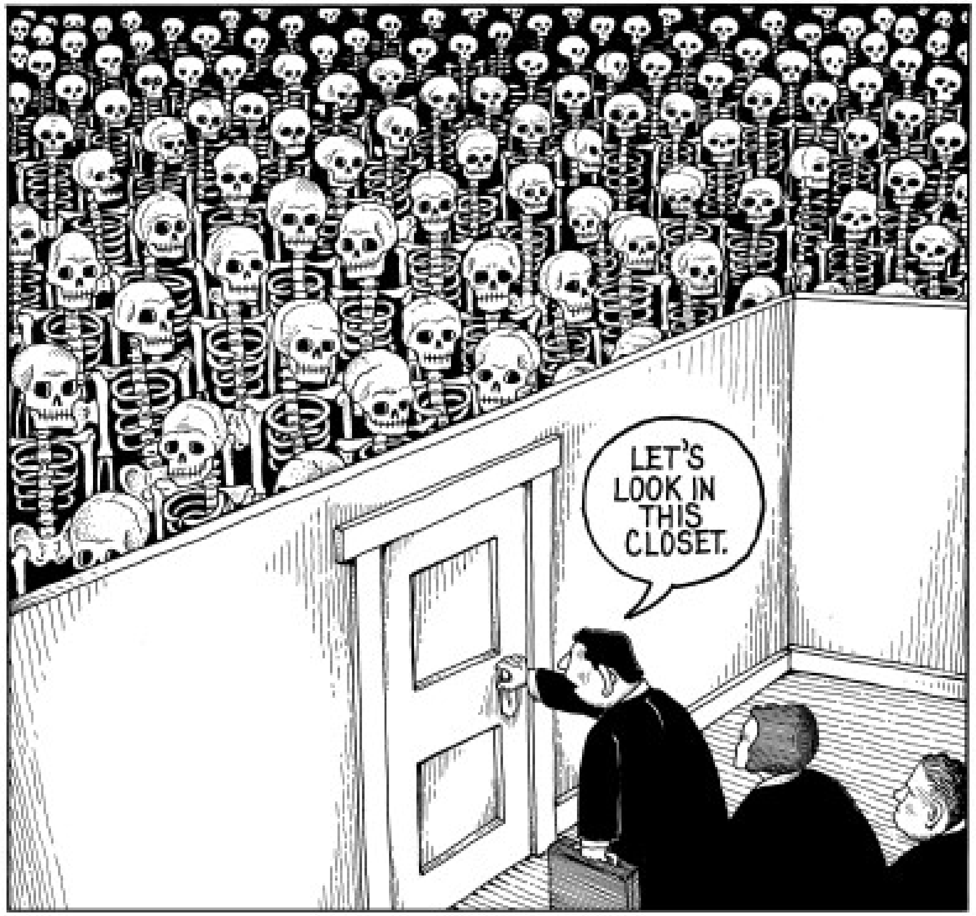
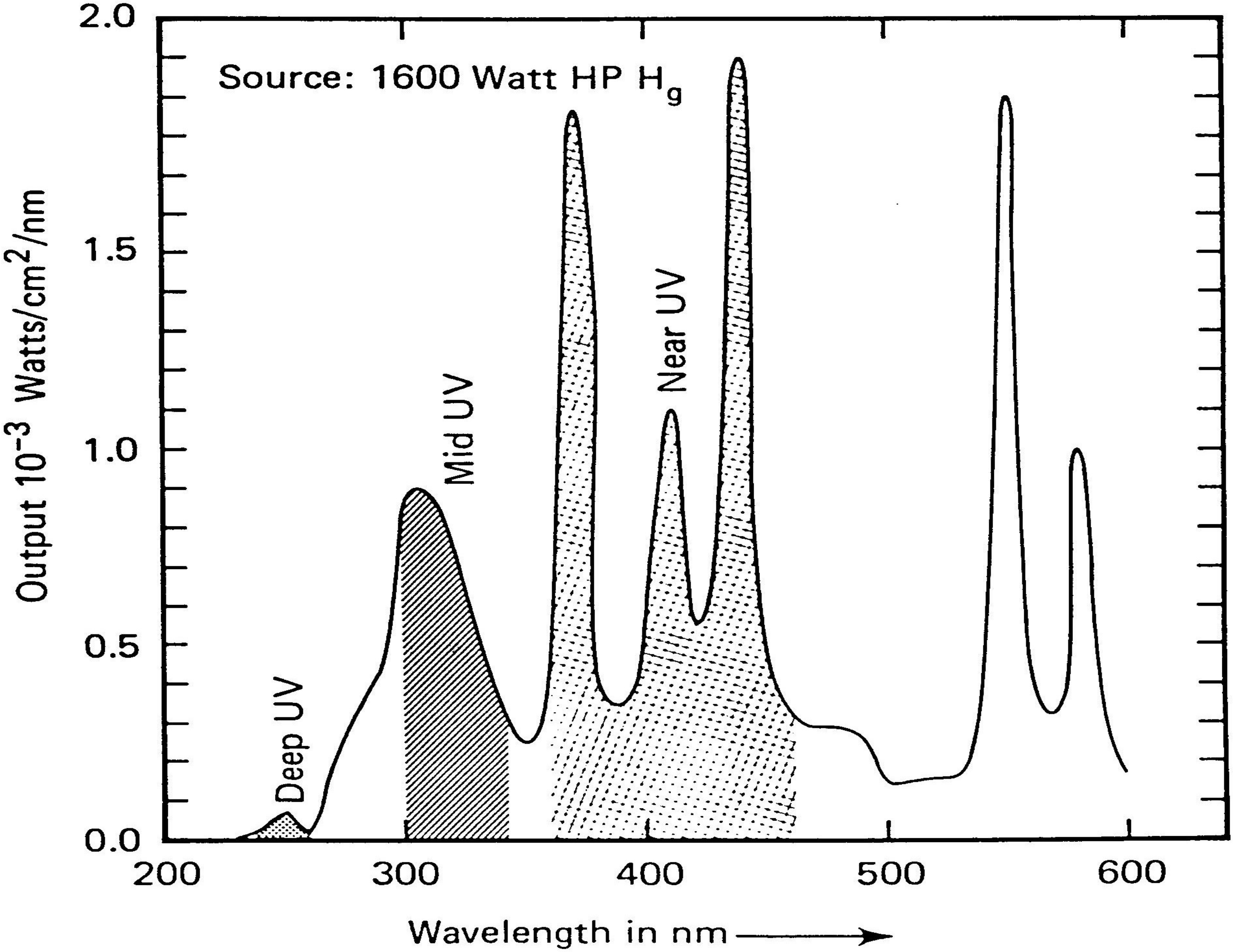
Lecture 14

Chemical Engineering for Micro/Nano Fabrication



Incident Power at the Wafer Plane PE-500



Intrinsic Reactivity — Quantum Yield

$$A \xrightarrow{h\nu} B$$

$$\Phi_A = \frac{\text{Molecules of "A" Consumed}}{\text{Photons of Light Absorbed}} = \frac{\text{Molecules}}{\text{Photon}}$$

$$\Phi_B = \frac{\text{Molecules of "B" Produced}}{\text{Photons of Light Absorbed}}$$

Measurement of Φ Simplified in Solution

1. Solution optically dense so that all incident photons absorbed.
2. Reactions run to low conversion so that rate of light absorption ~ constant
3. Diffusion is rapid in dilute solutions

Measurement More Difficult in Solid State

Diazoquinones $\Phi \sim 0.2 — 0.3$

Bis Azides $\Phi \sim 0.5 — 1.0$

Control of Resist Sensitivity

$$A + XPhotons \longrightarrow B$$

$$\Phi = B / X$$

$$B = [\Phi][X]$$

- Increased Conversion ot Product at Constant Dose Rate Demands:
  - –Increased absorption > X or
  - –Higher Quantum Efficiency > Φ

Chemical Amplification

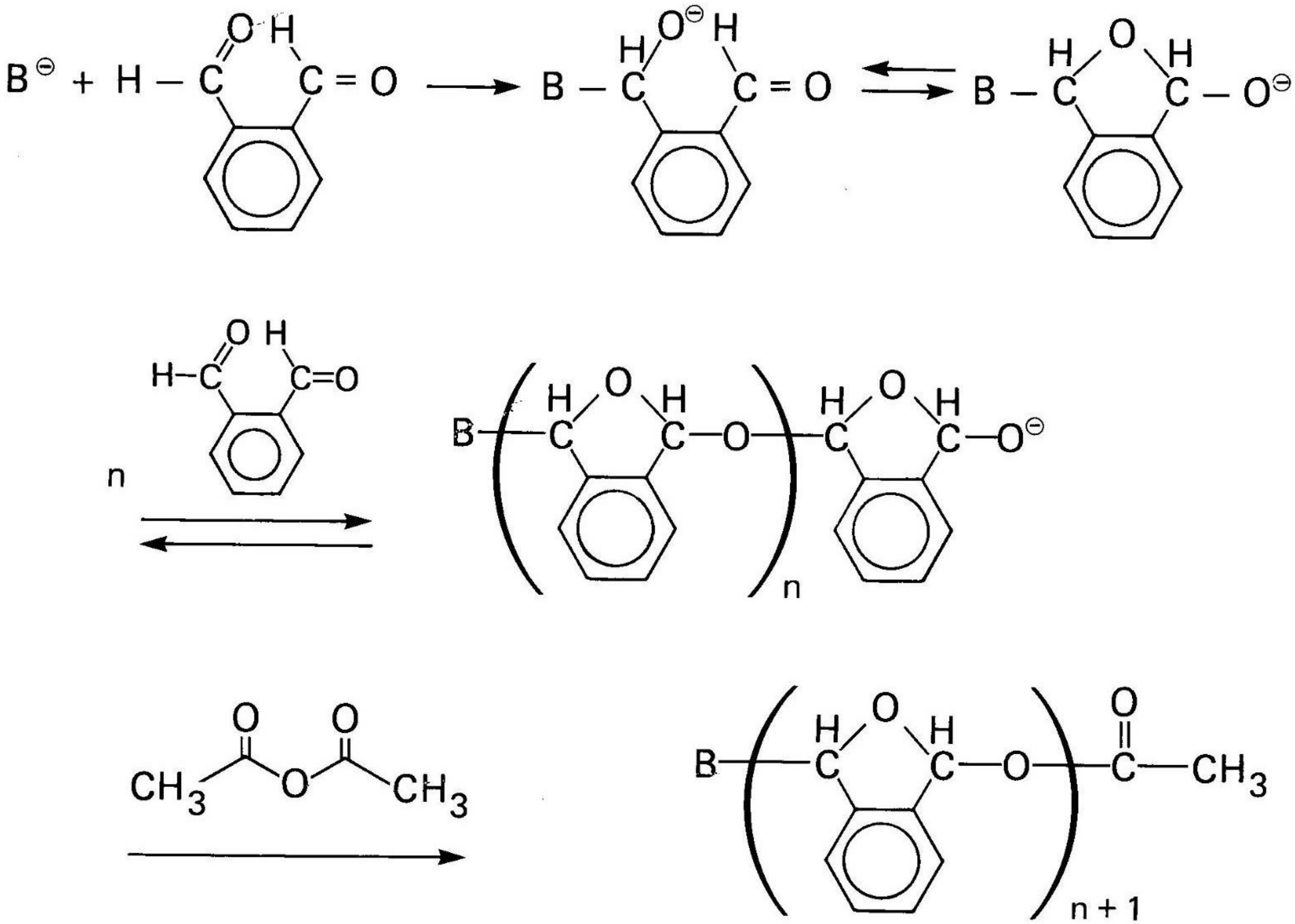
$$\text{Insoluble} \xrightarrow[\Phi < 1]{h\nu} \text{Soluble}$$

Generator

$\downarrow$ $h\nu$ $\Phi < 1$

$$\text{Insoluble} \xrightarrow{\text{Catalyst}} \text{Soluble} + \text{Catalyst}$$

Anionic polymerization of Phthalaldehyde



Ceiling Temperature, T_c

$$\sim\sim\sim\sim M^{\bullet} \quad + \quad M \rightleftharpoons \sim\sim\sim\sim M^{\bullet}_{n+1} \quad + \quad \text{Heat}$$

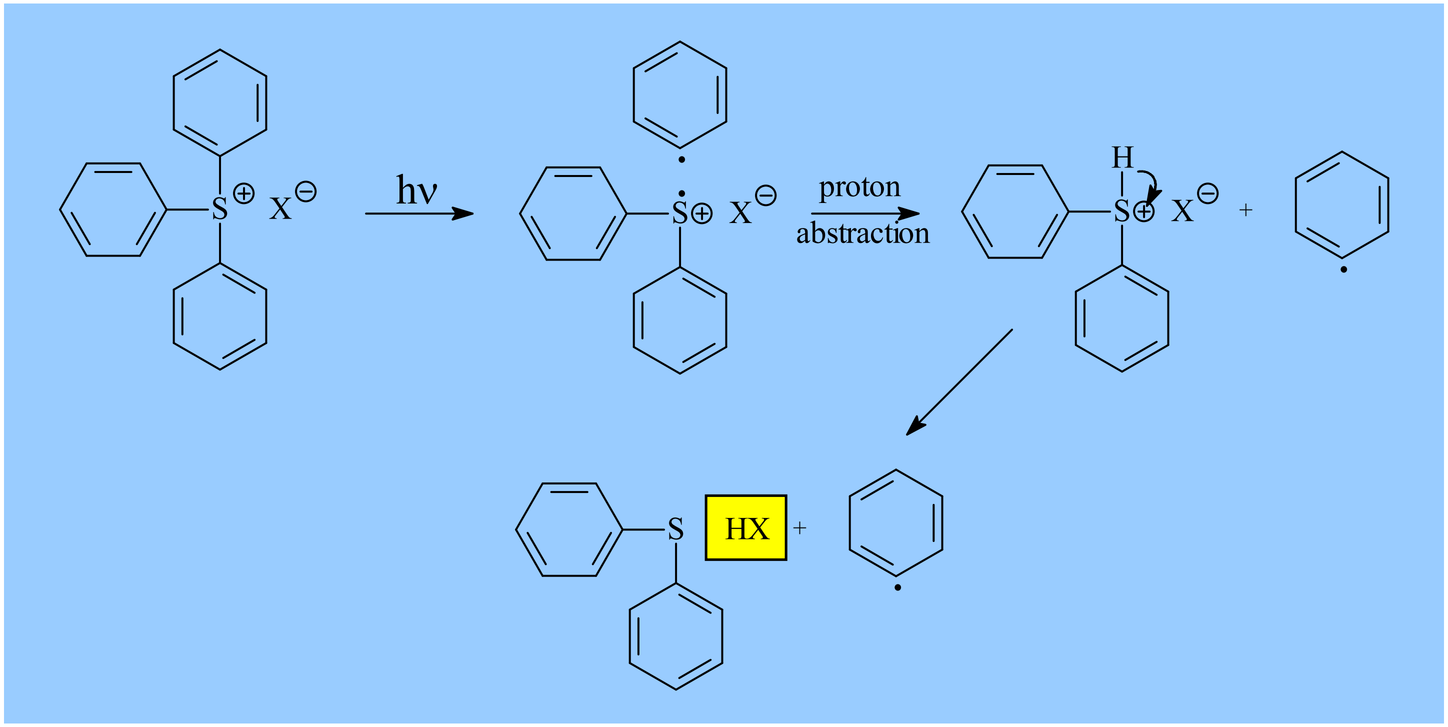
For reversible polymerizations, there is a temperature where the position of the monomer / polymer concentration is at equilibrium, where $\Delta G = 0$.

at equilibrium $\quad \Delta G = 0 = \Delta H - T\,\Delta S$

or, the Ceiling Temperture, $\quad T_c = \Delta H / \Delta S$

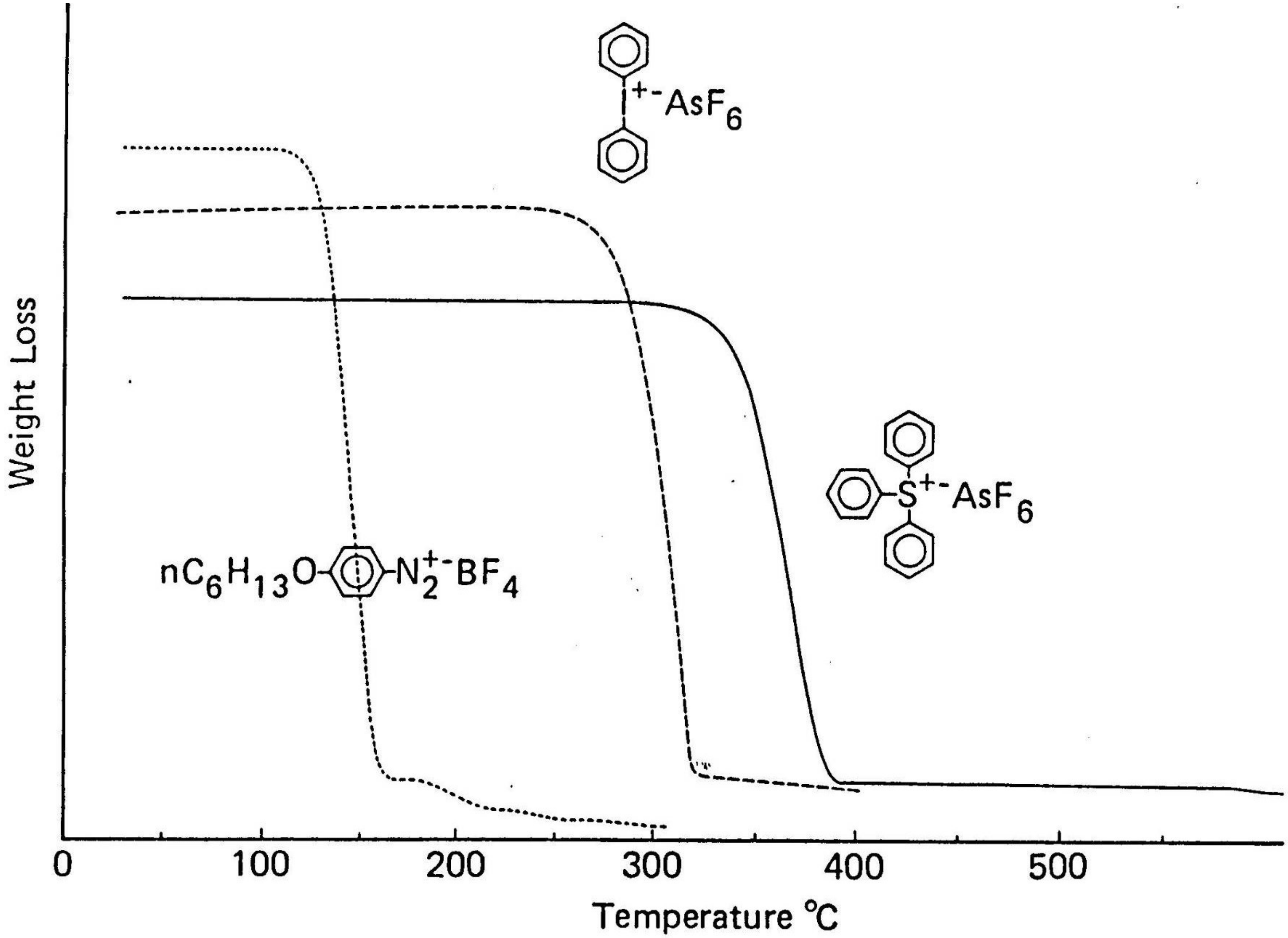
	T_c °C
α-methylstyrene	66
styrene	395

Photoacid Generation Mechanism of Aryl Sulfonium Salts

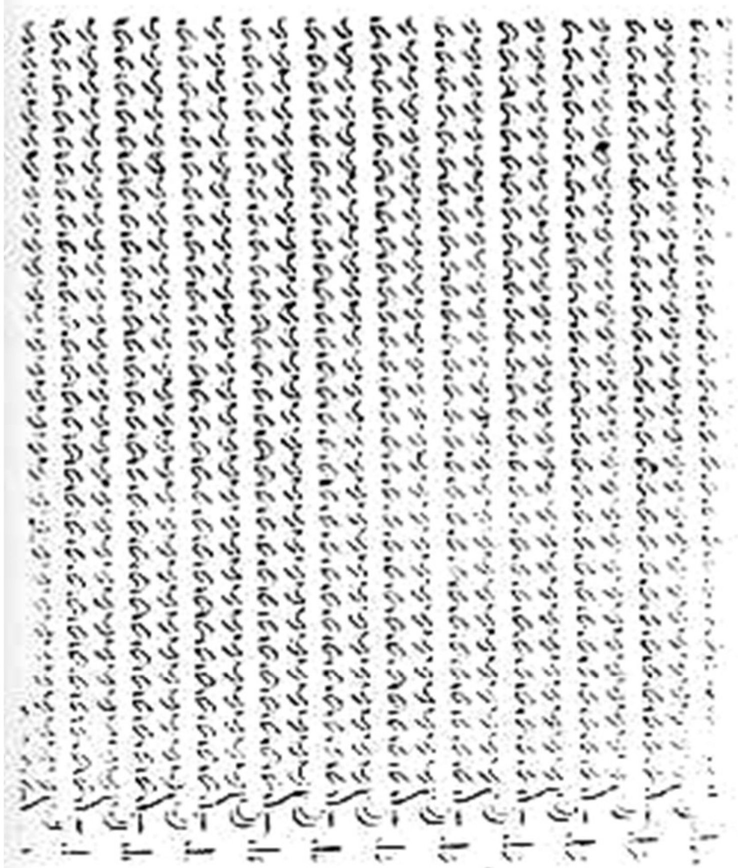


Dektar, J. L.; Hacker, N. P. *J. Am. Chem. Soc.* **1990**, *112*, 6004.

Thermogravimetric analysis of PAGs

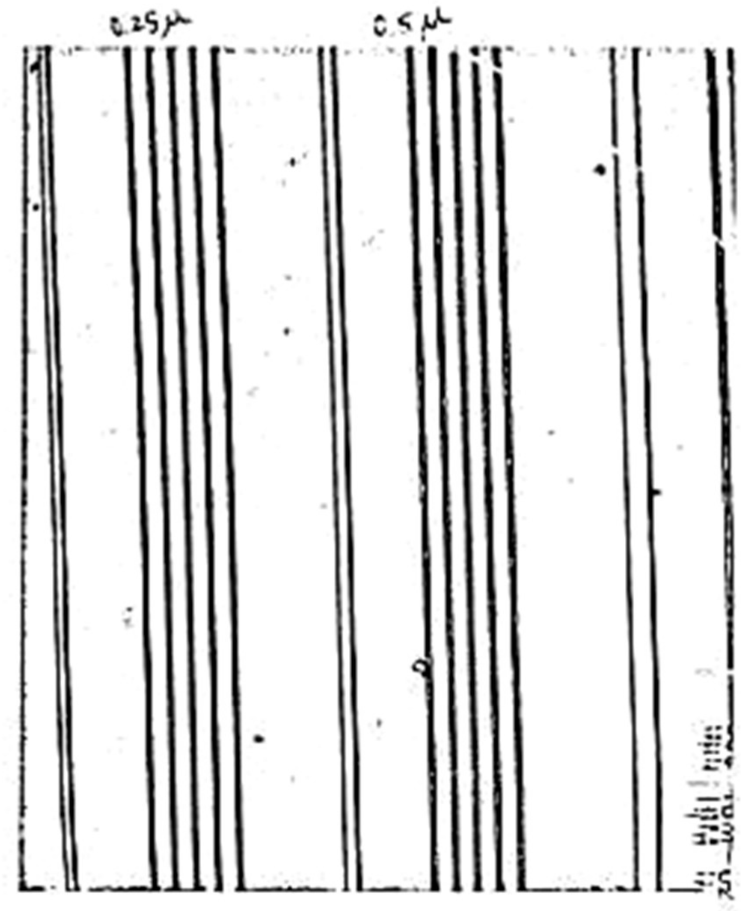


Optical Micrographs of "self-developed" Images in Polyphthalaldehyde



2.4 mj/cm^2 at 254 nm Deep UV Exposure

Minimum Feature 0.75μ

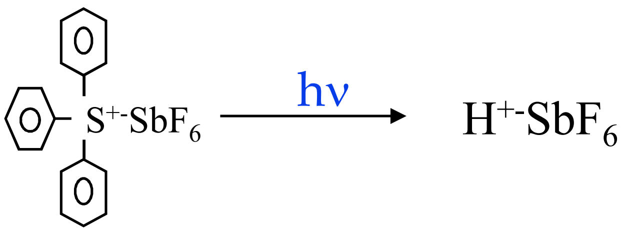


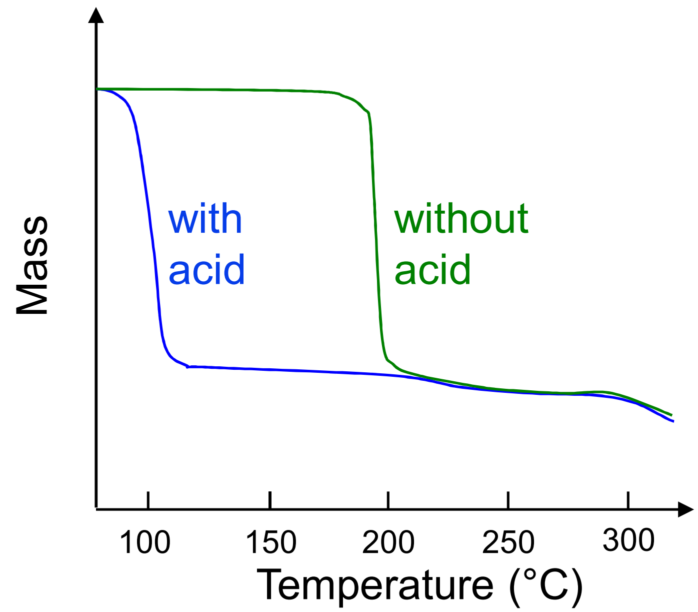
1.0μC/cm^2 e-Beam Exposure

Minimum Feature 0.25μ

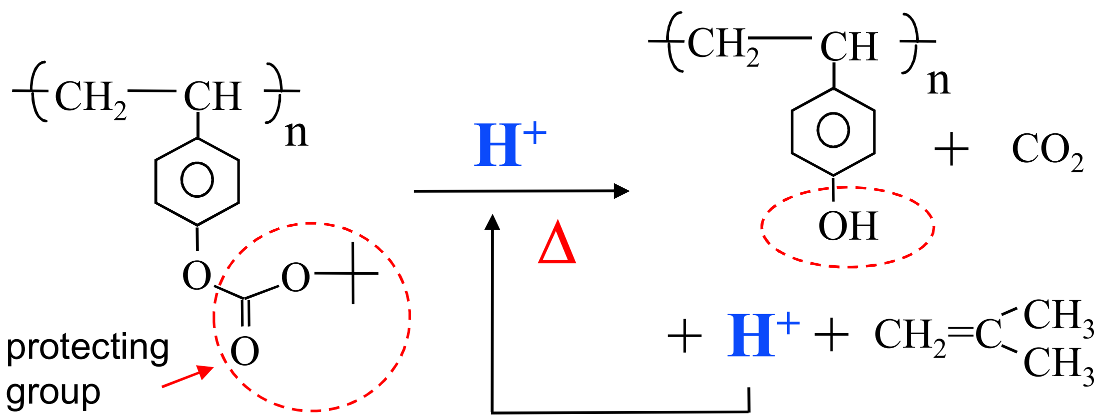
Chemically Amplified Deep UV Resists

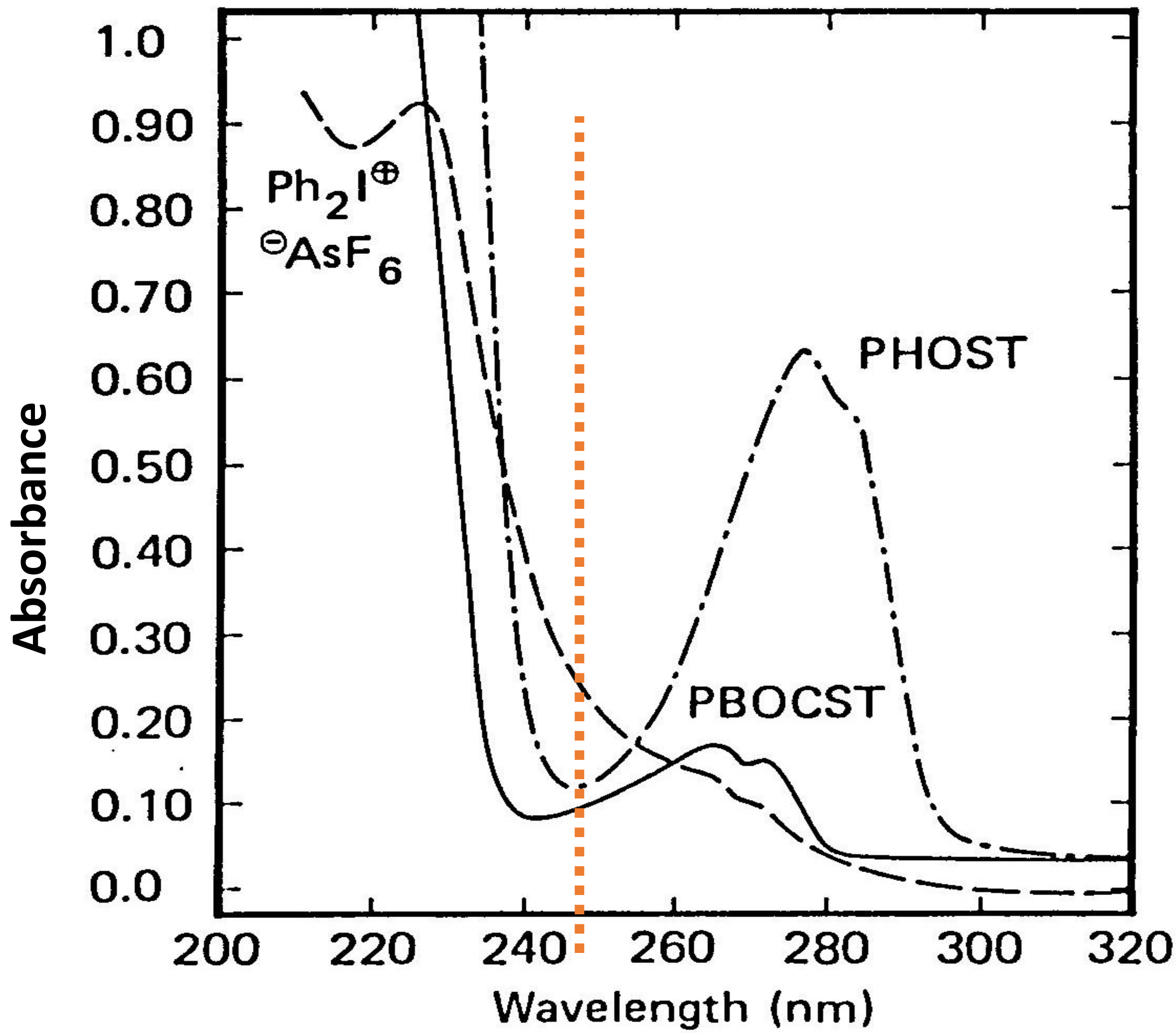
Photoacid Generation

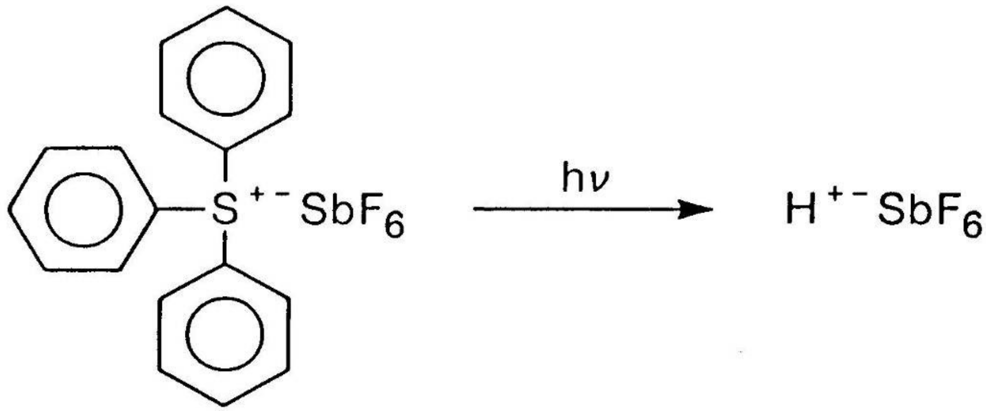


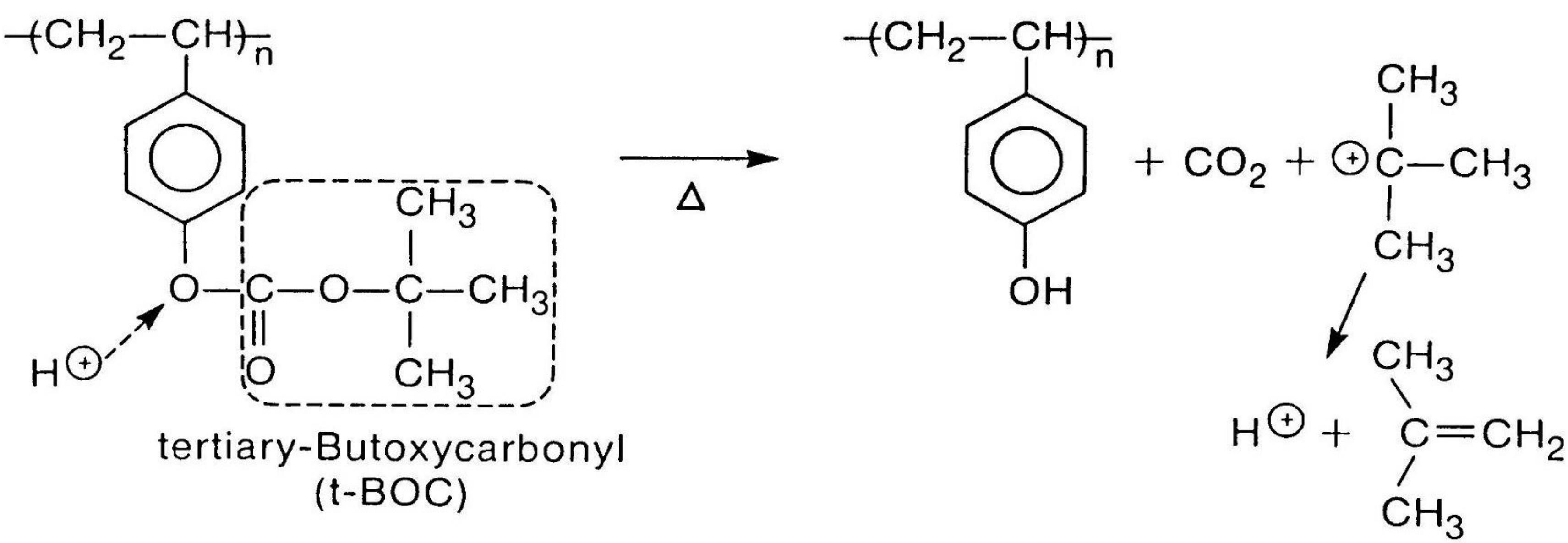


Acid-Catalyzed Deprotection



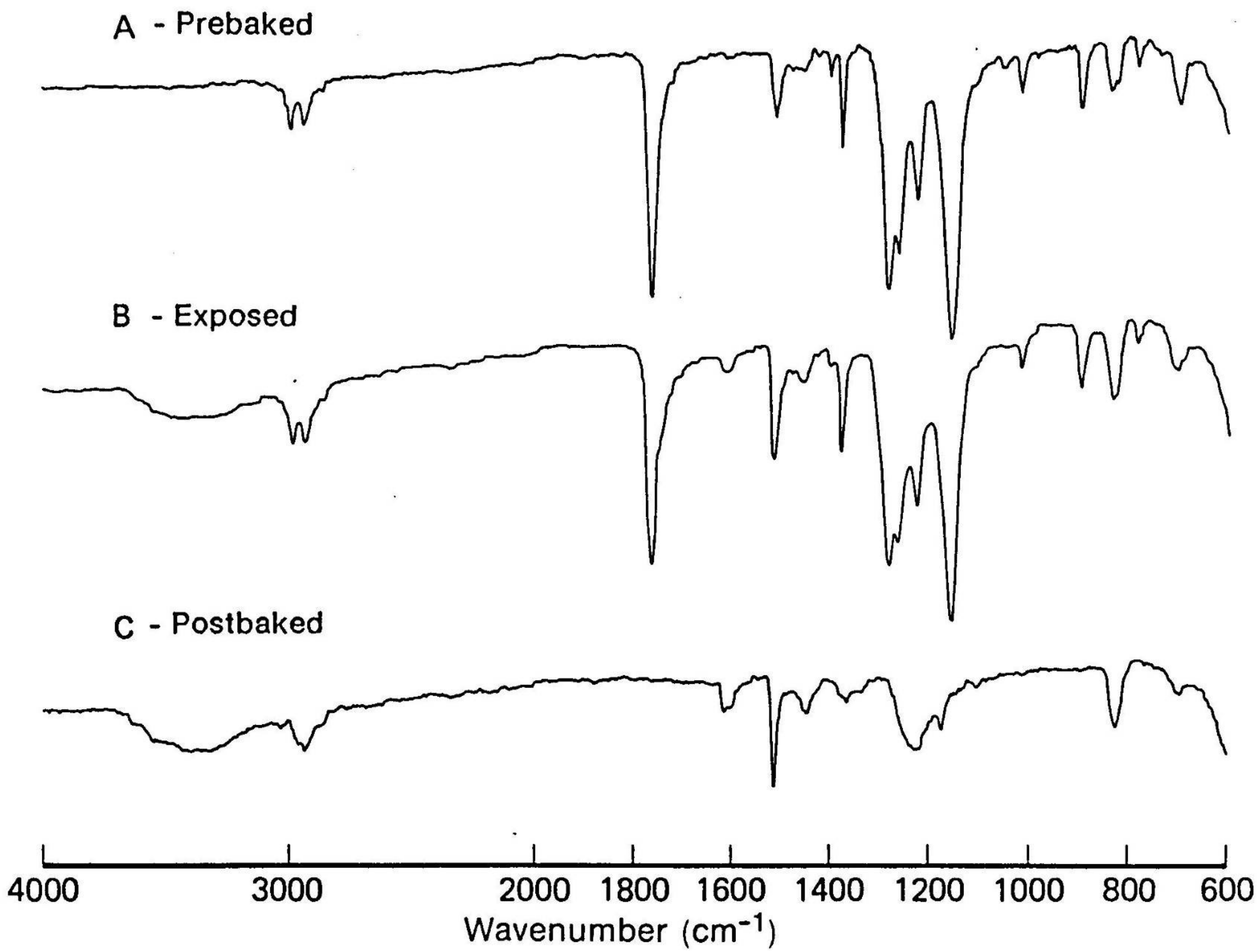

1.0
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.0
Absorbance
Ph$_2$I$^{\oplus}$
$^{\ominus}$AsF$_6$
PHOST
PBOCST
200
220
240
260
280
300
320
Wavelength (nm)



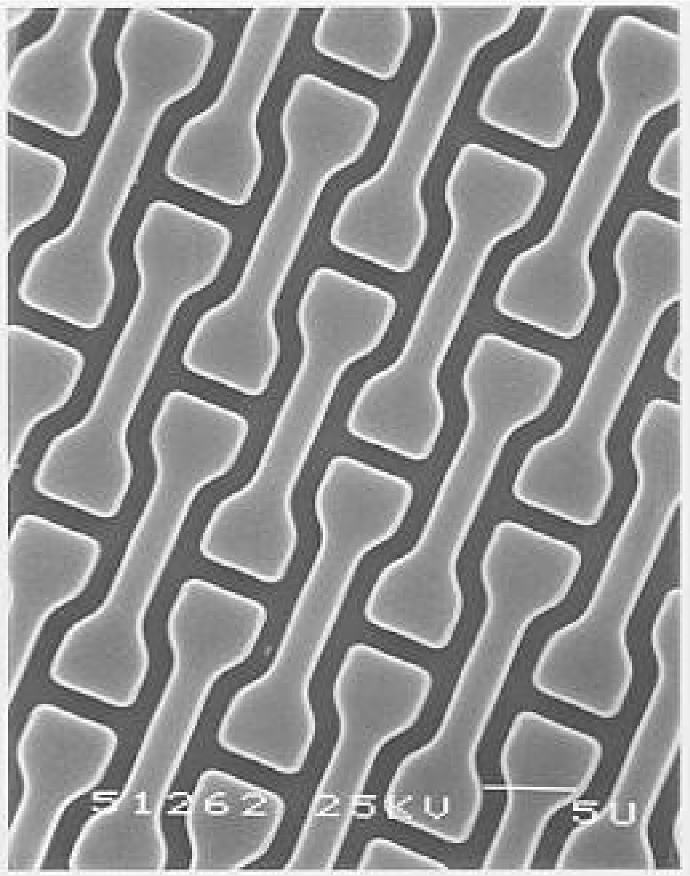


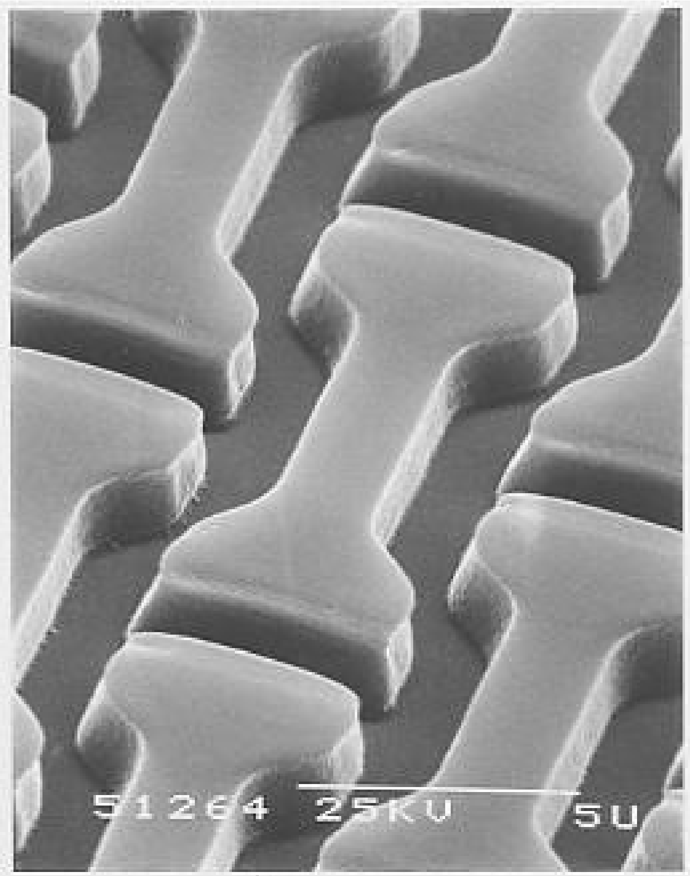
catalytic reaction — CHEMICAL AMPLIFICATION

Infrared analysis



First Commercial Implementation of Deep UV Photolithography

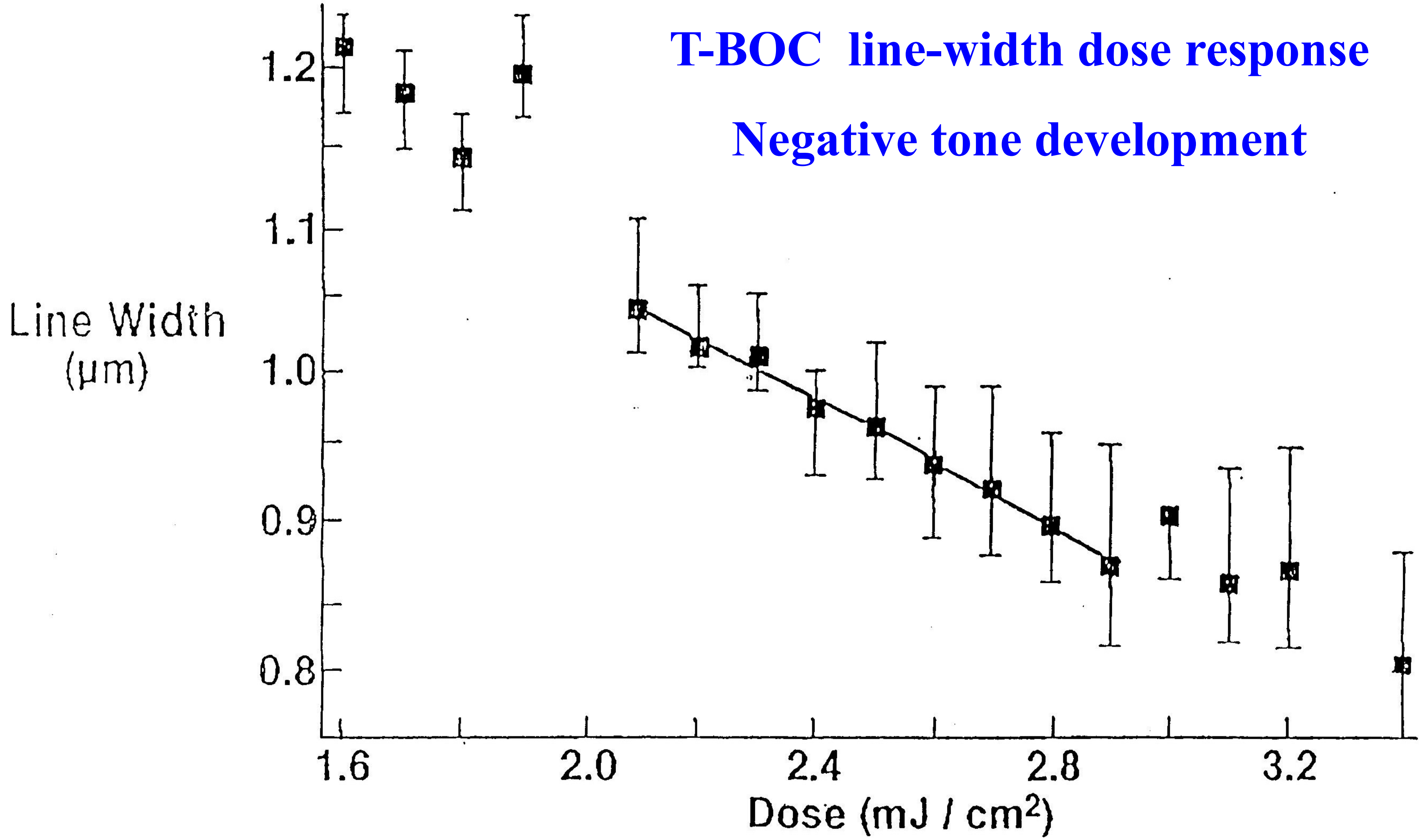




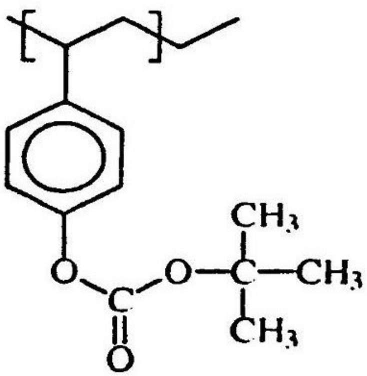
ROX level of 1M DRAM IBM

T-BOC line-width dose response

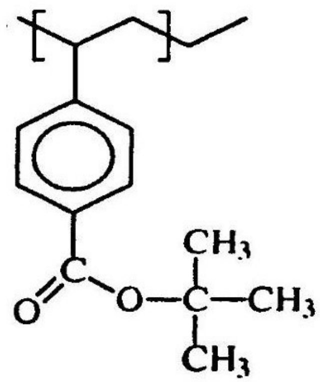
Negative tone development



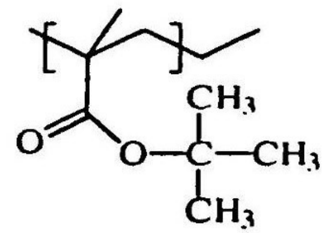
sample structures



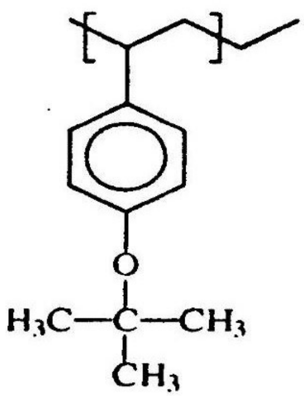
t-Butyl Carbonate



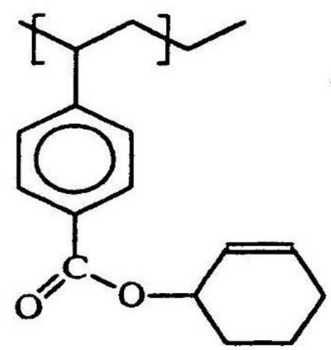
t-Butyl Ester



t-Butyl Ester

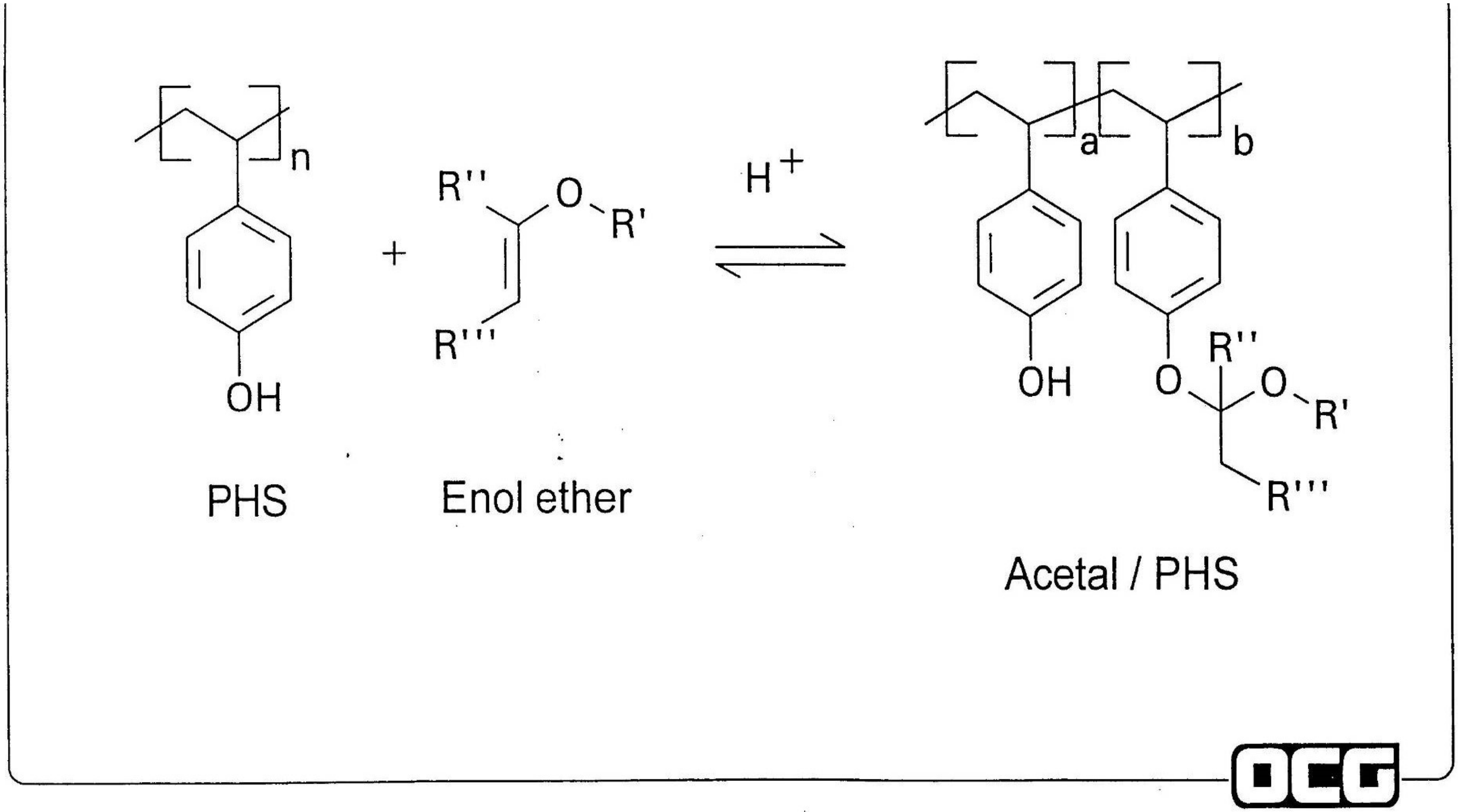


t-Butyl Ether

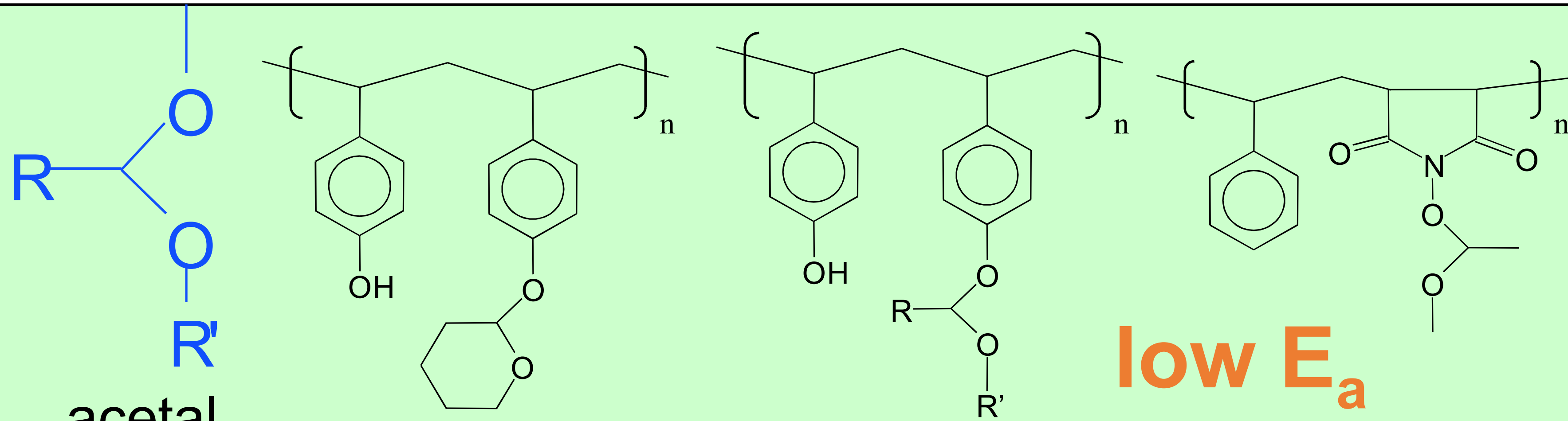


Secondary Allylic ester

Another approach



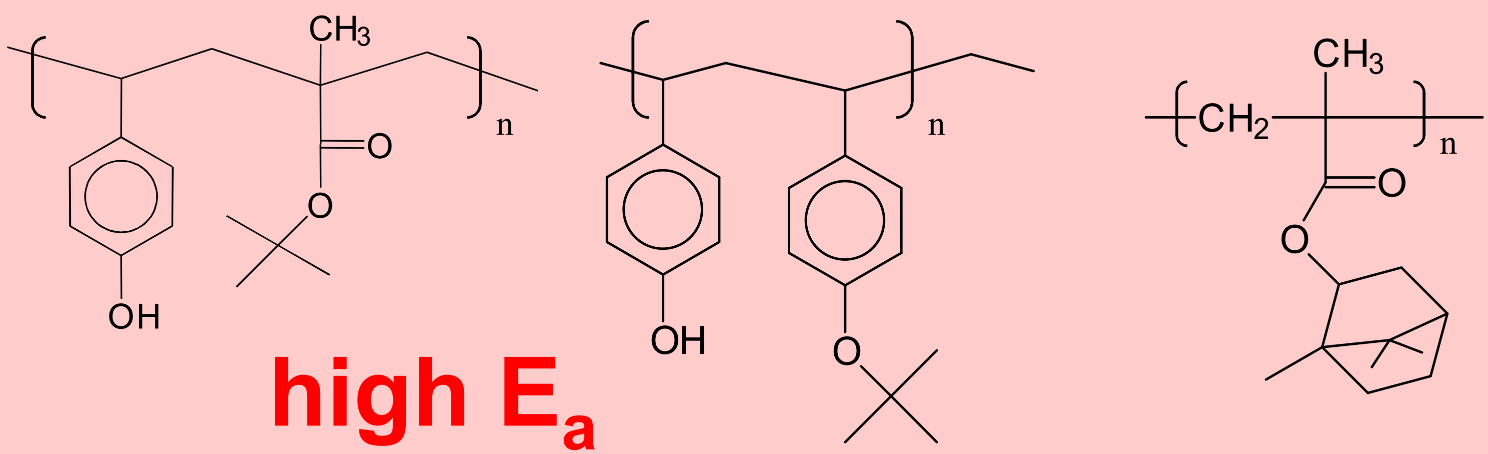
High And Low Activation Energy Protective Groups



acetal

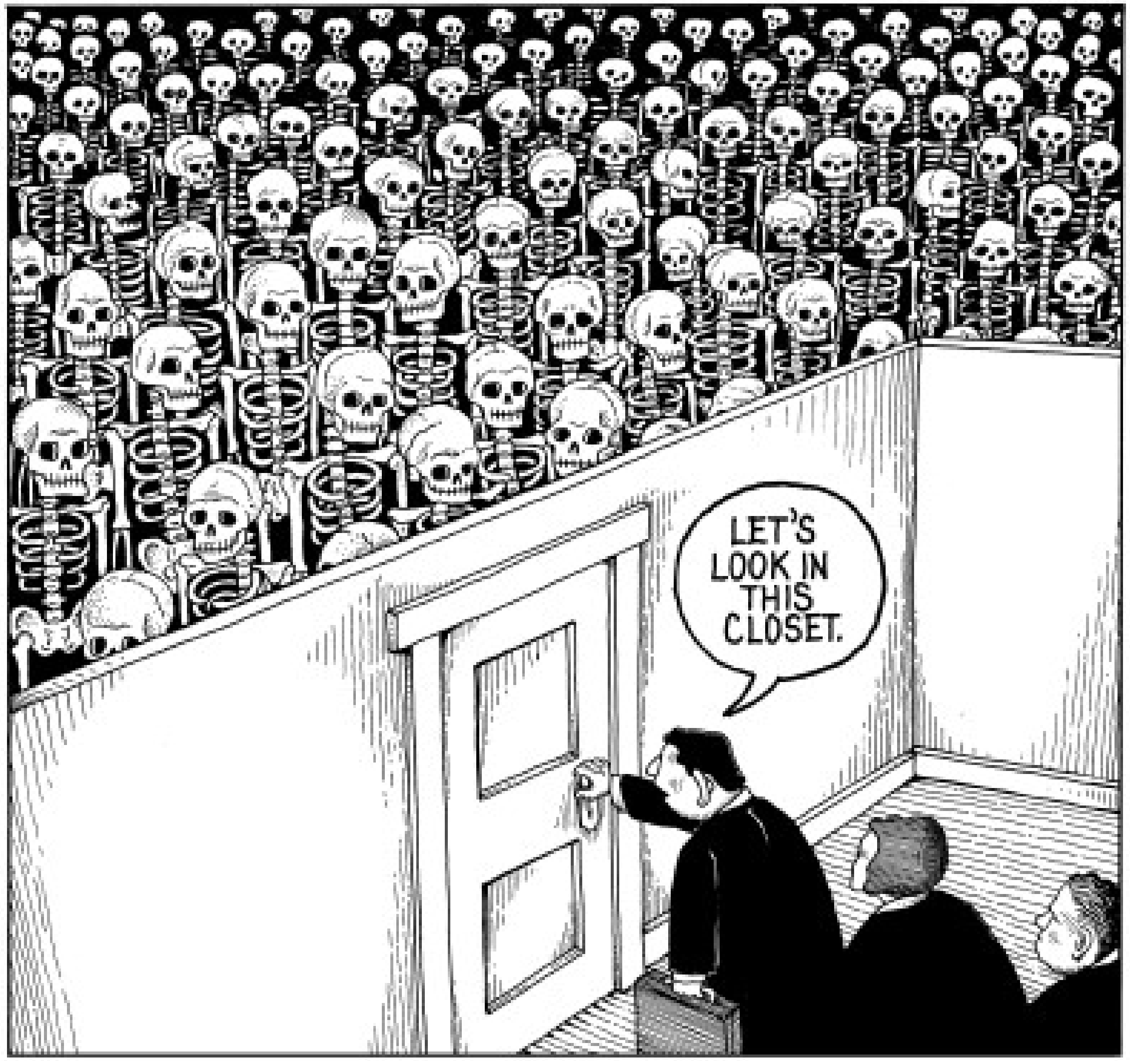
low E_a

t-butyl ester/ether, sec. alkyl

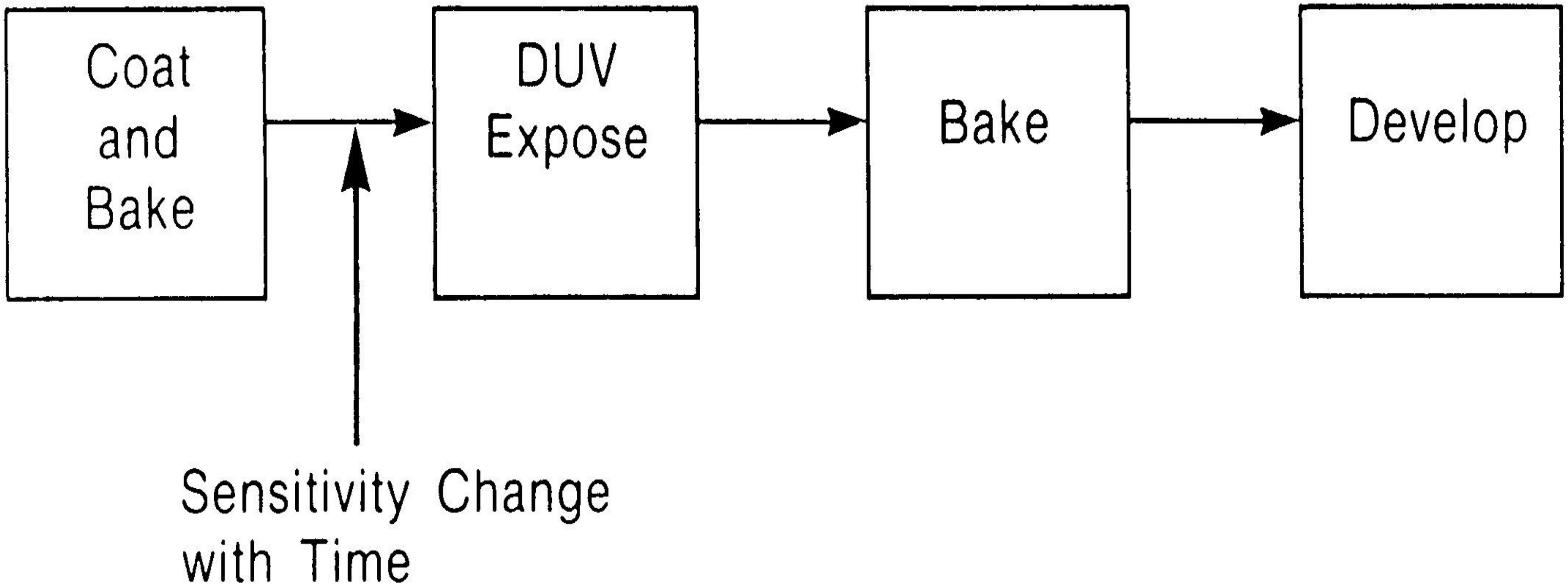


high E_a

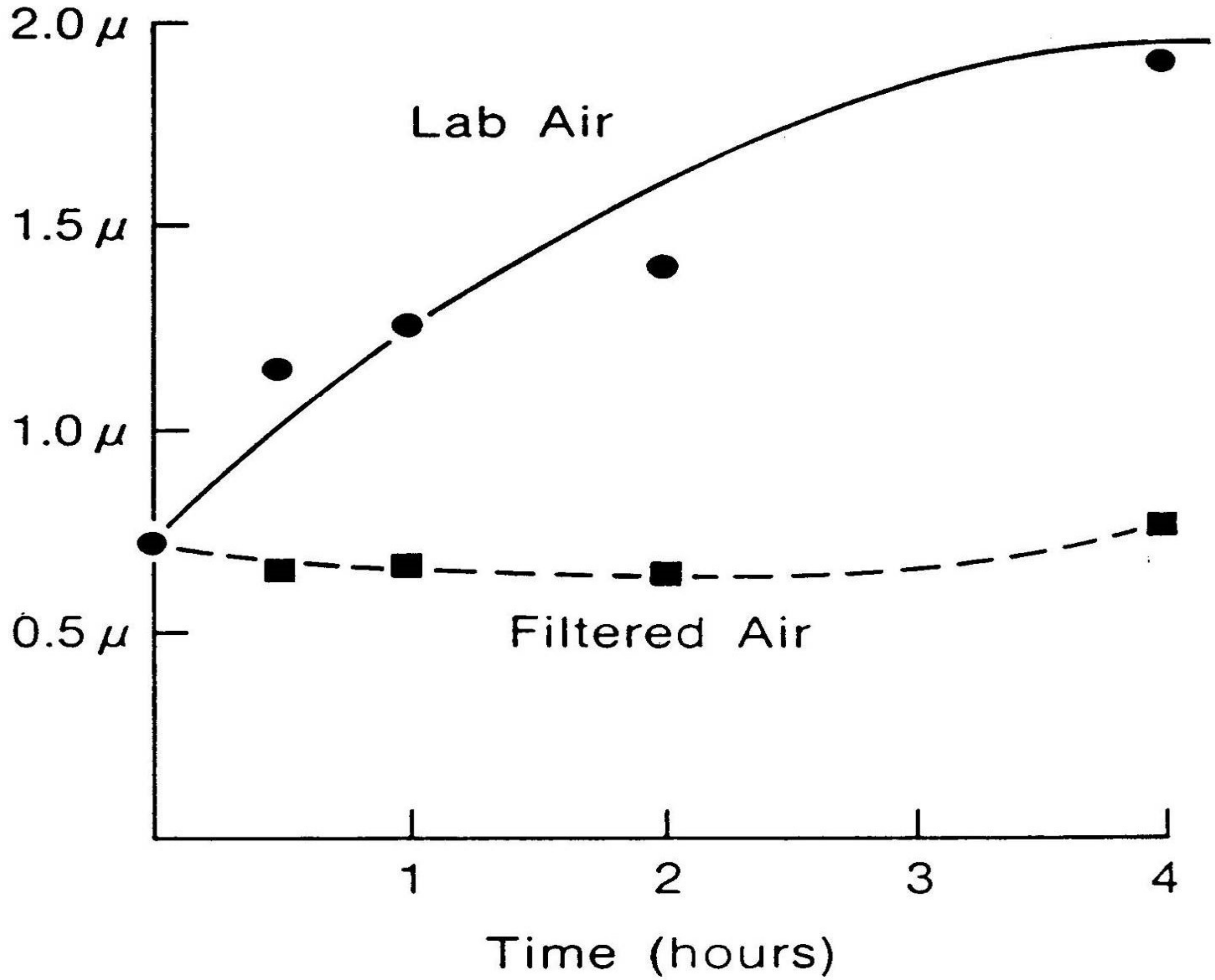
The Skeleton in the Closet



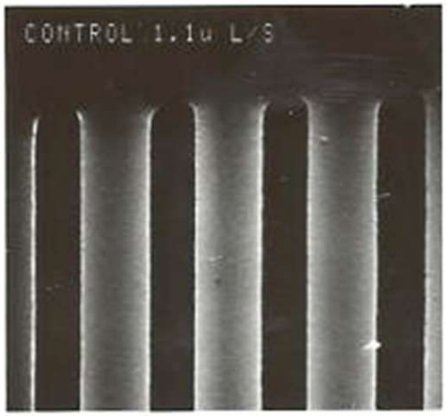
Resist Process Sequence



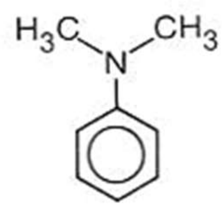
Effect of Delay Time
Lab Air vs. Filtered Air

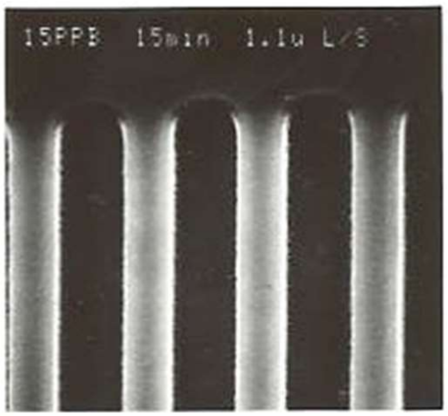


15 ppb of N,N-dimethylaniline



Control

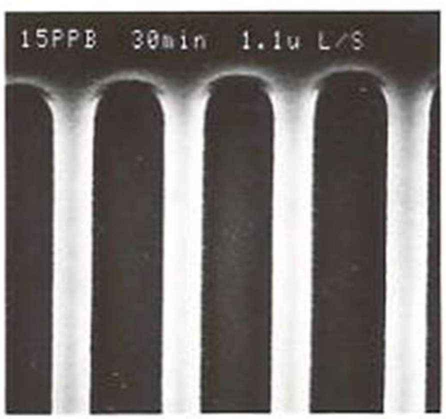




15 min

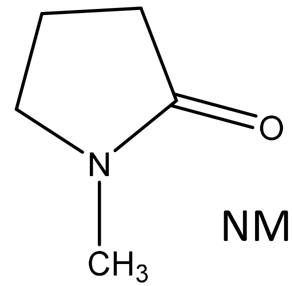
t-BOC Resist in negative tone

- anisole developer



30 min

"T" tops

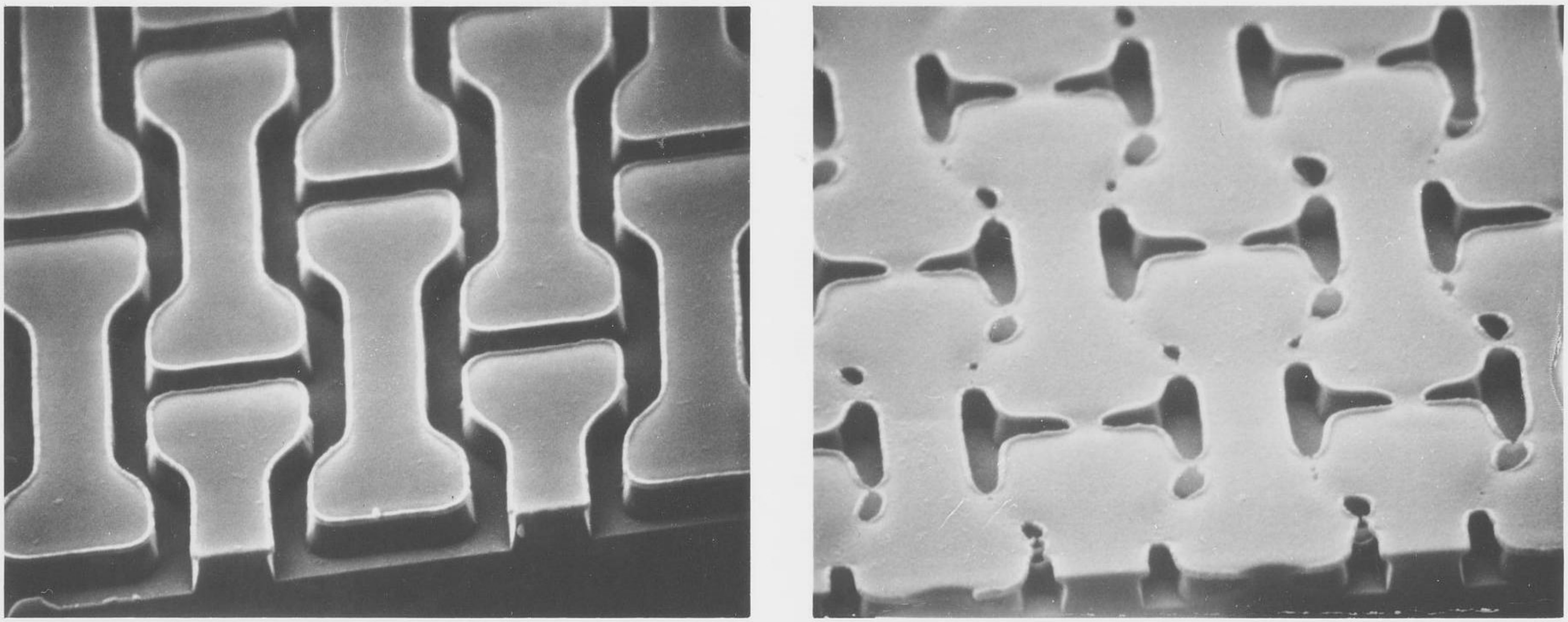


NMP

15 min in filtered air

15 min in 10ppb NMP before exposure

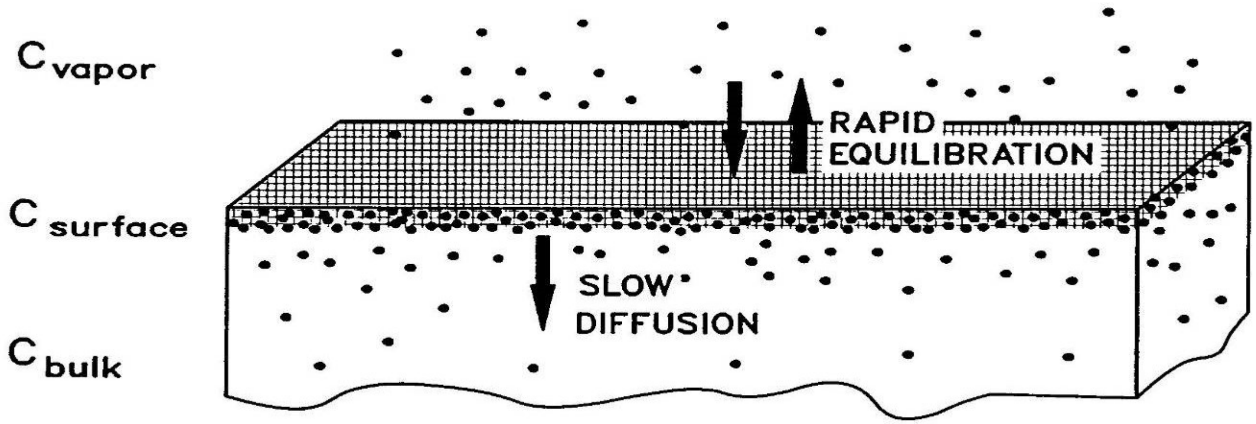
Positive Tone Image vs. Delay Time



No Delay

Post Coating Delay

Polymer Permability



$$C_{surface} = S \times C_{vapor}$$ (Henry's Law)

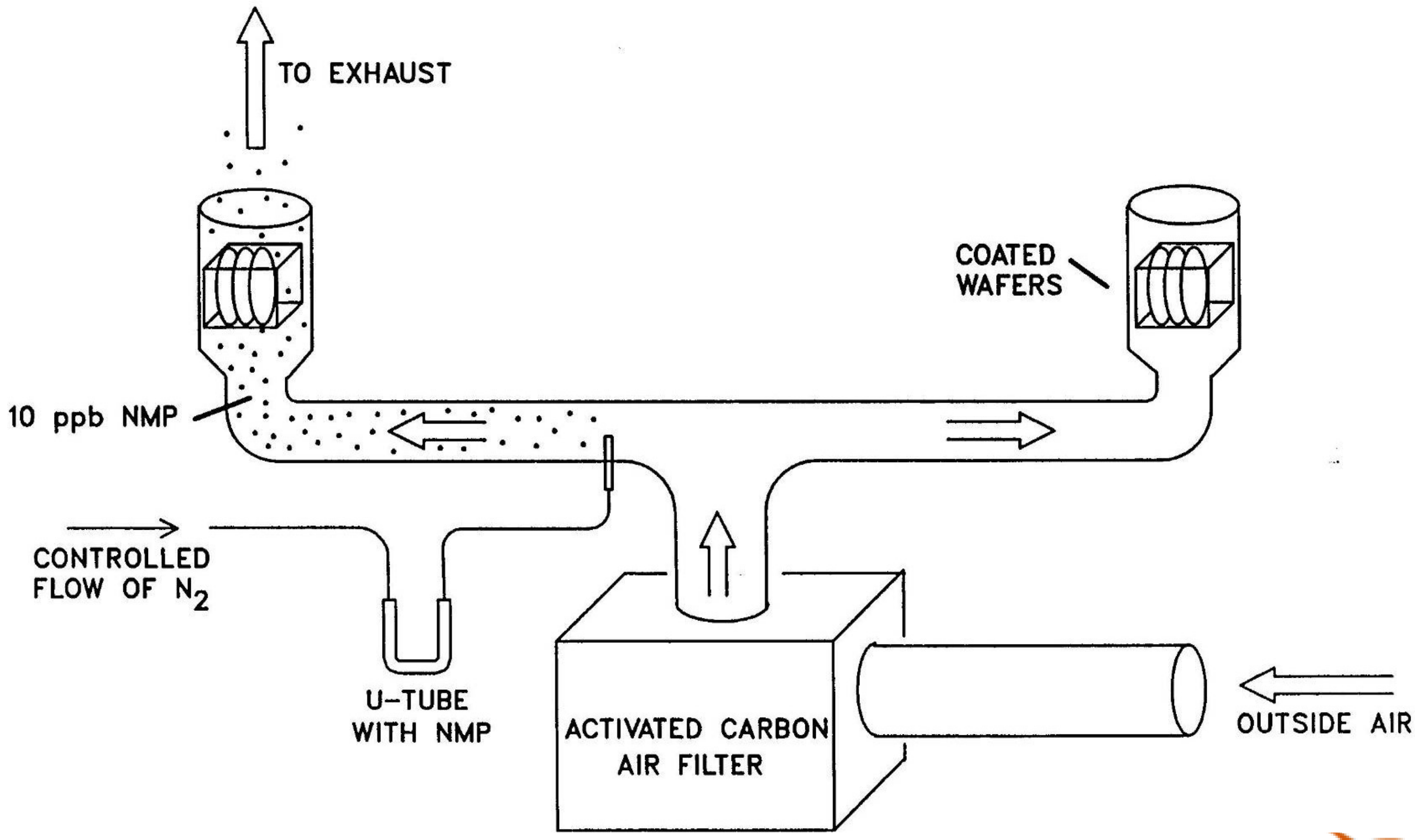
$$\text{Diffusion Rate} = -D \frac{dC}{dx}$$ (Fick's Law)

$$\frac{dC}{dx} = f\,(C_{surface})$$ so

$$\text{Sorption Rate} = f\,(\text{Solubility, Diffusivity})$$

W. Hinsberg, IBM

Experimental Apparatus



W.D. Hinsberg, et.al. IBM, Almaden

Polymer	NMP Content (ng/wafer)	Solubility Param. $(cal/cm^3)^{1/2}$	T_g (°C)
poly(methylmethacrylate)	70	9.1	115
poly(4–t–BOC–styrene)	547	9.5	135
poly(4–t–BOC–styrene) from Maruzen PHOST	400	9.5	115
m–cresol novolac	164	13.0	100
poly(4–hydroxystyrene)	758	12.6	180
poly(styrene)	64	8.5	100
epoxy cresol novolac	18	10.0	39
poly(MMA–TBMA–MAA)	296	9.4	145
poly(α–Me–styrene–co–Bz–MA)	107	9.1	110
poly(t–Bu–vinylbenzoate)	882	9.6	160
poly(3,5–Me_2–4–t–BOC–styrene)	362	9.9	130
poly(t–butyl methacrylate)	25	8.3	118
poly(TBMA–MMA)	23	8.7	115
poly(3,5–Me_2–4–hydroxystyrene)	870	11.4	175
poly(α–Me–styrene) (low MW)	49	9.0	168
poly(α–Me–styrene) (high MW)	36	9.0	168
poly(acrylic acid)	36	14.4	106
poly(4–t–butylstyrene)	315	9.0	145
poly(4–acetoxystyrene)	332	9.9	115
poly(methacrylic acid)	315	13.6	228
poly(4–MeO–styrene)	135	9.7	89
poly(4–MeO–styrene–co–4–t–BOC–styrene)	426	9.6	112
poly(3–t–BOC–styrene)	50	9.5	90
p(3–Me–4–hydroxystyrene)	340	11.3	135