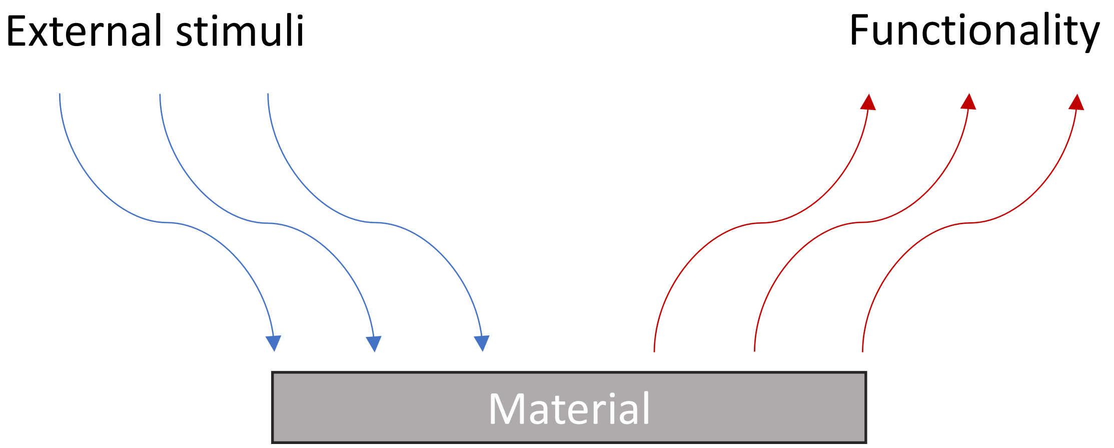
Responsive Functional Materials

Assist.-Prof. Dr. Heidi A. Schwartz

Photoactive Hybrid Materials

Universität Innsbruck



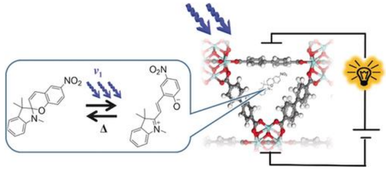
https://www.uibk.ac.at/en/aatc/ag-schwartz/

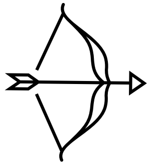
heidi.schwartz@uibk.ac.at

L01.063

Outline for today´s lecture

1. Short conclusion of last lecture



2. Learning objectives 

- Fundamentals and functional materials in everyday life II

- Next time: Analyzation tools and characterization methods I

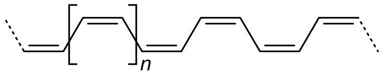
What you will learn the next weeks

1. Introduction into Material Sciences I
2. **Introduction into Material Sciences II**
3. Analyzation Tools I
4. Analyzation Tools II
5. Porous Materials I
6. Invited Speaker: Artem Mikhailov (Nancy)
7. Porous Materials II
8. Responsive materials
9. Photochromism and Luminescence
10. Hybrid Materials

A functional material could be defined as being prepared from a “target-motivated” approach

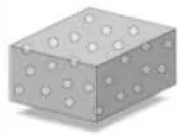
Ceramics

Polymers

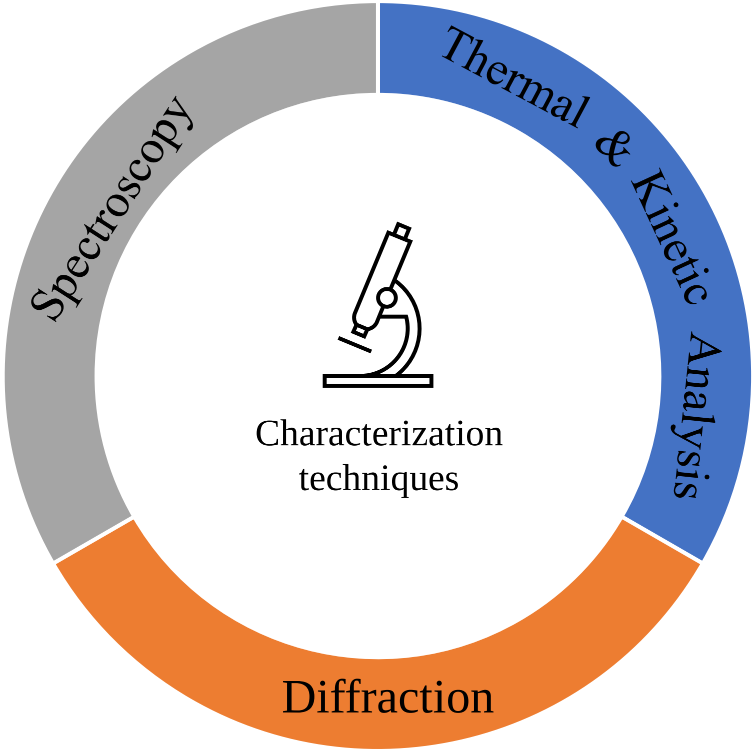


Metals

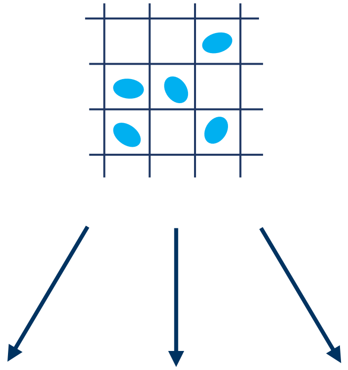
Composites



Glasses



Innovative Materials



Biomaterials

Nanomaterials

Semiconductors

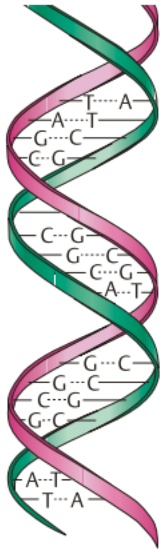
…

Porous materials

Functional Material - an overview | ScienceDirect Topics (3rd March, 2023)

Polymers – nothing would work without them

"Polymers" are chemical compounds, which are build up from repetitively connected macromolecules. They are divided into biopolymers and synthetic polymers.



DNS, the most important polymer.

Chemie. Mortimer C, Müller U, ed. *13. Auflage*. Stuttgart: Thieme; **2019**.

Polyamide – Wikipedia (4th March, 2023)

Acrylonitrile butadiene styrene – Wikipedia (4th March, 2023)

Chitin – Wikipedia (4th March, 2023)

Recycled plastic bottles leach more chemicals into drinks, review finds | Plastics | The Guardian (4th March, 2023)

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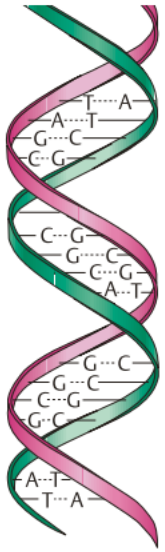
Types of polymers

Homopolymers and Copolymers

Homopolymers	Copolymers
Polyethylene	Most biopolymers
Polypropylene	Butyl rubber
Polyvinylchloride	Acrylonitrile butadiene styrene
Natural rubber	

Note: polymers can also be inorganic
e.g., polysiloxanes!



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White Board

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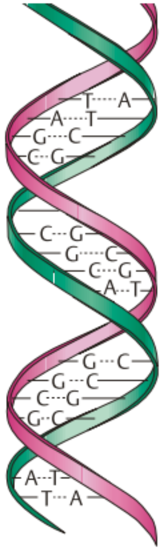
PET bottles.



DNS, the most important polymer.

Copolymer ABS.

Chitin.

Nylon.

Chemie. Mortimer C, Müller U, ed. *13. Auflage*. Stuttgart: Thieme; **2019**.
Acrylonitrile butadiene styrene – Wikipedia (4th March, 2023)
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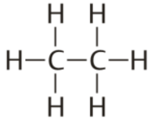
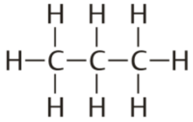
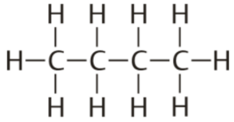
Chitin – Wikipedia (4th March, 2023)

White Board

Bonding situation

Fundamentals structure organic molecules

Most organic molecules are hydrocarbons, where C and H are covalently bound.

William D. Callister, David G. Rethwisch, Materialwissenschaften und Werkstofftechnik, WILEY-VCH, **2013**.

[Lessons | MATSE 81: Materials In Today's World](#) (19th February, 2025)

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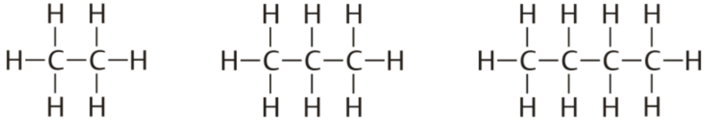
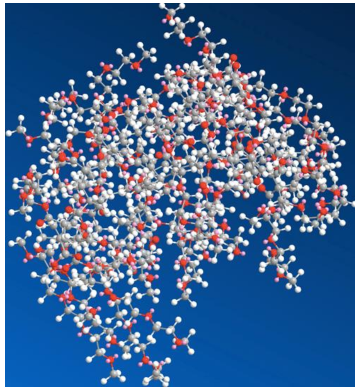
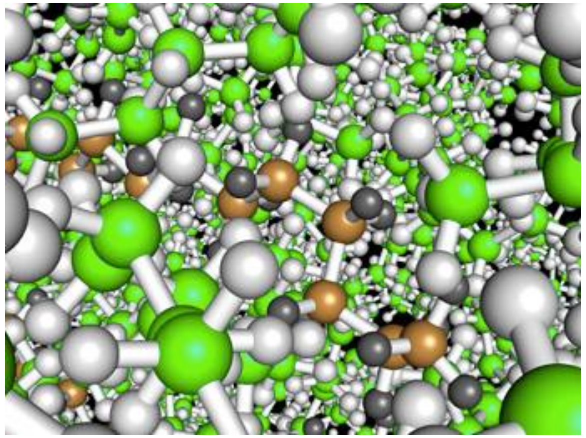


Polymers – made up of many monomers!

Polymers are very large molecules – macromolecules – consisting of repeating subunits. These units can be the same (<u>homo</u>polymer) und differ from each other (<u>co</u>polymer).





William D. Callister, David G. Rethwisch, Materialwissenschaften und Werkstofftechnik, WILEY-VCH, **2013**.

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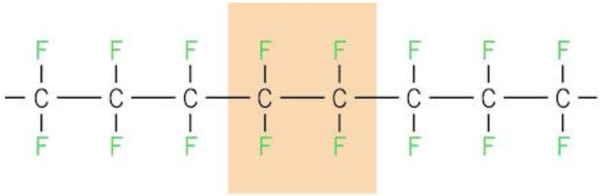
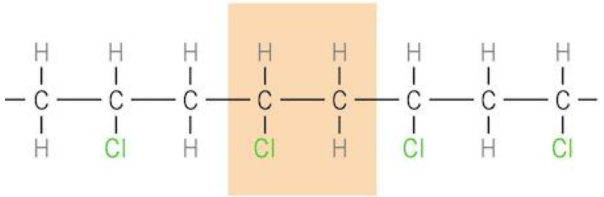
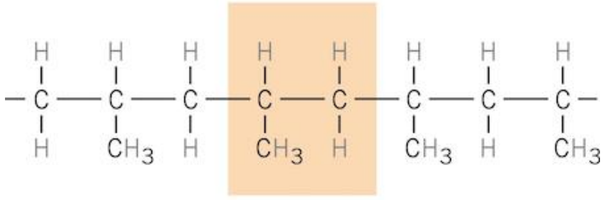
Typical repetition units



Polytetrafluorethylene



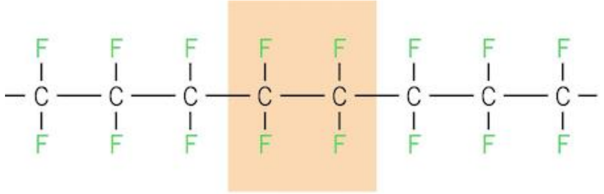
Polyvinylchloride



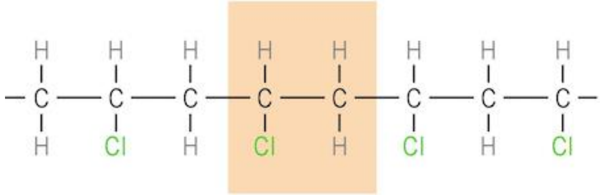
Polypropylene

William D. Callister, David G. Rethwisch, Materialwissenschaften und Werkstofftechnik, WILEY-VCH, **2013**.

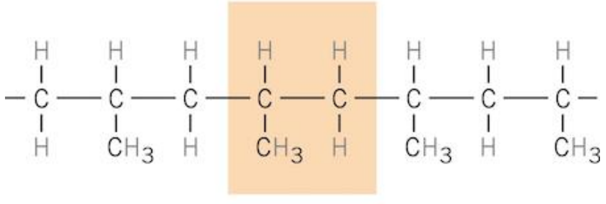
Typical repetition units



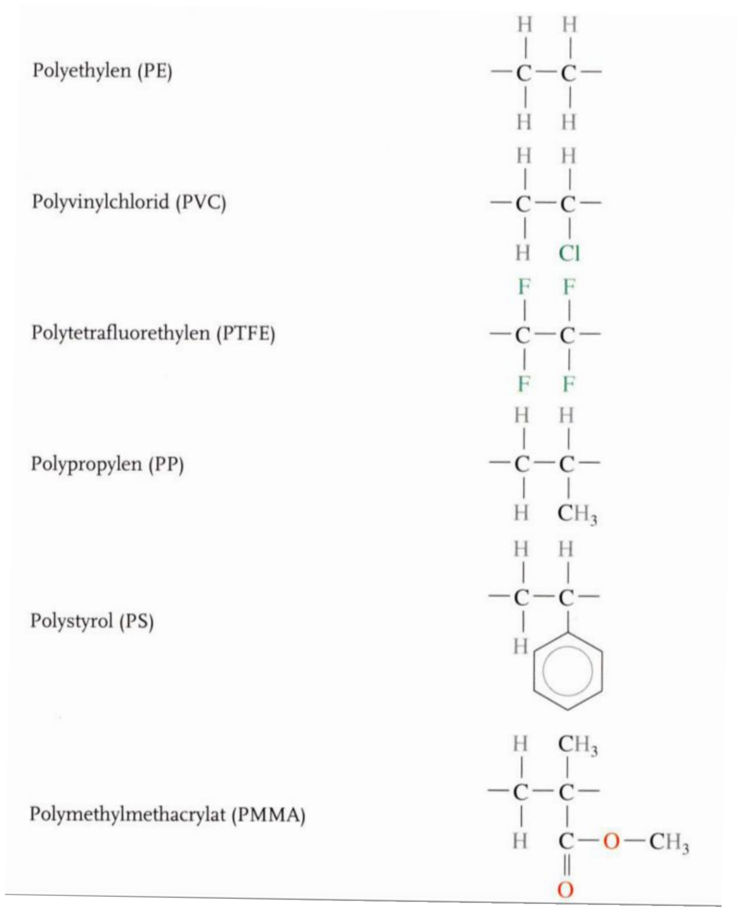
Polytetrafluorethylene



Polyvinylchloride



Polypropylene



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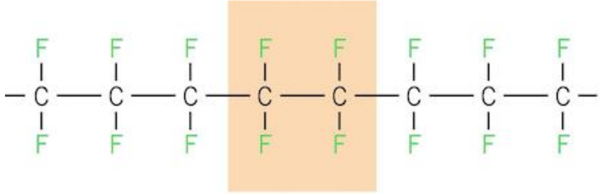

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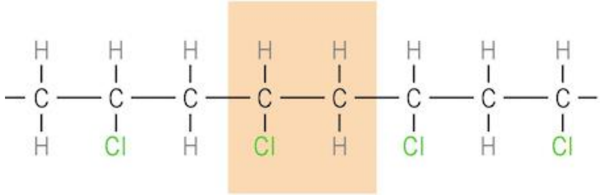

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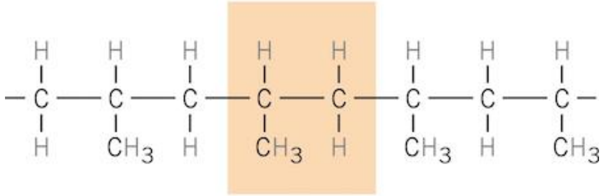
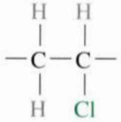


Polypropylene

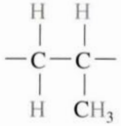
Polyethylen (PE)

Polyvinylchlorid (PVC)

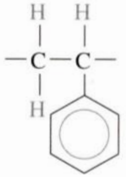


Polytetrafluorethylen (PTFE)

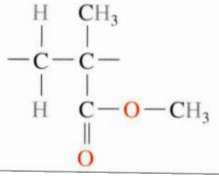
Polypropylen (PP)



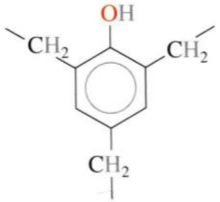
Polystyrol (PS)



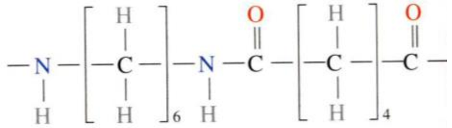
Polymethylmethacrylat (PMMA)



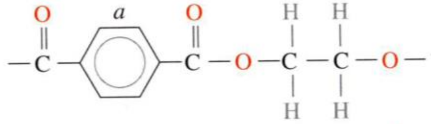
Phenolformaldehydharz (Bakelit)



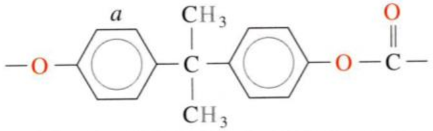
Polyhexamethylenadipamid
(Polyamid PA 6,6 Nylon)



Polyethylenterephthalat (PET, ein Polyester)



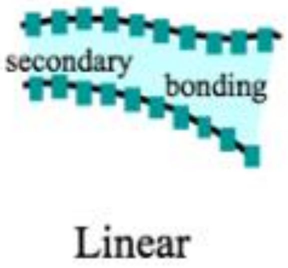
Polykarbonat (PC)



Das Symbol *a* bezeichnet einen aromatischen Ring.

William D. Callister, David G. Rethwisch, Materialwissenschaften und Werkstofftechnik, WILEY-VCH, **2013**.

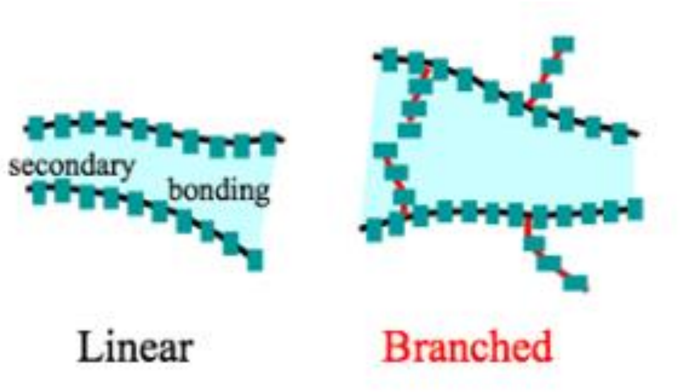
Basic Polymer Structures



- *van der Waals* or H bonding
- material can be re-molded by heating
- thermoplastics

William D. Callister, David G. Rethwisch, Materialwissenschaften und Werkstofftechnik, WILEY-VCH, **2013**.
[Lessons | MATSE 81: Materials In Today's World] (19th February, 2025)

Basic Polymer Structures



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- shorter chains
- less dense than lp
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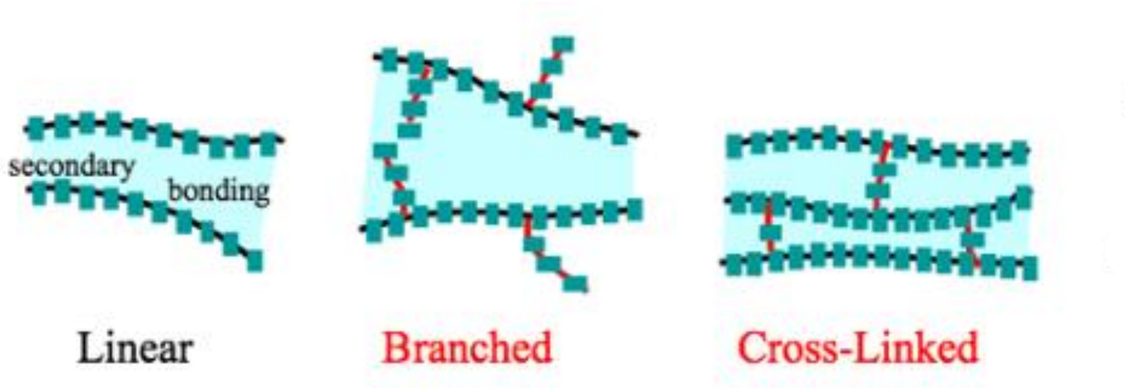

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- resemble ladders with linked chains
- covalent bonds
- thermosets

William D. Callister, David G. Rethwisch, Materialwissenschaften und Werkstofftechnik, WILEY-VCH, **2013**.
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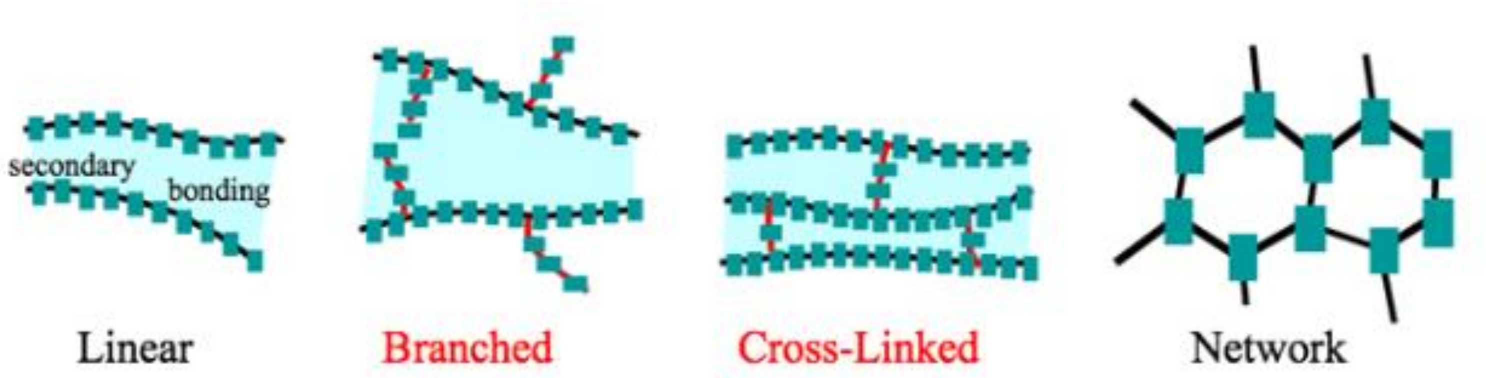

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- heaviliy linked
- nearly impossible to soften → degrading
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William D. Callister, David G. Rethwisch, Materialwissenschaften und Werkstofftechnik, WILEY-VCH, **2013**.
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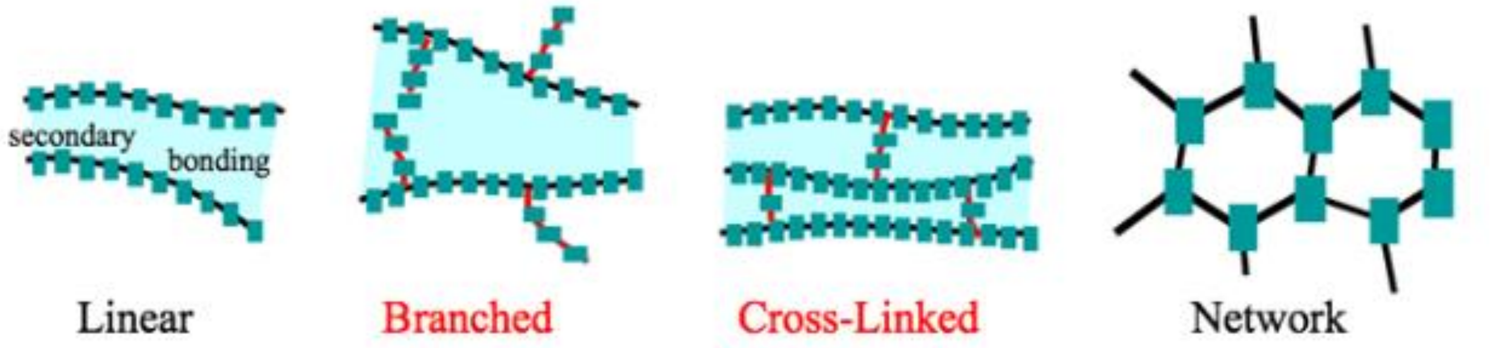

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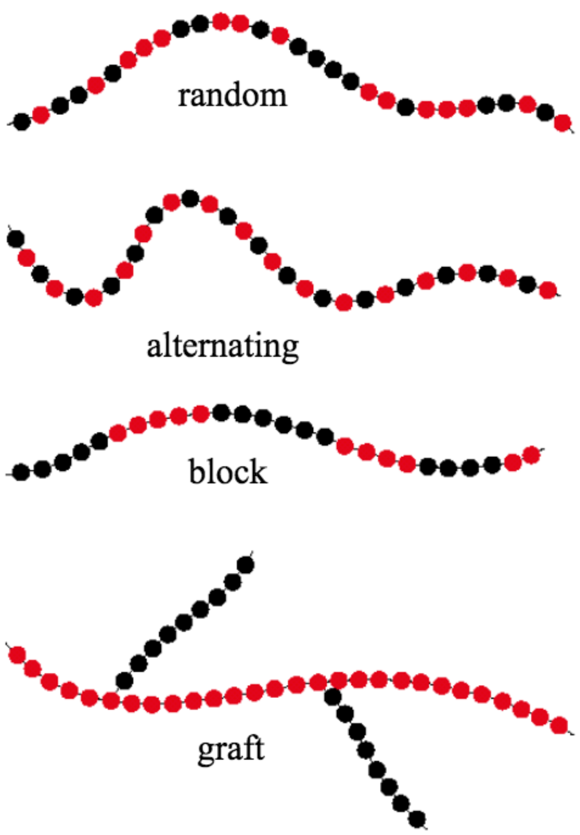
Copolymers
Two distinct starting monomers lead to several possible structures: **random**, **alternating**, **block** and **graft**.
Randomly ordered monomers result in a **random** copolymer.



William D. Callister, David G. Rethwisch, Materialwissenschaften und Werkstofftechnik, WILEY-VCH, **2013**.
[Lessons | MATSE 81: Materials In Today's World](#) (19th February, 2025)

Group-/Tandem-Work

Which biopolymers you know?

Where do we find polymers in our daily life?

What are they used for?

15 min

Biopolymers and …

IUPAC: Biopolymers are polymers produced by living organisms. Three main classes of biopolymers: polynucleotides, polypeptides and polysaccharides.

William D. Callister, David G. Rethwisch, Materialwissenschaften und Werkstofftechnik, WILEY-VCH, **2013**.
Biopolymer – Wikipedia (24th February, 2025)

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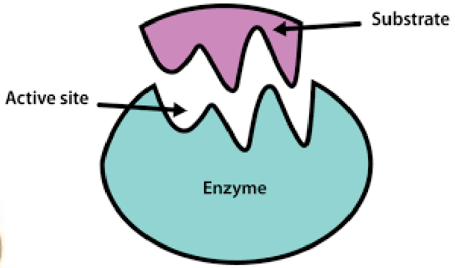
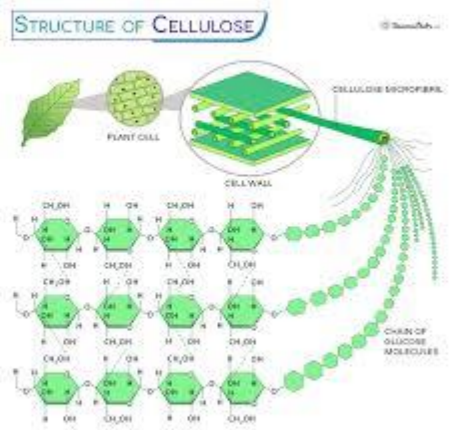
Proteins
Enzymes
Starch
Cellulose





Wood
Rubber
Whool
Leather
Silk
Cotton

William D. Callister, David G. Rethwisch, Materialwissenschaften und Werkstofftechnik, WILEY-VCH, **2013**.
Biopolymer – Wikipedia (24th February, 2025)

… synthetic polymers

Synthetic polymers are typically made out of petroleum oil under controlled conditions. Synthesis is carried out under heat and pressure and mostly the presence of a catalyst.

William D. Callister, David G. Rethwisch, Materialwissenschaften und Werkstofftechnik, WILEY-VCH, **2013**.
Synthetic Polymer - an overview | ScienceDirect Topics (25th February, 2025)

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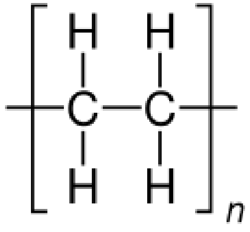
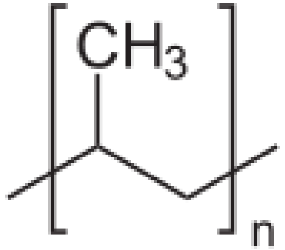
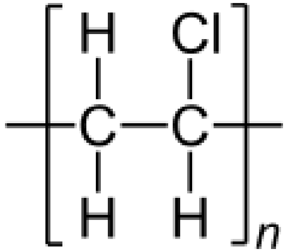


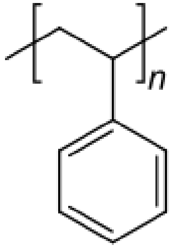
Polyethylene



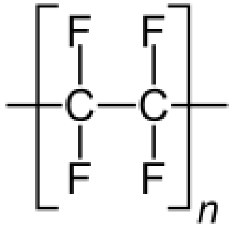
Polypropylene



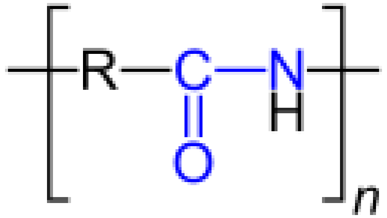
Polyvinylchloride



Polystyrene



Polytetrafluormethylene

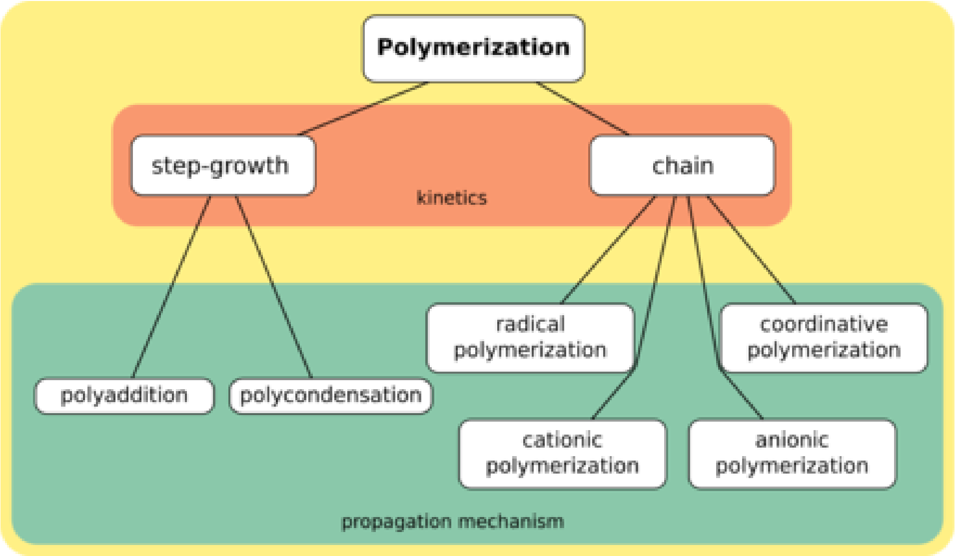


Polyamide

William D. Callister, David G. Rethwisch, Materialwissenschaften und Werkstofftechnik, WILEY-VCH, **2013**.
Synthetic Polymer - an overview | ScienceDirect Topics (25th February, 2025)
Pictures are taken from Wikipedia

Classification and technically relevant properties

Synthesis of polymers is done *via* three ways: polymerization, addition polymerization and condensation polymerization of (different) monomers.



Polymer – Wikipedia (4th March, 2023)

Details on Synthesis

Polymerization reactions can occur in bulk (without solvent) in solution, emulsion, suspension, or a gas-phase.

Chain growth mechanism
An initiator adds to a carbon-carbon double bond of an unsaturated substrate to yield a reactive intermediate (initiation). Intermediate reacts with a second molecule (propagation). Chain termination occurs by reaction with another reactive species.

William D. Callister, David G. Rethwisch, Materialwissenschaften und Werkstofftechnik, WILEY-VCH, **2013**.
Polymerization - an overview | ScienceDirect Topics (24th February, 2025)
John E. McMurry, Organic Chemistry, 8th edition, Brooks/Cole Cengage Learning, **2012**.

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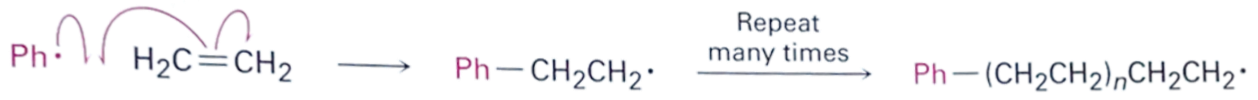

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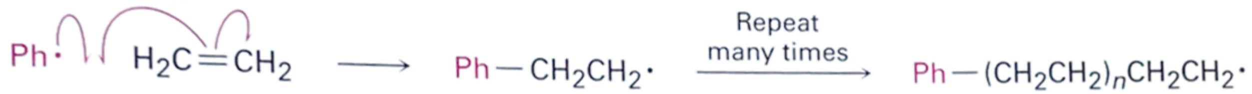

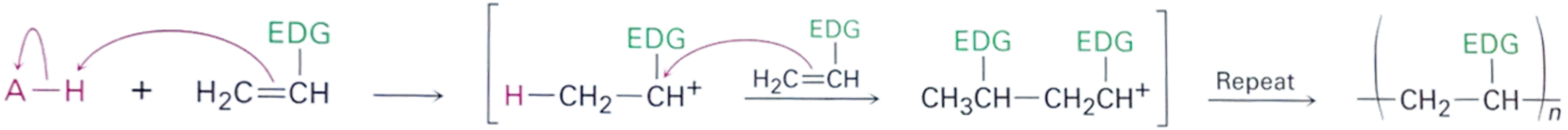

where EDG = an electron-donating group

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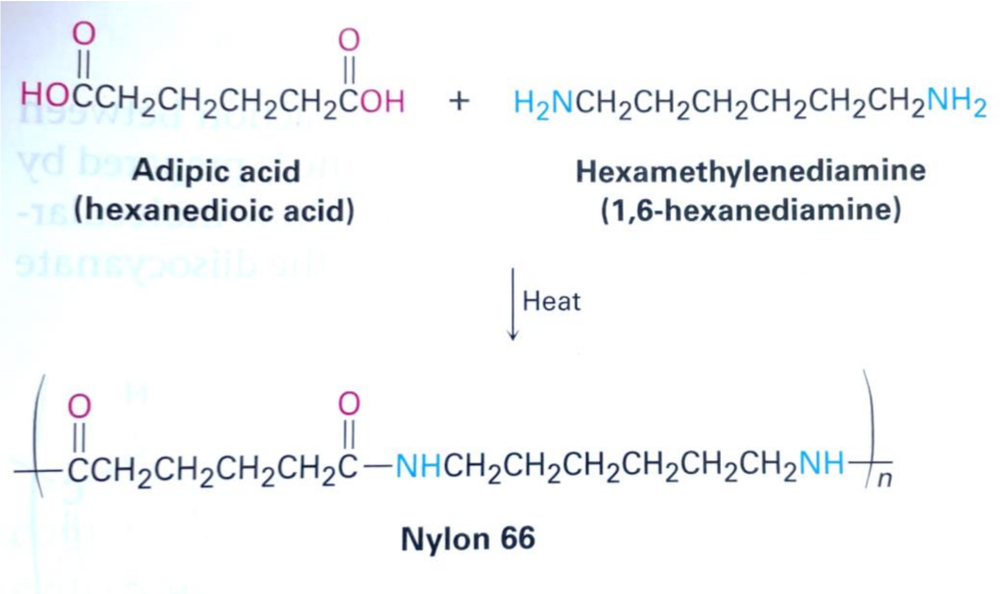

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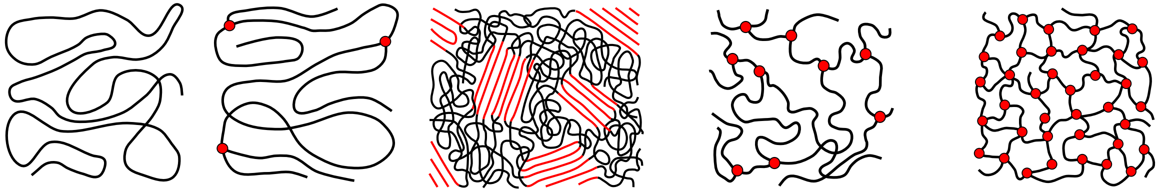
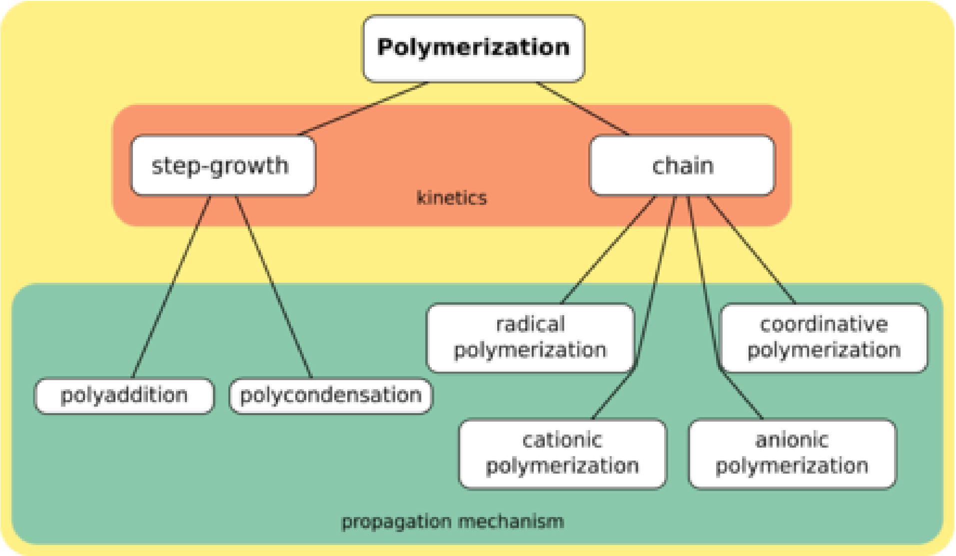


thermoplastics

elastomers

thermosets

resulting in



Polymer – Wikipedia (4th March, 2023)

White Board

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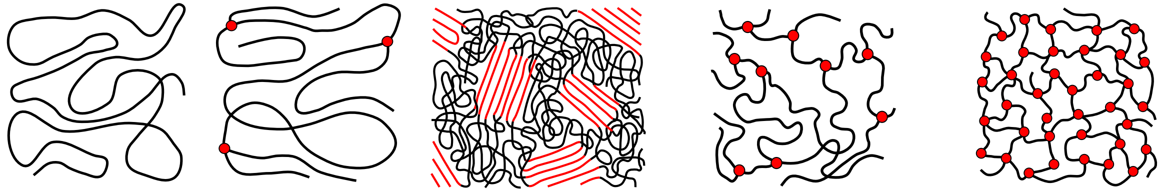

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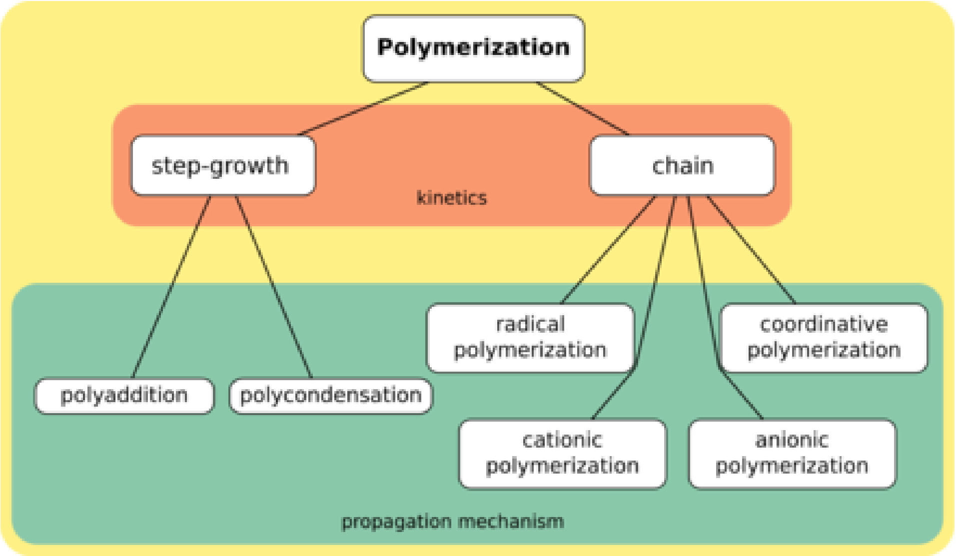

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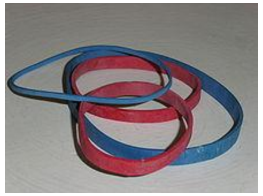

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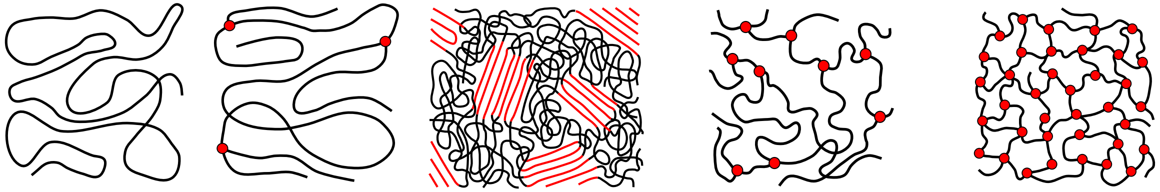

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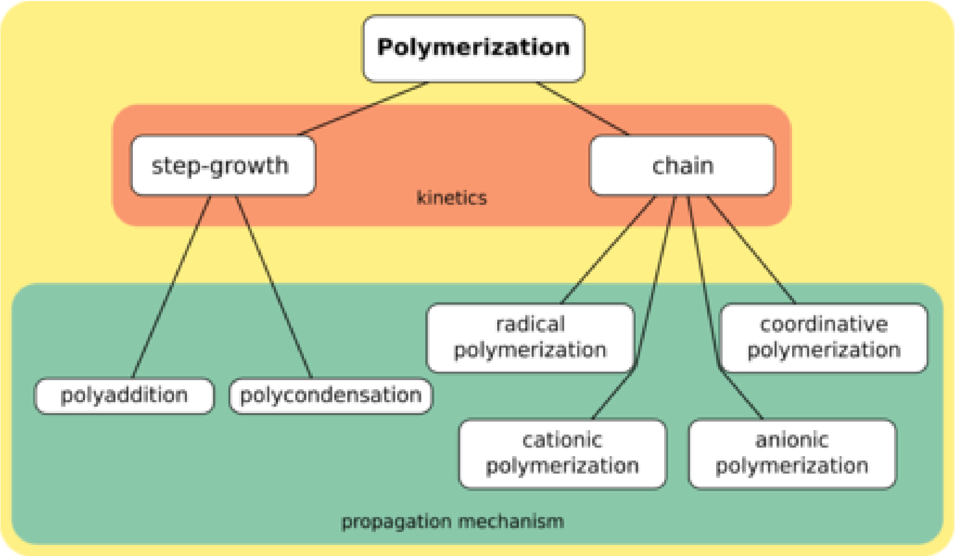

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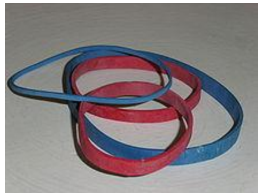

further applications

Conductive polymers for solarcells, (O)LEDs,…

Polymer – Wikipedia (4th March, 2023)

Analogously to metals and ceramics, properties of polymers are a direct result of structure of material.

Applications of polymers

William D. Callister, David G. Rethwisch, Materialwissenschaften und Werkstofftechnik, WILEY-VCH, **2013**.

Applications of polymers

Only one out of 50 teeth had the quality standard needed
→ extinction of elephants

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Until 1912, made from ivory.

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Reaction of **phenol** with **formaldehyde**
The product is a **liquid** that slowly solidifies into a **transparent, amber-colored solid**
Named by the inventor: Bakelite

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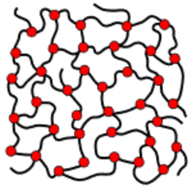
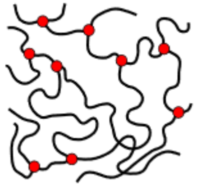
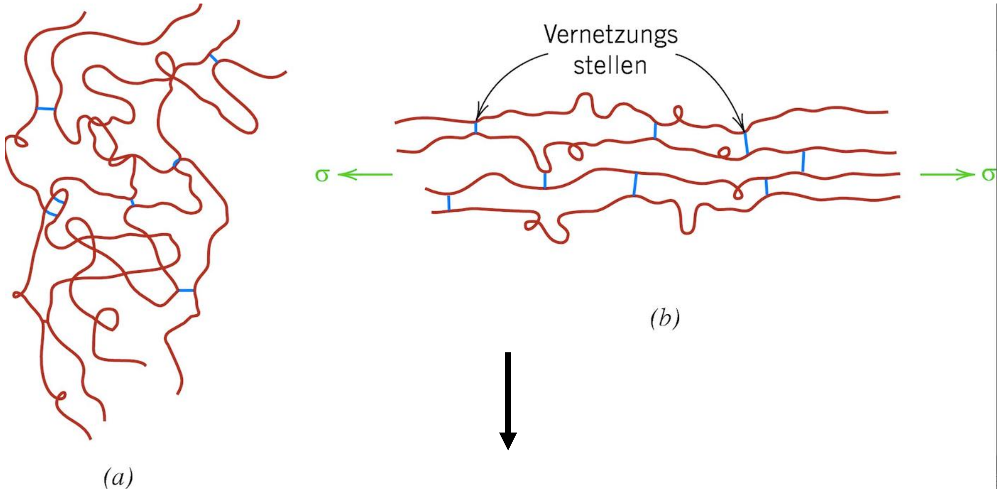


Phenol-formaldehyde is a **thermosetting polymer (thermoset)**
Heat-resistant and hard, as well as **significantly less brittle than many ceramics**
Relatively **inexpensive** and **easily colorable**
Elastic properties are **very similar to those of ivory**

William D. Callister, David G. Rethwisch, Materialwissenschaften und Werkstofftechnik, WILEY-VCH, **2013**.

Elastomers





Main properties

- very flexible at low temperatures
- weak intermolecular forces – extensive stretching
- specific working temperature varies depending on seal design and media compatibility

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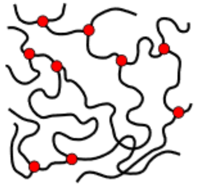
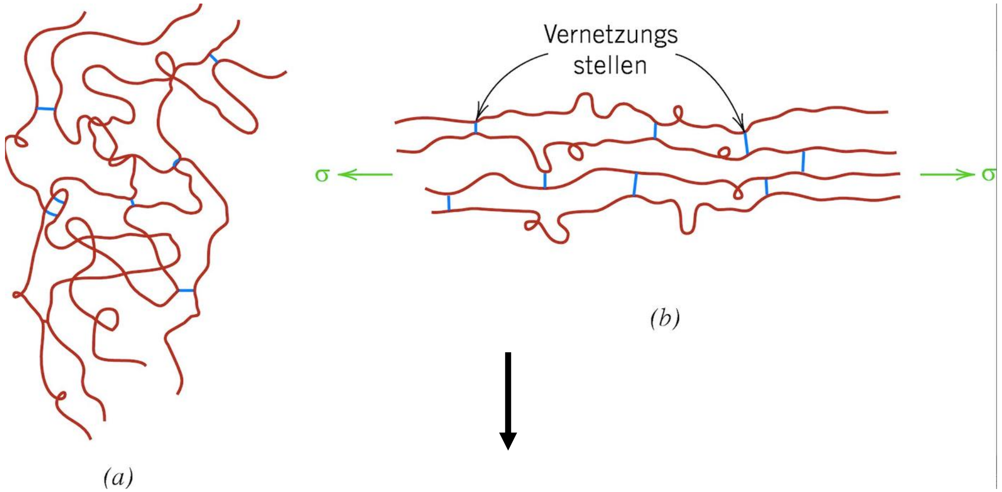


Natural rubber
Most important synthetic elastomer: **SBR – Styrene-butadiene copolymer (Buna S)**;
mixed with carbon black: **car tires**



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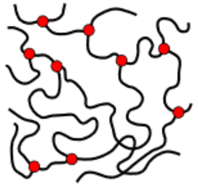

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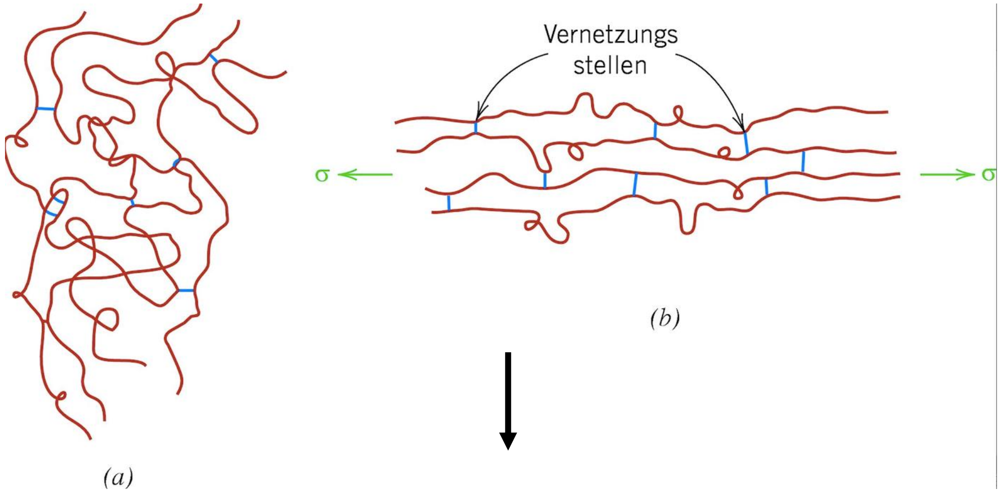
Silicone rubbers
- High flexibility over a wide temperature range (-90 to +250 °C)
- High **biocompatibility**, making them well-suited for **medical applications** (tubing for blood and blood products)
- Good **vulcanizability** at RT (**RTV resins: room temperature vulcanization**)



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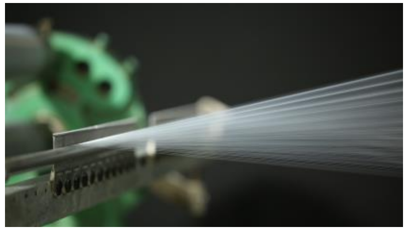
Fibres

Polymer fibres can be drawn into long filaments with a **length-to-diameter ratio of 100:1**

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- **High tensile strength, elastic modulus & abrasion resistance**
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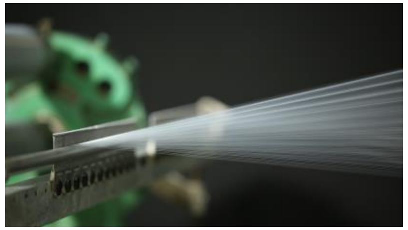
- **Tensile strength increases with crystallinity**, so **highly crystalline polymers are preferred**



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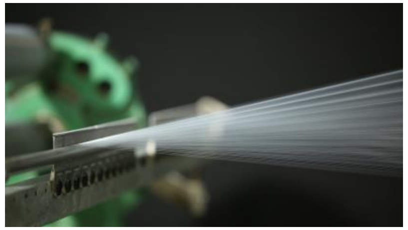
    - **Flame-resistant and suitable for tumble drying**



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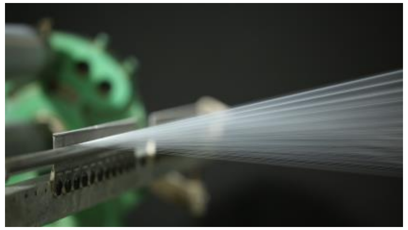

Where to find polymer fibres

- Polyester, Polyamide and Elasthane (textiles)
- Polyacryl (mostly whool-analogue textiles)
- Aramid (fracture- and impact-resistant – armour textiles, formula 1, …)
- Polypropylene (functional textiles, underwear)
- …

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Coatings / Lacquers

William D. Callister, David G. Rethwisch, Materialwissenschaften und Werkstofftechnik, WILEY-VCH, **2013**.
Lack – Wikipedia (24th February, 2025)

Coatings / Lacquers

Properties and functions

- Liquid or powdery
- Chemical or physical processes lead to a thin coating
- consist of binders, such as resins, dispersions, or emulsions, as well as fillers, pigments, solvents, and additives

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- **Protection:** Protecting the object from environmental influences
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Many components of **coating materials** are **polymers**, mostly of **organic origin**, such as:

- **Paint**
- **Varnish**
- **Enamel**
- **Clear lacquer**
- **Shellac** (a **natural polymer**, secreted by the **lac bug**)

Latices (**Latex** is a stable **suspension** of small, **insoluble polymer particles** in water)

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Adhesives

Two types of bonding mechanisms

Mechanical/physical:

- Adhesive penetrates **pores and crevices** of the surface
- **Interlocking** on a microscopic level
- Drying, cooling, gel formation

Chemical:

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Natural adhesives
Bone glue, casein, starch, resin

Synthetic adhesives (*Advantage: different materials can be bonded together, such as metals, ceramics, polymers, composites, leather, and combinations of these*)
Polyurethanes, Polysiloxanes, Polyimides, Acrylics, Rubbers

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Selection factors of adhesives

- **Type of materials** to be bonded
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- **Low-viscosity liquids** ensure **uniform and fully wetted surfaces**, maximizing **chemical bond interactions**.
- Bonding occurs when the **low-viscosity liquid solidifies or cross-links** through:
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High shear strength, peel resistance & fracture resistance

Advantages of Adhesive Bonding

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- Higher fatigue resistance
- Lower process costs
- Precise positioning
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Disadvantages of Adhesive Bonding

- Temperature sensitive (max. 300 °C)

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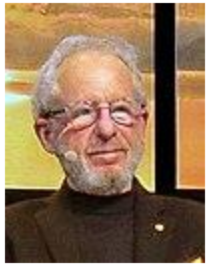
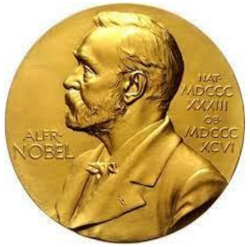
It´s not always bad to make mistakes!



“for their discovery and development of conductive polymers”

Nobel prize in Chemistry 2000

Alan J. Heeger
Alan MacDiarmid
Hideki Shirakawa



[Chemie-Nobelpreis 2000: Elektrisch leitende Kunststoffe könnten die Technik des 21. Jahrhunderts bestimmen - wissenschaft.de]
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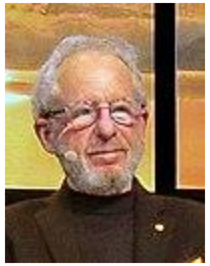

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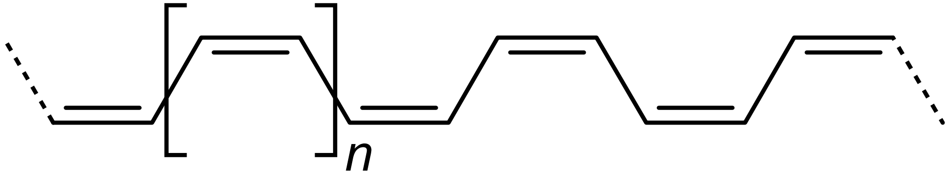
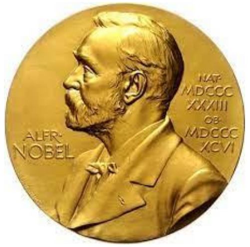
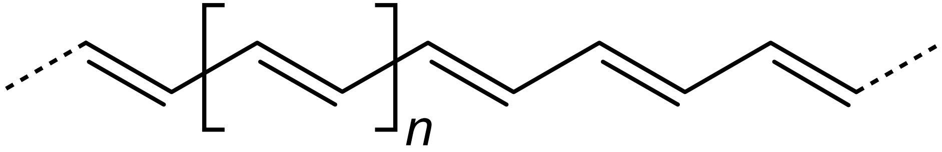


Copper colored film

Alan J. Heeger
Alan MacDiarmid
Hideki Shirakawa

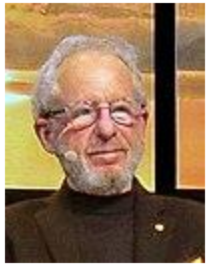




Silver colored film

[Chemie-Nobelpreis 2000: Elektrisch leitende Kunststoffe könnten die Technik des 21. Jahrhunderts bestimmen - wissenschaft.de](#) (4th March, 2023)

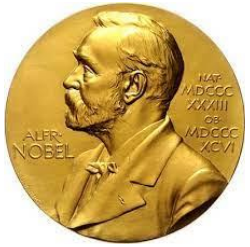
It´s not always bad to make mistakes!

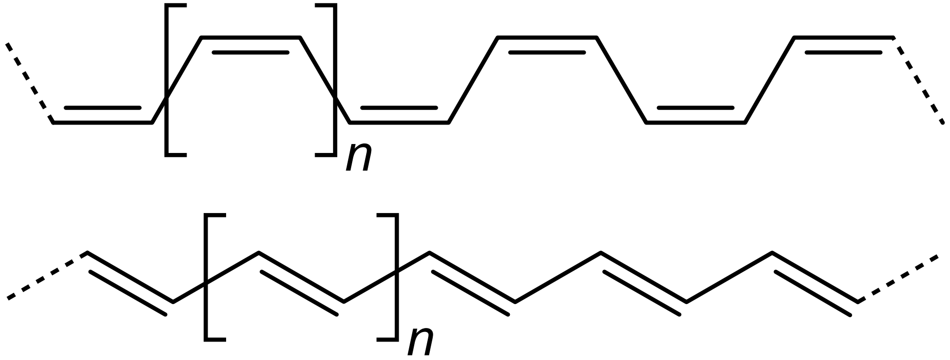


Nobel prize in Chemistry 2000

“for their discovery and development of conductive polymers”

Alan J. Heeger
Alan MacDiarmid
Hideki Shirakawa





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Shirakawa made a mistake during the synthesis of polyacetylen

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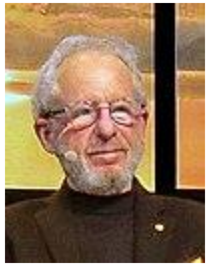

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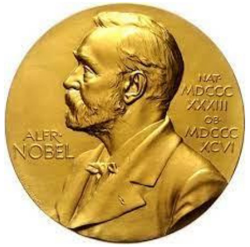

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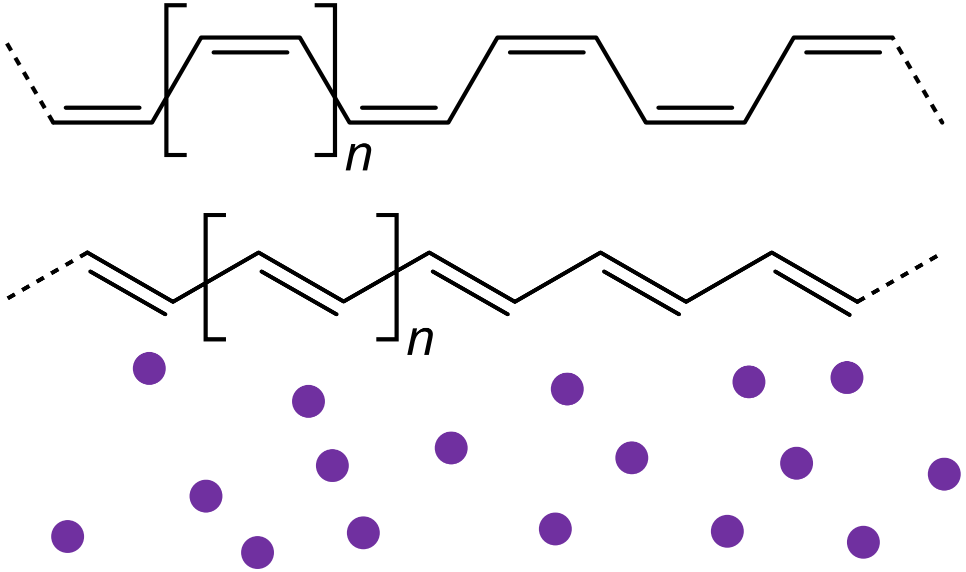

Copper colored film

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Oxidation of *E*-PE with gaseous iodine

Chemie-Nobelpreis 2000: Elektrisch leitende Kunststoffe könnten die Technik des 21. Jahrhunderts bestimmen - wissenschaft.de (4th March, 2023)

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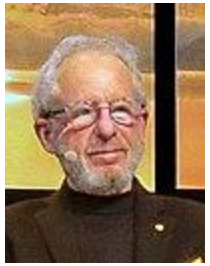  

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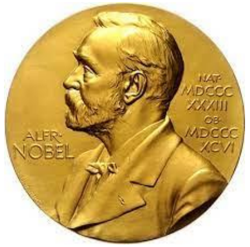

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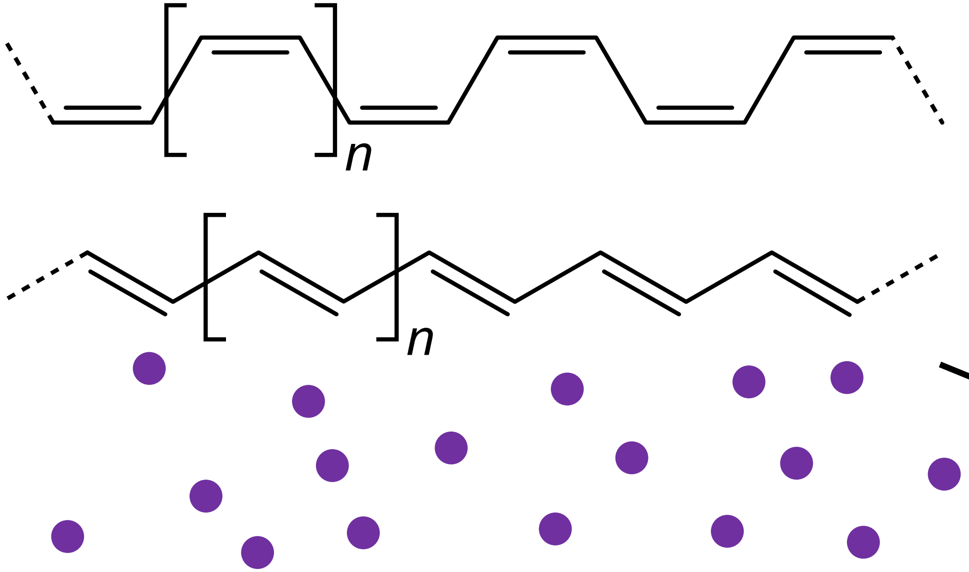


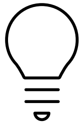
Copper colored film

Silver colored film

Shirakawa made a mistake during the synthesis of polyacetylen

as a result of impurity

Oxidation of *E*-PE with gaseous iodine



Note: Fundament for organic electronics!

[Chemie-Nobelpreis 2000: Elektrisch leitende Kunststoffe könnten die Technik des 21. Jahrhunderts bestimmen - wissenschaft.de](#) (4th March, 2023)

3D conductance like a metal!

Problem
Linear ballistic transport along polymer chains – not between layers or strands due to missing or weak inter-molecular ordering and coupling.

Article | Published: 05 February 2025

Two-dimensional polyaniline crystal with metallic out-of-plane conductivity

Tao Zhang, Shu Chen, Petko St. Petkov, Peng Zhang, Haoyuan Qi, Nguyen Ngan Nguyen, Wenjie Zhang, Jiho Yoon, Peining Li, Thomas Brumme, Alexey Alfonsov, Zhongquan Liao, Mike Hambsch, Shunqi Xu, Lars Mester, Vladislav Kataev, Bernd Büchner, Stefan C. B. Mannsfeld, Ehrenfried Zschech, Stuart S. P. Parkin, Ute Kaiser, Thomas Heine, Renhao Dong, Rainer Hillenbrand & Xinliang Feng

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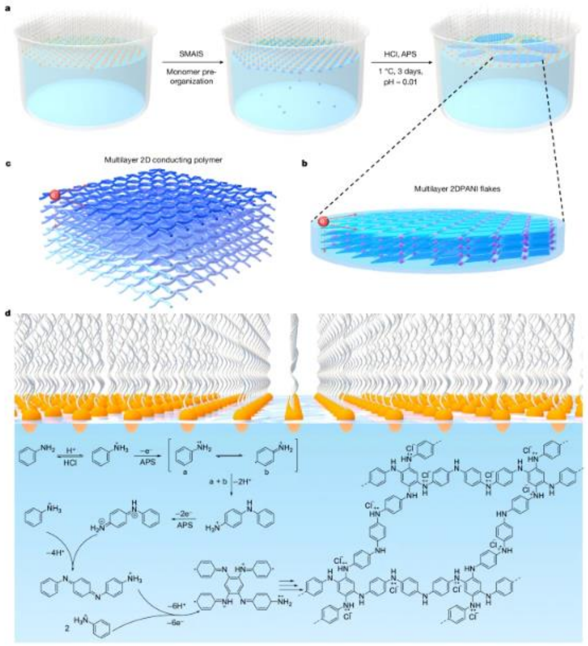

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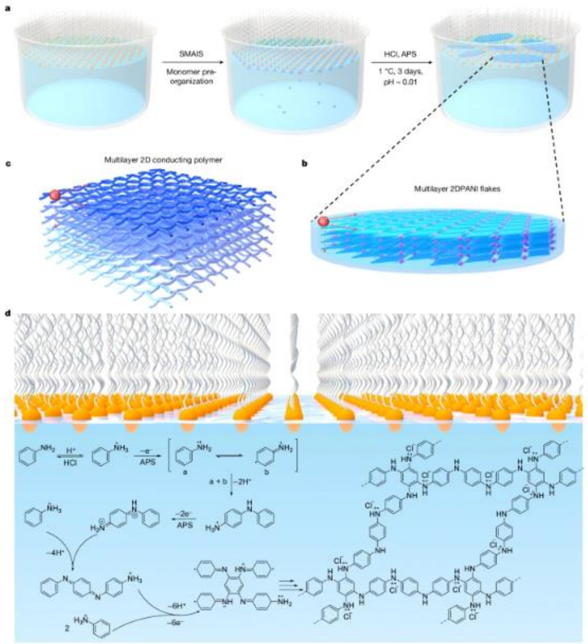

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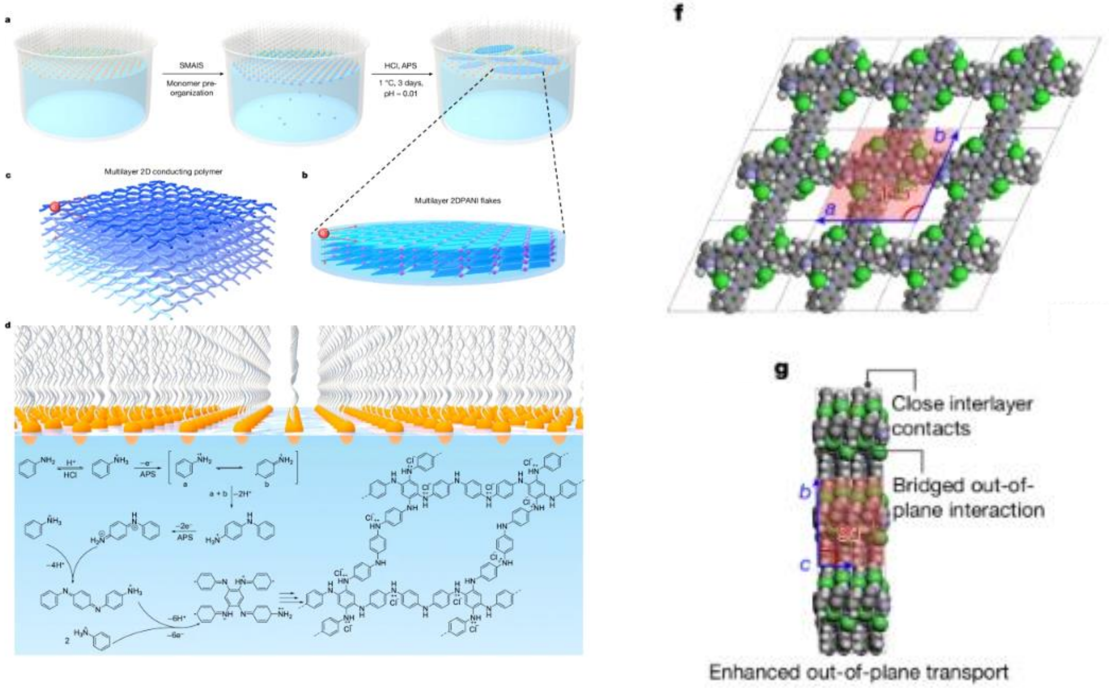

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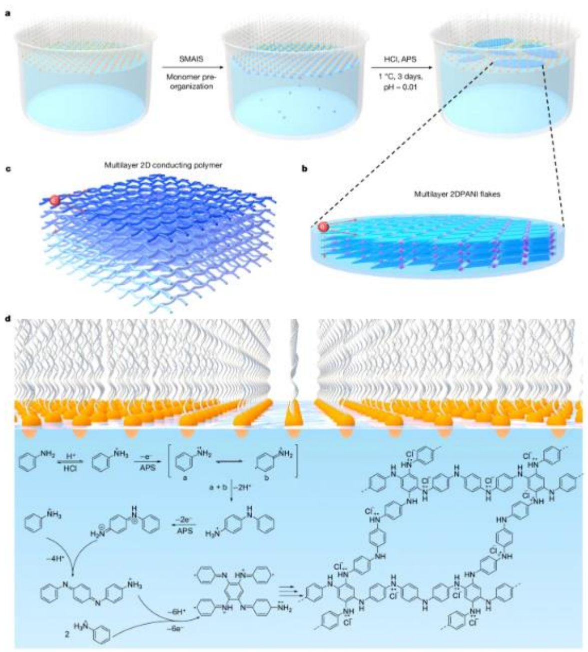

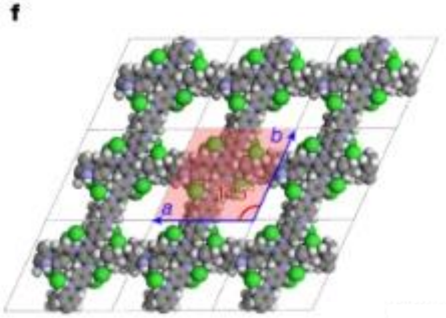

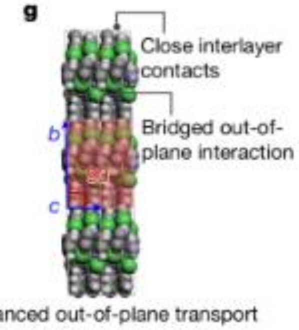

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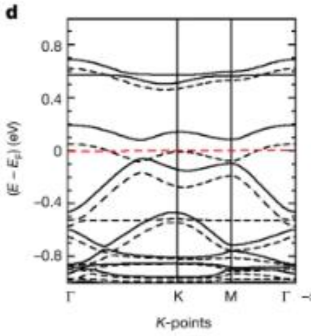
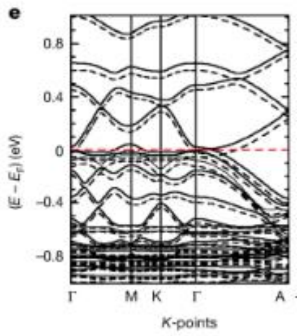
As a result of structure →

Metallic out-of-plane charge transport / 3D conduction



Mono-layer



layer-stacked

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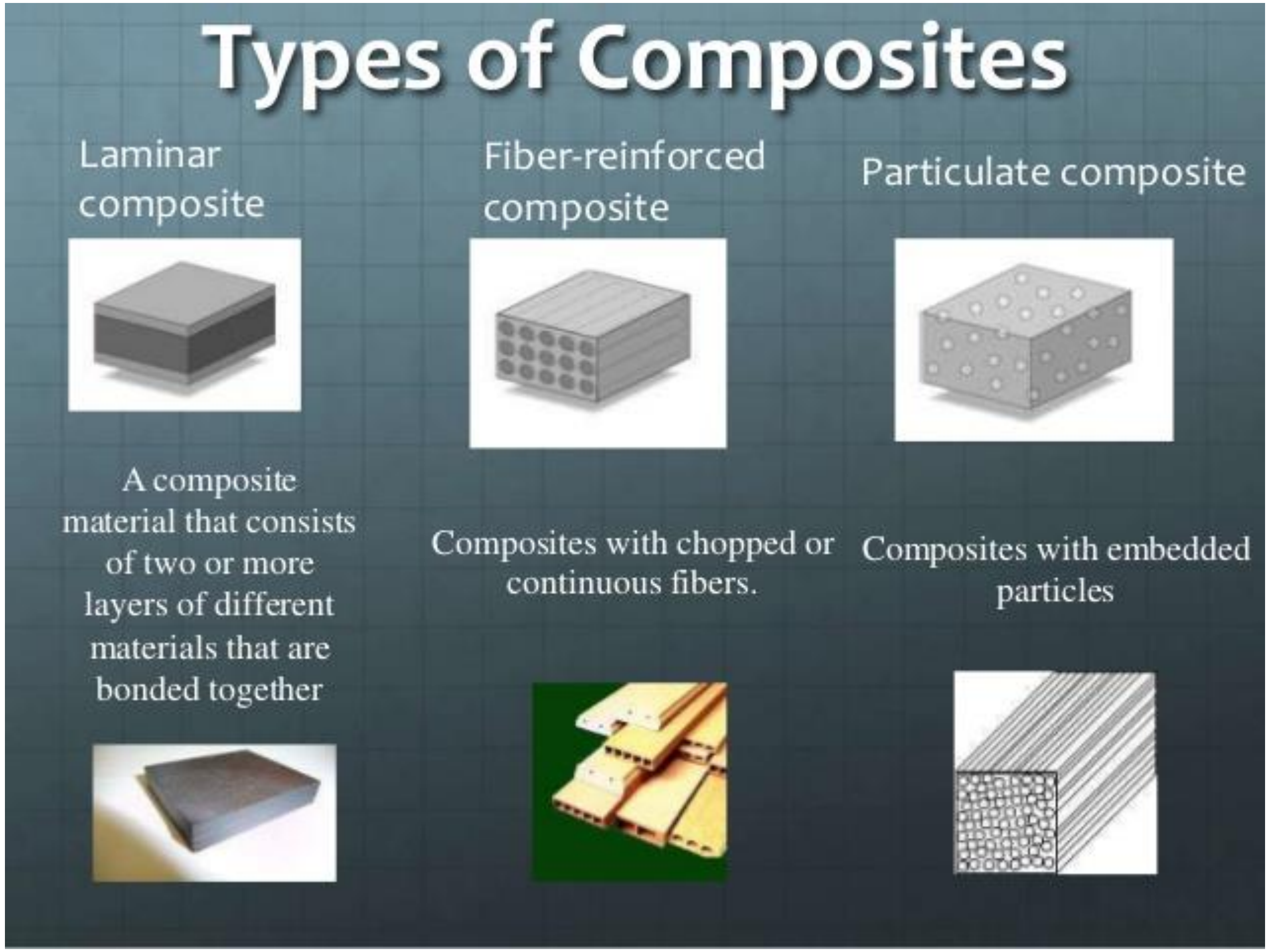
Composites/Compounds – Stronger together

Definition composite material

- combinations of two or more distinct materials components, resulting in enhanced properties that individual materials do not possess

Principle of combined action!



Classification of Composites Based on Reinforcement – Online Textile Academy (12th February, 2025)
Verbundwerkstoffe (24th February, 2025)
Lesson 9: Types and Applications of Composites | MATSE 81: Materials In Today's World (24th February, 2025)

Composites/Compounds – Stronger together

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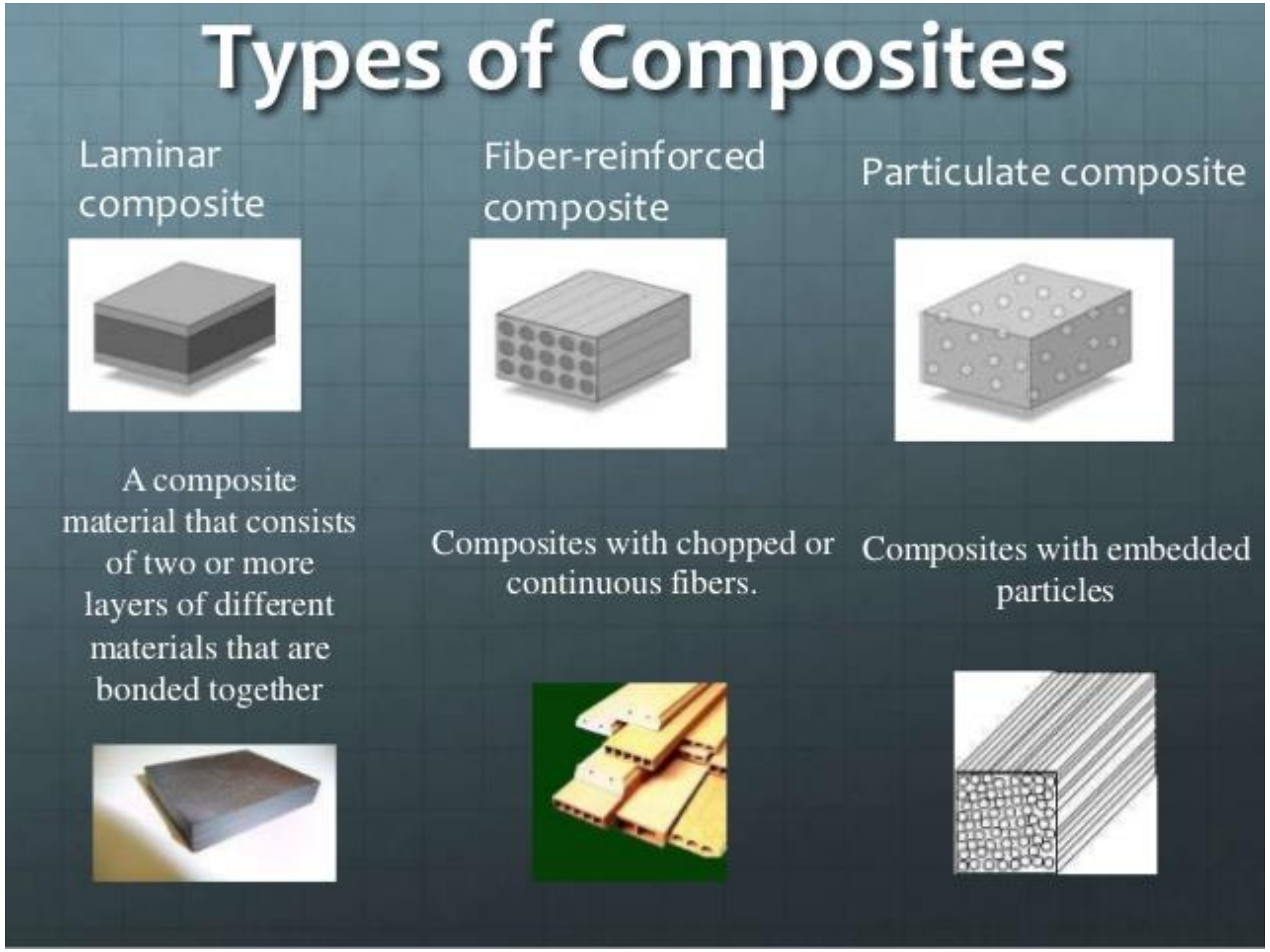
Principle of combined action!

Main components of composites

- **Matrix:** The continuous phase that binds the reinforcement together and distributes stress
- **Dispersed phase:** is dispersed in matrix in various concentrations and geometries

Single components remain intact!



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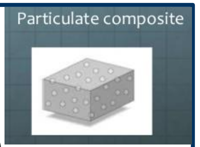
Types of composites and examples

Particulate composite



- Grinding wheel (ceramic, polymer/glass)
- Cemented carbide (WC, cobalt)
- Concrete (aggregate, fluid cement)

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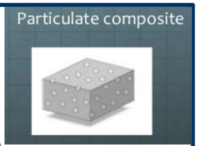

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Fiber-reinforced composite

- Fibre cement (fibres, cement)
- Ceramic matrix composite (fibres, ceramic)

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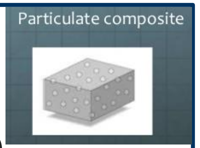

- Grinding wheel (ceramic, polymer/glass)
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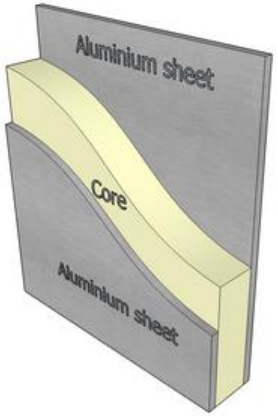
- Concrete (aggregate, fluid cement)

Structural composite

- Plywood (plies of wood sticked together with glue)
- Sandwich panel (*e.g.*, aluminum and polymer/porous mineral)
- Bimetall (*e.g.*, brass and iron)



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… and many more…

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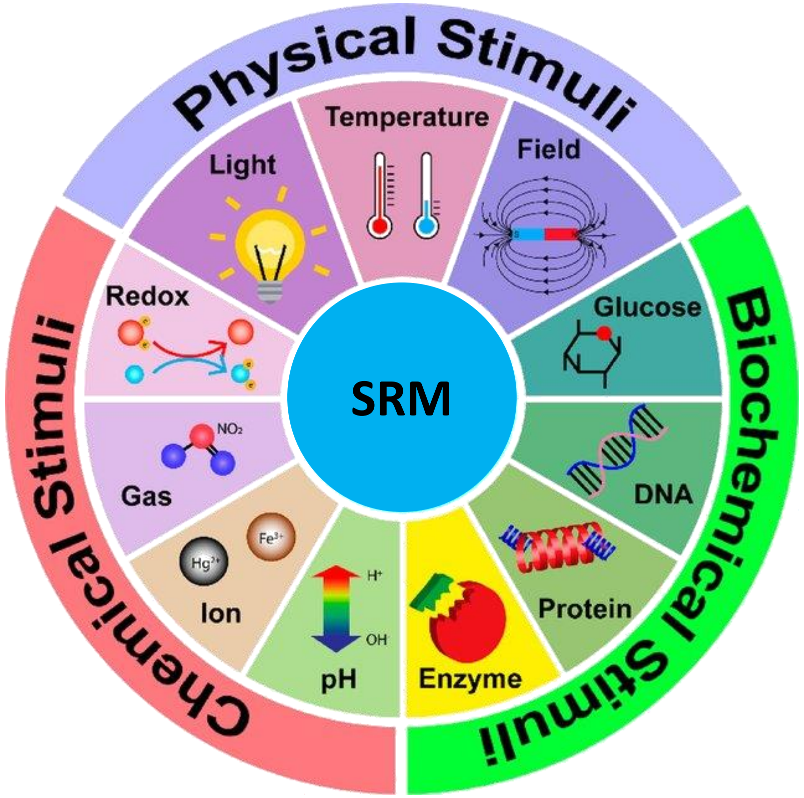
[Verbundwerkstoffe](#) (24th February, 2025)
[Lesson 9: Types and Applications of Composites | MATSE 81: Materials In Today's World](#) (24th February, 2025)

Taking materials a step further

Stimuli-responsive materials (SRM) are materials that can react to the presence of or changes in external stimuli.



[Stimuli-responsive materials: A smart way to study dynamic cell responses – ScienceDirect]() (3rd March, 2023)

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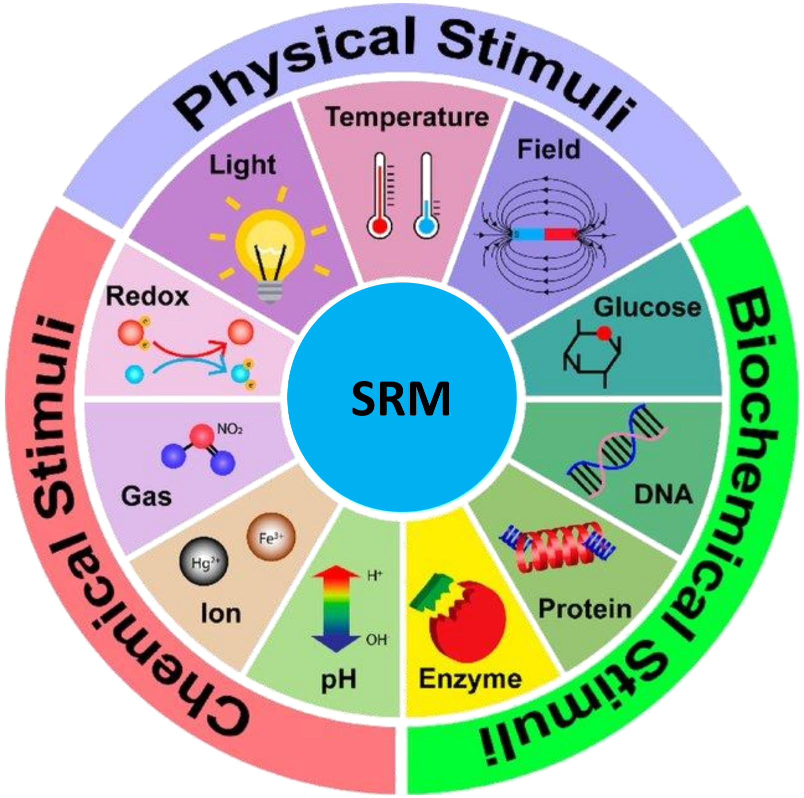


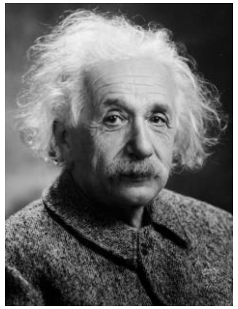
as a response to these stimuli, the material shows changes in its

- shape
- molecular assembly
- physical properties
- chemical properties
- mechanical properties

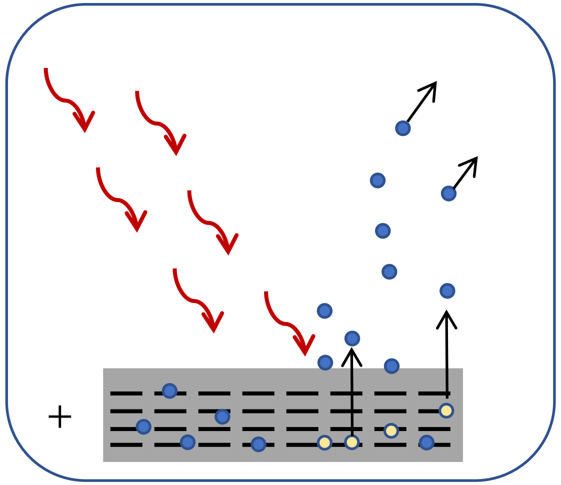
[Stimuli-responsive materials: A smart way to study dynamic cell responses – ScienceDirect]() (3rd March, 2023)

Photoelectric & photovoltaic effect

“excitation of electrons to a higher-energy state, when a material is exposed to electromagnetic radiation”



A. Einstein



Electrons leave the material.

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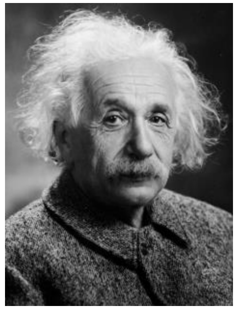

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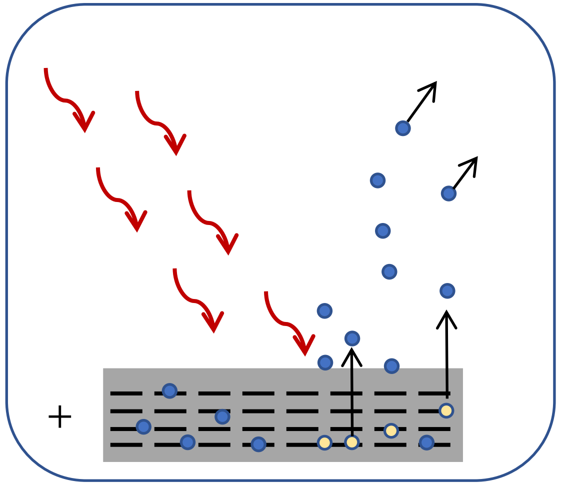

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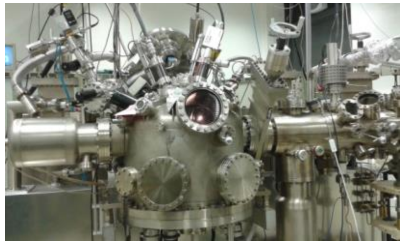

XPS.

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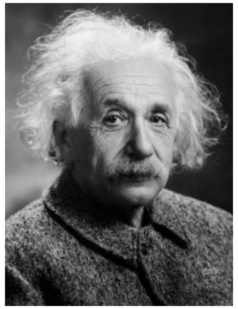

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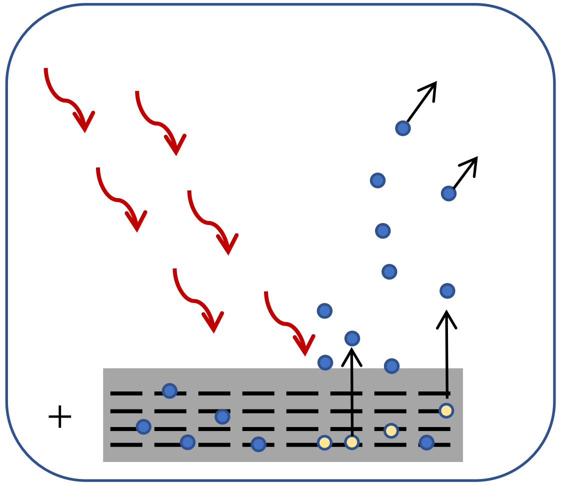

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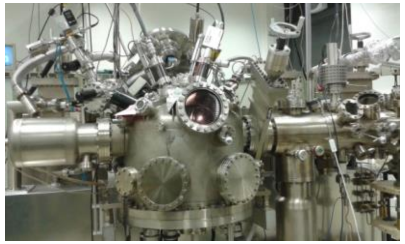

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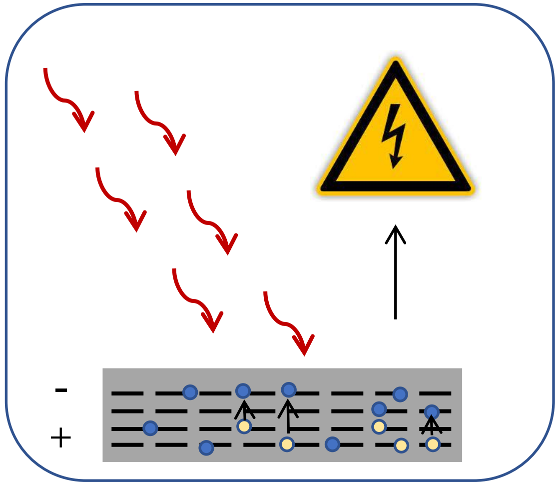

Electrons stay within the material.

E. Becquerel

Happy birthday Edmond Becquerel | IEC (4th March, 2023)

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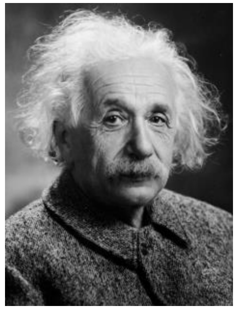

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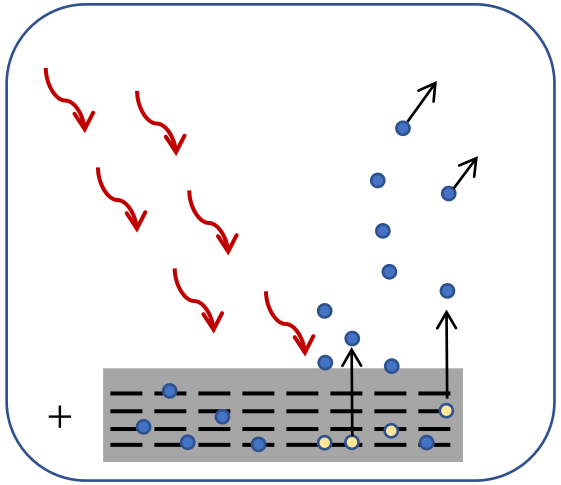

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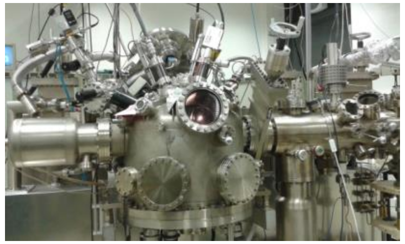

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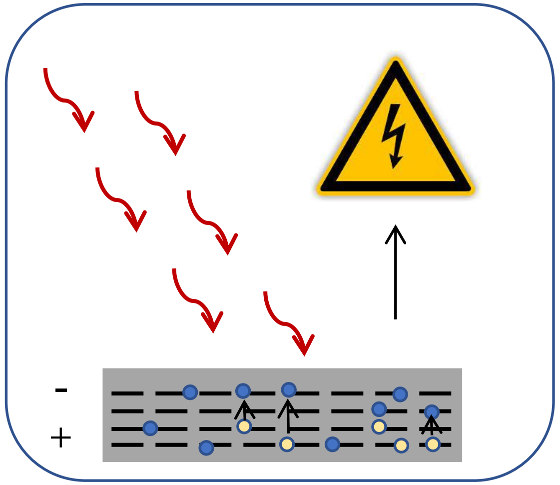

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Photovoltaic effect is also called the inner photoelectric effect.

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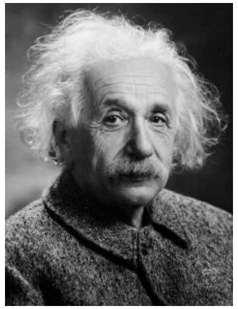

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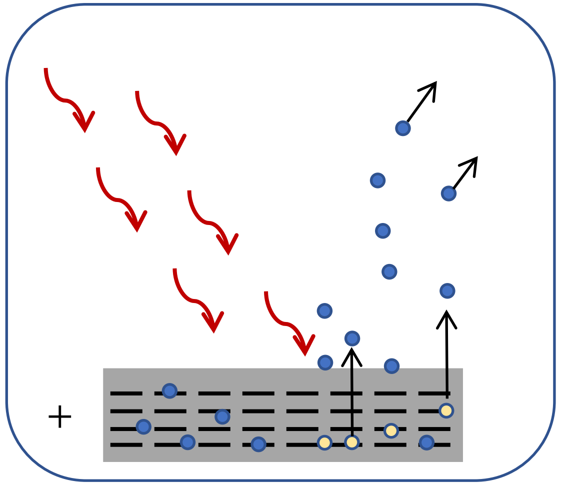

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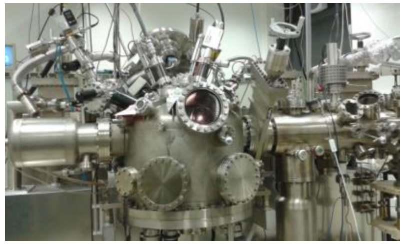
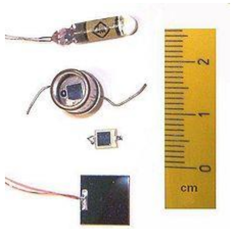
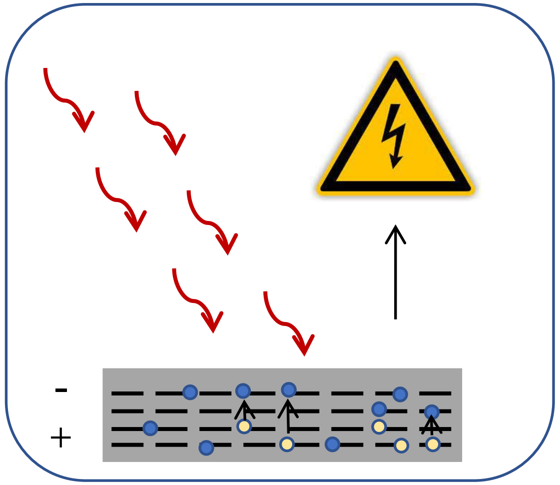


XPS.

Solar cell.



Photodiode.



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Questions?