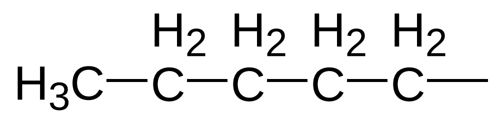
EE-527: MicroFabrication

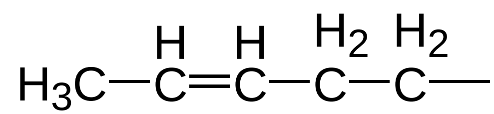
Negative Photoresists

A Little Structural Organic Chemistry - 1

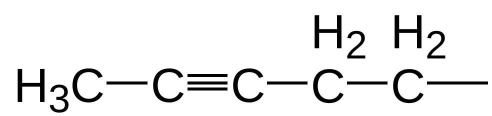
alkanes: (no double bonds):



alkenes: (at least 1 double bond):



alkynes: (at least 1 triple bond):



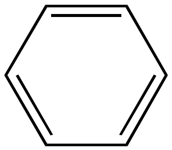
[alkenes and alkynes are unsaturated hydrocarbons.]

A Little Structural Organic Chemistry - 2

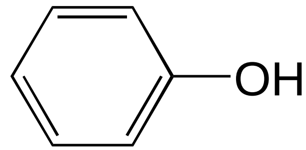
R—OH	alcohol
R—O—R'	ether
R—CHO	aldehyde
O R—C—R'	ketone
O R—C—OH	acid
O R—C—O—R'	ester
R—O—OH	hydroperoxide
R—O—O—R'	peroxide

CH_3OH	methanol
HCHO	formaldehyde
HCOOH	formic acid

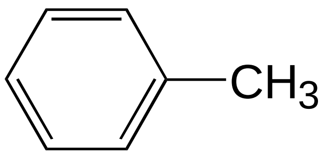
A Little Structural Organic Chemistry - 3



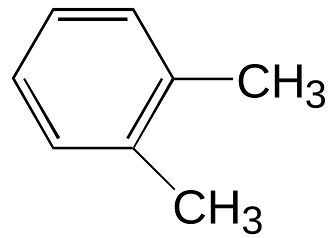
benzene



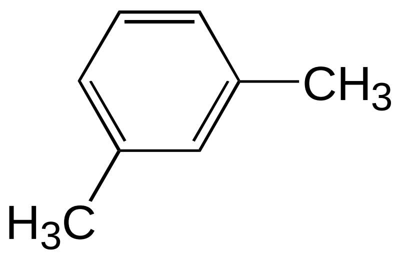
phenol



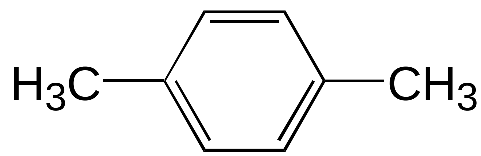
toluene



(ortho-)
xylene



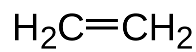
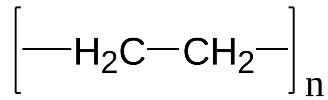
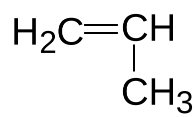
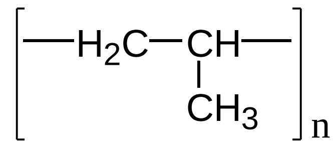
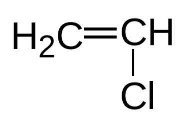
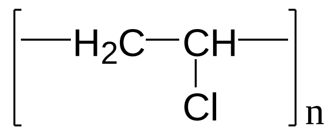
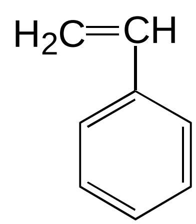
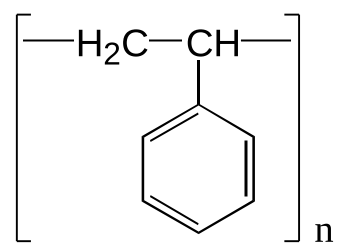
(meta-)
xylene



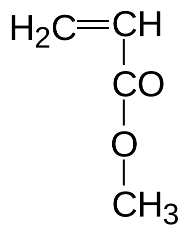
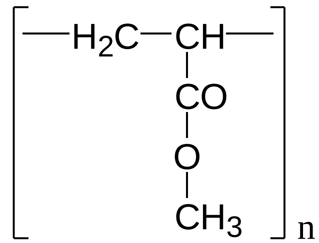
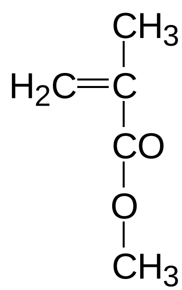
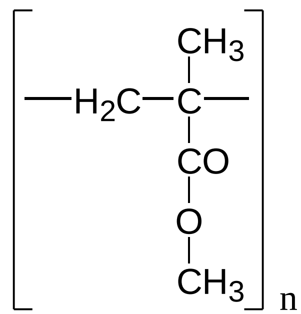
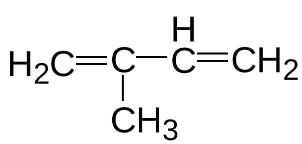
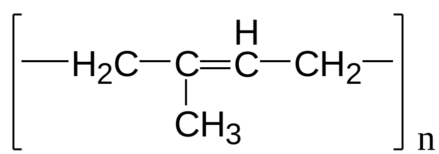
(para-)
xylene

ortho-	means straight out
meta-	means beyond
para-	means opposite

Common Monomers and Their Polymers - 1

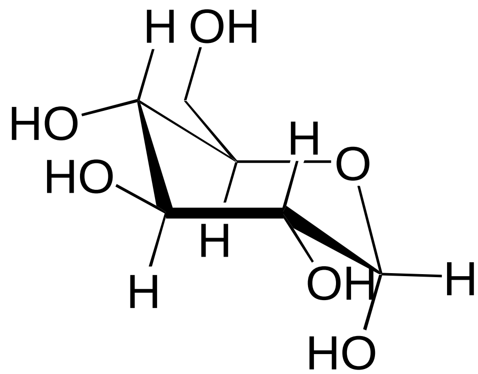
MONOMER	POLYMER
 ethylene	 polyethylene (PE)
 propylene	 polypropylene (PP)
 vinyl chloride	 polyvinyl chloride (PVC)
 styrene	 polystyrene (PS)

Common Monomers and Their Polymers - 2

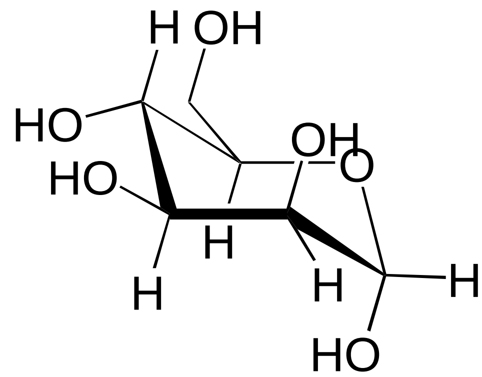
MONOMER	POLYMER
 methyl acrylate	 polymethyl acrylate (PMA)
 methyl methacrylate	 polymethyl methacrylate (PMMA)
 isoprene (2-methyl-1,3-butadiene)	 polyisoprene (PI)

All rubbers are diene polymers

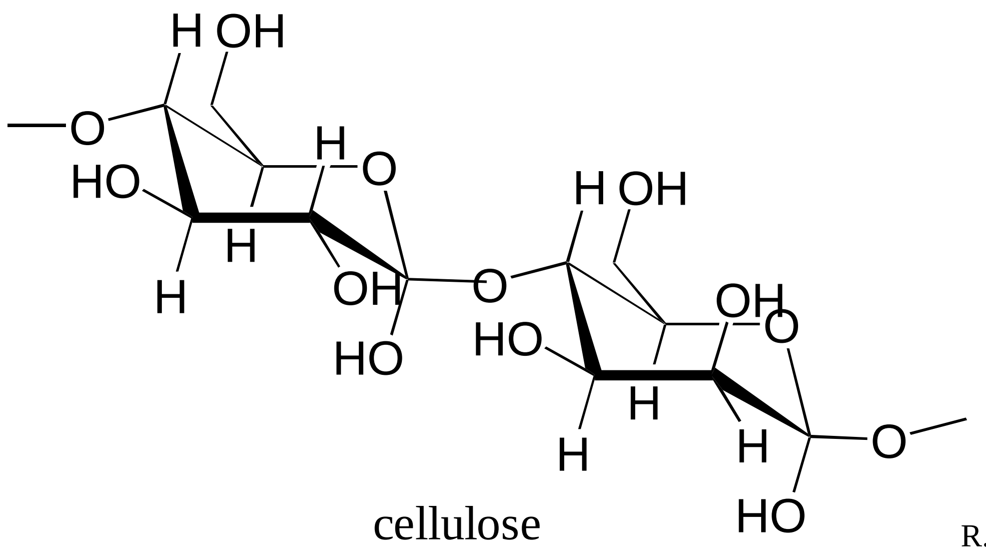
Common Monomers and Their Polymers - 3



D-glucose



D-manose



cellulose

Atomic Weights

hydrogen	1.0079
carbon	12.011
nitrogen	14.0067
oxygen	15.9994
silicon	28.0855
sulfur	32.06
chlorine	35.453

(distribution of isotopes gives rise to fractional atomic weights)

Molecular Weights

ethylene	C_2H_4	2(12.011) + 4(1.0079) = 28.05 g/mole
propylene	C_3H_6	3(12.011) + 6(1.0079) = 42.08 g/mole
vinyl chloride	C_2H_3Cl	2(12.011) + 3(1.0079) + 35.453 = 62.50 g/mole
styrene	C_8H_9	8(12.011) + 9(1.0079) = 105.16 g/mole
methyl acrylate	$C_4H_6O_2$	4(12.011) + 6(1.0079) + 2(15.9994) = 86.09 g/mole
methyl methacrylate	$C_5H_8O_2$	5(12.011) + 8(1.0079) + 2(15.9994) = 100.12 g/mole
isoprene	C_5H_8	5(12.011) + 8(1.0079) = 68.12 g/mole

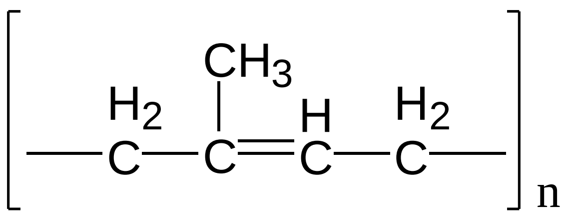
1 mole is Avogadro's number of particles: $N_A = 6.023 \times 10^{23}$

Molecular Weight of a Polymer

- $M_p = nM_m$
  - n = number of units
  - M_m = molecular weight of monomer
  - M_p = molecular weight of polymer
- For use in a photoresist resin, need a molecular weight of around 100,000 - 200,000 for proper viscosity, melting point, softening point, and stiffness.
- Example:
  – To get M_p = 100,000 using isoprene (M_m = 68.12 g/mole), need to get chains of average length of n = 100,000/68.12 = 1468 units.
  – This would lead to a molecule that is too long for proper photolithographic resolution, so need to coil the chains to make the lengths shorter and to increase the mechanical stiffness.

Polyisoprene Rubber

- 2-methyl-1,3-butadiene (isoprene) spontaneously polymerizes into natural latex rubber (polyisoprene).
- Polyisoprene becomes sticky and looses its shape at warm temperatures.
- Natural latex rubber is the only known polymer which is simultaneously:
  - elastic
  - air-tight
  - water-resistant
  - long wearing
  - adheres well to surfaces

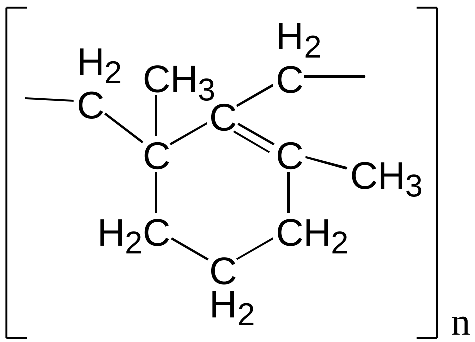


polyisoprene

C_5H_8

Cyclicized Poly(cis-isoprene) - 1

- Poly(cis-isoprene) is the substrate material for nearly all negative photoresists.
  - cis- CH_3 groups are on the same side of the chain
  - trans- CH_3 groups are on alternatingly opposite sides of the chain
  - cis-isoprene is needed in order to curl the chains up into rings; (trans-isoprene will not work; CH_3 groups would hit each other).
- Two protons are added to cis-isoprene to further saturate the polymer and induce curling into cyclicized versions.



monocyclic poly(cis-isoprene)
$C_{10}H_{16}$

Bicyclic and tricyclic forms are also possible. (This is usually part of the proprietary part of photoresist manufacture.

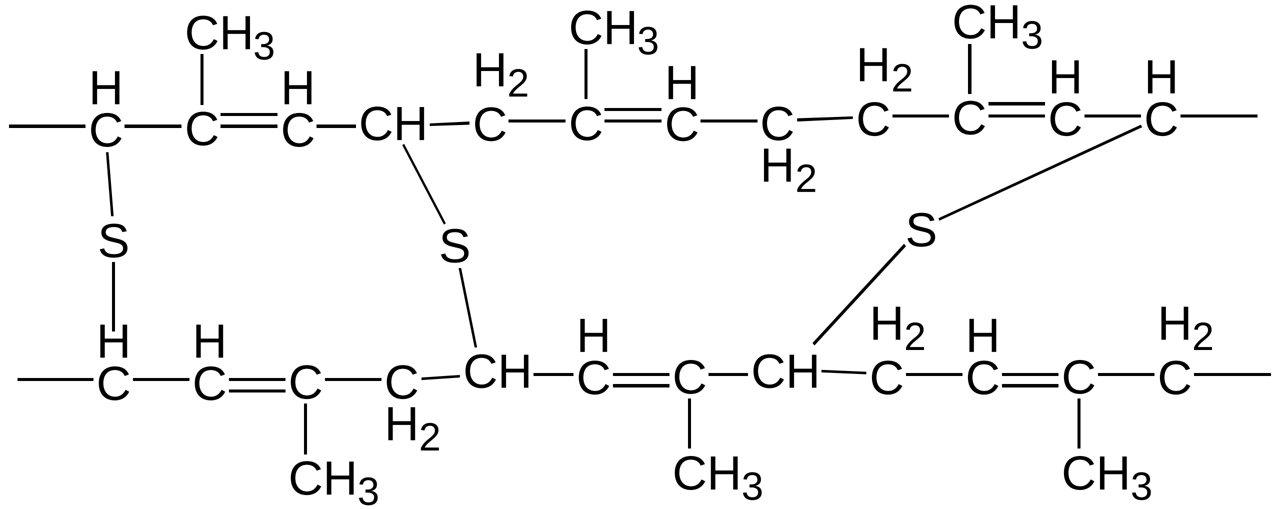
Cyclicized Poly(cis-isoprene) - 2

- Cyclicized poly(cis-isoprene) allows greater solids content in coating solutions and is less subject to thermal cross-linking.

Property	Uncyclicized	Cyclicized
Average Molecular Weight	~ 10^6	~ 10^4
Density	0.92 g/mL	0.99 g/mL
Softening Point	28 C	50-65 C
Intrinsic Viscosity	3-4	0.36-0.49
Unsaturation	14.7 mmole/g	4-8 mmole/g

Vulcanization (Cross-Linking) of Rubber

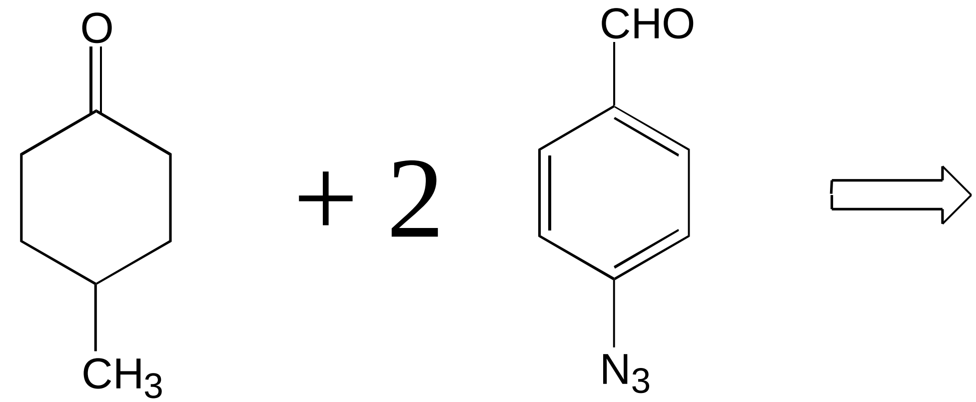
- Vulcanization of rubber uses sulfur atoms to form bridging bonds (cross-links) between polymer chains.
- Sulfur is thermally activated; it is not photosensitive.



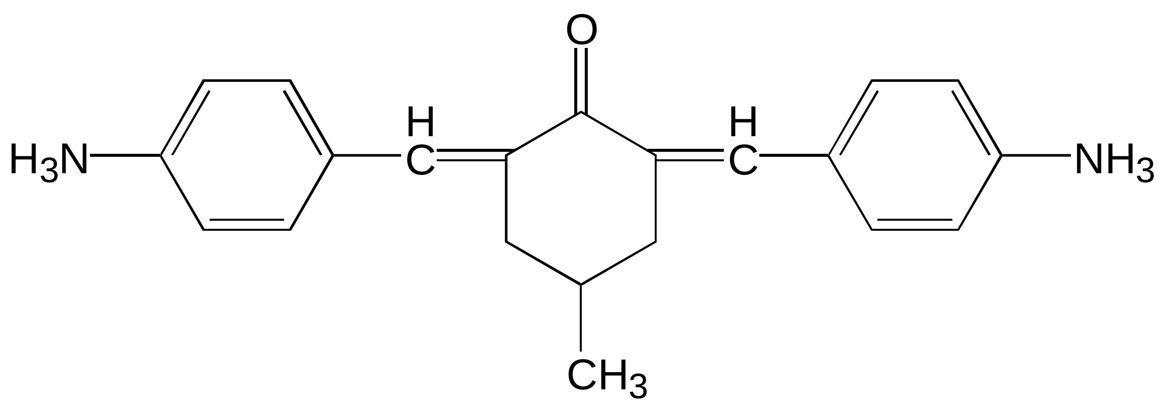
Components of a Negative Photoresist

- 1. Non-photosensitive substrate material
  - About 80 % of solids content
  - Usually cyclicized poly(cis-isoprene)
- 2. Photosensitive cross-linking agent
  - About 20 % of solids content
  - Usually a bis-azide ABC compound
- 3. Coating solvent
  - Fraction varies
  - Usually a mixture of n-butyl acetate, n-hexyl acetate, and 2-butanol
- Example: Kodak KTFR thin film resist:
  - work horse of the semiconductor industry from 1957 to 1972.

ABC Photosensitive Cross-Linking Agent



4-methylcyclohexanone 4-azidobenzaldehyde



2,6-bis(4-azidobenzal)-4-methylcyclohexanone

"ABC"

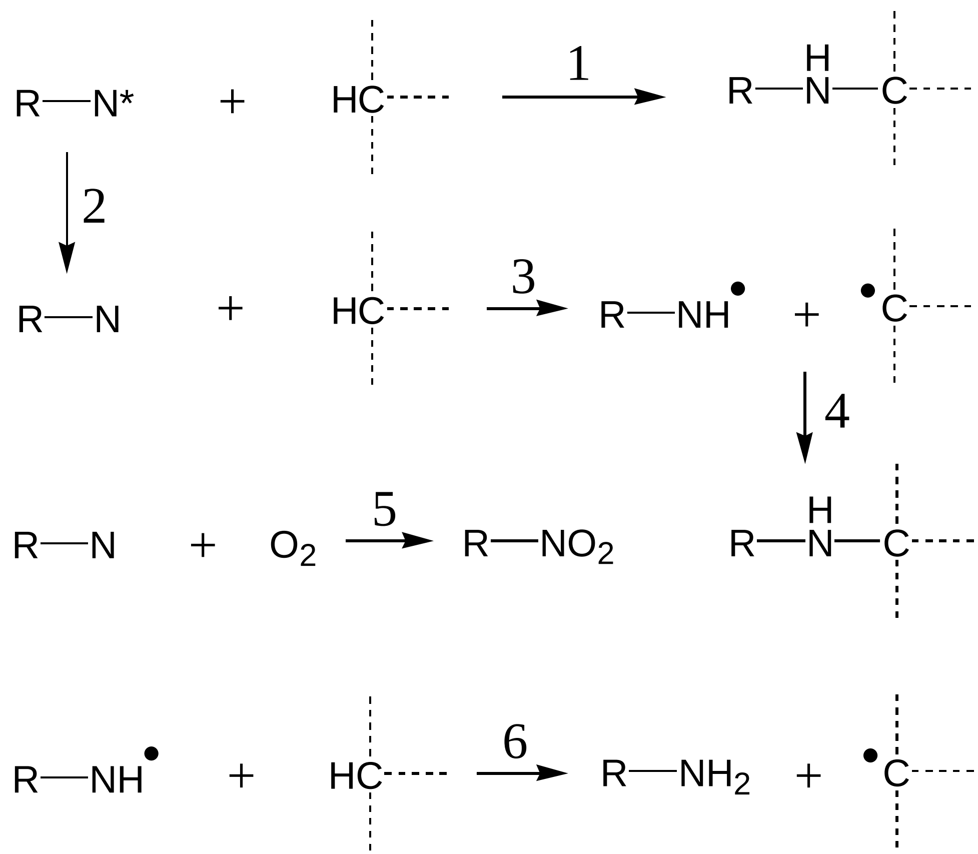
Bis-Azide Cross-Linking Agents

- "bis" means oppositely oriented---needed to attach both ends of the cross linker to two different substrate strands.
- It plays the same role as sulfur in vulcanization of rubber.
- The ABC bis-azide compound is photosensitive instead of being thermally activated.
- Photosensitivity arises from explosophore groups on ends:
  - N_3 azide group
  - NO_2 nitro group
  - Lead azide $Pb(N_3)_2$ is a primary explosive...
- Nitrenes are photoionized azide groups with a triplet ground state and a singlet excited state which is extremely reactive and capable of bonding to hydrocarbon chains.

Bis-Azide Cross-Linking Chemistry - 1

$$R{-}N_3 \xrightarrow{h\nu} R{-}N^* + N_2$$

photolysis of nitrene group: the only photoreaction



Bis-Azide Cross-Linking Chemistry - 2

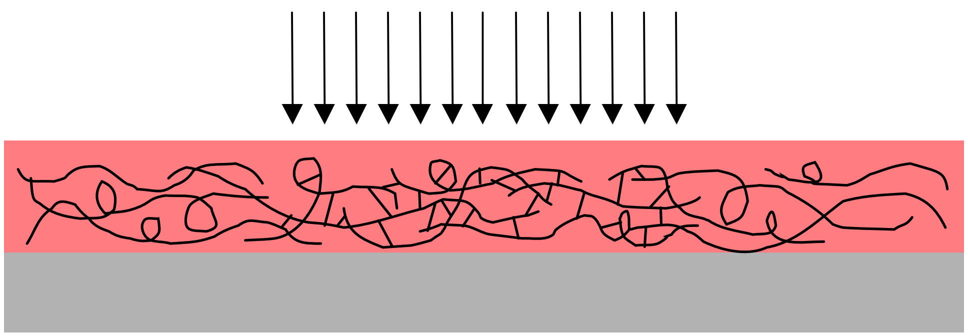
- Photolysis of nitrene group by ultraviolet light is the only photoreaction.
- Reaction 1 is the desired pathway which leads to one end of the ABC compound being cross-linked to an isoprene strand.
- Reactions 2, 3, and 4 are an alternative pathway to the same result, involving an intermediate ground state and a radical state of the nitrene.
- The ground state nitrene can combine with O_2. (Reaction 5)
  - This competes with cross-linking.
  - This can be used in an image reversal process.
- The radical state nitrene can steal an additional proton from an isoprene strand and terminate the ABC compound without forming a cross link. (Reaction 6)
  - This competes with cross-linking, also.

Cross-Linking Efficiency

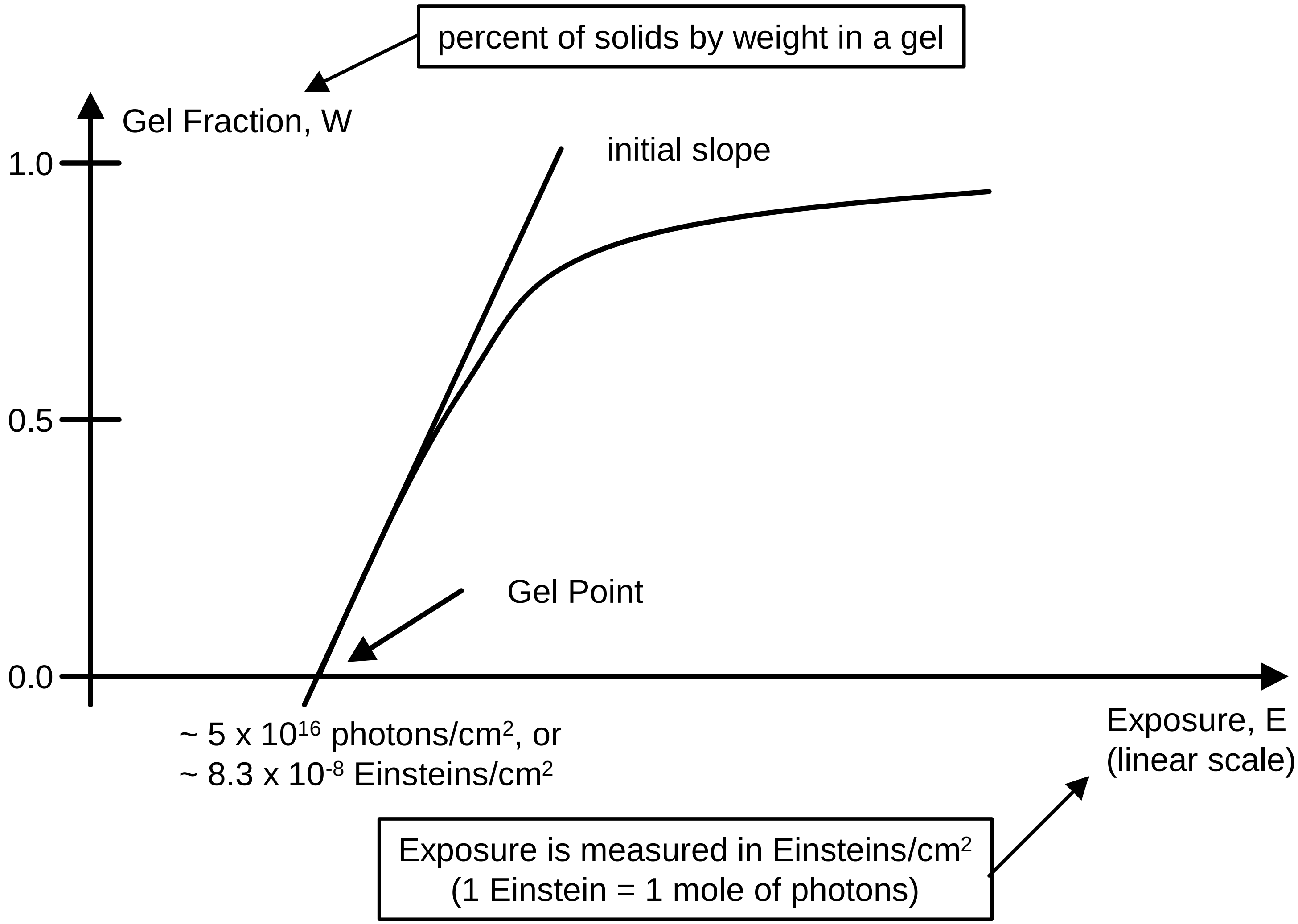
- χ is the efficiency of thermal cross-linking of nitrene groups to isoprene strands, set by the rates of reactions 1,2,3,4 versus 5,6.
- ϕ is the quantum efficiency of photolysis of the azide groups, set by the wavelength and absorption of the resist.
- $\Phi = \phi\chi$ is the quantum yield of cross-link bond formation.
- For a bis-azide resist, two bonds are needed (one on each end) to form a cross-link between isoprene strands; thus:
- $\Phi = \phi^2\chi^2$
  - This requires two photons per cross-link, and thus has very low photographic speed.
  - This allows great variety in the substrate polymer chains.

The Gel Point

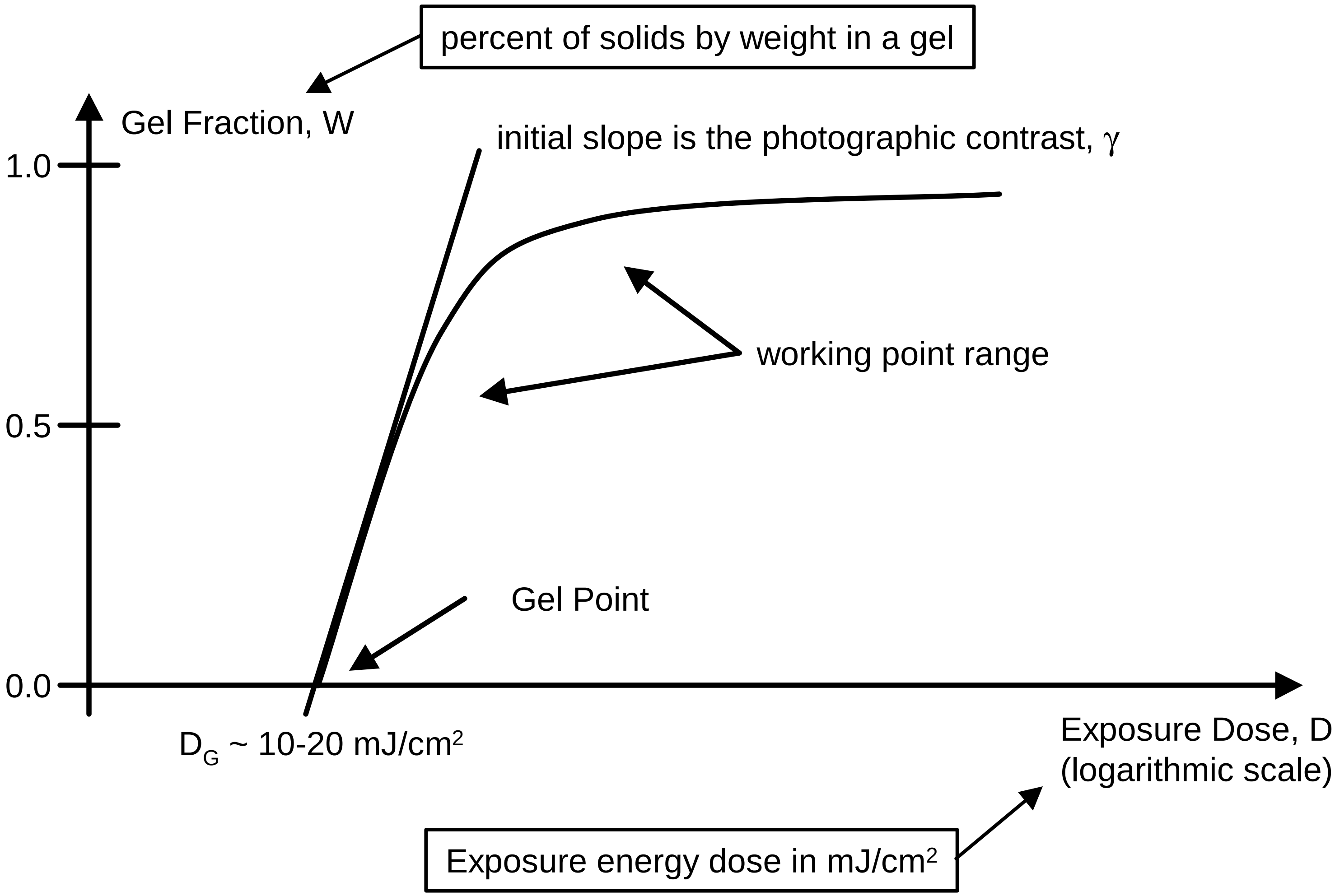
- All sites for cross-linking (chromophores) are equally likely; thus, larger polymer chains are more likely to bind together than small ones.
- A many-branched supermolecule results from increased exposure.
- This supermolecule permeates the irradiated area forming a lattice which solvent atoms can penetrate, but not disperse.
- The polymer chains have at this point been rendered insoluble to the solvent, and the exposure required to produce this is called the Gel Point.



The Gel Curve



The Sensitometric Curve



Exposure and Dose Calculations

N_A = Avogadro's number = 6.022 x 10^{23} particles/mole
h = Planck's constant = 6.626 x 10^{-34} J-s
c = speed of light in vacuum = 2.998 x 10^{8} m/s

$N_A hc$ = 0.1196 J-m/mole

E = exposure in Einsteins/cm^2
D = exposure energy dose in mJ/cm^2

Assume nearly monochromatic exposure illumination of wavelength λ

$$\frac{hc}{l}$$ is the energy per photon

$$\frac{N_A hc}{l}$$ is the energy in a mole of photons (one Einstein)

Therefore: $$D = \frac{E N_A hc}{l}$$

Optical Absorption by the Resist

A = fraction of light that is absorbed by the photoresist layer

d_r = thickness of the photoresist layer

α_r = optical absorption coefficient of the photoresist layer

ρ_r = density of the photoresist layer

R_1 = reflectivity of the air - photoresist boundary

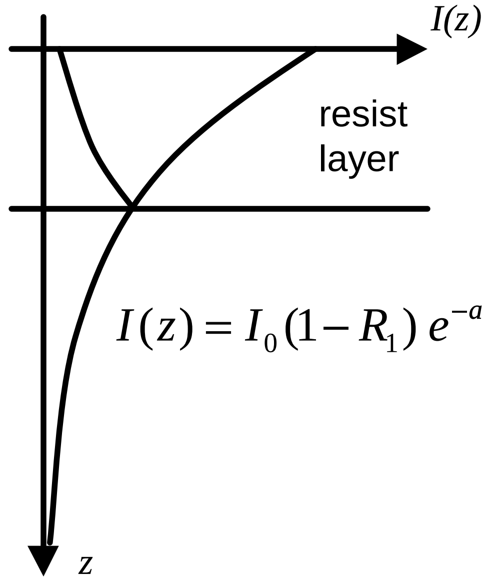
R_2 = reflectivity of the photoresist - substrate boundary

single pass:

$$A = (1 - R_1)(1 - e^{-a_r d_r})$$

double pass:

$$A = (1 - R_1)(1 - e^{-a_r d_r})\left[1 + R_2 e^{-a_r d_r}\right]$$



$$I(z) = I_0 (1 - R_1)\, e^{-a_r z}$$

Cross-Link Fraction

E = exposure in Einsteins/cm^2

A = absorbed fraction of light

Φ = quantum efficiency of cross-link formation

C = cross-link fraction

$EA\Phi$ = number of formed cross-links in moles/cm^2

$d_r\rho_r$ = mass of resist in grams/cm^2

$d_r\rho_r/2M_m$ = number of possible cross-links in moles/cm^2

therefore, the fraction of possible cross-links is proportional to the exposure:

$$C = \frac{EA\Phi 2M_m}{d_r r_r}$$

Gel Point Exposure

- The gel point occurs when each polymer strand, on average, has one cross-link. Thus,

$$C_{gel} = \frac{M_m}{M_p} = \frac{1}{n}$$

The gel point exposure is thus:

$$E_{gel} = \frac{d_r r_r}{A\Phi 2 M_m n} = \frac{d_r r_r}{A\Phi 2 M_p}$$

For $\Phi = 1$, $A = 1$, $d_r = 1$ µm, $M_p = 10^5$ g/mole, and $\lambda = 365$ nm, obtain that

$E_{gel} = 0.25 \times 10^{-9}$ Einsteins/cm^2 and $D_{gel} = 0.1$ mJ/cm^2.

This is a benchmark for negative resist systems.

The Flory Function - 1

W = gel fraction (fraction of solids)

C = cross-link fraction

n = degree of polymerization (an integer) = M_p/M_m

$f(n)$ = distribution of polymerization, a log-normal distribution

β = dispersity, typically 0.6 - 2.2

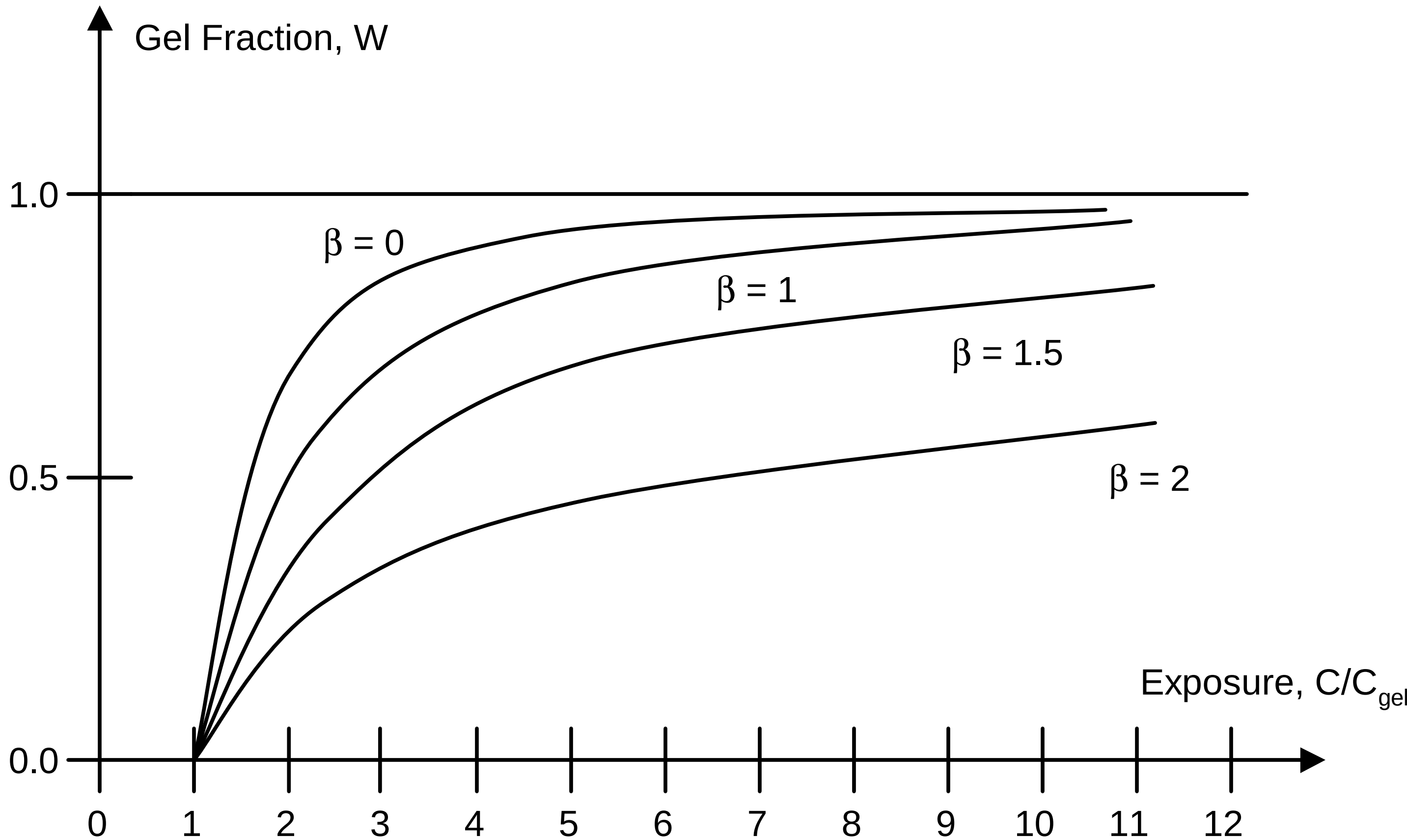
n_0 = average polymer chain length

The Flory function relates the cross-link fraction C (proportional to exposure) to the resulting gel fraction W (solids content) as a function of the average chain length and dispersity of the polymer.

$$f(n) = \exp\left\{ -\frac{(\ln n - \ln n_0)^2}{2b^2} \right\}$$

$$W = 1 - \frac{\sum_{n=1}^{\infty} n\ f(n)\,[1 - CW]^n}{\sum_{n=1}^{\infty} n\ f(n)}$$

The Flory Function - 2



Dispersity and Contrast

- The slope of the sensitometric curve is the photographic contrast of the resist:

$$\left(\frac{dW}{dE}\right)_{\text{gel point}} = \frac{2}{E_{gel}} e^{-b^2}$$

$$\left(\frac{dW}{d(\log E)}\right)_{\text{gel point}} = 2\ln(10)\, e^{-b^2} = 4.606\, e^{-b^2} = \gamma$$

- Desire a minimally dispersed polymer to optimize the sensitometric curve.
  - Age increases the dispersity of the polymer.
  - This is a key factor in limiting the shelf life of photoresist.

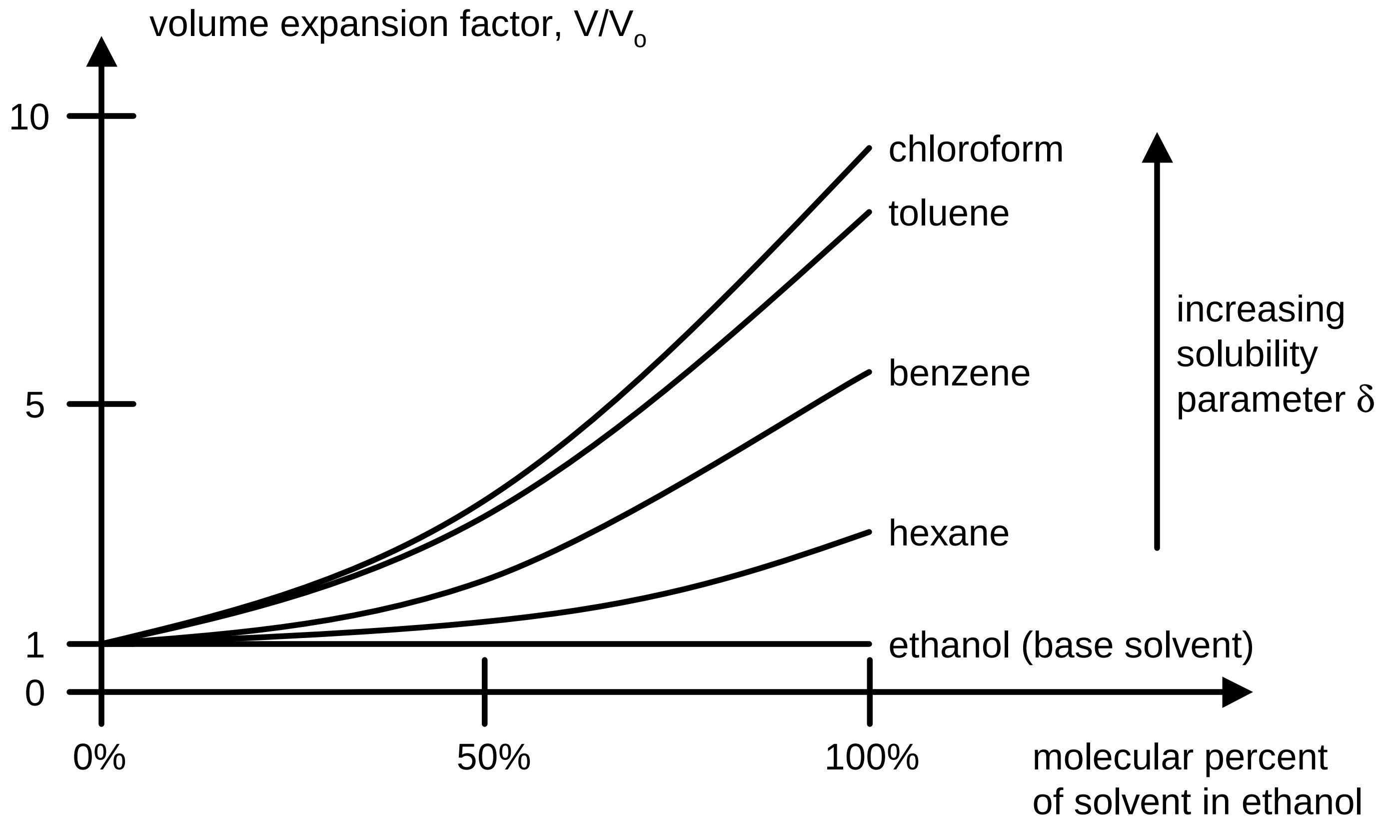
Negative Photoresist Ingredients

- 1. Non-photosensitive substrate material
- 2. Photosensitive cross-linking agent
- 3. Coating solvent
- 4. Other additives: (usually proprietary)
  - antioxidants
  - radical scavengers
  - amines; to absorb O_2 during exposure
  - wetting agents
  - adhesion promoters
  - coating aids
  - dyes

Negative Photoresist Development - 1

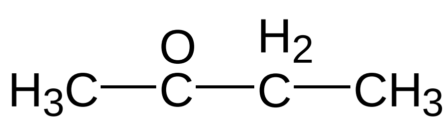
- The unexposed (uncross-linked) areas of resist as well as polymer chains that have not been cross-linked to the overall network of the gel must be dissolved during development.
- Negative photoresist developers are solvents which swell the resist, allowing uncross-linked polymer chains to untangle and be washed away.
- A sequence of solvents is often used to keep the swelling reversible.
- The swelling of the resist during development is the largest contributor to loss of features and linewidth limitations.

Negative Photoresist Development - 2

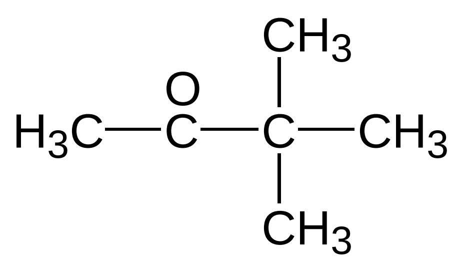


Negative Photoresist Strippers

- Most commonly used are:
  - Methyl ethyl ketone (MEK)
  - Methyl isobutyl ketone (MIBK)



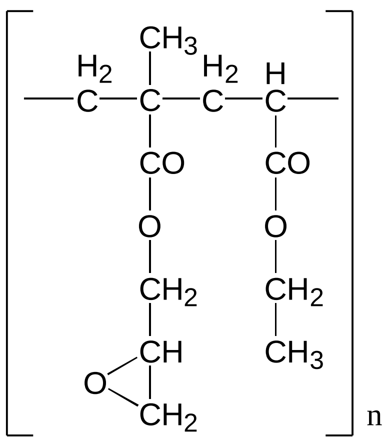
methyl ethyl ketone (MEK)

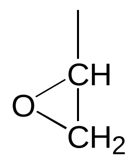


methyl isobutyl ketone (MIBK)

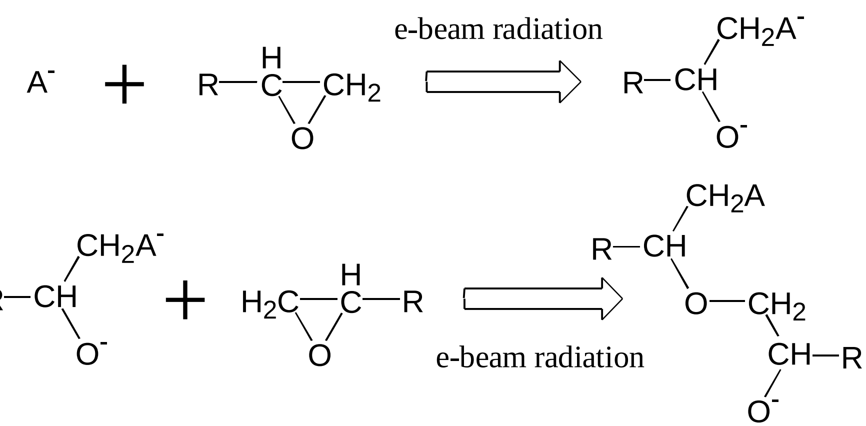
Single Component Negative Photoresists

- Electron beam irradiation produces cross-linking.
- An anion A^- is needed to complete the reaction.





epoxide group



glycidyl methacrylate and ethyl acrylate copolymer