INSTITUT DE CIÈNCIA DELS MATERIALS de la Universitat de València

Introducció a la ciència dels materials i dels nanomaterials

ICMUV · 4 – 8 de juliol de 2022

Macromolecules & Colloids for Sustainable Materials

MacroCoSM

Materials polimèrics

Rafael Muñoz-Espí
rafael.munoz@uv.es
Institut de Ciència dels Materials (ICMUV)

Is this the first thing you think about polymers?

Polymers are everywhere! Imagine one day without polymers…

Exercise for the coffee break: combine the names of polymers with the pictures



Poly(ethylene glycol) (PEG)

Polycarbonate

Nylon

Poly(ethylene terephthalate) (PET)

Polyisoprene


Polyhydroxyethylmethacrylate (PHEMA)

Polyurethane

Polystyrene

Polytetrafluoroethylene

Polysiloxane

Hyaluronic acid





Outline

1. Definitions and General Aspects
2. Sustainability Aspects: Recycling and Bio-Based Polymers
3. Polymers in the Solid State
4. Preparation of Polymers
   - Polymer Nanoparticles and Nanocapsules

1. Definitions and General Aspects

Definition of Polymer and Macromolecule

According to the International Union of Pure and Applied Chemistry:

polymer
A substance composed of macromolecules.

macromolecule
A molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass.

However, most commonly, the terms *polymer* and *macromolecule* are used **interchangeably.**

In general: **polymer = repetition of a monomer**

Examples of Common Polymers (I)

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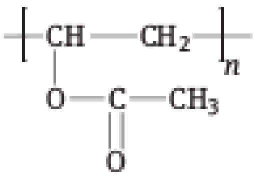
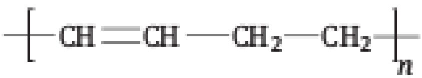
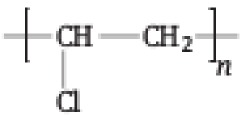
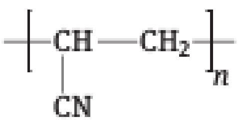
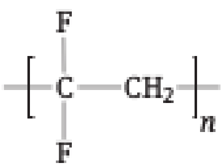
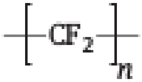
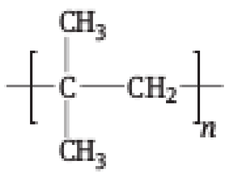
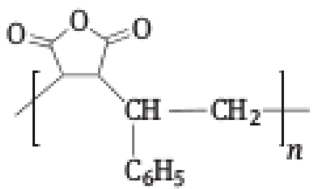
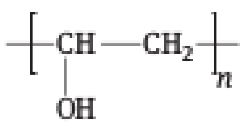
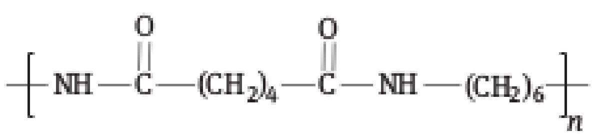
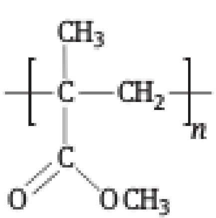
Table 8: Structure-based, source-based, and retained traditional names for some common polymers[a] [8, 13].

Structure	Structure-based names	Source-based names	Retained traditional names
	Poly(1-acetoxyethylene)	Poly(vinyl acetate) Poly(ethenyl acetate)	
	Poly(but-1-ene-1,4-diyl)[b]	Poly(buta-1,3-diene)	Polybutadiene[c]
	Poly(1-chloroethylene)	Poly(vinyl chloride) Poly(chlorethene)	
	Poly(1-cyanoethylene)	Polyacrylonitrile Poly(prop-2-enenitrile)	
	Poly(1,1-difluoroethylene)	Poly(1,1-difluoroethene)	
	Poly(difluoromethylene)[d]	Poly(tetrafluoroethene)	Polytetrafluoroethylene

Examples of Common Polymers (II)

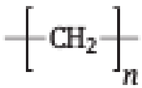
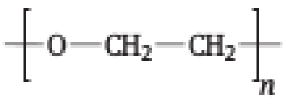
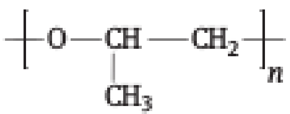
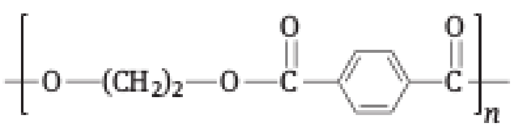
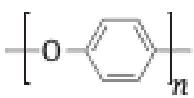
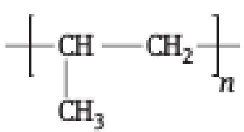
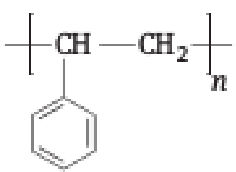
Table 8 (continued)

Structure	Structure-based names	Source-based names	Retained traditional names
	Poly(1,1-dimethylethylene)	Poly(2-methylpropene)	Polyisobutene
	Poly[(2,5-dioxotetrahydrofuran-3,4-diyl)(1-phenylethylene)]	Poly[(maleic anhydride)-*alt*-styrene]	
	Poly(1-hydroxyethylene)	Poly(vinyl alcohol)	
	Poly(azanediyladipoylazanediylhexane-1,6-diyl)	Poly[*N*,*N*'-(hexane-1,6-diyl)hexanediamide]	
	Poly[1-(methoxycarbonyl)-1-methylethylene]	Poly(methyl methacrylate)	

Source: *Pure Appl. Chem.* **2020**, *92*, 797–813

Examples of Common Polymers (III)

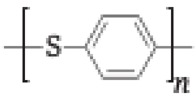
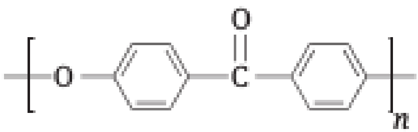
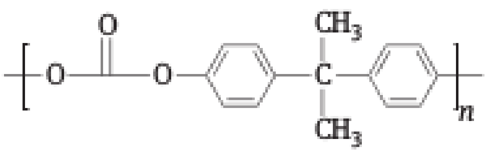
Table 8 (continued)

Structure	Structure-based names	Source-based names	Retained traditional names
	Poly(methylene)[d]	Polyethene	Polyethylene
	Poly(oxyethylene)	Poly(oxirane)	Poly(ethylene oxide)
	Poly[oxy(1-methylethylene)]	Poly(methyloxirane)	Poly(propylene oxide)
	Poly(oxyethyleneoxyterephthaloyl)	Poly(ethylene terephthalate)	
	Poly(oxy-1,4-phenylene)	Poly(1,4-phenylene oxide)	
	Poly(1-methylethylene)	Polypropene	Polypropylene
	Poly(1-phenylethylene)	Polystyrene Poly(ethenylbenzene) Poly(vinylbenzene)	

Source: *Pure Appl. Chem*. **2020**, *92*, 797–813

Examples of Common Polymers (IV)

Table 8 (continued)

Structure	Structure-based names	Source-based names	Retained traditional names
	Poly(sulfanediyl-1,4-phenylene)	Poly(1,4-phenylene sulfide)	
	Poly(oxy-1,4-phenylenecarbonyl-1,4-phenylene)		
	Poly[oxycarbonyloxy-1,4-phenylene(dimethyl-methylene)-1,4-phenylene]	Poly[(dimethylmethylene) bis(4,1-phenylene) carbonate]	

[a]There is no 1:1-correlation between structure-based names, source-based names, and retained traditional names for polymers.
[b]This assumes polymerization of buta-1,3-diene in the '-1,4-' mode, for which the CRU is usually written $-[-CH_2-CH{=}CH-CH_2-]_n-$. This is correct, but not the preferred CRU, which is as shown in the Table. Similarly, the preferred CRU for isoprene polymerized in the '-1,4-' mode is $-[-C(CH_3){=}CH-CH_2-CH_2-]_n-$ and named poly(1-methylbut-1-ene-1,4-diyl).
[c]The traditional name polybutadiene should not be used if the structure of the polymer is known. In such circumstances the structure-based name should be used.
[d]Structure-based representations $-[-CH_2-]_n-$ and $-[-CF_2-]_n-$ are preferred for poly(methylene) and poly(difluoromethylene), respectively. However, because of past usage, and as an attempt to retain some similarity to the CRU formulae of homopolymers derived from other ethene derivatives, the CRU representations $-[-CH_2-CH_2-]_n-$ and $-[-CF_2-CF_2-]_n-$ are also acceptable.

Source: *Pure Appl. Chem*. **2020**, *92*, 797–813

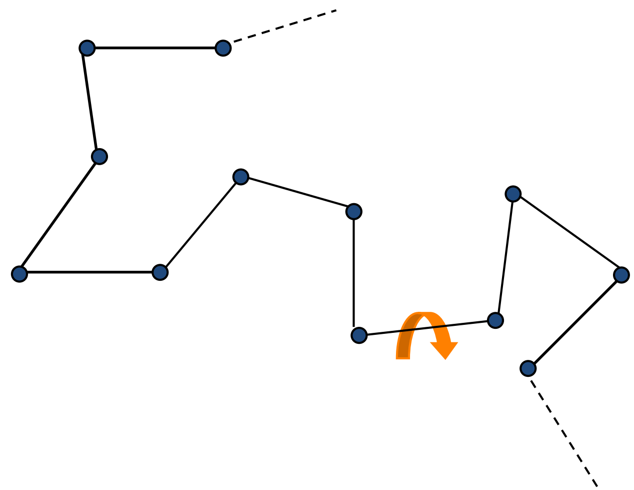
Characteristics of Polymers

Macromolecules or *polymers* are molecules with a covalent structure and a high molecular mass.

- Polymers are formed by the union of *monomers*

$$\underset{\text{ethylene}}{x\,(\mathrm{CH_2{=}CH_2})} \rightarrow \underset{\text{polyethylene}}{—(—\mathrm{CH_2\text{-}CH_2}—)_x—}$$

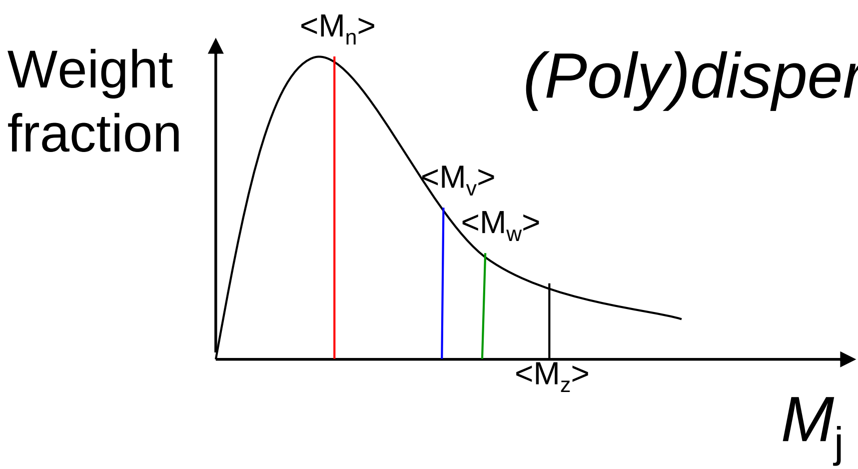
- Polymers are <u>in general</u> *polydisperse*
- Polymers are flexible



Molar Mass Distributions in Polymers

During polymer synthesis, a distribution of chain lengths is obtained → "mixture" of different molecular weights

$$\overline{M}_n \leq \overline{M}_v \leq \overline{M}_w \leq \overline{M}_z$$



(Poly)dispersity $Đ = \overline{M}_w / \overline{M}_n \geq 1$

The broading of the distribution depends on the synthetic method (mechanism and conditions)

Molar Mass Distributions in Polymers

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Number fraction of molecules of size *i*:

$$n_i = \frac{N_i}{\sum N_i}$$

Number average molecular weight

$$\overline{M}_n = \frac{\sum_{i=1}^{i=\infty} M_i N_i}{\sum_{i=1}^{i=\infty} N_i} = \sum_{i=1}^{i=\infty} M_i \frac{N_i}{\sum N_i} = \sum M_i n_i$$

Mass fraction of molecules of size *i*:

$$w_i = \frac{W_i}{\sum W_i}$$

Weight average molecular weight

$$\overline{M}_w = \frac{\sum_{i=1}^{i=\infty} M_i W_i}{\sum_{i=1}^{i=\infty} W_i} = \sum M_i w_i$$

According to the origin

monodisperse

Naturals
- *cellulose, natural rubber, resins...*
- *biopolymers (proteins, polynucleotides)*

Organic synthetic polymers — *polystyrene, polyethylene*

Semisynthetic polymers
- *nitrocellulose*
- *cellulose esters*

Silicon polymers
- *Synthetic polysiloxans:* $–Si(CH_3)_2 – O –$
- *Natural silicates:* $[SiO_4]^{4-}$

Classification of Polymers

According to monomer composition

homopolymers -AAAAAAA-

copolymers

- random -ABAABABBBAAA-
- alternate -ABABABABA-
- block -AAABBBAAABBB-
- graft -AAAAA-

```
-AAAAA-
 |
  BBBBBB-
```

Terpolymers (3 monomers)

According to the chain structure

linear chains:

-A-A-A-A-

branched chains:

```
      A-A-A-A-
       |
-A-A-A-A-
          |
        A-A-A-
```

network polymers: 2D o 3D

```
      |
-A-A-A-A-A-A-
      |     |
-A-A-A-A-A-A-A-A-A-
            |     |
 -A-A-A-A-A-A-A
     |        |
```

ladder polymer:

```
-A-A-A-A-A-A-A-A-A-
     |    |    |
-A-A-A-A-A-A-A-A-A-
```

Definition: Plastic

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Merriam-Webster SINCE 1828

JOIN MWU | GAMES | BROWSE THESAURUS | WORD OF THE DAY | VIDEO | WORDS

plastic

DICTIONARY THESAURUS

CITE

plastic [2]

noun

Definition of PLASTIC

1 : a plastic substance; *specifically* : any of numerous organic synthetic or processed materials that are mostly thermoplastic or thermosetting polymers of high molecular weight and that can be made into objects, films, or filaments

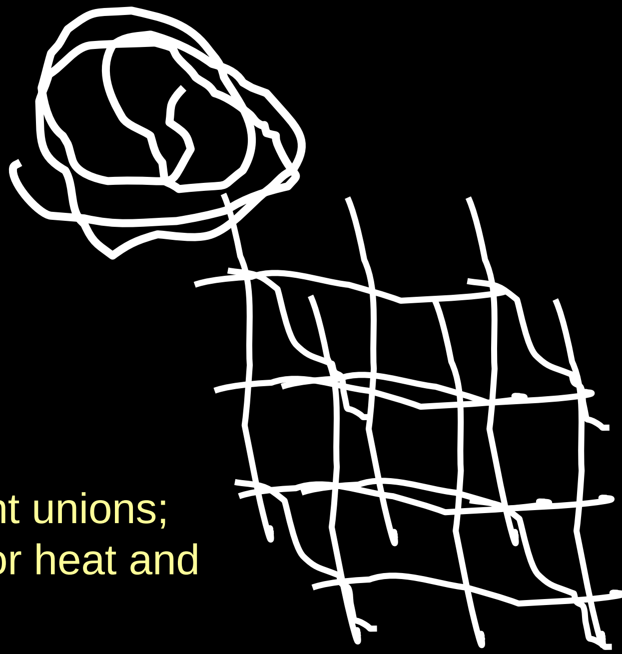
2 : credit cards used for payment — called also *plastic money*

Classification of Polymers/Plastics

According to the properties

Thermoplastics

Soft and ductil within a certain temperature range

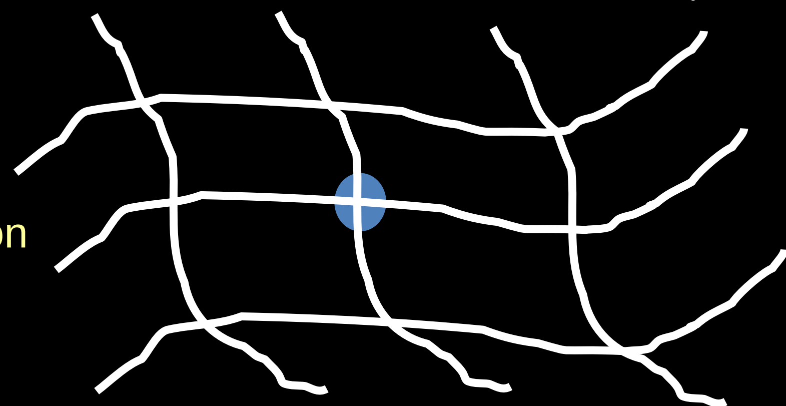


Thermosets

Reticular structures with covalent unions; cross-linking produced by heat or heat and pressure during polymerization

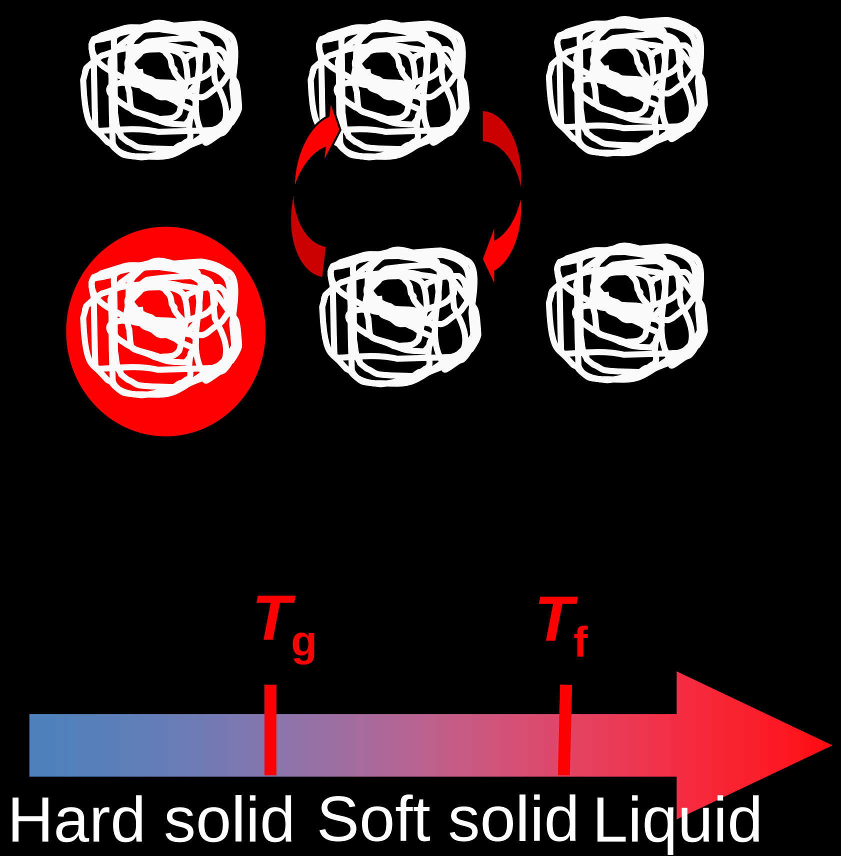
Elastomers

Great elastic deformation

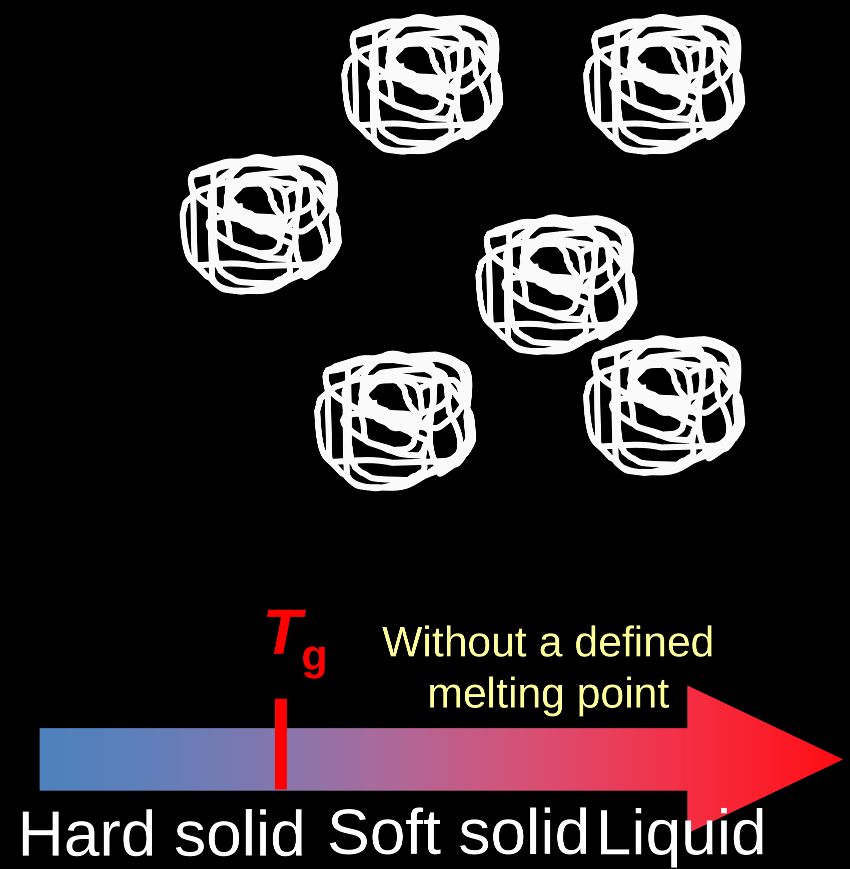


Thermoplastics

semicrystalline



amorphous



2. Sustainability Aspects: Recycling and Bio-based Polymers


The famous plastic island in the
Pacific Ocean...

Plastic Coding System

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1 PETE	2 HDPE	3 PVC	4 LDPE	5 PP	6 PS	7 OTHER
polyethylene terephthalate	high-density polyethylene	polyvinyl chloride	low-density polyethylene	polypropylene	polystyrene	other plastics, including acrylic, polycarbonate, polyactic fibers, nylon, fiberglass
soft drink bottles, mineral water, fruit juice containers and cooking oil	milk jugs, cleaning agents, laundry detergents, bleaching agents, shampoo bottles, washing and shower soaps	trays for sweets, fruit, plastic packing (bubble foil) and food foils to wrap the foodstuff	crushed bottles, shopping bags, highly-resistant sacks and most of the wrappings	furniture, consumers, luggage, toys as well as bumpers, lining and external borders of the cars	toys, hard packing, refrigerator trays, cosmetic bags, costume jewellery, audio cassettes, CD cases, vending cups	an example of one type is a polycarbonate used for CD production and baby feeding bottles

Definitions: Recycling and Reuse

Reuse

The general term *reuse* encompasses all the options available for the processing of plastics, regardless of whether the waste products are directly processed into new plastics or whether they are reused in a different manner. This term also includes so-called *energy utilization* in particular, that is, the use of plastic waste for the purpose of producing energy.

Recycling

The recycling of plastic waste refers to the processing of old waste into new plastics, or their being processed to be put to another use, with the exception of energy recovery. Recycling thus refers to all types of *material utilization*.

The relationship between these terms can thus be described by the following equation:

$$\text{Reuse} = \text{Recycling} + \text{Energy utilization}$$

Koltzenburg, Maskos & Nuyken. *Polymer Chemistry*. Springer, 2017.

Energy Utilization

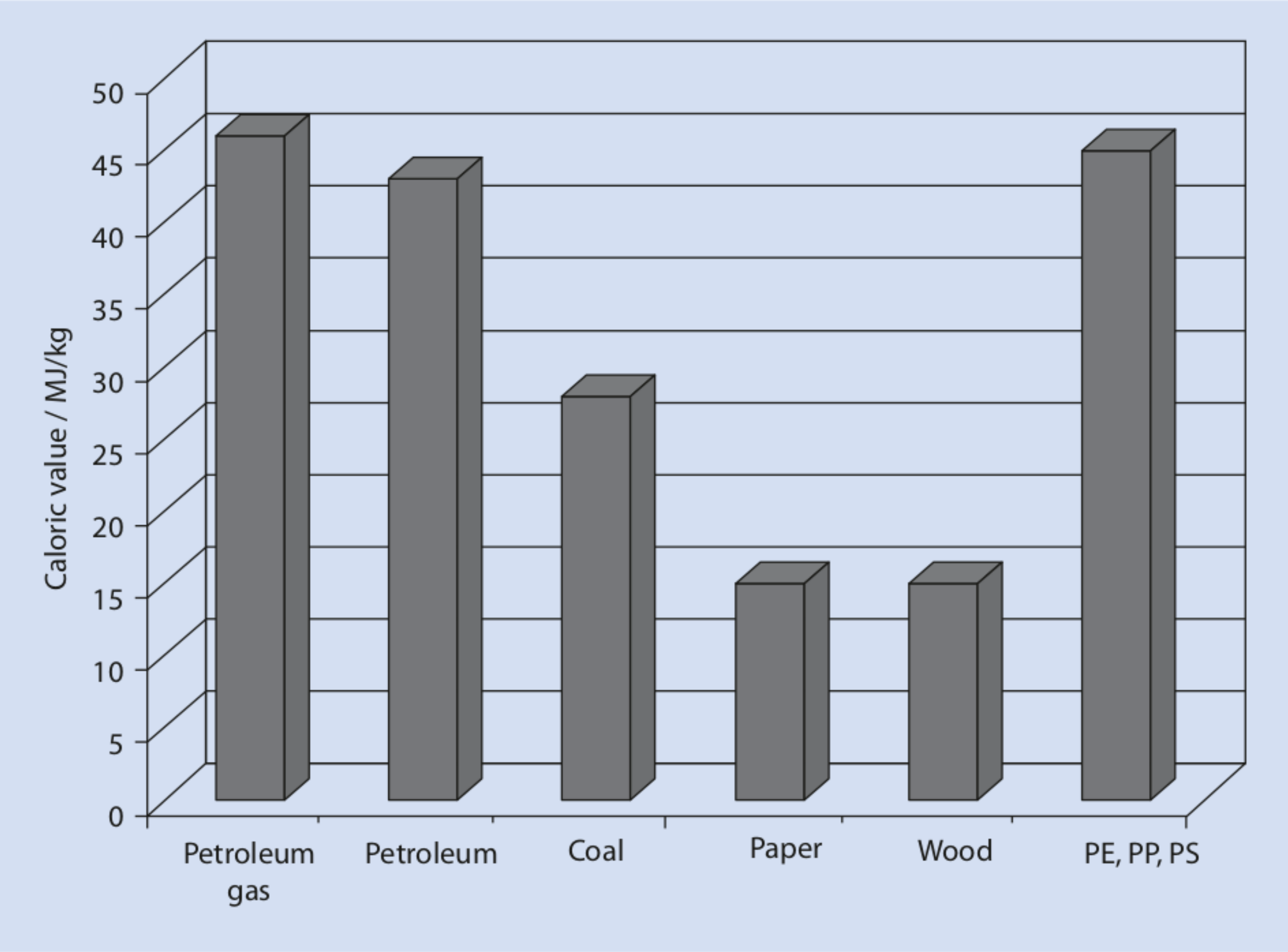


Fig. 21.4 Calorific value of selected materials

Koltzenburg, Maskos & Nuyken. *Polymer Chemistry*. Springer, 2017.

Biopolymer, Bioplastic and Bio-based Polymer

- The terminology is extremely confusing and contradictory
- Strictly speaking, a **BIOPOLYMER** is an ***unmodified naturally occurring polymer*** (e.g., protein, DNA, polysaccharide)
    - This definition is very restrictive, but very often the term is used for any bio-based polymer.
    - "**BIO-BASED POLYMER**" is a more general term, which includes any polymer originating from natural resources, also after modification (e.g., poly(L-lactic acid)).

Bio-Based Polymers: Classification

- **Proteins**
  - Collagen, gelatin, gluten...
- **Nucleic acids**: DNA and RNA
- **Polysaccharides**
  - **Neutral:** dextran, starch, cellulose, chitin
  - **Cationic:** chitosan, pullulan
  - **Anionic**: alginate, heparin, pectin
- **Phenolic macromolecules**
  - Lignin
- **Others**
  - Natural rubber (polyisoprene)

BIOPOLYMERS *stricto sensu*

- **Polyesters by microbial fermentation**
  - Polyhydroxyalcanoate (PHA)
  - Polyhydroxybutyrate (PHB)
- **Semi-synthetic bio-based polymers**
  - Carboxymethylcellulose
  - Nitrocellulose
- **Synthetic bio-based polymers**
  - Poly(lactic acid) (PLA)
  - Polycaprolactone (PCL)
  - Poly(vinyl alcohol) (PVA)

Bio-Based Polymers

! Bio-based ≠ biodegradable

A large number of monomers used for synthetic polymers can be produced from renewable resources:

- Ethene (glucose → ethanol → ethene) ***polyethylene***
- Ethylene oxide (from bio-ethene) ***poly(ethylene oxide)***
- Diacids (e.g., for ***polyesters*** or ***polyamides***)
- Polyols (e.g., for ***polyurethanes***)

➢ The properties of the polymers obtained are not dependent on whether the building blocks are derived from renewable or fossil raw materials and the biodegradability of these materials is just as limited as their synthetic analogs.

Koltzenburg, Maskos & Nuyken. *Polymer Chemistry*. Springer, 2017.

4. Polymers in the Solid State

Polymers in the Solid State

Polymers in the solid state →
- **Amorphous**
- **Semicrystalline**
- Single crystal

Amorphous, Semicrystalline: Very common, important

Single crystal → Unusual, technologically Irrelevant

In crystalline solids, upon heating:
crystalline → amorphous liquid
(first-order phase transition)

T_m Melting temperature

In amorphous solids, upon heating:
vitreous solidified amorphous state → amorphous melt
(second-order phase transition)

T_g Glass transition temperature

Amorphous polymers: They are in a disordered state, similar to that of liquids and gases. They can be, therefore, classified as "undercooled liquids". The chains take the random coil conformation.

- When heated, they undergo a gradual process of softening.
  - At room temperature, they are usually rigid solids (**glassy state**).
  - When heated, they soften and become deformable (viscous **rubbery state**) → T_g
  - If temperature is further increased, they can become liquid.

Crystalline polymers: highly ordered polymers. The polymer chains pack to form crystals. They undergo melting upon increase of temperature and are characterized by a melting temperature (T_m).

- Because polymers are long macromolecular chains, they cannot pack easily, with exception of rare cases of polymerization from 100% crystalline monomers. Therefore, it is nearly impossible to find 100% crystalline polymer.

- In general, “crystalline” polymers have a crystallinity between **30 and 80%**, that is, they are actually **“semicrystalline”** solids with both an **amorphous region** and a **crystalline region**. Accordingly, they have both T_g and T_m.

Important Techniques of Thermal Analysis

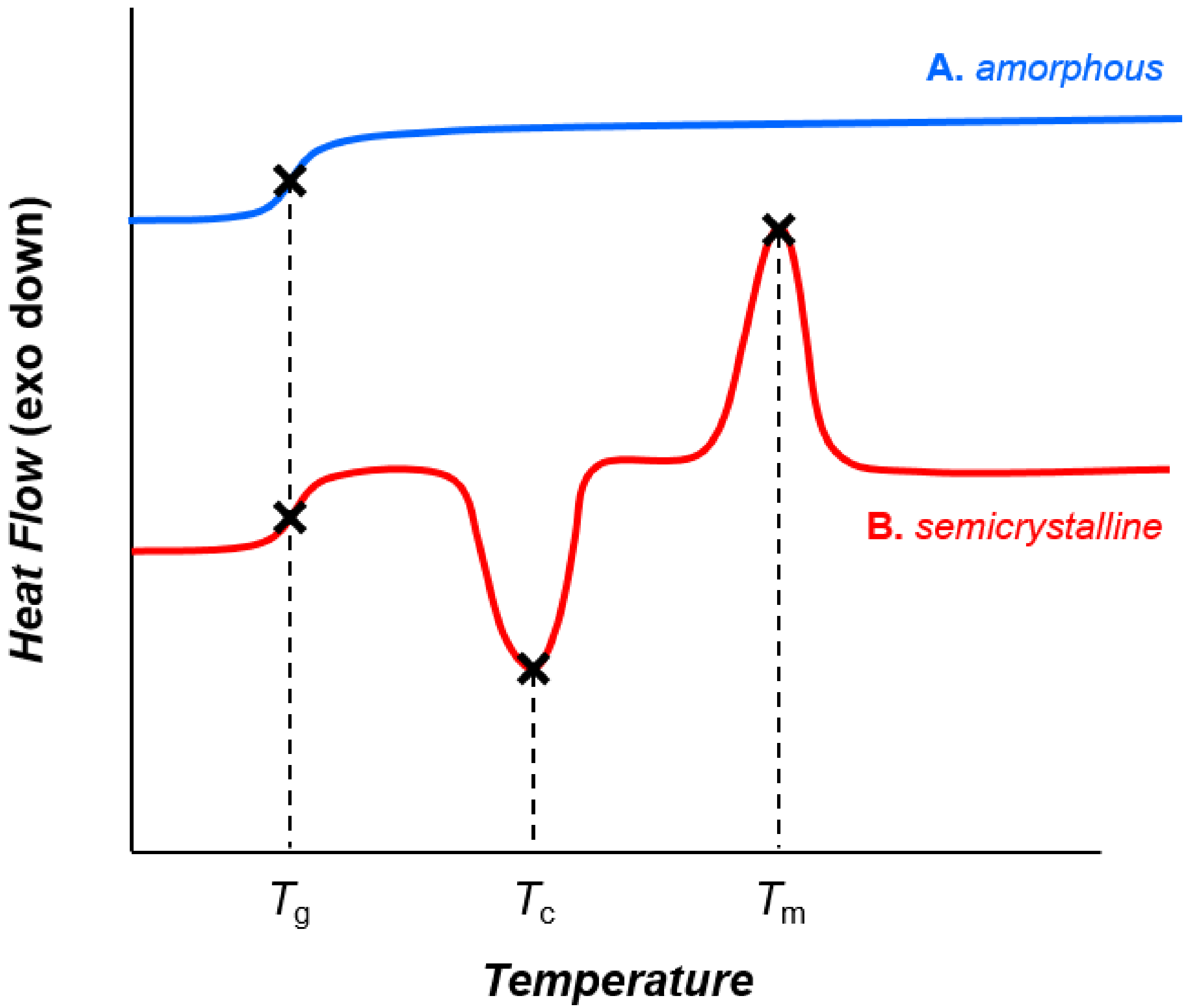
- Thermogravimetrical Analysis (**TGA**)
- Thermomechanical Analysis (**TMA**)
- Differential Scanning Calorimetry (**DSC**)
- Dynamic Mechanical Analysis (**DMA**)

Differential Scanning Calorimetry (DSC)

- The heat flow *to* and *from* a **sample** and a **reference** material is measured as a function of temperature.
- The sample is heated, cooled or held at constant temperature.
- The measurement signal is the energy absorbed by or released by the sample in milliwatts.
- DSC allows you to detect **endothermic** and **exothermic** effects, measure peak areas (transition and reaction enthalpies), determine temperatures that characterize a peak or other effects, and measure specific heat capacity.

Thermal Analysis of Polymers: Selected Applications, Mettler-Toledo.

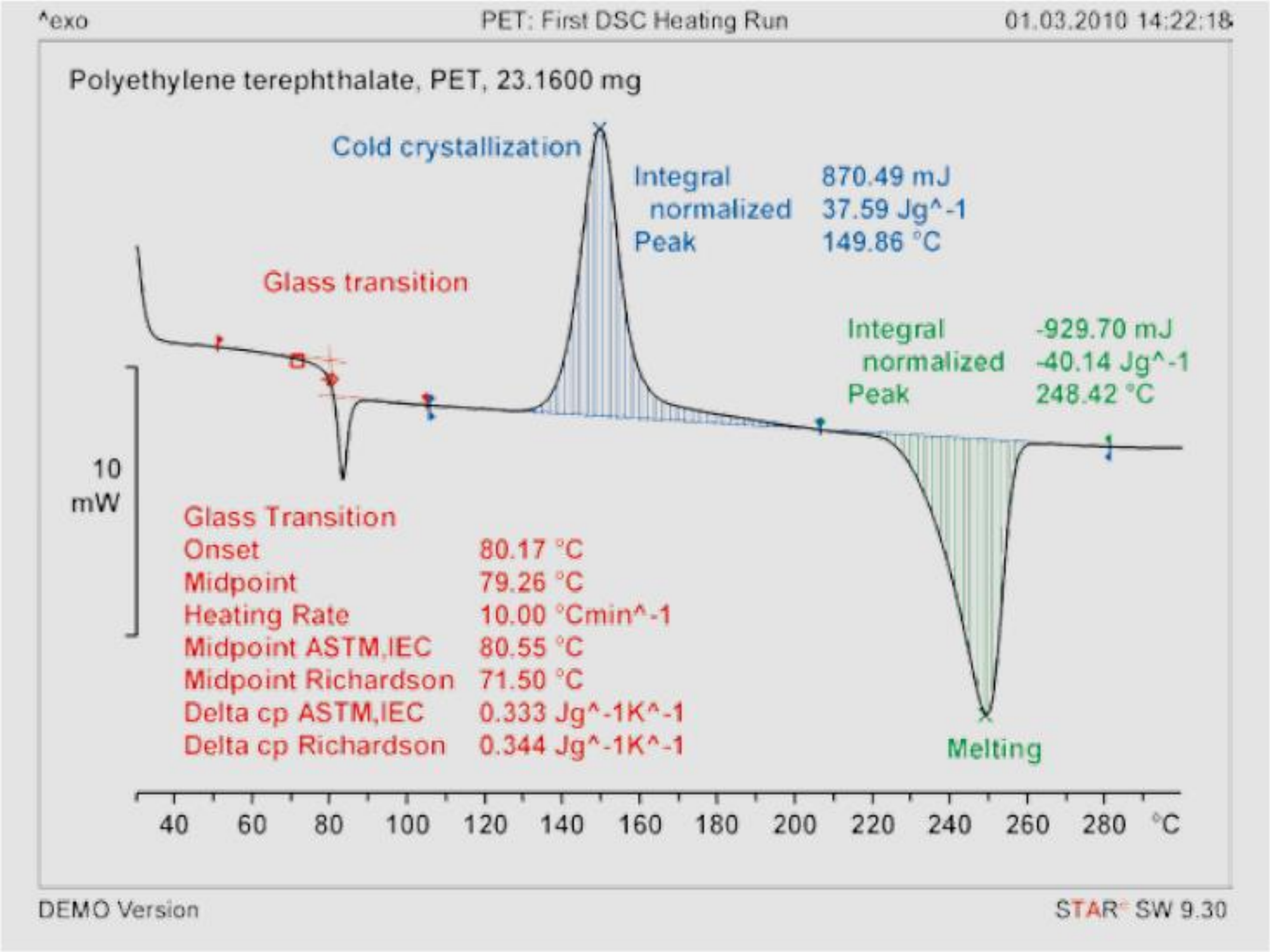
Differential Scanning Calorimetry (DSC)



Differential Scanning Calorimetry (DSC)

Pay attention to the direction of EXO, both directions are possible.

Figure 3.
The main effects measured by DSC using PET as a sample. Temperature range 30–300 °C; heating rate 20 K/min; purge gas nitrogen at 50 mL/min.



Thermal Analysis of Polymers: Selected Applications, Mettler-Toledo.

4. Preparation of Polymers

Classification of Polymerization Reactions

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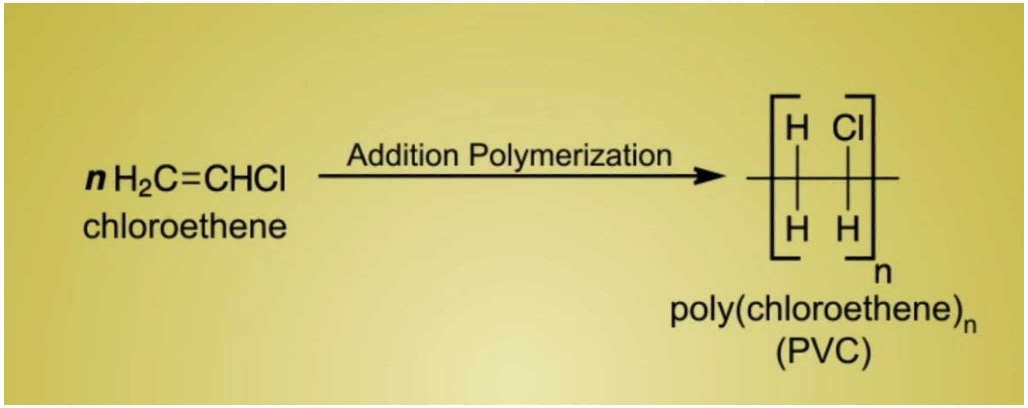
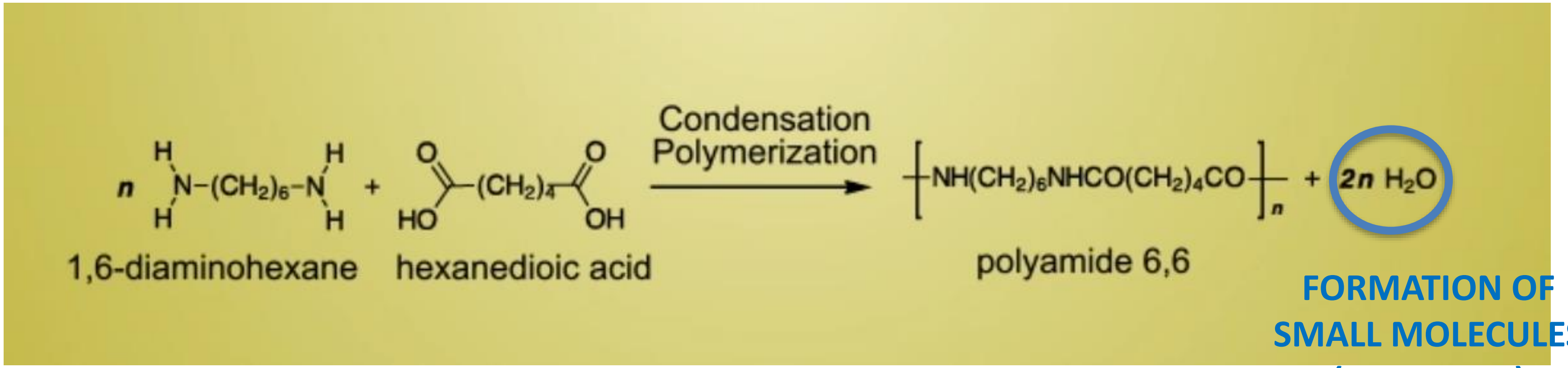
I. Addition Polymerization



II. Condensation Polymerization



FORMATION OF SMALL MOLECULES (e.g., water)

Image source: JoVE video, “Polymerization Protocols”

Classification of Polymerization Reactions

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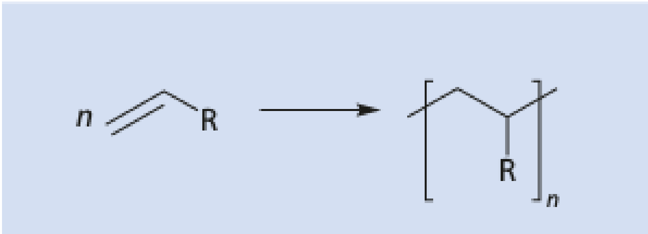
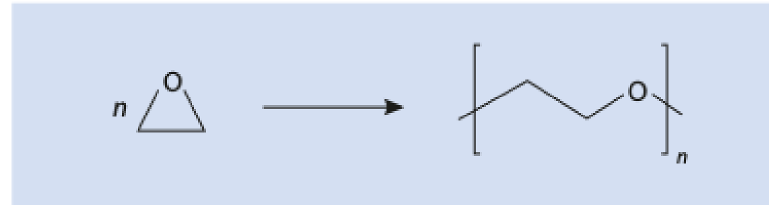
I. Chain-Growth Reactions



Polymerization of an olefinically unsaturated compound



Ring-opening polymerization
(from ethylene oxide)

II. Step-Growth Reactions

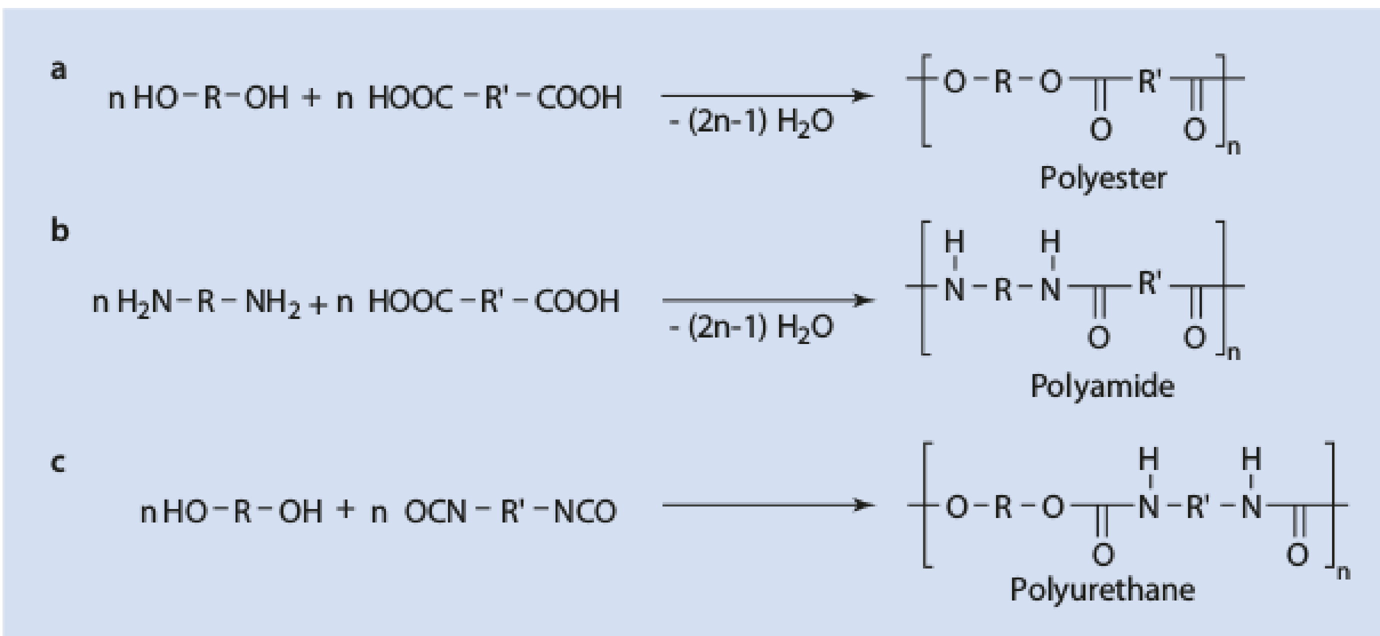
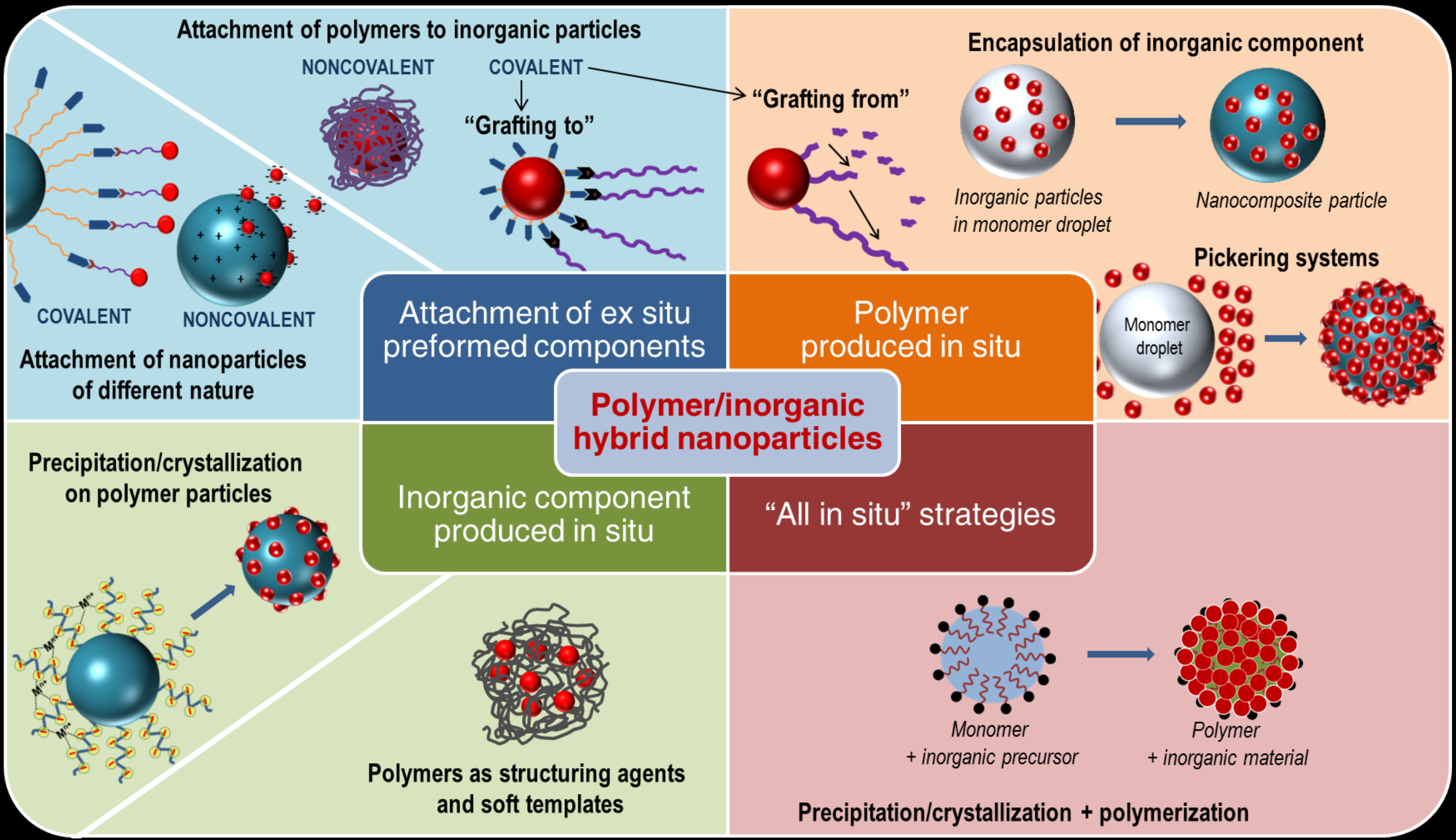


Image source: Koltzenburg, Maskos & Nuyken. *Polymer Chemistry*. Springer, 2017.

Laboratory Practice this Afternoon

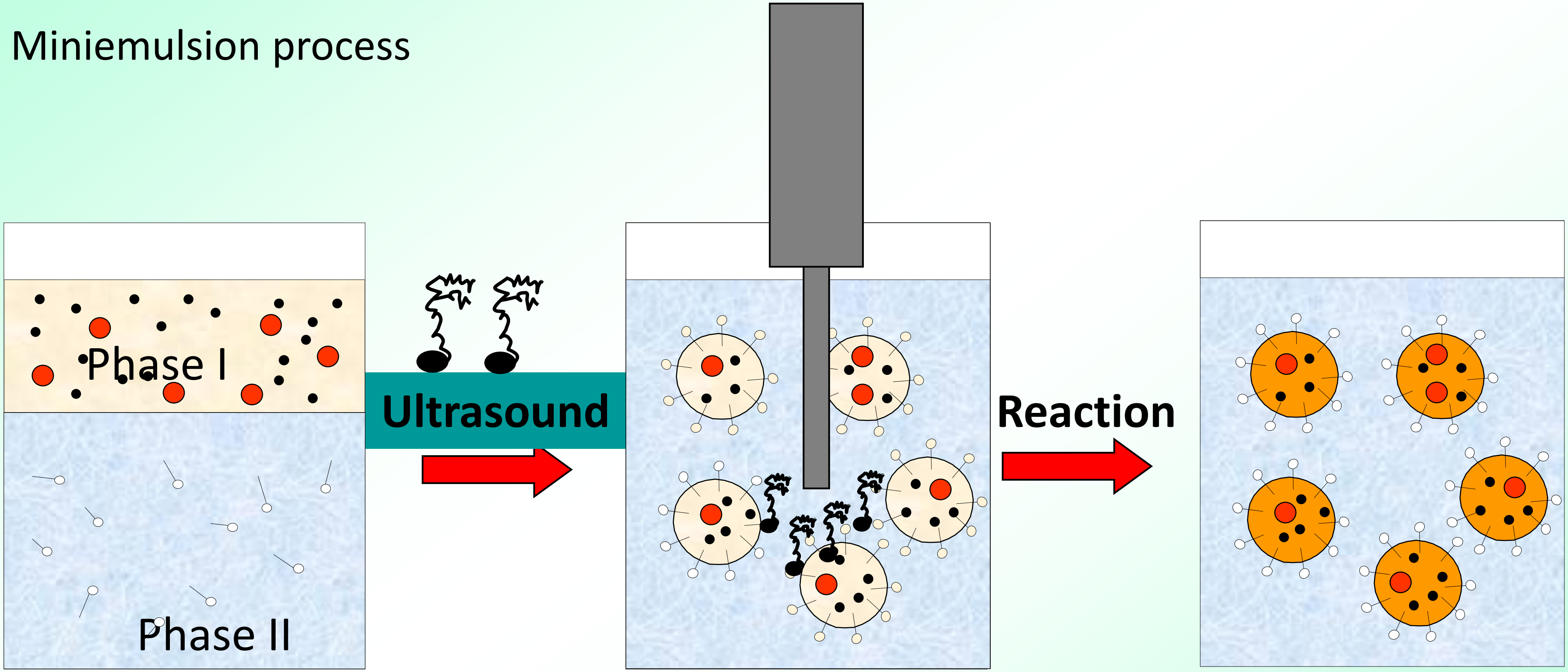
Polymer Nanoparticles and Nanocaspules



Attachment of polymers to inorganic particles
NONCOVALENT
COVALENT
"Grafting to"
COVALENT
NONCOVALENT
Attachment of nanoparticles of different nature
"Grafting from"
Encapsulation of inorganic component
Inorganic particles in monomer droplet
Nanocomposite particle
Pickering systems
Monomer droplet
Attachment of ex situ preformed components
Polymer produced in situ
Polymer/inorganic hybrid nanoparticles
Inorganic component produced in situ
"All in situ" strategies
Precipitation/crystallization on polymer particles
Polymers as structuring agents and soft templates
Monomer + inorganic precursor
Polymer + inorganic material
Precipitation/crystallization + polymerization

Preparation of Small Droplets and Particles

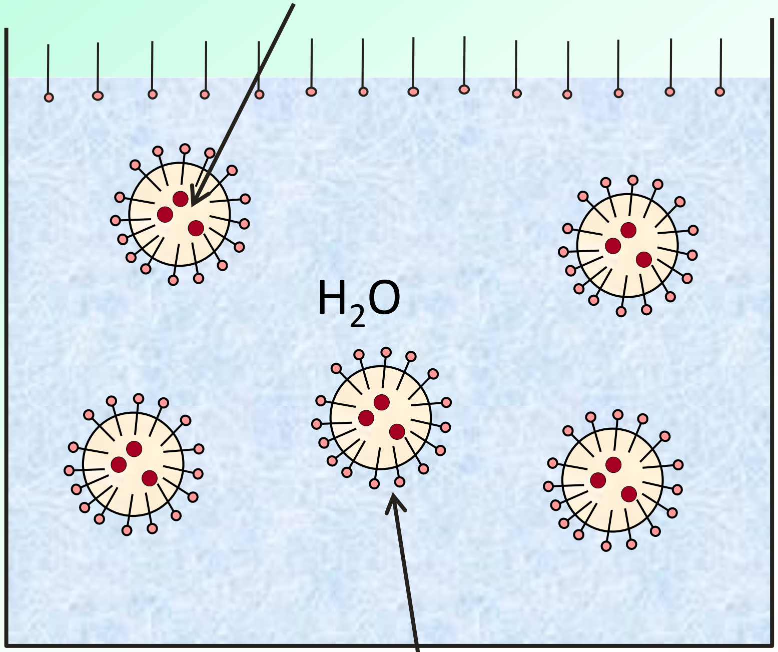
Miniemulsion process



Stable, small and narrowly distributed nanodroplets as small reaction spaces (30–500 nm)

Direct and Inverse Miniemulsions

non-polar phase
and *hydro*phobe

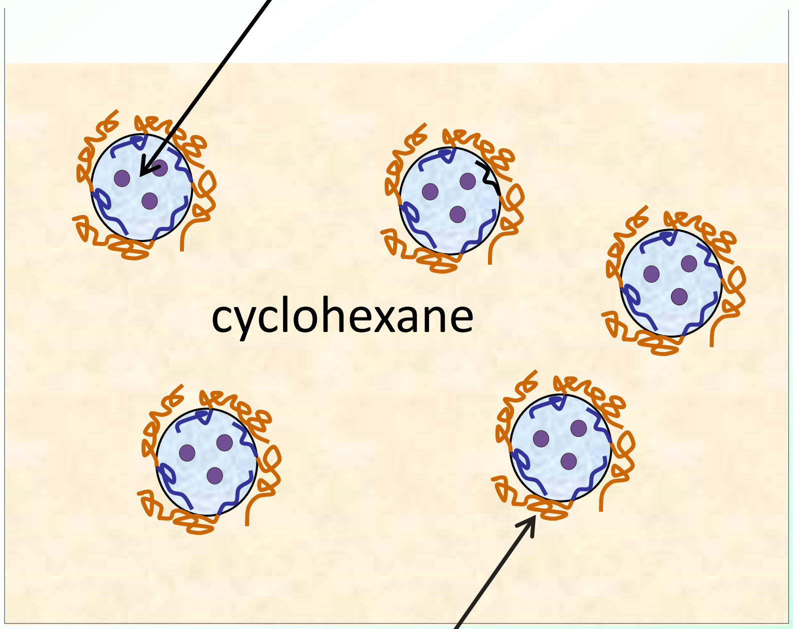


surfactant

e.g. sodium dodecylsulfate (**SDS**)
cetyltrimethylammonium chloride
(**CTMA-Cl**)

Milk, body lotion

polar phase
and *lipo*phobe (e.g. salt)



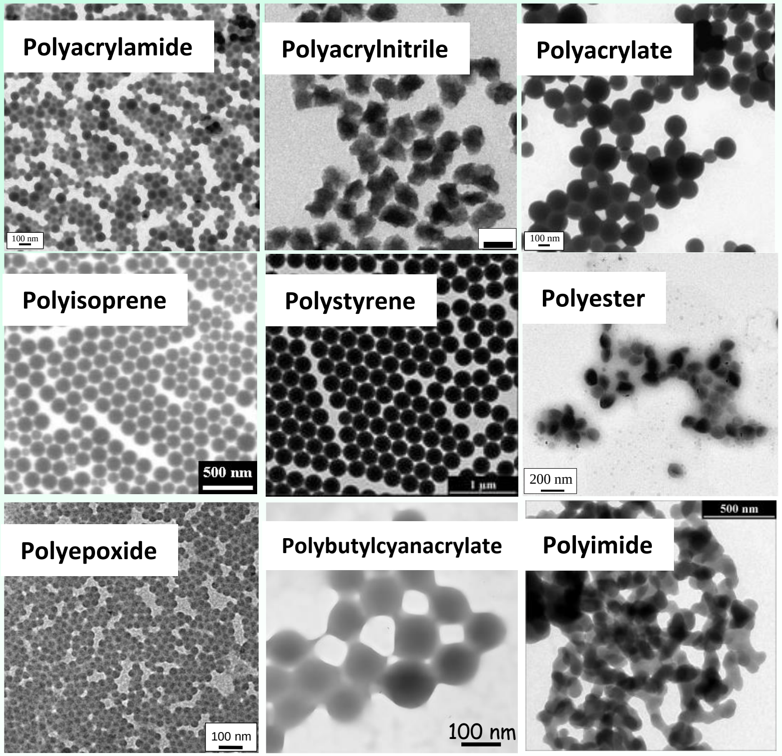
surfactant

block copolymer
e.g. poly[(ethylene-*co*-butylene)-*b*-(ethylene oxide)]

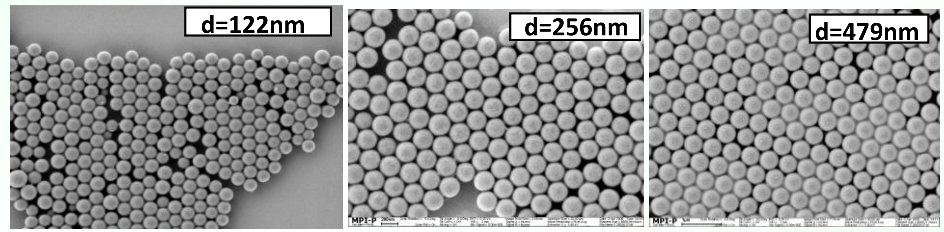
Butter, hand creme

Variation of Parameters

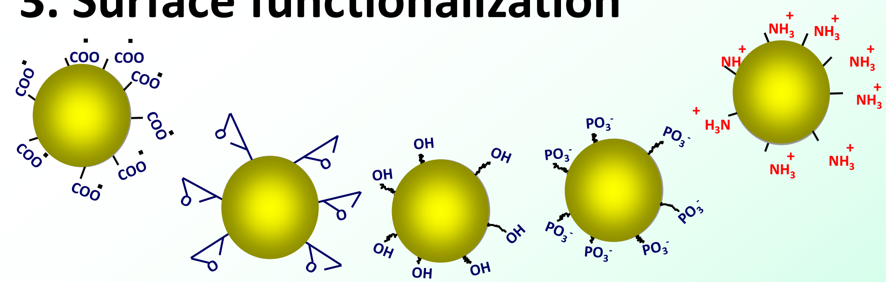
1. Polymer Material



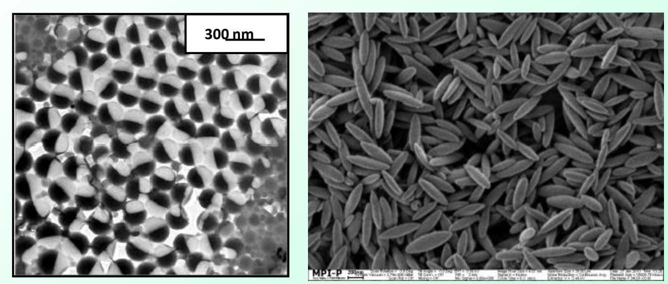
2. Size



3. Surface functionalization



4. Form

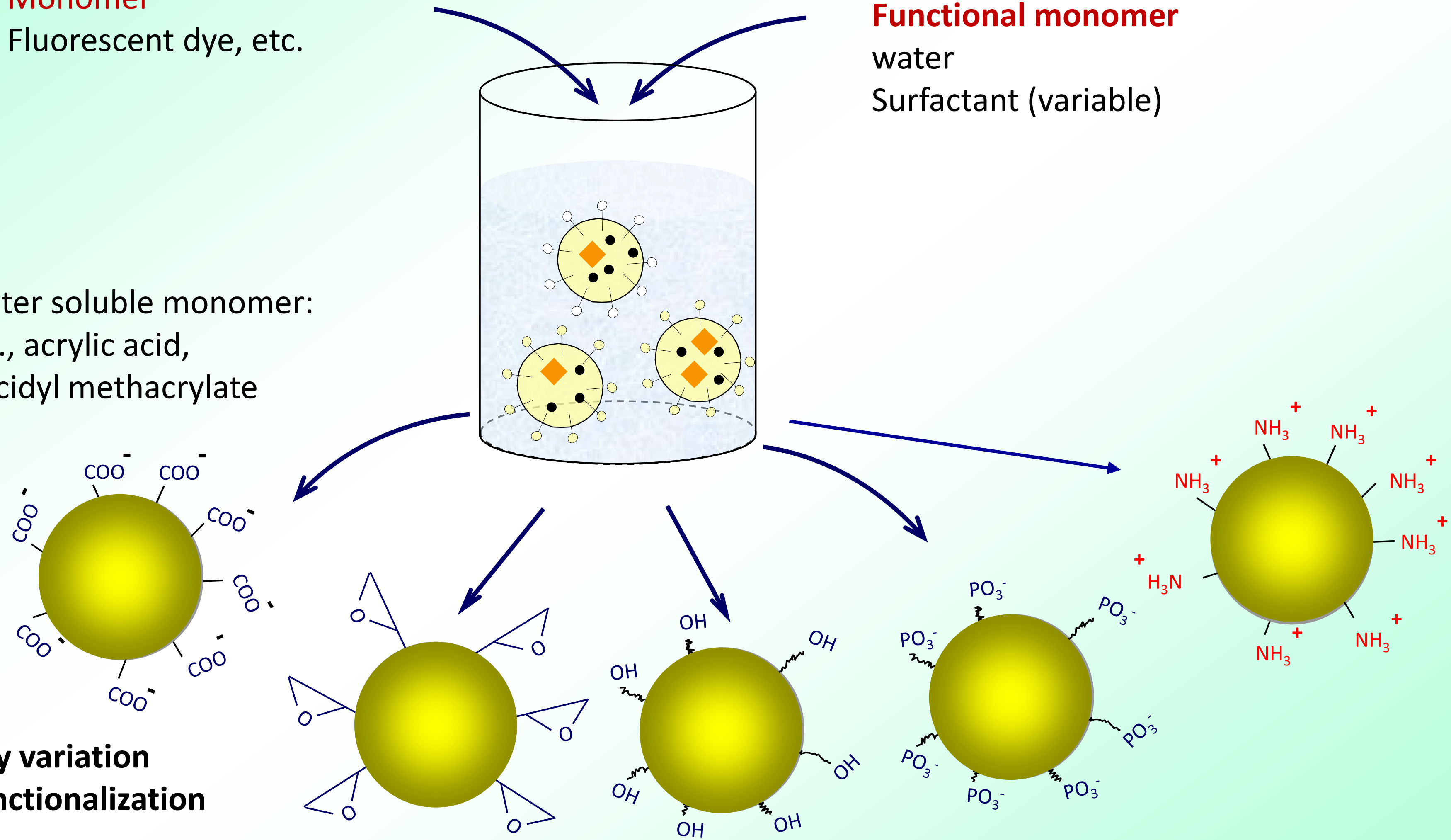


Synthesis of Surface-Functionalized Nanoparticles

Oil phase
Monomer
Fluorescent dye, etc.

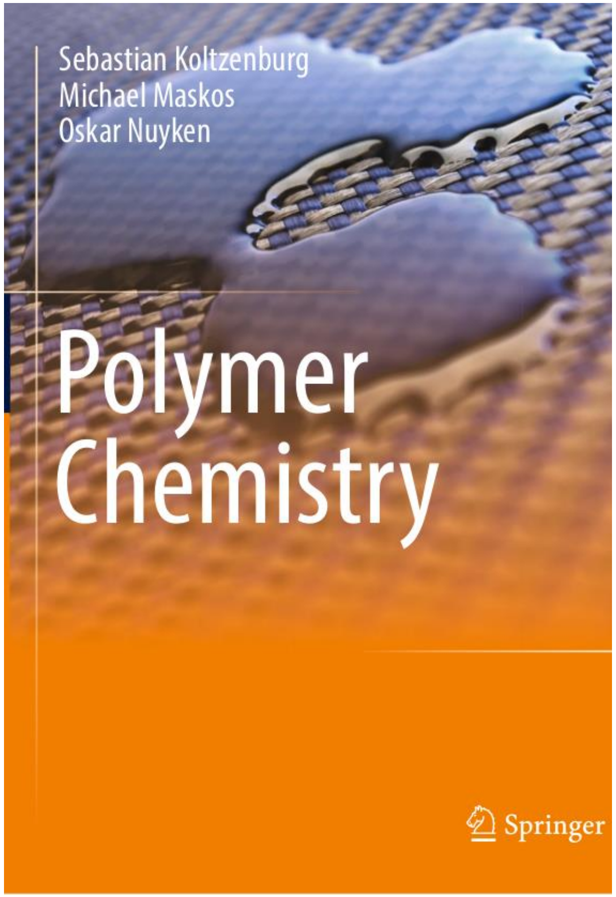
Aqueous phase
Functional monomer
water
Surfactant (variable)

Water soluble monomer:
e.g., acrylic acid,
glycidyl methacrylate



- **Density variation**
- **Bio-functionalization**

Recommended Manuals



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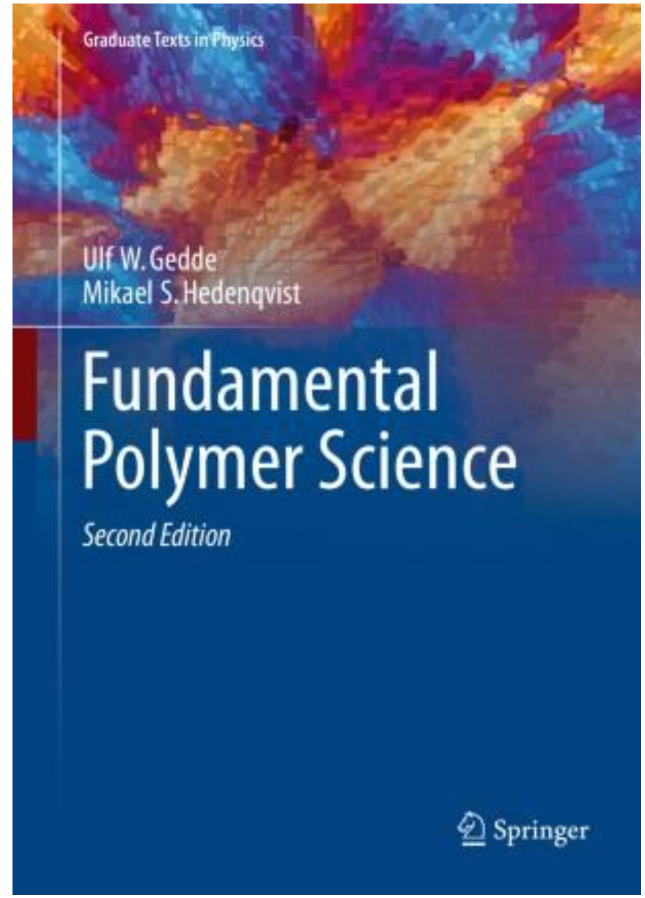

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