A Little Structural Organic Chemistry - 1

alkanes: (no double bonds):
\[
\text{H}_3\text{C} - \text{H}_2 - \text{C} - \text{H}_2 - \text{C} - \text{H}_2 - \text{C} - \text{H}_2 - \text{C} - \text{H}_2 - \text{C} - \text{H}_2
\]

alkenes: (at least 1 double bond):
\[
\text{H}_3\text{C} - \text{H} - \text{C} - \text{H}_2 - \text{C} - \text{H}_2 - \text{C} - \text{H}_2 - \text{C} - \text{H}_2 - \text{C} - \text{H}_2
\]

alkynes: (at least 1 triple bond):
\[
\text{H}_3\text{C} - \text{C} - \text{C} - \text{H}_2 - \text{C} - \text{H}_2 - \text{C} - \text{H}_2 - \text{C} - \text{H}_2 - \text{C} - \text{H}_2
\]

[alkenes and alkynes are unsaturated hydrocarbons.]

Common Monomers and Their Polymers - 1

<table>
<thead>
<tr>
<th>MONOMER</th>
<th>POLYMER</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{C} = \text{CH}_2)</td>
<td>(\text{H}_2\text{C} = \text{CH}<em>2)</em>(\text{n}) polyethylene (PE)</td>
</tr>
<tr>
<td>(\text{H}_2\text{C} = \text{CH}_2)</td>
<td>(\text{H}_2\text{C} = \text{CH}<em>2)</em>(\text{n}) polypropylene (PP)</td>
</tr>
<tr>
<td>(\text{H}_2\text{C} = \text{CHO})</td>
<td>(\text{H}<em>2\text{C} = \text{CHO})</em>(\text{n}) polyvinyl chloride (PVC)</td>
</tr>
<tr>
<td>(\text{H}_2\text{C} = \text{CH}_2)</td>
<td>(\text{H}_2\text{C} = \text{CH}<em>2)</em>(\text{n}) polystyrene (PS)</td>
</tr>
</tbody>
</table>

Common Monomers and Their Polymers - 2

<table>
<thead>
<tr>
<th>MONOMER</th>
<th>POLYMER</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{C} = \text{CH}_2)</td>
<td>(\text{H}_2\text{C} = \text{CH}<em>2)</em>(\text{n}) polymethyl acrylate (PMA)</td>
</tr>
<tr>
<td>(\text{H}_2\text{C} = \text{CH}_2)</td>
<td>(\text{H}_2\text{C} = \text{CH}<em>2)</em>(\text{n}) polymethyl methacrylate (PMMA)</td>
</tr>
</tbody>
</table>

All rubbers are diene polymers.

(2-methyl-1,3-butadiene)

A Little Structural Organic Chemistry - 2

\(\text{R} - \text{OH}\) alcohol
\(\text{R} - \text{O} - \text{R}'\) ether
\(\text{R} - \text{CHO}\) aldehyde
\(\text{HO}_2\text{C} - \text{OH}\) acid
\(\text{R} - \text{O} - \text{O} - \text{R}'\) peroxide
\(\text{R} - \text{O} - \text{H}\) hydroperoxide
\(\text{CH}_3\text{OH}\) methanol
\(\text{HCHO}\) formaldehyde
\(\text{HCOOH}\) formic acid
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 \( (M_m = 68.12 \text{ g/mole}) \), need to get chains of average length of \( n = \frac{100,000}{68.12} = 1468 \) 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 loses 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

Cyclicized Poly(cis-isoprene) - 1

- Poly(cis-isoprene) is the substrate material for nearly all negative photoresists.
  - cis- \( \text{CH}_2 \) groups are on the same side of the chain
  - trans- \( \text{CH}_2 \) 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 groups would hit each other).

- Two protons are added to cis-isoprene to further saturate the polymer and induce curling into cyclicized versions.

Atomic Weights

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

Molecular Weights

- ethylene \( \text{C}_2\text{H}_4 \) 2(12.011) + 4(1.0079) = 28.05 g/mole
- propylene \( \text{C}_3\text{H}_6 \) 3(12.011) + 6(1.0079) = 42.08 g/mole
- vinyl chloride \( \text{C}_2\text{H}_3\text{Cl} \) 2(12.011) + 3(1.0079) + 35.453 = 62.50 g/mole
- styrene \( \text{C}_8\text{H}_8 \) 8(12.011) + 8(1.0079) = 105.16 g/mole
- methyl acrylate \( \text{C}_4\text{H}_6\text{O}_2 \) 4(12.011) + 6(1.0079) + 2(15.9994) = 86.09 g/mole
- methyl methacrylate \( \text{C}_5\text{H}_8\text{O}_2 \) 5(12.011) + 8(1.0079) + 2(15.9994) = 100.12 g/mole
- isoprene \( \text{C}_5\text{H}_10 \) 5(12.011) + 10(1.0079) = 86.12 g/mole

1 mole is Avogadro number of particles: \( N_A = 6.023 \times 10^{23} \)
Cyclicized Poly(cis-isoprene) - 2

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

<table>
<thead>
<tr>
<th>Property</th>
<th>Uncyclized</th>
<th>Cyclicized</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Molecular Weight</td>
<td>~ 10^6</td>
<td>~ 10^4</td>
</tr>
<tr>
<td>Density</td>
<td>0.92 g/mL</td>
<td>0.99 g/mL</td>
</tr>
<tr>
<td>Softening Point</td>
<td>28°C</td>
<td>50-65°C</td>
</tr>
<tr>
<td>Intrinsic Viscosity</td>
<td>3.4</td>
<td>0.36-0.49</td>
</tr>
<tr>
<td>Unsaturation</td>
<td>14.7 mmole/g</td>
<td>4-8 mmole/g</td>
</tr>
</tbody>
</table>

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 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.
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 O₂. (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.
• Φ = χφ 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:
  • Φ = φ²χ²
    – This requires two photons per cross-link, and thus has very low photographic speed.
    – This allows great variety in the substrate polymer chains.

Exposure and Dose Calculations

\[ \frac{h c}{\lambda} \] is the energy per photon
\[ N_e \frac{h c}{\lambda} \] is the energy in a mole of photons (one Einstein)
Therefore: \[ D = \frac{E N_e h c}{\lambda} \]

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 Flory Function - 1

\[ W = \text{gel fraction (fraction of solids)} \]
\[ C = \text{cross-link fraction} \]
\[ n = \text{degree of polymerization (an integer)} = M_p/M_m \]
\[ f(n) = \text{distribution of polymerization, a log-normal distribution} \]
\[ \beta = \text{dispersity, typically 0.6 - 2.2} \]
\[ \bar{n}_e = \text{average polymer chain length} \]

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.

\[ f(n) = \exp\left(-\frac{\ln(n) - \ln(n_e)}{2\beta^2}\right) \]
\[ W = 1 - \frac{\sum_{n} n f(n) [1 - CW]}{\sum_{n} n f(n)} \]

The Flory Function - 2

Gel Fraction, \( W \)

Cross-Link Fraction

\[ E = \text{exposure in Einsteins/cm}^2 \]
\[ A = \text{absorbed fraction of light} \]
\[ \Phi = \text{quantum efficiency of cross-link formation} \]
\[ C = \text{cross-link fraction} \]

\[ \text{number of formed cross-links in moles/cm}^2 \]
\[ d \rho_r = \text{mass of resist in grams/cm}^2 \]
\[ M_p/2M_m = \text{number of possible cross-links in moles/cm}^2 \]

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

\[ C = \frac{EA\Phi2M_m}{d \rho_r} \]

Gel Point Exposure

\[ \text{The gel point occurs when each polymer strand, on average, has one cross-link. Thus,} \]
\[ C_{gel} = \frac{M_p}{M_p} = \frac{1}{n} \]

The gel point exposure is thus:

\[ E_{gel} = \frac{d \rho_r}{A\Phi2M_m} = \frac{d \rho_r}{A\Phi2M_p} \]

For \( \Phi = 1, A = 1, d_r = 1 \mu m, M_p = 10^5 \text{ g/mole}, \) and \( \lambda = 365 \text{ nm}, \) obtain that \( E_{gel} = 0.26 \times 10^8 \text{ Einsteins/cm}^2 \) and \( A_{gel} = 0.1 \text{ mJ/cm}^2. \)

This is a benchmark for negative resist systems.

Optical Absorption by the Resist

\[ \alpha = \text{fraction of light that is absorbed by the photoresist layer} \]
\[ d_r = \text{thickness of the photoresist layer} \]
\[ \alpha_r = \text{optical absorption coefficient of the photoresist layer} \]
\[ \rho_r = \text{density of the photoresist layer} \]
\[ R_1 = \text{reflectivity of the air - photoresist boundary} \]
\[ R_2 = \text{reflectivity of the photoresist - substrate boundary} \]

single pass:

\[ A = (1 - R_1)(1 - e^{-\alpha d_r}) \]

double pass:

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

Disperisty and Contrast

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

\[ \left(\frac{dW}{dE}\right)_{at} = \frac{2}{E_{gel}}e^{-3\gamma} \]

\[ \left(\frac{dW}{d(\log E)}\right)_{at} = 2\ln(10) e^{-3\gamma} = 4.606 e^{-3\gamma} = \gamma \]

- 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 the resist.
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 O₂ 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.

Single Component Negative Photoresists

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

\[
\begin{align*}
\text{glycidyl methacrylate and ethyl acrylate copolymer} & \quad \rightarrow \quad \text{cross-linked polymer} \\
\text{H₂C=CH₂} & \quad + \quad \text{CH₂=CH₂} & \quad \overset{\text{e-beam radiation}}{\rightarrow} & \quad \text{H₂C=CH₂} \\
\text{epoxide group} & \quad \text{CHO} & \quad \overset{\text{e-beam radiation}}{\rightarrow} & \quad \text{CHO} \\
\text{glycidyl methacrylate and ethyl acrylate copolymer} & \quad \rightarrow \quad \text{cross-linked polymer} \\
\end{align*}
\]

Negative Photoresist Strippers

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

Negative Photoresist Development - 2

<table>
<thead>
<tr>
<th>Volume Expansion Factor, ( V/V_0 )</th>
<th>Chloroform</th>
<th>Toluene</th>
<th>Benzene</th>
<th>Hexane</th>
<th>Ethanol (Base Solvent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>0.0</td>
<td>0.5</td>
<td>1.0</td>
<td>2.0</td>
<td>10.0</td>
</tr>
<tr>
<td>50%</td>
<td>5.0</td>
<td>7.5</td>
<td>10.0</td>
<td>12.5</td>
<td>25.0</td>
</tr>
<tr>
<td>100%</td>
<td>10.0</td>
<td>15.0</td>
<td>20.0</td>
<td>25.0</td>
<td>50.0</td>
</tr>
</tbody>
</table>

Increasing solubility parameter \( \delta \) with molecular percent of solvent in ethanol.