23.1 Polymerization Reactions for Synthetic Polymers
23.2 Applications for Synthetic Polymers
23.3 Liquid Crystals
23.4 Natural Polymers
Kevlar

General Chemistry II
Multichip Module

Cross section of PI thin film multi chip module.
Photoresist (PR)

A material whose properties (e.g. solubility) can be changed by irradiation.

Positive Type PR

Deprotection in the exposed area

Solubility: Enhanced

Negative Type PR

Crosslinking in the exposed area

Solubility: Decreased
Organic Electronics

*Organic Transistor, LEDs, Solar Cells and more*

- Lightweight
- Flexible
- Low temperature processing
- Inexpensive

Printed electronic calculator on a plastic

http://www.dupont.com/displays/

High Viewing Angle Flat-Panel Displays
Flexible and Transparent Display

Samsung “Galaxy Fold”


LG Electronics, Transparent and Foldable Smartphone, US Patent 10,254,863
Flexible and Transparent Display

Polyimides

![Diagram of underwater tunnel with transparent capsules]

Evaluation of aquatic highways, air taxis, and space hotels for life in 50 years time.
Historical Overview of the Synthetic Polymers

Polymerization of Vinyl Chloride & Styrene (Vulcanization of Rubber)

1838, 1839

Celluloid

1868

Rayon

1890

1893

1910

1920

X-Ray Diffraction (H. Mark)

1929

1930

Urea-formaldehyde Resins

General Acceptance of the Macromolecular Hypothesis

Polymerization Reaction (Wallace H. Carothers)

Covalent Bonded Macromolecular Structure (Herman Staudinger)

Nobel Prize in 1953

Styrene-Diene Copolymers & Phenolic Resin "Bakelite" (Lee Baekeland)

1838, 1839

Polymerization of Vinyl Chloride & Styrene (Vulcanization of Rubber)

1929

PMMA

PVAc

Nylon 66 Manufacture

By DuPont

Neoprene Rubber

Polysulfide Rubber (Thiokol)

Melamine-formaldehyde Resins

1931 1936 1937

1945

1960

Epoxy Resin

ABS, Polyesters, PC, PAN

Polyisobutylene (USA)

Polyethylene (UK)

Polyurethane (Ger)

AN-BD Rubber (Ger)

HDPE, LLDPE, PP

(Karl Ziegler & Giulio Natta)

Nobel Prize in 1963

Olefin Polym. by Metallocene (Kaminski)

Controlled Polymerization (Matyjaszewski, Grubbs)

Dendrimers (Tomalia, Newcomb, Frechet)

Conducting Polyacetylene (Shirakawa, MacDiarmid, Heeger)

Nobel Prize in 2000

Anionic Living Polym. (Szwarc)

Functional Polymers

Tailor-Made Polymers

1980

LLS

1990

SPM

2015

X-Ray Diffraction (H. Mark)

1931

1936

1937

1945

1960

NMR, FTIR

Physical Chemistry of Macromolecules

(Paul J. Flory)

Nobel Prize in 1974

1980

Epoxy Resin

ABS, Polyesters, PC, PAN

Polysiloxane (Silicones)

Fluorocarbon Polymers

E. H. Mark

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Styrene-Diene Copolymers

& Phenolic Resin "Bakelite"

(Lee Baekeland)
In 1920, Hermann Staudinger, then professor of organic chemistry at the Eigenössische Technische Hochschule in Zurich, created a stir in the international chemical community when he postulated that materials such as natural rubber have very high molecular weights. In a paper entitled "Über Polymerisation," Staudinger presented several reactions that form high molecular weight molecules by linking together a large number of small molecules. During this reaction, which he called "polymerization," individual repeating units are joined together by covalent bonds.

This new concept, referred to as "macromolecules" by Staudinger in 1922, covered both synthetic and natural polymers and was the key to a wide range of modern polymeric materials and innovative applications. Today, the molecular architectures of synthetic polymers and biopolymers are tailored with high precision to meet the demands of modern technology. The products of polymer chemistry are diverse, from food packaging, textile fibers, auto parts and toys, to membranes for water desalination, carriers used in controlled drug release and biopolymers for tissue engineering.
Why are organic polymers (macromolecules) so useful?

ائه Unique properties with high performance/cost ratio
- lightweight, high toughness and modulus
- excellent electrical properties
- good durability in various environment
- easy processing
- versatile structure

ياه Factors that govern physical properties of polymeric materials
- Chemical factors
  Molecular structure
    [Primary bond strength, Resonance stabilization, Crosslinking and branching
    Molecular symmetry (structure regularity)]
  Mechanism of bond cleavage
  Secondary (hydrogen) bonding or van der Waals' bond forces
- Physical factors
  Molecular weight and molecular weight distribution
  Morphology
    [Orientation, Crystallinity]
The three states of matter

A Gas: Molecules are far apart and fill the available space

B Liquid: Molecules are close together but move relative to each other

C Solid: Molecules are tightly packed in a regular array and move very little relative to each other
Hydrocarbons

Gas

\[ \text{H} - \text{C} - \text{H} \quad \text{H} - \text{C} - \text{C} - \text{H} \quad \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \quad \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \]

Liquid

\[ \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \quad \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \]

Solid

\[ \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \]

Polymers

\[ \left( \text{H}_2\text{C} - \text{CH}_2 \right)_n \]

Polyethylene (PE)

\[ \left( \text{H}_2\text{C} - \text{CH} - \text{CH}_3 \right)_n \]

Polypropylene (PP)
Figure 9.31. Alternation of crystalline and amorphous regions in a rapidly cooled melt of semicrystalline polyethylene.

Fringed micelle

Folded-chain lamella
Polymers (고분자): Poly = many, mer = part, Macromolecules (거대분자) macromolecules built up by the linking together (polymerization) of large numbers of smaller molecules (monomers)

Types of Polymers and Polymerizations

Composition or Structure (Carothers)
- Condensation
- Addition

Polymerization Reaction Mechanism (Flory)
- Step
- Chain

A polymer is classified as a condensation polymer,
if a) its synthesis involves the elimination of small molecules
or b) it contains functional groups as part of the polymer chain
or c) its repeating unit lacks certain atoms that are present in the (hypothetical) monomer to which it can be degraded.

If a polymer does not fulfill any of these requirements, it is classified as an addition polymer.
Examples (Condensation Polymers)

a) polyamides

\[ \begin{align*}
   &n \text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 + n \text{HO-C-CH}_2\text{CH}_2\text{CH}_2\text{H} - \text{COH} \\
   \quad &\downarrow \\
   &\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH-C-CH}_2\text{CH}_2\text{CH}_2\text{C} - \text{O} _n + (2n - 1) \text{H}_2\text{O}
\end{align*} \]

b) polyurethanes

\[ \begin{align*}
   &n \text{HO-R-OH} + n \text{O=C=N-R'-N=C=O} \\
   \quad &\downarrow \\
   &\text{HO-R-O-C-NH-R'-NH-C-O}_n \text{R-O-C-NH-R'-N=C=O}
\end{align*} \]

c) phenol-formaldehyde polymers

\[ \begin{align*}
   &n \text{OH} + n \text{H-C-H} \rightarrow \text{OH} \quad \text{H-C-CH}_2\text{CH}_2\text{CH}_2\text{NH}_n + (n - 1) \text{H}_2\text{O}
\end{align*} \]
## Polymerization mechanism

Step and chain polymerizations differ in the length of time required for the complete growth of full-sized polymer molecules.

<table>
<thead>
<tr>
<th>Chain Polymerization</th>
<th>Step Polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Only growth reaction adds repeating units one at a time to the chain.</td>
<td>Any two molecular species present can react.</td>
</tr>
<tr>
<td>Monomer concentration decreases steadily throughout reaction.</td>
<td>Monomer disappears early in reaction: at DP* 10, less than 1% monomer remains.</td>
</tr>
<tr>
<td>High polymer is formed at once; polymer molecular weight changes little throughout reaction.</td>
<td>Polymer molecular weight rises steadily throughout the reaction.</td>
</tr>
<tr>
<td>Long reaction times give high yields but affect molecular weight little.</td>
<td>Long reaction times are essential to obtain high molecular weights.</td>
</tr>
<tr>
<td>Reaction mixture contains only monomer, high polymer, and about $10^{-8}$ part of growing chains.</td>
<td>At any stage all molecular species are present in a calculable distribution.</td>
</tr>
</tbody>
</table>

The two classifications, polymerization mechanism and polymer structure, cannot always be used interchangeably.

---

General Chemistry II
### Step-growth Mechanism (Condensation Polymerization)

- **Monomer**: (AB or AA + BB Type)
  - A, B: Reactive

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 + 1 = 2</td>
<td>(dimer)</td>
</tr>
<tr>
<td>1 + 2 = 3</td>
<td>(monomer)</td>
</tr>
<tr>
<td>2 + 2 = 4</td>
<td></td>
</tr>
<tr>
<td>2 + 2 = 4</td>
<td></td>
</tr>
<tr>
<td>3 + 2 = 5</td>
<td></td>
</tr>
<tr>
<td>3 + 4 = 7</td>
<td></td>
</tr>
<tr>
<td>4 + 4 = 8</td>
<td></td>
</tr>
</tbody>
</table>

### Chain-growth Mechanism (Addition Polymerization)

- **Initiator**
  - Monomer

**Initiation >> Propagation**

- Initiator
- Reactive chain-end

**Reaction of monomer with Polymer end-groups**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 + 1 = 2</td>
<td></td>
</tr>
<tr>
<td>2 + 1 = 3</td>
<td></td>
</tr>
</tbody>
</table>
| 3 + 1 = 4 | ...
| n + 1 = n+1 | |
Chain growth

Living

Step growth

Molecular weight

Conversion

0%

100%

“High Polymer” weight
23.1 POLYMERIZATION REACTIONS FOR SYNTHETIC POLYMERS

- **Addition polymerization 1** ~ free radical chain reaction

**Ex.** Polymerization of vinyl chloride, \( \text{CH}_2\text{=CHCl} \rightarrow \text{Poly(vinyl chloride)} \) (PVC)

Initiator ~ peroxide, \( \text{R–O–O–R'} \)

- **Initiation:**

  \[
  \text{R–O–O–R'} \rightarrow \text{R–O}^- + \cdot\text{O–R'}
  \]

  \[
  \text{R–O}^- + \text{CH}_2\text{=CHCl} \rightarrow \text{R–O–CH}_2\text{–C}^-\cdot
  \]

- **Propagation**

  \[
  \text{R–O–CH}_2\text{–C}^-\cdot + \text{CH}_2\text{=C–CH}_2\text{–C}^-\cdot \rightarrow \text{R–O–CH}_2\text{–C–C–CH}_2\text{–C}^-\cdot
  \]
➢ **Termination 1 (Coupling)**

\[
R-O-(CH_2-CHCl)_mCH_2-C\cdot + \cdot C-CH_2-(CHCl-CH_2)_nO-R' \rightarrow \\
R-O-(CH_2-CHCl)_mCH_2-C-C-CH_2-(CHCl-CH_2)_nO-R'
\]

➢ **Termination 2 (Disproportionation)**

\[
R-O-(CH_2-CHCl)_mCH_2-C-C\cdot + \cdot C-CH_2-(CHCl-CH_2)_nO-R' \rightarrow \\
R-O-(CH_2-CHCl)_mCH=CHCl + CH_2Cl-CH_2-(CHCl-CH_2)_nO-R'
\]
❖ **Branched polymeric chain**

![Diagram of branched polymeric chain]

- Hydrogen atom abstraction
- Growing second chain terminates
- New radical site generated
- Branch grows by addition polymerization from new radical site

❖ **Addition polymerization 2 ~ ion initiated chain reaction**

❖ **Polymerization of acrylonitrile**

\[
\begin{align*}
  n & \quad \text{CH}_2\equiv\text{CH} \\
  & \quad \text{C} \equiv \text{N} \\
\end{align*}
\]

\[
\rightarrow \quad \left[ \begin{array}{c} 
  \text{CH}_2\text{CH} \\
  | \\
  \text{C} \equiv \text{N} \\
\end{array} \right]^n
\]

Initiator for this process: butyl lithium, \((\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)^{-}\text{Li}^{+}\) or \(\text{Bu}^{-}\text{Li}^{+}\)
➢ **Initiation**

\[
\text{Bu}^\ominus\text{Li}^\oplus + \text{CH}_2=\text{CH} \rightarrow \text{Bu}--\text{CH}_2--\text{CH}^\ominus\text{Li}^\oplus
\]

\[
\text{C}≡\text{N} \quad \text{C}≡\text{N}
\]

➢ **Propagation**

\[
\text{Bu}--\text{CH}_2--\text{CH}^\ominus\text{Li}^\oplus + \text{CH}_2=\text{CH} \rightarrow \text{Bu}--\text{CH}_2--\text{CH}^\ominus\text{Li}^\oplus + \text{CH}_2=\text{CH}
\]

\[
\text{C}≡\text{N} \quad \text{C}≡\text{N}
\]

➢ **Termination**

\[
\text{-(CH}_2--\text{CH})_n\text{CH}_2--\text{CH}^\ominus\text{Li}^\oplus + \text{H}_2\text{O} \rightarrow
\]

\[
\text{-(CH}_2--\text{CH})_n\text{CH}_2--\text{CH}_2 + \text{Li}^\oplus + \text{OH}^\ominus
\]

\[
\text{C}≡\text{N} \quad \text{C}≡\text{N}
\]
Chain Polymerization

Radical

\[ R^\cdot \overset{\text{Cl}}{\longrightarrow} R\overset{\text{Cl}}{\longrightarrow} R\overset{\text{Cl}}{\longrightarrow} R\overset{\text{Cl}}{\longrightarrow} R\overset{\text{Cl}}{\longrightarrow} V \]

Anionic

\[ \overset{\text{Nu}}{\text{N}} \overset{\text{C}}{\longrightarrow} \overset{\text{C}}{\overset{\text{Nu}}{\longrightarrow}} \overset{\text{N}}{\overset{\text{C}}{\longrightarrow}} \overset{\text{C}}{\overset{\text{Nu}}{\longrightarrow}} \overset{\text{N}}{\overset{\text{C}}{\longrightarrow}} \overset{\text{C}}{\overset{\text{Nu}}{\longrightarrow}} \overset{\text{N}}{\overset{\text{C}}{\longrightarrow}} \overset{\text{C}}{\overset{\text{Nu}}{\longrightarrow}} AN \]

Cationic

\[ \overset{\text{E}^\cdot}{\overset{\text{OR}}{\longrightarrow}} \overset{\text{Nu}}{\overset{\text{OR}}{\longrightarrow}} \overset{\text{OR}}{\overset{\text{E}^\cdot}{\longrightarrow}} \overset{\text{OR}}{\overset{\text{E}^\cdot}{\longrightarrow}} \overset{\text{OR}}{\overset{\text{E}^\cdot}{\longrightarrow}} \overset{\text{OR}}{\overset{\text{E}^\cdot}{\longrightarrow}} V \]
Chain-growth Mechanism (Addition Polymerization)

Radical

\[ R^\bullet + \text{Cl} \rightarrow R^\bullet \text{Cl} \rightarrow \text{VC} \rightarrow R\text{Cl}^\bullet \rightarrow R\text{Cl} \rightarrow \text{VC} \rightarrow \]

Anionic

\[ \text{Nu} + \text{C} = \text{Nu} \rightarrow \text{Nu} \text{C} \rightarrow \text{AN} \rightarrow \text{Nu} \text{C} \rightarrow \text{AN} \rightarrow \]

Cationic

\[ \text{E}^+ + \text{OR} \rightarrow \text{Nu} \text{OR}^+ \rightarrow \text{VE} \rightarrow \text{E} \text{OR}^+ \rightarrow \text{VE} \rightarrow \]

Initiation >> Propagation

Reaction of monomer with Polymer end-groups

\[ 1 + 1 = 2, \quad 2 + 1 = 3, \quad 3 + 1 = 4, \quad \ldots, \quad n + 1 = n+1 \]
Condensation polymerization (A step polymerization)

→ A small molecule (e.g. H₂O) is split off as each monomer unit is attached to the growing polymer

Ex. Polymerization of 6-aminohexanoic acid → “Nylon 6”

Adipic acid       +       Hexamethylenediamine → “Nylon 66”
**Step-growth Mechanism (Condensation Polymerization)**

**Monomer**
(AB or AA + BB Type)  
A, B : Reactive

1 + 1 = 2 (dimer)  
1 + 2 = 3  
2 + 2 = 4

2 + 2 = 4  
3 + 2 = 5  
3 + 4 = 7  
4 + 4 = 8
Copolymers

- Polymerization with two or more types of monomers into irregular sequence along the polymer chain

**random** – A and B randomly vary in chain

**alternating** – A and B alternate in polymer chain

**block** – large blocks of A alternate with large blocks of B

**graft** – chains of B grafted on to A backbone
Cross-Linking: Nonlinear Synthetic Polymers

◆ Phenol-formaldehyde copolymer ~ adhesives for plywood

❖ With excess phenol, acid catalyst...

(1) Addition of formaldehyde to phenol to give methylolphenol

\[
\text{Ph} + \text{H}_2\text{C} = \text{O} \rightarrow \text{PhCH}_2\text{OH}
\]

(2) Condensation reaction to form a linear polymer, novalac

\[
2n \text{PhCH}_2\text{OH} \rightarrow \left[\text{PhCH}_2\text{OH}\right]_n + 2n \text{H}_2\text{O}
\]
Fig. 23.3 A mixture of phenol / formaldehyde dissolved in acetic acid + HCl → Phenol-formaldehyde polymer
With excess formaldehyde …

These monomers can form cross-linked polymers.

“Bakelite” (1907), later became “Catalin”

Revolutionary non-flammable first artificial plastic made by Baekeland
Phenolic resin made from cross-linked phenol and formaldehyde
◆ “Bakelite” (1907), later became “Catalin”

Revolutionary non-flammable first artificial plastic made by Baekeland
Phenolic resin made from cross-linked phenol and formaldehyde
Molecular Shape of Macromolecules

- Linear
- Branched
- Block
- Grafted
- Crosslinked
- Ladder
- Star
- Hyperbranched
- Dendrimer
23.2 APPLICATIONS FOR SYNTHETIC POLYMERS

■ Fibers

◆ Cellulose

~ Made by chemical regeneration of the natural polymer cellulose, a condensation polymer of glucose that is made by plants.

Glucose $\rightarrow$ Cellulose + $2n\ H_2O$
Cellulose fibers in plant cell wall

Cellulose structure

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**Rayon** ~ “semisynthetic” fiber

**Viscous rayon process**

~ Digestion of cellulose with conc. NaOH:

\[ \text{–OH groups} \rightarrow \text{–O}^-\text{Na}^+ \text{ ionic groups} \]

~ Reaction with CS\(_2\):

\[ \text{–C–O}^-\text{Na}^+ + \text{CS}_2 \rightarrow \text{–C–O–C–S}^-\text{Na}^+ \]

~ Ripening step:

Xanthate groups are removed to recover CS\(_2\)

~ Addition of H\(_2\)SO\(_4\):

Neutralize NaOH

Spin out (wet spinning) viscous rayon to form fibers
Filter paper (cellulose) will dissolve in a concentrated ammonia solution containing $[\text{Cu(NH}_3\text{)}_4]^{2+}$ ions. When the solution is extruded into aqueous sulfuric acid, a dark blue thread of rayon (regenerated cellulose) precipitates.
◆ Nylon

1930s Carothers (DuPont)
Condensation polymerization
to form amide linkage

Wallace H. Carothers
(US, 1896-1937)

35 ft. leg with a nylon stocking, L.A.
➢ Condensation reaction:

\[
\begin{align*}
\text{HO} - \text{C} - (\text{CH}_2)_4 - \text{C} - \text{OH} + \text{H} - \text{N} - (\text{CH}_2)_6 - \text{NH}_2 & \rightarrow \\
\text{Hexamethylenediamine} & \\
\text{Adipic acid} & \\
\text{HO} - \text{C} - (\text{CH}_2)_4 - \text{C} - \text{N} - (\text{CH}_2)_6 - \text{NH}_2 + \text{H}_2\text{O}
\end{align*}
\]

➢ Repeating the above process gives “nylon 66”

\[
\left[\begin{array}{c}
\text{O} \\
\text{C} - (\text{CH}_2)_4 - \text{C} - \text{N} - (\text{CH}_2)_6 - \text{N} \\
\text{H} \\
\text{H} \\
\end{array}\right]_n
\]

- 66 → 6 carbon atoms on the starting diamine and 6 on the carboxylic acids
➢ Hexamethylenediamine dissolved in water (lower layer)
➢ Adipyl chloride dissolved in hexane (upper layer).

At the interface between the layers, nylon forms and is drawn out onto the stirring bar.
**Polyester** → Dicarboxylic acid + Dialcohol

Ex. Polyethylene terephthalate, “PET” “Dacron”

![Polyester reaction diagram]

➢ Repeating the above process gives “Dacron”
- **Polyester** → Dicarboxylic acid + Dialcohol

Ex. Polyethylene terephthalate, “PET” “Dacron”
<table>
<thead>
<tr>
<th>Name</th>
<th>Structural Units</th>
<th>Properties</th>
<th>Sample Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rayon</td>
<td>Regenerated cellulose</td>
<td>Absorbent, soft, easy to dye, poor wash and wear</td>
<td>Dresses, suits, coats, curtains, blankets</td>
</tr>
<tr>
<td>Acetate</td>
<td>Acetylated cellulose</td>
<td>Fast drying, supple, shrink-resistant</td>
<td>Dresses, shirts, draperies, upholstery</td>
</tr>
<tr>
<td>Nylon</td>
<td>Polyamide</td>
<td>Strong, lustrous, easy to wash, smooth, resilient</td>
<td>Carpeting, upholstery, tents, sails, hosiery, stretch fabrics, rope</td>
</tr>
<tr>
<td>Dacron</td>
<td>Polyester</td>
<td>Strong, easy to dye, shrink-resistant</td>
<td>Permanent-press fabrics, rope, sails, thread</td>
</tr>
<tr>
<td>Acrylic (Orlon)</td>
<td>$\text{CH}_2\underbrace{-\text{CH}}_n\text{C}=-\text{N}$</td>
<td>Warm, lightweight, resilient, quick-drying</td>
<td>Carpeting, sweaters, baby clothes, socks</td>
</tr>
</tbody>
</table>
Plastics

Polymeric materials that can be molded or extruded into desired shapes and that harden upon cooling or solvent evaporation

Bakelite ~ first synthetic plastic, phenol-formaldehyde resin

Polyethylene

Low-density polyethylene (LDPE) < 0.94 g cm\(^{-3}\)

Free-radical-initiated addition polymerization of ethylene monomer at high pressure (1000~3000 atm) and at 300~500°C

Free radicals frequently abstract hydrogen from the middle of the chain

Resulting PE is not a perfect linear chain, heavily branched

Difficulty in packing of irregularly branched chains leads to LDPE

Soft, coating, trash bags, squeeze bottles
➢ **High-density polyethylene (HDPE)**

~ 0.96 g cm$^{-3}$

~ Linear PE synthesized with

  Ziegler catalyst (1954) $\text{TiCl}_4 / \text{Al(C}_2\text{H}_5)_3$

~ Monomer added only to the coordination sphere of $\text{Ti}^{4+}$

~ Hard, molding into bowls, toys

➢ **Linear low density polyethylene (LLDPE)**

~ Same metal-catalyzed reactions as HDPE

~ Deliberate copolymer with other 1-alkenes

~ Contains controlled short length of side groups
HDPE
(high density polyethylene)

LDPE
(low density polyethylene)

LLDPE
(linear low density polyethylene)

Isotactic Polypropylene

Syndiotactic Polypropylene
Structure and Properties of Polyolefins

\[
\left[ \text{H}_2\text{C} - \text{CH}_2 \right]_n \\
\text{Polyethylene (PE)}
\]

\[
\left[ \text{H}_2\text{C} - \text{C} - \text{CH}_3 \right]_n \\
\text{Polypropylene (PP)}
\]

**HDPE**  \( T_m = 135 \degree C \)

**Isotactic PP**  \( T_m = 165 \degree C \)

**Syndiotactic PP**  \( T_m = 150 \degree C \)

**Atactic PP**  Amorphous
Polypropylene

- Substitution of H in ethylene by a –CH₃ group
- Stiffer and harder than HDPE, higher m.p., endure high T
- Medical instruments (sterilization at high temp)

Different conformations of methyl groups

- **Isotactic form**
  - All methyl groups are arranged on the same side
  - Ziegler catalyst

- **Syndiotactic form**
  - Methyl groups are arranged alternately in a regular fashion
  - Natta catalyst (VCl₄)

- **Atactic form** ~ random positioning of methyl groups
Fig. 23.6 Structures of (a) isotactic, (b) syndiotactic, and (c) atactic polypropylene.
Nobel Prize Winner in Organic Chemistry

"for their discoveries in the field of the chemistry and technology of high polymers" (1963)

K. Ziegler  G. Natta

Ziegler, Max-Planck-Institut, Mülheim, Germany

Aufbau reaction (1940's)

\[
\begin{align*}
n & \text{CH}_2=\text{CH}_2 & \text{Et}_3\text{Al} & \text{Al} \{ (\text{C}_2\text{H}_4)_n \text{Et} \}_3 & \text{O}_2 & \text{HO-} (\text{CH}_2-\text{CH}_2)_n - \text{Et} \\
& n = 1-12
\end{align*}
\]

Accident?

\[
\begin{align*}
n & \text{CH}_2=\text{CH}_2 & \text{Et}_3\text{Al} & \text{Ni(II)} & \text{CH}_3-\text{CH}_2-\text{CH} = \text{CH}_2 \\
& & & & \text{Only!}
\end{align*}
\]

1953

\[
\begin{align*}
n & \text{CH}_2=\text{CH}_2 & \text{Et}_3\text{Al} & \text{TiCl}_4 & -(\text{CH}_2-\text{CH}_2)_n^- \\
& & & & \text{(High Density Polyethylene, HDPE)}
\end{align*}
\]
Polymers with other elements beyond C and H

- Polyvinyl chloride (PVC)
- Polytetrafluoroethylene (Teflon)
  - Discovered by Plunkett at DuPont (1938)
  - Almost completely inert
  - Excellent heat stability (260°C)
  - Non-stick surface coating (frying pans)

Roy J. Plunkett
(US, 1910-1994)
<table>
<thead>
<tr>
<th><strong>Polyethylene</strong></th>
<th>(\text{(\text{CH}_2-\text{CH}_2)}_n)</th>
<th>High density: hard, strong, stiff</th>
<th>Molded containers, lids, toys, pipe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene</td>
<td>(\text{(\text{CH}_2-\text{CH})}_n)</td>
<td>Low density: soft, flexible, clear</td>
<td>Packaging, trash bags, squeeze bottles</td>
</tr>
<tr>
<td></td>
<td>(\text{(\text{CH}_3)}_n)</td>
<td>Stiffer, harder than high-density polyethylene, higher melting point</td>
<td>Containers, lids, carpeting, luggage, rope</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>(\text{(\text{CH}_2-\text{CH})}_n)</td>
<td>Nonflammable, resistant to chemicals</td>
<td>Water pipes, roofing, credit cards, records</td>
</tr>
<tr>
<td></td>
<td>(\text{(\text{Cl})}_n)</td>
<td>Brittle, flammable, not resistant to chemicals, easy to process and dye</td>
<td>Furniture, toys, refrigerator linings, insulation</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>(\text{(\text{CH}_2-\text{CH})}_n)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\text{(\text{(\text{CH}_2-\text{CH}_2)}_n)</td>
<td>(\text{(\text{CH}_3)}_n)</td>
<td></td>
</tr>
<tr>
<td>Phenolics</td>
<td>Phenol-formaldehyde copolymer</td>
<td>Resistant to heat, water, chemicals</td>
<td>Plywood adhesive, Fiberglass binder, circuit boards</td>
</tr>
</tbody>
</table>
◆ Elastomer

~ Polymers that can be deformed to a great extent and still recover its original form when the deforming stress is removed “Rubber” ~ term first used by Priestley (rub with pencil eraser)

❖ Natural rubber

~ Polymer of isoprene (2-methylbutadiene), all cis-form, unsaturated

❑ Gutta percha ~ all trans-form of polyisoprene, tough (golf ball)

➢ Free-radical addition polymerization of isoprene

mixture of cis- and trans-forms, useless as an elastomer!
From Rubber trees
Fig. 23.8 In the polymerization of isoprene, a cis or trans configuration can form at each double bond in the polymer. The blue arrows show the redistribution of the electrons upon bond formation.
Changing the architecture of the natural rubber (linear polyisoprene) to a crosslinked polymer dramatically changes the physical properties – makes the material useful.
❖ **Vulcanization of rubber**

~ Discovered by Goodyear (1839)
~ Addition of sulphur (< 5%)

To improve properties of natural rubber

Sulphur bridge between methyl groups on different chains

❖ **Synthetic rubbers**

SBR rubber (Styrene-butadiene rubber)

NBR rubber (Acronitrile-butadiene rubber)

All-**cis** polybutadiene

~ Ziegler-Natta catalysts
Electrically Conducting Polymers

“Synthetic metals”

\( \pi \)-conjugated chain of polymer backbone

Ground-state for the polymer chain \( \rightarrow \) insulator

Doping \( \rightarrow \) conducting polymers

Partial oxidation or reduction of polymers

Electron donating dopants: Na, K, Li \( \rightarrow \) \( n \)-type material

Electron accepting dopants: \( I_2, PF_6, BF_4 \) \( \rightarrow \) \( p \)-type material

Polyacetylene doped with iodine

\( \rightarrow \) conductivity of \( \sim 5 \times 10^4 \) S cm\(^{-1} \) (1/10 of Cu)

1 S(Siemens) = 1 A V\(^{-1} \) = 1 mho = 1 \([\Omega(ohm)]^{-1}\)
Conducting Organic Polymers
(Nobel Prize in Chemistry 2000)

Acetylene \[\rightarrow\] Polyacetylene

Remove one electron \[\rightarrow\] Resonance stabilized

Add one electron \[\rightarrow\] Resonance stabilized

Polyacetylene

Poly(p-phenylene vinylene)
trans-Polyacetylene

Polythiophene

Poly(para-phenylene)

Poly(para-pyridine)