Chapter 5
Selected Classes of Organic Compounds
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5.1
From Crude Oil to Base Chemicals and Polyolefins
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<th>Distillation Fractionation</th>
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<th>Paraffin Wax</th>
<th>Bitumen</th>
<th>Petroleum Coke</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>C₁–C₂</td>
<td>C₃–C₄</td>
<td>C₅–C₁₂</td>
<td>C₁₀–C₁₆</td>
<td>C₁₄–C₂₁</td>
<td>C₁₄–C₇₀</td>
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<td>120–220°C</td>
<td>150–270°C</td>
<td>200–350°C</td>
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<td>200–600°C</td>
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</table>
Base Chemical Production

- Acetic acid: 10 Mt, $1.14/kg
- Methanol: 29 Mt, $0.50/kg
- Formaldehyde: 8.7 Mt, $0.46/kg
- Terephthalic acid: 30 Mt, $0.93/kg
- o/m/p-xylene: 10.1 Mt, $1.06/kg
- Butadiene: 8.5 Mt, $1.19/kg
- Polybutadiene: 1.82 Mt, $1.19/kg
- MTBE: 22.2 Mt, $1.11/kg
- Polyvinyl chloride: 16 Mt, $1.91/kg
- Ethanol: 2.6 Mt, $0.42/kg
- Ethylene oxide: 11.2 Mt, $1.70/kg
- Ethanolamines: 0.84 Mt, $1.28/kg
- Vinyl chloride: 24 Mt, $0.75/kg
- Vinyl acetate: 3.8 Mt, $1.39/kg
- Propylene oxide: 4 Mt, $2.23/kg
- Acrylonitrile: 4.3 Mt, $2.99/kg
- Acrylic acid: 2 Mt, $2.43/kg
- Isopropanol: 2.3 Mt, $0.84/kg
- n-Butanols: 1.78 Mt, $1.50/kg
- Ethylene: 79 Mt, $1.30/kg
- Polyethylene: 41 Mt, $1.87/kg
- Butane/ethenes: Mixture
- Oil coke
- Heavy fuel oil
- Jet fuel
- Light fuel/diesel oil
- Naphtha
- Natural gas liquids (methane, ethane, propane)
- BTX
- Diisocyanates: 2.23 Mt, $2.2/kg
- Toluene: 7.85 Mt, $1.03/kg
- Benzene: 24.9 Mt, $1.19/kg
- Cyclohexane: 5.1 Mt, $0.76/kg
- Cyclohexanone, Nylon-6,6: 3.4 Mt, $1.10/kg
- Phenol: 3.4 Mt, $1.70/kg
- Styrene: 19.2 Mt, $1.32/kg
- Polystyrene: 5.18 Mt, $2.15/kg
- SBR, ABS, SAN, resins
- Acetone: 3.4 Mt, $1.70/kg
- Cumene: 8 Mt, $1.36/kg
- Ethylbenzene: 19.7 Mt, $1.27/kg
- Propylene glycol: 0.97 Mt, $1.33/kg
- Acrylic fibres, nitrile rubber, ABS, SAN
- Polyethylene glycol: 0.84 Mt, $1.28/kg
- Ethylene glycol: 9.7 Mt, $1.60/kg
Oxidation of Alkanes

- **Complete Oxidation (Combustion)**

  \[ C_{2n+2}H_{2n+2} + (3n/2 + 1/2)O_2 \rightarrow nCO_2 + (n + 1)H_2O \]

  \[ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H = -892 \text{ kJ/mol} \]

- **Partial Oxidation**

  \[ ^0\text{CH}_4 + 1/2O_2 \rightarrow \text{CH}_3\text{OH} \]
  methanol

  \[ ^0\text{CH}_4 + 2/2O_2 \rightarrow \text{HCHO} + H_2O \]
  formaldehyde

  \[ ^0\text{CH}_4 + 3/2O_2 \rightarrow \text{HCOOH} + H_2O \]
  formic acid

  \[ ^0\text{CH}_4 + 4/2O_2 \rightarrow \text{CO}_2 + 2H_2O \]
  carbon dioxide

  \[ ^0\text{CH}_4 + 5/2O_2 \rightarrow \text{H}_2\text{CO}_3 \]
  carbonic acid
• Preparation of Simple Haloalkanes by Halogenation of Alkanes

\[
\begin{align*}
\text{CH}_4 & \xrightarrow{1/2 \text{Cl}_2} \text{H}_2\text{HCl} & & \text{chloromethane} & & \text{methyl chloride} & & \text{b.p. } -24^\circ\text{C} & & 1.86 \text{ D} \\
& & & & & & & & \\
\text{CH}_3\text{CH}_3 & \xrightarrow{1/2 \text{Cl}_2} \text{Cl}_2\text{HCl} & & \text{dichloromethane (DCM)} & & \text{methylene chloride} & & \text{b.p. } 40^\circ\text{C} & & 1.60 \text{ D} \\
& & & & & & & & \\
\text{CH}_3\text{CH}_3 & \xrightarrow{1/2 \text{Cl}_2} \text{Cl}_2\text{Cl} & & \text{trichloromethane} & & \text{chloroform} & & \text{b.p. } 61^\circ\text{C} & & 1.04 \text{ D} \\
& & & & & & & & \\
\text{CH}_3\text{CH}_3 & \xrightarrow{1/2 \text{Cl}_2} \text{Cl}_2\text{Cl}_2 & & \text{tetrachloromethane} & & \text{tetrachlorocarbon (tetra)} & & \text{b.p. } 76^\circ\text{C} & & \\
\end{align*}
\]

• Industrial Production of Alkenes by Thermal Cracking of Alkanes (followed by Fractionation)

\[
\begin{align*}
\text{H}_3\text{C}==\text{CH}_3 & \xrightarrow{> 1000^\circ\text{C}} \text{H}_2\text{H} + \text{H}_2 \\
& & \text{H}_2\text{O} \\
\text{H}_3\text{C}==\text{CHCH}_3 & \xrightarrow{> 1000^\circ\text{C}} \text{H}_2\text{H} + \text{CH}_4 \\
& & \text{H}_2\text{O} \\
\text{H}_3\text{C}==\text{CHCH}_3 & \xrightarrow{> 1000^\circ\text{C}} \text{H}_3\text{C}==\text{CH}_2 + \text{H}_2 \\
& & \text{H}_2\text{O} \\
\end{align*}
\]
High-Density Polyethylene (HDPE) and Polypropylene (PP)

- free radical polymerization of ethylene at high pressure in the gas phase

\[
\begin{align*}
\text{H}_2\text{C}=\text{CH}_2 & \xrightarrow{300^\circ\text{C}, 1000\text{ bar}} \text{O}_2 / \text{H}_2\text{O}_2 \quad \rightarrow \quad \text{n}\text{} \\
\end{align*}
\]

- low-density polyethylene (LDPE) \( (d \approx 0.92 \text{ g cm}^{-3}) \)
- high degree of branching (2–4% Me, <0.5% longer branches), low tensile strength (12 MPa)
- low crystallinity (40–50%), \( T_g \approx -110^\circ\text{C}, T_m \approx 100–110^\circ\text{C} \)

- propylene (and higher olefins) cannot be polymerized via radical polymerization

\[
\begin{align*}
\text{H}_2\text{C}=\text{CH}_3 & \xrightarrow{+ \text{R}^\bullet} \text{H}_2\text{C}=\text{CH}_2 \quad \leftrightarrow \quad \text{H}_2\text{C}=\text{CH}_2 \\
\end{align*}
\]
High-Density Polyethylene (HDPE) and Polypropylene (PP)

- Catalytic polymerization of ethylene and propylene in the gas phase using Ziegler Natta catalysts

\[
\text{Ziegler Natta} \quad \text{H} = \text{H} \quad \text{CH}_3 \quad \text{H} = \text{H} \quad \rightarrow \quad \left[\text{H}_2\text{C}_n\text{H}_{2n+2}\right]_n
\]

- High-density polyethylene (HDPE) \((d \approx 0.95 \text{ g cm}^{-3})\), 60 Mt/a
  - Low degree of branching (<0.1%), high tensile strength \((\leq 32 \text{ MPa})\)
  - High crystallinity (>90%), \(T_g \approx -110^\circ\text{C}, T_m \leq 141^\circ\text{C}\)

- Isotactic polypropylene (iPP) \((d \approx 0.91 \text{ g cm}^{-3})\), 55 Mt/a
  - High tensile strength \((\leq 30 \text{ MPa})\)
  - Low crystallinity (>90%), \(T_g \approx -10^\circ\text{C}, T_m \leq 165^\circ\text{C}\)
Polymerization of Alkenes (Olefins)

- Radical Polymerization

\[
\text{Initiator} \rightarrow \text{Initiator} + \text{Monomer} \rightarrow \text{Initiator} \rightarrow \text{Initiator} - \text{H}^* \rightarrow \text{Initiator}
\]

- Anionic Polymerization

\[
\text{Nu}^- \rightarrow \text{Nu}^- + \text{Monomer} \rightarrow \text{Nu}^- \rightarrow \text{Nu}^- + \text{End Group} \rightarrow \text{Nu}^-
\]

- Cationic Polymerization

\[
\text{El}^+ \rightarrow \text{El}^+ + \text{Monomer} \rightarrow \text{El}^+ \rightarrow \text{El}^+ - \text{H}^+ \rightarrow \text{El}^+
\]
General Reaction Stages in the Example of Radical Polymerizations

- **initiator decomposition**
  \[
  \text{initiator} \xrightarrow{-N_2 \uparrow} 2 \text{ initiator radical}
  \]

- **initiation**
  \[
  \text{initiator radical} + \text{monomer} \rightarrow \text{monomer radical}
  \]

- **propagation (chain growth)**
  \[
  \text{monomer radical} \xrightarrow{n} \text{polymer radical}
  \]

- **termination (e.g., combination)**
  \[
  \text{polymer radicals} \rightarrow \text{cross-linked polymer}
  \]
Azobis(isobutynitrile) (AIBN)  
\[ \text{Initiator Decomposition} \]

\[ \text{NC} \quad \text{N} \quad \text{N} \quad \text{CN} \quad 40-80^\circ C \quad - N_2 \uparrow \quad 2 \quad \text{CH}_3 \quad \text{CN} \]

\[ \text{or photolysis @ 366 nm} \]

Di(tert.-butylperoxide) (DTPO)  
\[ \text{X} \quad \text{O} \quad \text{O} \quad \text{X} \quad 100-140^\circ C \quad 2 \quad \text{CH}_3 \quad \text{O}_2 \]

Dicumylperoxide (DCPO)  
\[ \text{Ph} \quad \text{O} \quad \text{O} \quad \text{Ph} \quad 80-120^\circ C \quad 2 \quad \text{Ph} \quad \text{O}_2 \]

Dibenzoylperoxide (DBPO)  
\[ \text{Ph} \quad \text{O} \quad \text{O} \quad \text{Ph} \quad 60-100^\circ C \quad 2 \quad \text{Ph} \quad \text{O}_2 \quad - 2 \text{CO}_2 \uparrow \quad 2 \quad \text{Ph} \]
Important Vinyl Monomers in Radical Polymerization

- Ethene (PE)
- Chloroethene (PVC)
- 1,1-Difluoroethene (PVDF)
- Tetrafluoroethene (PTFE)
- Vinyl acetate (PVAc)
- Phenylethene (PS)
- 2-Vinylpyridine (P2VP)
- 2-Methylbutadiene (PI)
- Butadiene (PB)
- Propenoic acid (PAA)
- Methyl propenoate (PMA)
- Propenoic amide (PAAm)
- N-Isopropyl acrylamide (PNIPAAm)
- 2-Methylpropenoic acid (PMAA)
- Methyl 2-methylpropenoate (PMMA)
- 2-Methylpropenoic amide (PMAAm)
- Hydroxyethyl methacrylate (PHEMA)
• Polymers do not have defined molar masses but **molecular weight distributions (MWD)**
• Different molecular weight averages, width, and shape
• Molecular weight averages are “moments” of the molecular weight distribution

\[
\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i}
\]

number average molecular weight

\[
\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}
\]

weight average molecular weight

\[
\bar{M}_z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2}
\]

centrifuge average molecular weight

\[
\bar{M}_{z+1} = \frac{\sum n_i M_i^4}{\sum n_i M_i^3}
\]

z+1 average molecular weight
Thermal Transitions of Polymers

- **Highly crystalline**
- **Partially crystalline**
- **Amorphous, glassy**

**Melting transition** $T_m$

**Glass transition** $T_g$

**Polymer melt**

- **Highly crystalline**
- **Partially crystalline**
- **Amorphous, glassy**
Mechanical Properties of Polymers

- **flexible polymers** ($T_g < r.t.$)
  - viscous liquid
  - thermoplastic elastomer
  - elastomer

- **rigid polymer chains** ($T_g > r.t.$)
  - amorphous thermoplastic
  - crystalline thermoplastic
  - durometer
  - fiber axis
  - fiber
• Young's modulus $E$ (slope in the elastic deformation region) is a measure for stiffness
• Energy at break (area under stress-strain curve) is a measure for toughness
• Yield stress (maximum at the end of the elastic deformation region) is a measure for strength
Synthesis and Properties of Polystyrene (PS)

- Polymerization in suspension (in hydrocarbons); transparent beads
- Glassy amorphous thermoplastic ($T_g \approx 100^\circ C$)
- High stiffness and hardness (but often low toughness)
- Used for foams, injection-molded objects
Synthesis and Properties of Polymethylmethacrylate (PMMA)

- Polymerization in bulk (but also solution, emulsion)
- Glassy amorphous thermoplastic \( T_g \approx 100^\circ C \)
- High stiffness, hardness, strength (but often low toughness)
- Used for plexiglass, injection-molded objects
5.2
Surfactants and Colloids
Surfactants in Everyday Life

- Surfactants: „surface active agents“
- Cleaning, washing, food, cosmetics, surface modification
Fatty Acids and Fats

- Fatty acids are the building blocks of fats, they are long chain ($C_{12}-C_{18}$) carboxylic acids
- Fatty acids may also contain double bonds
- Soap molecules are the simplest class of surfactants, sodium or potassium salts of fatty acids

<table>
<thead>
<tr>
<th>fatty acids</th>
<th>fats</th>
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</thead>
<tbody>
<tr>
<td>lauric acid</td>
<td>glyceryl esters of fatty acids</td>
</tr>
<tr>
<td>palmitic acid</td>
<td></td>
</tr>
<tr>
<td>stearic acid</td>
<td></td>
</tr>
<tr>
<td>oleic acid</td>
<td></td>
</tr>
</tbody>
</table>

\[
\text{glycerine} \rightarrow \text{fatty acids} \rightarrow \text{fats}
\]
What is Soap?

- Soap is obtained by hydrolysis of fats under alkaline conditions

\[
\text{Fatty acid} + \text{NaOH} \rightarrow \text{Soap} + \text{Water}
\]

- Saponification under alkaline conditions (irreversible)

\[
\text{R-COOH} + \text{OH}^- \rightarrow \text{R-COO}^- + \text{H}_2\text{O}
\]
Synthesis of Carboxylic Acids

- Other ways to obtain carboxylic acids and their salts
  - Oxidation of paraffins (industrial route)
    \[ R-\text{CH}_2\text{CH}_2R' + \text{O}_2 \rightarrow R-\text{COOH} + R'-\text{COOH} \]
  - Oxidation of primary alcohols and aldehydes (industrial route)
    \[ R-\text{CH}_2\text{OH} \xrightarrow{\text{KMnO}_4} R-\text{COOH} \]
    \[ R-\text{CHO} \xrightarrow{\text{KMnO}_4} R-\text{COOH} \]
  - Hydrolysis of esters (laboratory scale)
  - Hydrolysis of nitrils (accessible via S\(_\text{N}\)2 reaction of haloalkanes, laboratory scale)
    \[ R-\text{CN} \xrightarrow{\text{OH}^-} R-\text{COOH} \]
    \[ R-\text{CN} \xrightarrow{\text{H}^+} R-\text{COOH} \]
Hydrolysis of Nitriles

- Hydrolysis of nitriles under acidic conditions leads to primary amides:

\[
\begin{align*}
R-CN & \xrightarrow{\text{H}^+\text{H}_2\text{O}} R-\text{NH}_2^+ \\
R-\text{NH}_2^+ & \xrightarrow{\text{H}_2\text{O}} R-\text{NH}_2 \\
R-\text{NH}_2 & \xrightarrow{\text{H}^+} \text{R-COOH} \\
\end{align*}
\]

- Hydrolysis of primary amides under acidic conditions leads to carboxylic acids:

\[
\begin{align*}
\text{R-COOH} & \xrightarrow{\text{H}^+} \text{R-\text{NH}_2^+} \\
\text{R-\text{NH}_2} & \xrightarrow{\text{H}_2\text{O}} \text{R-COOH} + \text{NH}_3 \\
\text{R-COOH} & \xrightarrow{\text{NH}_3} \text{R-COOH}^+ \\
\end{align*}
\]
Overview of different classes of surfactants

- **Anionic**, **cationic**, **nonionic** and **zwitterionic** surfactants
- Common motif: surfactants are amphiphilic, they have incompatible molecular segments (e.g. hydrophilic head, a hydrophobic tail)
Emulsions

- Emulsions are (surfactant stabilized) mixtures of “oil” (organic solvents) and water, that is mixtures of immiscible fluids.

- Emulsions consist of a **continuous phase** and a **discontinuous phase**.

- Depending on the ratio of oil and water, either **oil-in-water emulsions (o/w)**, or **water-in-oil emulsions (w/o)** are formed.

![Diagram of oil-in-water and water-in-oil emulsions](image)
### Important Organic Solvents

<table>
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<tr>
<th>Polar Protic</th>
<th>Polar Aprotic</th>
<th>Weakly Polar</th>
<th>Unpolar</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>dimethyl formamide (DMF)</td>
<td>acetone</td>
<td>dioxane</td>
</tr>
<tr>
<td>water</td>
<td>N-methyl pyrroldoine (NMP)</td>
<td>ethyl acetate (EA)</td>
<td></td>
</tr>
<tr>
<td>H₃C–OH</td>
<td>methanol (MeOH)</td>
<td>tetrahydrofuran (THF)</td>
<td>diethyl ether (DE)</td>
</tr>
<tr>
<td>ethanol (EtOH)</td>
<td>acetonitrile (MeCN)</td>
<td>toluene</td>
<td></td>
</tr>
<tr>
<td>isopropanol (PrOH)</td>
<td>dimethylsulfoxide (DMSO)</td>
<td>dichloromethane (DCM)</td>
<td>cyclohexane (CH)</td>
</tr>
<tr>
<td>acetic acid (AcOH)</td>
<td>pyridine</td>
<td>chloroform</td>
<td>heptane</td>
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Polarity of Organic Solvents

- Non-polar solvents, polar aprotic solvents, polar protic solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Boiling point [°C]</th>
<th>Dielectric constant</th>
<th>Density [g/mL]</th>
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<tbody>
<tr>
<td>Pentane</td>
<td>36</td>
<td>1.84</td>
<td>0.626</td>
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<td>Hexane</td>
<td>69</td>
<td>1.88</td>
<td>0.655</td>
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<tr>
<td>Benzene</td>
<td>80</td>
<td>2.3</td>
<td>0.879</td>
</tr>
<tr>
<td>Toluene</td>
<td>111</td>
<td>2.38</td>
<td>0.867</td>
</tr>
<tr>
<td>Chloroform</td>
<td>61</td>
<td>4.81</td>
<td>1.498</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>66</td>
<td>7.5</td>
<td>0.886</td>
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<tr>
<td>Dimethyl sulfoxide</td>
<td>189</td>
<td>46.7</td>
<td>1.092</td>
</tr>
<tr>
<td>Formic acid</td>
<td>101</td>
<td>58</td>
<td>1.21</td>
</tr>
<tr>
<td>Ethanol</td>
<td>79</td>
<td>24.55</td>
<td>0.789</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>118</td>
<td>6.2</td>
<td>1.049</td>
</tr>
<tr>
<td>Water</td>
<td>100</td>
<td>80</td>
<td>1.000</td>
</tr>
</tbody>
</table>

- Usually organic solvents have a lower density than water (exception: chlorinated solvents, such as CHCl₃, CH₂Cl₂)
Water and Other Protic Solvents are “Structured Solvents”

- Permanent dipole moment of water due to differences in electronegativity between oxygen and hydrogen
- Permanent dipole moment leads to short range order in water
The Classical and Non-Classical Hydrophobic Effect

- **Classical hydrophobic effect** (temperature dependant): entropy-driven, degrees of freedom for water decrease at the oil water interface, hydrogen bonds reorient in a way to minimize disturbance of the hydrogen bonds

- **Non-classical hydrophobic effect** (independant of temperature): enthalpic component, at the interface water molecules have less interaction with other H$_2$O molecules by H-bonding

\[
\Delta G = \Delta H - T \Delta S
\]

Phase segregation, interface minimization
Critical Micelle Concentration (CMC)

- Surfactants cover first the interface between water and air
- Above the **critical micelle concentration** (CMC) surfactants start to aggregate
- Determination of CMC is possible by monitoring of surface tension

\[ \sigma [\text{mN/m}] \]

\[ \text{cmc} \]

\[ \ln [c(\text{surfactant})] \]

- Abrupt change of surface tension at the cmc due to micelle formation
Molecular parameters of surfactants determine size and shape of micelles

- hydrophobic contribution (due to hydrocarbon chains sequestering themselves)
- surface term (due to opposing tendencies of surfactant head groups to crowd together to minimize hydrocarbon-water contacts and to spread apart)
- packing term (due to the hydrophobic interior of the aggregates excluding water and head groups)

\[ N_s = \frac{v}{la_0} \]

- \( N_s \): surfactant parameter
- \( v \): volume of the hydrophobic portion of the surfactant molecule
- \( l \): length of hydrocarbon chains
- \( a_0 \): effective area per head group
Different Types of Micelles

cone

wedge

cylinder

V / (a•l) \leq 1/3

V / (a•l) \leq 1/2

V / (a•l) \leq 1

spherical micelle
cylinder micelle
sheet micelle
vesicle (liposome)
Phospholipids

- Natural, zwitterionic surfactants (found in eggs, soy beans, milk, sunflowers, marine sources)

![Phosphatidylcholine structure](image)

- Building blocks of biological membranes in animals and plants (fluid mosaic model for cell membranes)

![Cell membrane diagram](image)
5.3

π-Conjugated Molecules for Organic Dyes and Semiconductors
• examples of natural and synthetic dyes that have a range of different colors

indigo

malachite green

anthocyanidin

• these dyes are organic molecules with extended conjugated $\pi$-electron systems

• interaction with the visible part of the spectrum of electromagnetic radiation gives rise to color
• electromagnetic radiation of suitable **wavelength/energy** will interact with molecules

\[
E = h\nu \\
\nu = \frac{c}{\lambda} \\
E = \frac{hc}{\lambda}
\]

• visible spectrum with wavelengths of **780–380 nm** with an energy of **1.5–3.2 eV**

• on the order of the energy difference between the **HOMO** and **LUMO** of some molecules
Electronic Excitation of a Molecule by Absorption

- photon of suitable energy is absorbed leading to electronic excitation of a molecule

\[ E = h\nu \]
\[ \nu = \frac{c}{\lambda} \]
\[ E = \frac{hc}{\lambda} \]

- absorption of a photon with frequency \( \nu \) occurs when \( E_{\text{photon}} = \Delta E \) of the HOMO-LUMO gap
- colours of organic molecules can directly arise as result of the absorption process

**wavelength of absorbed light**

**resulting complementary color**
Excitation in Simple Organic Molecules

- different organic molecules have different **HOMO** and **LUMO** energies

![Diagram showing energy levels and transitions](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>( \Delta E ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>150</td>
<td>8.3</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_2 )</td>
<td>165</td>
<td>7.5</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_2 )</td>
<td>217</td>
<td>5.7</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_2 )</td>
<td>300</td>
<td>4.1</td>
</tr>
</tbody>
</table>

- different **types of transitions**; in excitation processes **non-bonding orbitals** can play a role
- small organic molecules are colorless to the human eye as **absorption occurs in the UV region**
Optical Gap and Degree of Delocalization

- increasing the size of the system of **conjugated π-electrons** decreases the HOMO-LUMO gap

![Absorption spectrum of thiophene and octathiophene](image)

- with increasing **conjugation length** the main absorption shifts towards longer wavelengths
- **color** of the different molecules changes; from **colorless to red** for the octathiophene
Jablonski diagram illustrates the electronic states of a molecule and the transitions between them.

- Intersystem crossing (ISC) is a non-radiative transition to a state with a different spin multiplicity.
- The much larger time scale of phosphorescence is caused by a “spin-forbidden” transition.
• **absorption** and **emission** (fluorescence) spectra of a perylene bisimide in solution

**Fluorescence and Stokes Shift**

- Emission is usually **at higher wavelengths** compared to absorption
- **Stokes shift** is the difference in the wavelengths of maximum absorption and emission
organic molecules can also appear colored through an emission process

dye + excitation $\rightarrow$ excitation of the dye; dye emits energy (fluorescence)
HOMO-LUMO gap and energy of the emission depend on the molecular structure of the dye
the wavelength of the emitted light determines the color of the material
changes in the system of conjugated π-electrons lead to a change of the colour: phenolphthalein

- \( pH = 0-8.2 \) : colourless
- \( pH < 0 \) : red
- \( pH = 8.2-12.0 \) : pink

broken conjugation when the system of conjugated π-electrons is out of plane
Synthesis Example: Preparation of Phenolphthalein

• mechanism of the Friedel-Crafts acylation:
The poinsettia plant can be used to make an indicator solution to test for pH. This is because the red leaves contain anthocyanin pigments, the structure of which subtly changes at varying pH. Red cabbage contains similar pigments, and as such can also be used. Some possible structures & colours are shown below.

Poinsettia plants have a false reputation for being poisonous. Whilst eating a lot of the leaves could cause stomach pain and vomiting, this is unlikely due to their awful taste!

- **changes in the system of conjugated π-electrons lead to a change of the colour**: anthocyanidins

  - at different pH the conjugation changes and the colour changes accordingly
  - a variety of plants are coloured by anthocyanidins and their derivatives (e.g., berries, grapes, cabbage)
Extended Conjugated Systems – Dye Molecules

terpenes (isoprenoids)

- Lycopene
- β-carotene

isoprene

retinol (vitamin A₁)

tetrapyrroles

- Porphyrin
- Phthalocyanine
- Chlorophyll a

M = H, Zn, Cu, Fe...

Mg

RO

OMe
From Organic Dyes to Organic Electronic Materials

- organic molecules with extended conjugated $\pi$-electrons can also transport charges

**organic solar cells**

**organic light-emitting diodes**

**organic field-effect transistors**

**potential advantages:**
- device flexibility
- lighter devices
- low-cost production
- large-area usage
- resource efficiency
Extended Conjugated Systems – Organic Electronic Materials

- napthalene
- anthracene
- tetracene
- pentacene
- perylene
- terrylene
- pyrene
- coronene

- pentacene (in the crystal)
- perylene bisimide (in the crystal)

- electron-rich; p-type semiconductor
- electron-poor; n-type semiconductor
Selected Examples of Polymer Semiconductors

poly(acetylene)s

poly(phenylene)s

poly(thiophene)s

poly(phenylene vinylene)s

poly(phenylene)s

“ladder-type poly(phenylene)s

poly(pyrrrole)

PEDOT

e.g., P3HT

e.g., MEH-PPV

PPV

PPy
molecules with “conjugated \( \pi \)-electrons” have highly polarisable, delocalized electron system

- upon increasing the size of the conjugated system, the HOMO-LUMO gap narrows
- MO levels get closer, start to interact with one another, but still located MO, no bands
Electron Density Distribution of Increasingly Large $\pi$-Conjugated Systems

benzene  naphthalene  anthracene  tetracene  pentacene
- packing of the molecules in the solid (crystalline) state makes their $\pi$-conjugated systems interact

- layered arrangement of “standing” pentacenes, long axes tilted to layer normal
- “herringbone arrangement” within layers, herringbone angle between molecular planes
- intermolecular electron delocalization due to $\pi-\pi$ interactions results in narrow bands.

- Valence and conduction bands with band width $\omega \approx 1$ eV, much narrower than in inorganic materials.
- Small band width representative of low degree of (macroscopic) delocalization.
- Different charge carrier mobilities for different lattice directions of the crystal.
Synthesis Example: Preparation of Pentacene

- mechanism of the aldol condensation:

\[ \text{aldol condensation} \]

\[ \text{addition} \]

\[ \text{elimination} \]

\[ \text{etc.} \]
Charge transport in organic thin film devices occurs in thin 2D layer parallel to substrate.

- gate electrode induces charge carriers in the channel, serves as to “switch on/off” the device.
5.4
Polyesters, Polyamides, Polycarbonates, and Polyurethanes
Outline of the Lecture

- introduction and general background on polymers

- polymerization mechanisms (step-growth vs. chain-growth) and statistical analysis

- polycondensation polymers (polyamide, polyester, etc.) – synthesis, structure, properties

- quick overview of some polyaddition polymers (polycarbonate, polyurethane)
• definition of a polymer according to Hermann Staudinger:

“A polymer is a large molecule constituted from (identical) smaller structural ‘repeating units’ with a length sufficient such that molecules with n and n+1 repeating units are indistinguishable”

• if properties are indistinguishable, polymers are also inseparable; polymers are “polydisperse”!

• homopolymers: one type of repeating units (but different architectures)

- linear
- star
- branched
- hyperbranched
- network

• copolymers: different types of repeating units (and microstructures)

- random
- AB diblock
- ABC triblock
- segmented
- graft
- alternating
- ABA triblock
- miktoarm star
- tapered
- brush
• polymers do not have defined molar masses but molecular weight distributions (MWD)
• different molecular weight averages, width, and shape
• molecular weight averages are “moments” of the molecular weight distribution

\[
\begin{align*}
\overline{M}_n &= \frac{\sum n_i M_i}{\sum n_i} \\
\overline{M}_w &= \frac{\sum n_i M_i^2}{\sum n_i M_i} \\
\overline{M}_z &= \frac{\sum n_i M_i^3}{\sum n_i M_i^2} \\
\overline{M}_{z+1} &= \frac{\sum n_i M_i^4}{\sum n_i M_i^3}
\end{align*}
\]
Molecular Weight Averages and Polydispersity Index (PDI)

\[
\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{8 \cdot 5000}{8} = 5000
\]

\[
\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{8 \cdot 5000^2}{8 \cdot 5000} = 5000
\]

\[
PDI = \frac{\bar{M}_w}{\bar{M}_n} = 1 \quad \text{monodisperse (molecularly uniform)}
\]

\[
\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{4 \cdot 9000 + 4 \cdot 1000}{4 + 4} = 5000
\]

\[
\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i} = \frac{4 \cdot 9000^2 + 4 \cdot 1000^2}{4 \cdot 9000 + 4 \cdot 1000} = 8200
\]

\[
PDI = \frac{\bar{M}_w}{\bar{M}_n} = 1.64 \quad \text{polydisperse}
\]
Determination of Molecular Weights

Mass Spectrometry

Gel Permeation Chromatography
Polymerization Mechanisms: Step-Growth vs. Chain-Growth

- **chain-growth**: appending one monomer at a time to the activated growing chain (except termination)
  
  Example: polyolefins

  \[
  AB + AB^* \rightarrow (AB)_2^* \quad +AB \rightarrow (AB)_3^* \quad +AB \quad \cdots \quad +(AB)_m^* \rightarrow (AB)_n.
  \]

- **step-growth**: all chains may react through their end groups
  
  Example: polyesters, polyamides

  \[
  AB + AB \rightarrow (AB)_2 \quad +(AB)_m \rightarrow (AB)_{m+2} \quad +(AB)_x \quad \cdots \quad +(AB)_y \rightarrow (AB)_n.
  \]

- The statistical process of polymer growth is different for step-growth and chain-growth
- Control variables are not the same (e.g. **stoichiometry of monomers** vs. **initiator concentration**)
- The mechanism depends on the type of monomers to be polymerized
polymer chain growth is a statistical process (source of polydispersity)

polydispersity increases with conversion

conversion limits molecular weight (high molecular weight requires very high conversions)
Dependence of Molecular Weight on Conversion and Functional Group Stoichiometry

- ratio of monomers and functional groups
  \[ r = \frac{[\text{mon}_A]}{[\text{mon}_B]} = \frac{n_{A,0}}{n_{B,0}} \]

- total number of monomers
  \[ n_0 = \frac{n_{A,0}}{2} + \frac{n_{B,0}}{2} = \frac{n_{A,0}}{2} \cdot \left(1 + \frac{1}{r}\right) \]

- conversion of functional groups
  \[ x_p = \frac{n_{A,0} - n_A}{n_{A,0}} = \frac{n_{B,0} - n_B}{n_{B,0}} \]

- number of chains
  \[ n = \frac{n_A}{2} + \frac{n_B}{2} = \frac{n_{A,0}}{2} \cdot \frac{1 + r - 2x_pr}{r} \]

- degree of polymerization
  \[ \overline{P_n} = \frac{n_0}{n} = \frac{1 + r}{1 + r - 2x_p r} \]

Carothers Equation
Dependence of Molecular Weight on Conversion and Functional Group Stoichiometry

\[ P_n = \frac{1 + r}{1 - r} \]

for complete conversion \((x_p = 1)\)

Carothers Equation

\[ P_n = \frac{1 + r}{1 + r - 2x_p r} \]

\[ P_n = \frac{1}{1 - x_p} \]

for perfect stoichiometry \((r = 1)\)
Molecular Weight Distribution in Step Growth Reactions

- probability of finding an unreacted group
  \[ \pi_u = 1 - x_p \]

- probability of \( i \) coupling reactions
  \[ \pi_i = x^i_p \]

- probability of finding chain of length \( p \)
  \[ \pi_p = \pi_u \cdot \pi_{(p-1)} = (1 - x_p) \cdot x_p^{p-1} \]

- total number of chains
  \[ n = n_0 \cdot (1 - x_p) \]

- number of chains with length \( p \)
  \[ n_p = n \cdot \pi_p = n_0 \cdot (1 - x_p)^2 \cdot x_p^{p-1} \]

- weight fraction of chains with length \( p \)
  \[ \chi_p = \frac{m_p}{\sum m_p} = \frac{pM_{ru}n_p}{M_{ru}n_0} = p \cdot (1 - x_p)^2 \cdot x_p^{p-1} \]

Schulz-Flory Distribution
Schulz-Flory Distribution

\[ \chi_p = p \cdot (1 - x_p)^2 \cdot x_p^{p-1} \]

weight fraction \( x_p \)

degree of polymerization \( p \)

number average degree of polymerization

\[ \overline{P}_n = \frac{1}{1 - x_p} \]

weight average degree of polymerization

\[ \overline{P}_w = \frac{1 + x_p}{1 - x_p} \]

polydispersity index

\[ \text{PDI} = \frac{\overline{P}_n}{\overline{P}_w} = 1 + x_p \rightarrow 2 \]
Summary of the Kinetics of Step Growth Polyreactions

Carothers’ equation

\[ P_n = \frac{1}{1 - \text{conv}} \]

Polydispersity index (PDI)

\[ \text{PDI} = 1 + \text{conv} \]

Schulz–Flory distribution
Polycondensations are Step-Growth Reactions

- **Polycondensations** are substitutions of difunctional molecules under extrusion of molecules

- Water is formed and should be removed to drive the forward reaction

- Polyesters and polyamides are widely used polycondensation polymers

Polymerization net reaction of single type AB monomer

\[
\begin{align*}
\text{HO-} \text{R}_1 \text{NH}_2 + \text{HO-} \text{R}_2 \text{NH}_2 & \rightarrow \text{HO-} \text{R}_1 \text{N-} \text{R}_2 \text{OH} + \text{H}_2\text{O} \\
\text{HO-} \text{R}_1 \text{COOH} + \text{HO-} \text{R}_2 \text{OH} & \rightarrow \text{HO-} \text{R}_1 \text{C-} \text{O-} \text{R}_2 \text{OH} + \text{H}_2\text{O} \\
\text{HO-} \text{R}_1 \text{NH}_2 + \text{HO-} \text{R}_2 \text{OH} & \rightarrow \text{HO-} \text{R}_1 \text{N-} \text{R}_2 \text{OH} + \text{H}_2\text{O}
\end{align*}
\]
Important Polyamide Structures and Properties

- aliphatic

\[
\text{Nylon 6,6} \quad T_g = 70°C; T_m = 255°C
\]

- aromatic

\[
\text{Nomex} \quad T_g = 270°C; T_m = 360°C \text{ (dec.)}
\]

\[
\text{Kevlar} \quad T_m > 400°C \text{ (dec.)}
\]

- chain rigidity and intermolecular interactions govern the material properties
• partially to highly crystalline thermoplasts; fibers; composites with glass or carbon fibers
• high strength, toughness, hardness, low wear
• good thermal shape persistence
• good electric isolation
• good chemical robustness against solvents, acids, bases, oxidants
Polymerization of Nylons and Resulting Structure

**Step Reactions**

**AA**
Hexamethylene diamine

**BB**
Adipic acid

\[ \text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2 + \text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH} \rightarrow \text{H}_2\text{O} \rightarrow \text{Poly(hexamethylene adipamide)} \]

**Poly(hexamethylene adipamide)**
Nylon-6,6, PA-6,6

**AB**
\( \text{ADIC} \rightarrow \text{Nylon-6, PA-6} \)

\( \text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH} \)

\( \text{H}_2\text{O} \rightarrow \text{Polycaprolactam} \)

\( \text{Nylon-6, PA-6} \)

**PA 6,6** — \( T_g = 70°C; T_m = 255°C \)

**PA 6** — \( T_g = 60°C; T_m = 220°C \)
• melt polycondensation by salt dehydration

1,6-hexanedioic acid
(adipic acid)

H₂O / EtOH

1,6-diaminohexan
(hexamethylene diamine)

hexanediammonium adipate
“AH salt”

>270°C
(melt)

Poly(hexamethyleneadipamide)
Nylon 6,6
Technical Preparation of Nylons

- interfacial polycondensation (by Schotten-Baumann reaction)

1,10-decanedioic acid chloride
(sebacic acid chloride)

\[
\text{C}_2\text{H}_2\text{Cl}_4
\]

\[
\begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{C} \\
\text{O} \\
\text{Cl}
\end{array}
\]

\[
+ \quad \text{H}_2\text{N} \begin{array}{c}
\text{H}_2\text{O} / \text{NaOH}
\end{array}
\]

1,6-diaminohexane
(hexamethylene diamine)

\[
\begin{array}{c}
\text{H}_2\text{N} \\
\text{C} \\
\text{O} \\
\text{N} \\
\text{H}
\end{array}
\]

Poly(hexamethylenesebacamide)
Nylon 6,10
fiber drawn from interface
Technical Preparation of Nylons

- Schotten-Baumann reaction in polar aprotic solvents using hydrogen-bond breaking agents

\[
\text{terephthalic acid chloride} + \text{1,4-phenylene diamine} \rightarrow \overset{\text{excess Li}_2\text{CO}_3}{\text{poly(1,4-phenylene terephthalamide)}}
\]

\[
\text{p-aminobenzoyl chloride (HCl salt)} + N\text{-methylpyrrolidone (NMP)} \rightarrow \overset{\text{excess Li}_2\text{CO}_3}{\text{poly(p-benzoyleamide)}}
\]

Kevlar

Fiber B
Technical Preparation of Poly(ethylene terephthalate) PET

- transesterification polycondensation

\[
\begin{align*}
1,4\text{-benzenedicarboxylic acid} & \quad \text{terephthalic acid} \\
\text{ethylene glycol} & \quad \text{distill off}
\end{align*}
\]

\[
\begin{align*}
\text{excess} & \quad \text{pressure} \\
100\text{–}200^\circ\text{C} & \quad >250^\circ\text{C}
\end{align*}
\]

poly(ethylene terephthalate) PET
Step Reactions

- partially crystalline thermoplasts (used for bottles, fibers, composites)
- high strength and stiffness, low wear
- good chemical robustness

Poly(ethylene terephthalate) PET  
\[ T_g = 98^\circ C; T_m = 255^\circ C \]

Poly(butylene terephthalate) PBT  
\[ T_g = 60^\circ C; T_m = 223^\circ C \]

Ardel  
\[ T_{dec} \approx 400^\circ C \]
Polycaprolactone (PCL)

- ring opening polymerization (analogous to PA-6 synthesis)

- speciality polymer used in biomedical applications mainly

\[
\text{PA 6} \quad T_g = 60^\circ C; \quad T_m = 220^\circ C \\
\text{PCL} \quad T_g = -60^\circ C; \quad T_m = 60^\circ C
\]
amorphous thermoplasts; often in composites
high strength, toughness, hardness, up to 135°C
highly transparent
good electric isolation, good irradiation stability

\[
\text{bisphenol A} \xrightarrow{\text{phosgene}} \text{Polycarbonat A}
\]

\[
\begin{align*}
\text{T}_g &= 150^\circ\text{C}; T_{\text{soft}} = 220-260^\circ\text{C}
\end{align*}
\]
• partially crystalline thermoplasts; foams

\[
\text{HO} \quad \text{OH} \quad \text{N} \quad \text{N} \quad \text{CO} \quad \text{CO} \\
\text{H} \quad \text{N} \quad \text{O} \quad \text{O} \quad \text{x}
\]

\[
\begin{align*}
R-N=\text{C}=O & \quad + \quad \text{H}_2\text{O} & \quad \text{step 1} & \quad \rightarrow & \quad R-N-C-O-H \\
& \quad \text{decomposes} & \quad \rightarrow & \quad R-NH_2 & \quad + \quad \text{CO}_2^{\text{gas}}
\end{align*}
\]

\[
R-N=\text{C}=O & \quad + \quad R-NH_2 & \quad \text{step 3} & \quad \rightarrow & \quad R-N-C-N-R
\]
5.5

Amino Acids, Peptides, and Proteins
• primary structure
  defined polypeptide made from 20 standard amino acids

• secondary structure
  3D form of local segments (α-helices, β-sheets) is the result of defined patterns of hydrogen bonds

• tertiary structure
  geometric shape of the protein is the result of supramolecular interactions between the amino acid side chains (H-bonds, ionic, S–S, hydrophobic, and van der Waals)

• quaternary structure
  arrangement of multiple proteins into multi-subunit complex
## Amino Acid Pool

<table>
<thead>
<tr>
<th>Amino Acids with Electrically Charged Side Chains</th>
<th>Amino Acids with Polar Uncharged Side Chains</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Lysine" /></td>
<td><img src="image" alt="Serine" /></td>
</tr>
<tr>
<td><img src="image" alt="Aspartamic Acid" /></td>
<td><img src="image" alt="Asparginine" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Amino Acids with Hydrophobic Side Chains</th>
<th>Special Cases</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Alanine" /></td>
<td><img src="image" alt="Glycine" /></td>
</tr>
<tr>
<td><img src="image" alt="Phenylalanine" /></td>
<td><img src="image" alt="Cysteine" /></td>
</tr>
</tbody>
</table>

• pharmacology and medicine:

![Diagram of Peptides and Derivatives in Action]

- Recognition and binding
- Entry inhibitors
- Virus fusion
- Fusion inhibitors
- CD4-receptor
- CKR5 / CCR5 coreceptor
- Integration
- Integration inhibitors
- Nuclear entry
- Expression
- Reverse transcription
- Reverse transcription inhibitors
- Capsid protein
- Envelop
- Envelop protein
- Envelop glycoprotein
- Envelop glycoprotein inhibitors

- Enfuvirtide, T-20

• materials science and engineering:

![Diagram of Peptides and Derivatives in Action]

- Hydrogen bonding
- Aggregate network
- Tapes & nanofibers
- Single β-sheet
- Nanofiber
- β-sheet stacking
- Aggregate network
- Tapes & nanofibers
- Entanglement network
- Polymer matrix

![Diagram of Peptides and Derivatives in Action]

- Damping experiment
- Nanocomposites
- Blends
- Steel
- PIB200
- Smartane

- Amplitude (a.u.)
- Resonance frequency / Hz
- References
Peptide-Coupling Reactions: Peptide Coupling Reagents

- no amide (peptide), but salt formation between carboxylic acid and amine:

\[
\text{R} \text{OH} + \text{R'-NH}_2 \rightarrow \text{R} \text{O}^\ominus + \text{R'-NH}_3
\]

- solution: peptide coupling reagents

\[
\text{R} \text{OH} + \text{R'-NH}_2 \xrightarrow{\text{DIC}} \text{R} \text{N}^{\ominus} \text{H} \text{R'}
\]

\[
\text{R} \text{OH} + \text{N=C=N} \rightarrow \text{R} \text{O}^\ominus + \text{N=C=N} \rightarrow \text{N=O} \text{R}
\]

\[
\text{R'} \text{NH} + \xrightarrow{\text{S}_{\text{AE}}} \text{R} \text{N}^{\ominus} \text{H} \text{R'} + \text{HN-CONH-N}
\]

- the driving force of the reaction is the urea formation
Peptide-Coupling Reactions: Protecting Groups

\[\text{H}_2\text{N}-\text{C}-\text{N} \quad \text{O} \quad \text{H} \quad + \quad \text{H}_2\text{N} \quad \text{C} \quad \text{O} \quad \text{OH} \quad \xrightarrow{\text{DIC}} \quad ?\]
Peptide-Coupling Reactions: Protecting Groups

- **uncontrolled reaction between carboxylic acids and amines:**

  ![Chemical reaction diagram]

- **solution: orthogonal protection groups for the carboxylic acid and amine functionalities:**

  - **carboxylic acid:** tert-butyl ester (acid labile)
  - **amines:** Fmoc-group (base labile)
• synthesis of the tert-butyl esters:

\[ R\text{OH} + \text{DIC} \rightarrow R\text{O}^+ + \text{HN} = \text{C} = \text{N} \rightarrow R\text{O}^+ + \text{HN} = \text{C} = \text{N}^+ \rightarrow \text{HN} \text{O} \]

\[ \text{OH} + \text{HN} = \text{C} = \text{N} \rightarrow \text{O} \text{R} \text{O} \text{N} \text{C} \text{N}^+ \rightarrow \text{HN} \text{O} \text{R} \text{O} \text{N} \text{C} \text{N}^+ \rightarrow \text{HN} \text{O} \text{R} \text{O} \text{N} \text{C} \text{N}^+ \]

tert-butyl ester
Peptide-Coupling Reactions: Protecting Groups

- removal of the tert-butyl ester under *acidic conditions*: protonation of ester carbonyl, then elimination reaction releasing isobutene (driving force)

- the peptide chain can then be extended by using DIC and any tert-butyl-protected amino acid
• introduction of the Fmoc-group:

9-fluorenylmethanol → Fluorenylmethyloxycarbonyl chloride (Fmoc-Cl)

H₂N-ASN-ASN-ASN-OH → Fmoc-Cl
• removal of the Fmoc-group under *basic conditions*: abstraction of fluorenyl proton, then elimination reaction releasing CO$_2$ and 9-methylene-9H-fluorene (driving force)

![Chemical structure](image)

• the peptide chain can then be extended by using DIC and any Fmoc-protected amino acid
<table>
<thead>
<tr>
<th>amines</th>
<th>carboxylic acids</th>
<th>alcohols</th>
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