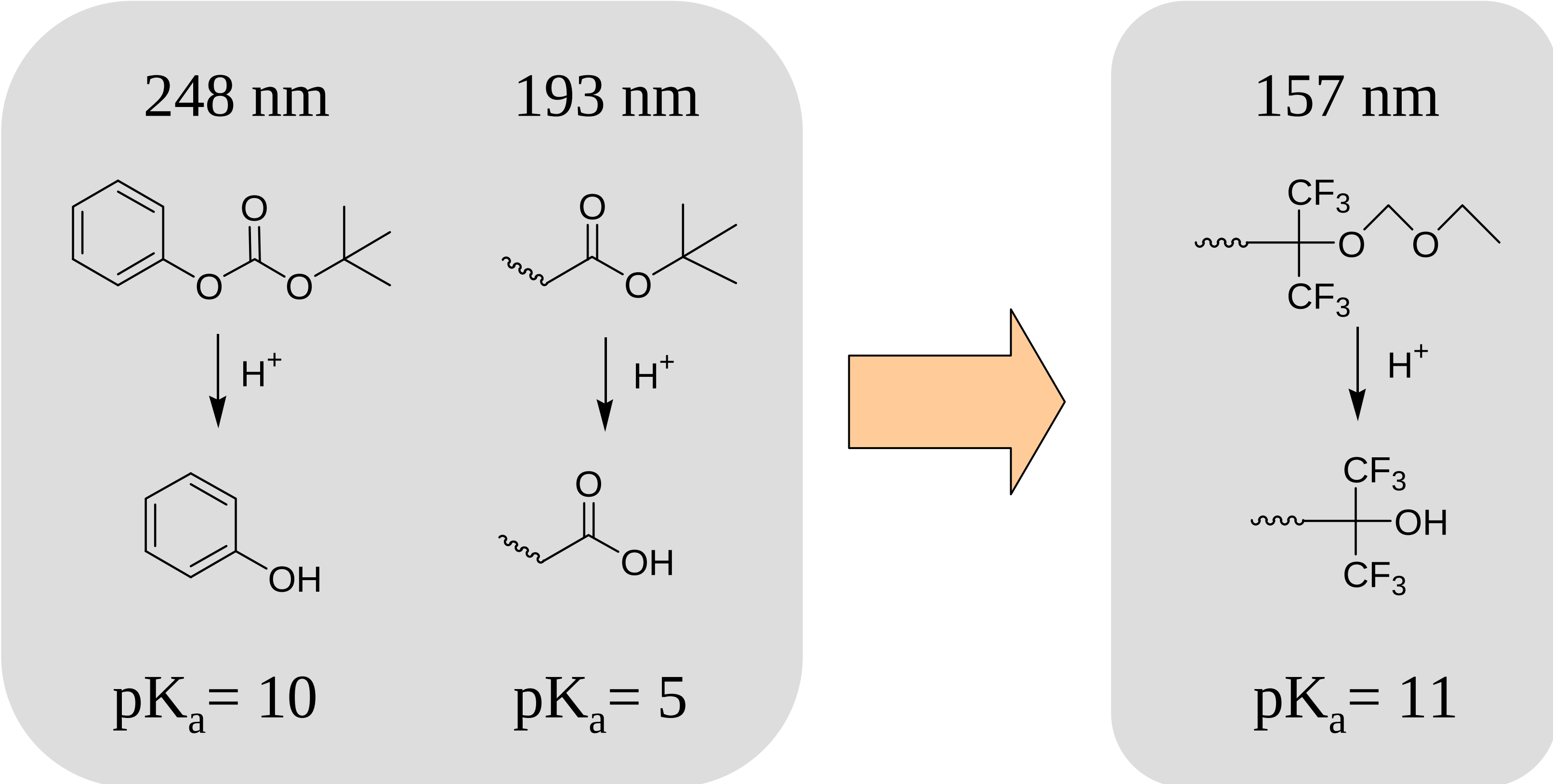


Alicyclic compound

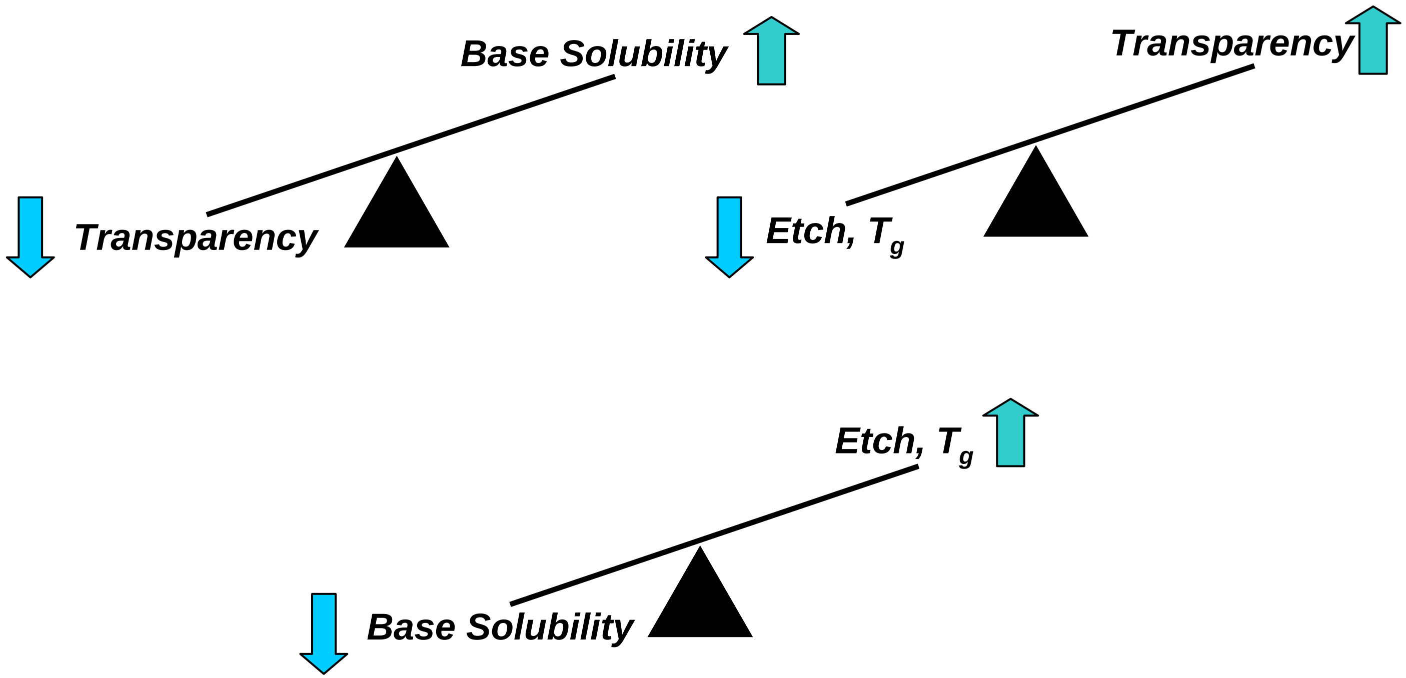




Protecting Group



Balancing photoresist properties at 157 nm



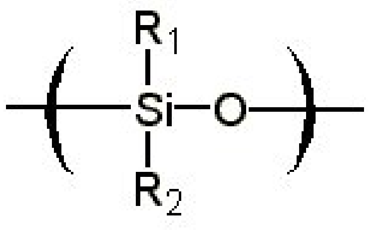
Approach to Design of Photoresist polymer

Patterson, *Proc*, SPIE **3999**, 365 (2000)

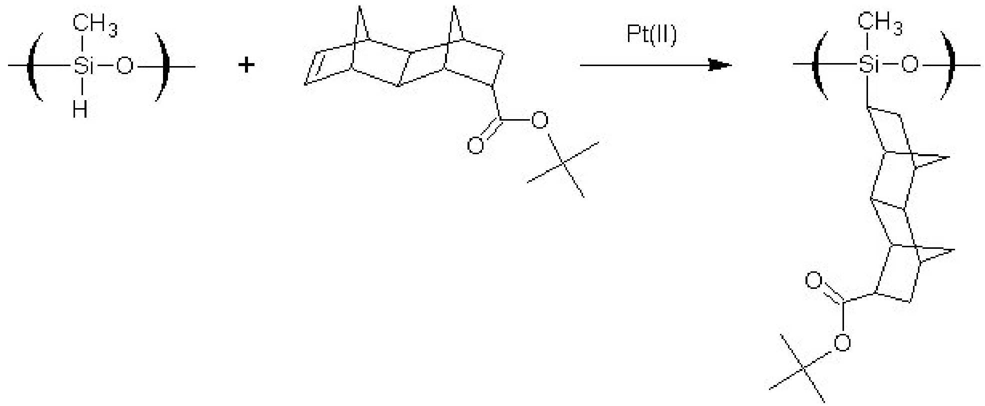
Backbone — Etch Resistance — Developer Solubility — Protecting Group

Transparency

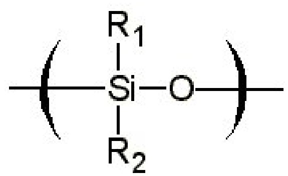
Siloxanes



R_1	R_2	Tg/°C
CH_3	H	-138
CH_3	CH_3	-125
CH_3	Phenyl	-90 to -75
CH_3	CH_2CH_3	-135
CH_3	$CH_2CH_2CH_3$	-120
CH_3	$CH_2CH_2CF_3$	-70
Phenyl	Phenyl	50 to 100

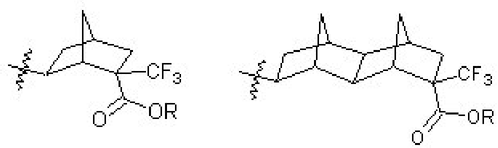


(T_g~ 90℃)



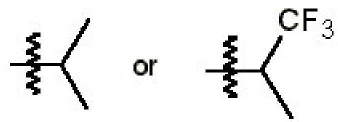
R_1

One of our transparent norbornene or dinorbornene monomers, eg.



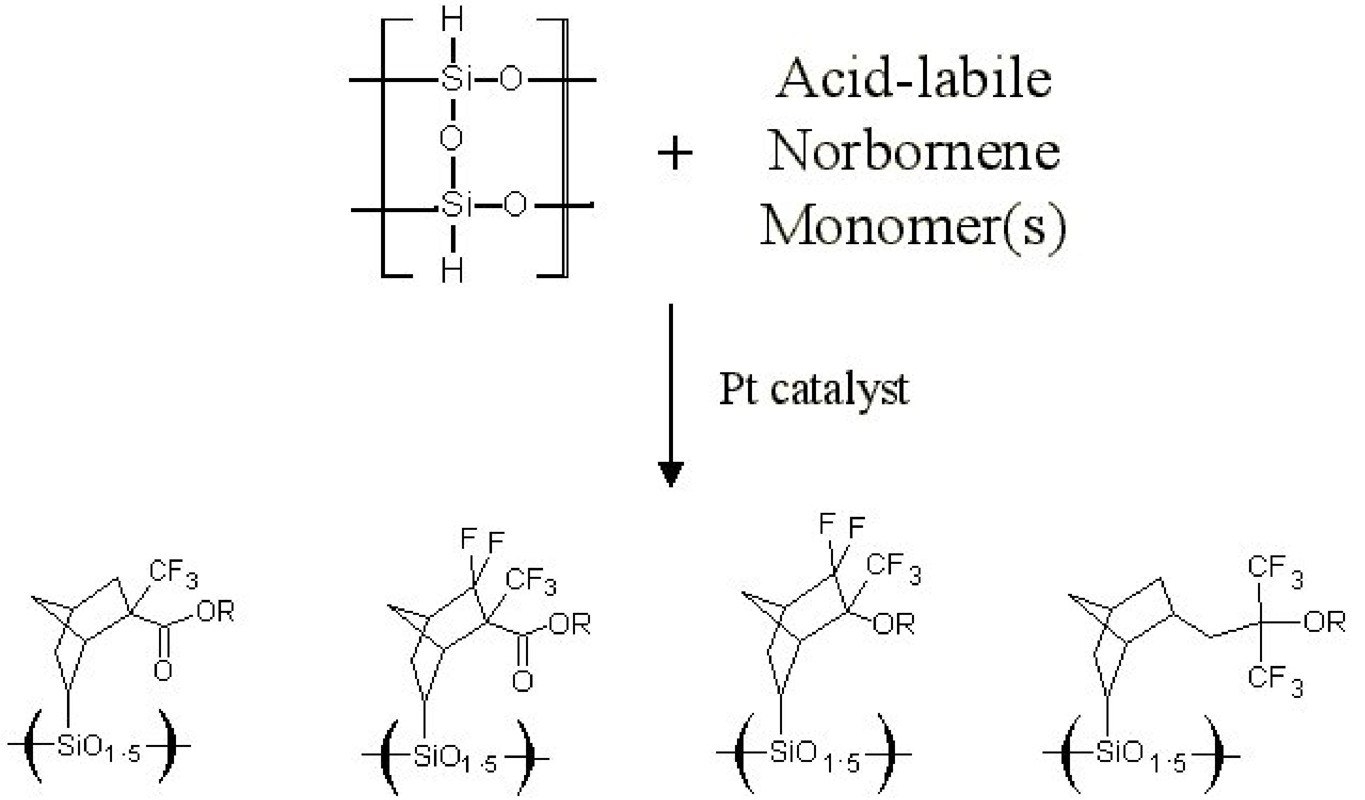
R_2

Substituent that imparts both transparency and high Tg characteristics, eg.



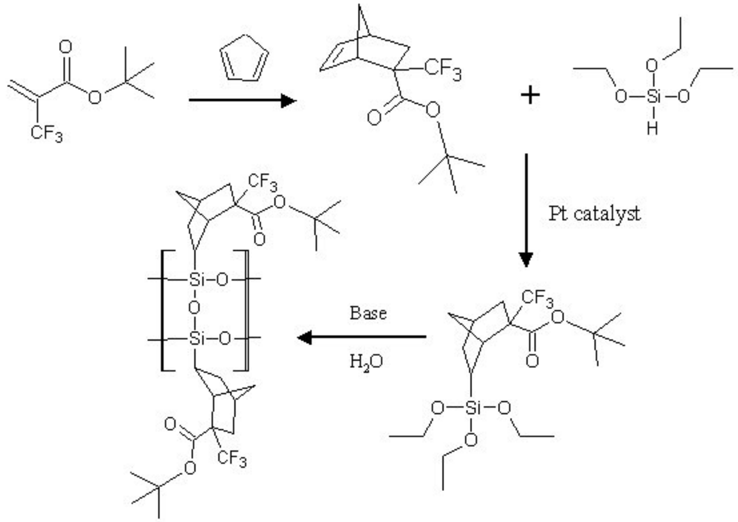
Fluorinated, high T_g polysiloxane

Silsesquioxanes

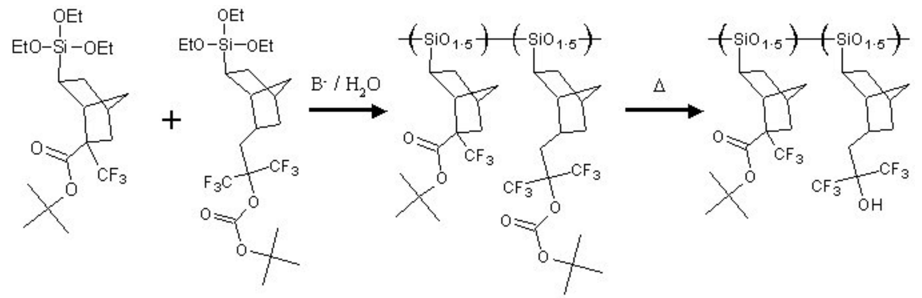


Silsesquioxanes from commercially available hydridosilsesquioxane

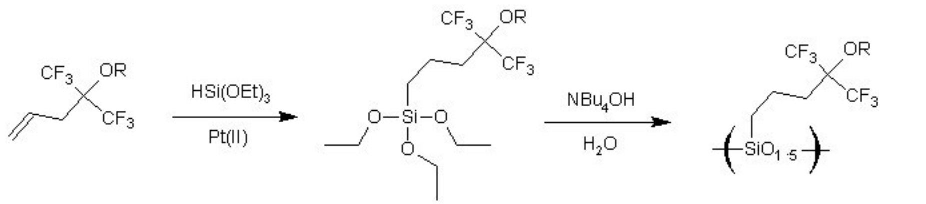
Silsesquioxanes



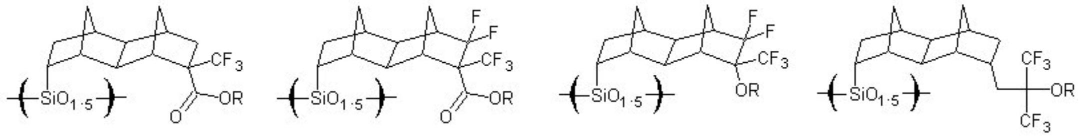
A silsesquioxane copolymer (for better adhesion, higher Tg)



Synthesis of an acid-labile, transparent silsesquioxane



A silsesquioxane from protected allylhexafluoroalcohol

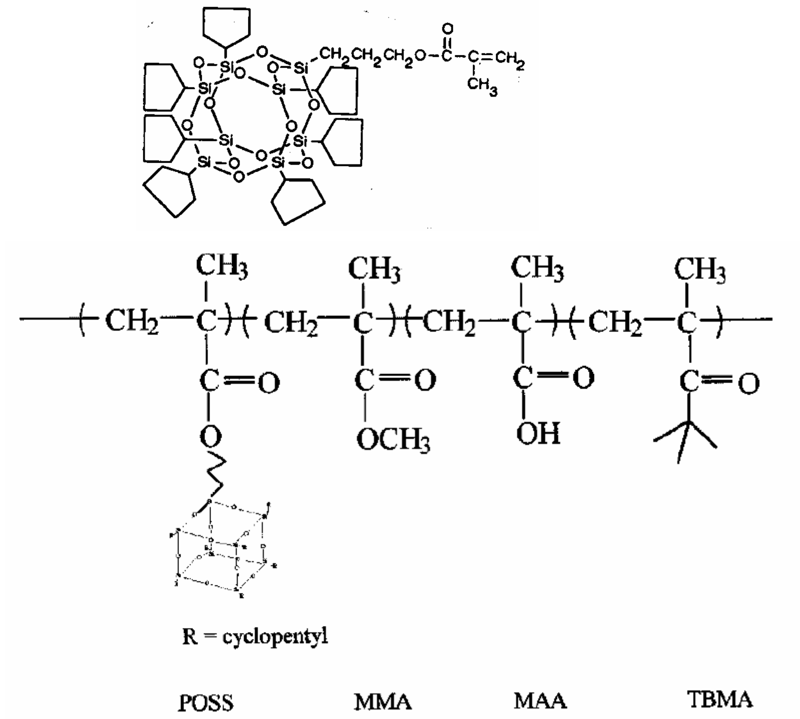


Dinorbornyl silsesquioxanes

Silsesquioxanes

Incorporation of polyhedral oligosilsesquioxane (POSS) in chemically amplified resists to improve their reactive ion etching resistance

- *Hengpeng Wu, M. J. Yacaman, J. Vac. Sci. Technol. B 19(3), **2001**, 851-855*



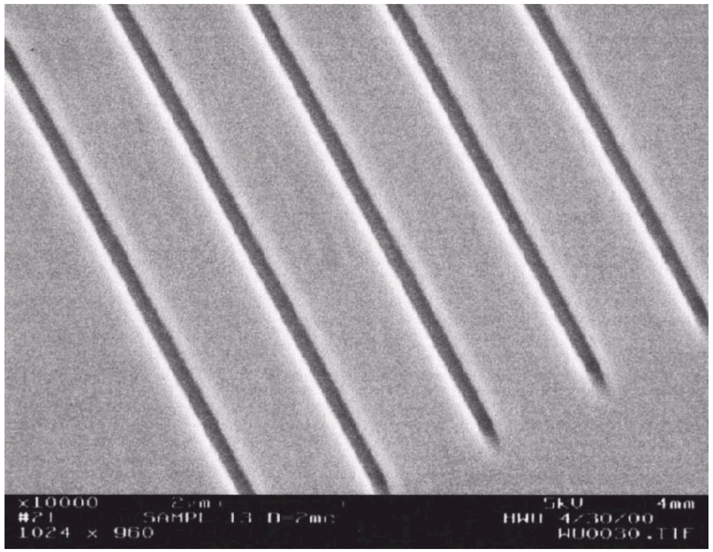
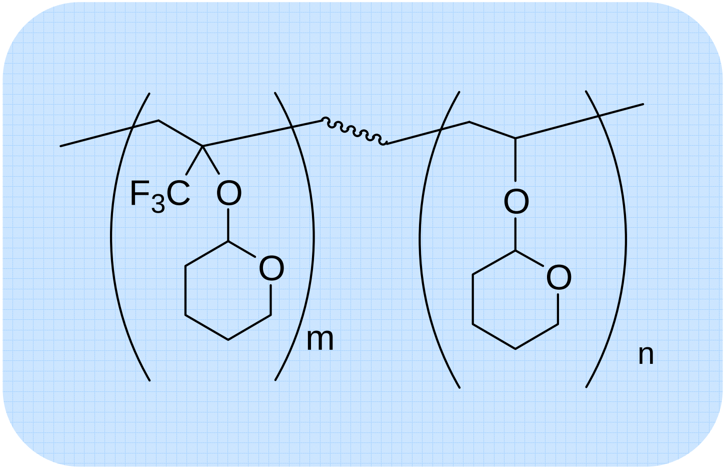
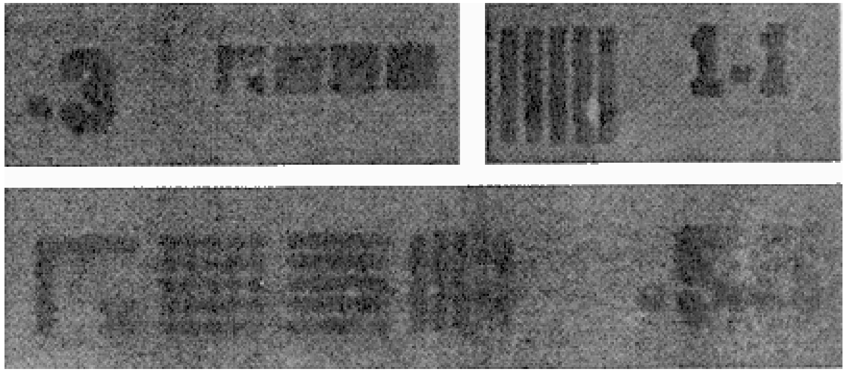


Fig. SEM micrograph of polymers
: Dose: 5 $\mu C/cm^2$; feature dimension: 240 nm

Hydrofluorocarbon Resist

Schmaljohann, *Proc*, SPIE **3999**, 330 (2000)





THP-protected poly(vinyl alcohol-*co*-α-trifluoromethyl vinyl alcohol)

: 0.55 μm pattern (m/n = 55/45)

: max. 70% protection with ATPB (cat.) instead of PTSA