Synthetic Methods in Chemistry

WS 2020/ 2021

wednesdays 9:15-10:45

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Information, times & dates

wednesdays – 9:15 –10:45 Online Seminar	
when	**what**
11.11.2020	1. Introduction to Polymer Science
25.11.2020	2. Polymers made by radical polymerisation
2.12.2020	2. Polymers made by radical polymerisation
9.12.2020	3. Polycondensates and high performance polymers
16.12.2020	4. Polymers made by polyaddition
6.1.2021	5. Elastomers
13.1.2021	6. Polymers made by transition metal-catalyzed polymerization (polyolefines)

Lecture slides can be found here

https://www.tu-chemnitz.de/chemie/polymer/lehresommer/lehre.php#Education

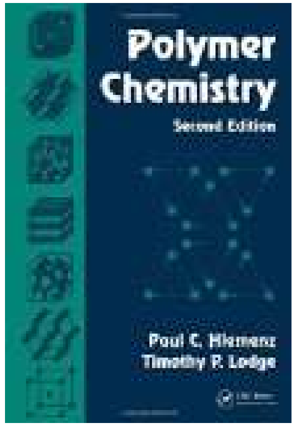
Online seminar takes place here

https://webroom.hrz.tu-chemnitz.de/gl/mic-otk-0g1-2ia

TECHNISCHE UNIVERSITÄT CHEMNITZ

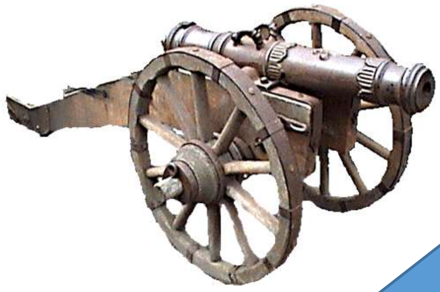
Literature

- J. M. G. Cowie: Chemie und Physik der synthetischen Polymeren, Vieweg-Verlag, Braunschweig Wiesbaden 1997
- H.-G. Elias, Makromoleküle, Wiley-VCH, Weinheim, 4 Bände
- P. C. Painter, M.M. Coleman, „Essentials of Polymer Science and Engineering“, DEStech Publication, Inc., Lancaster,PA, 2009
- S. Koltzenburg, M. Maskos, O. Nuyken, Polymere, Springer 2013
- Handbook of polymer synthesis, characterization and processing
- A. RUDIN, P. CHOI, The Elements of Polymer Science and Engineering, Elsevier 2013
- Hiemenz and Lodge, Polymer Chemistry, second Edition, CRC Press, Taylor& Francis, 2007



1. Introduction

Age naming according to materials



iron age

1000 B. C.

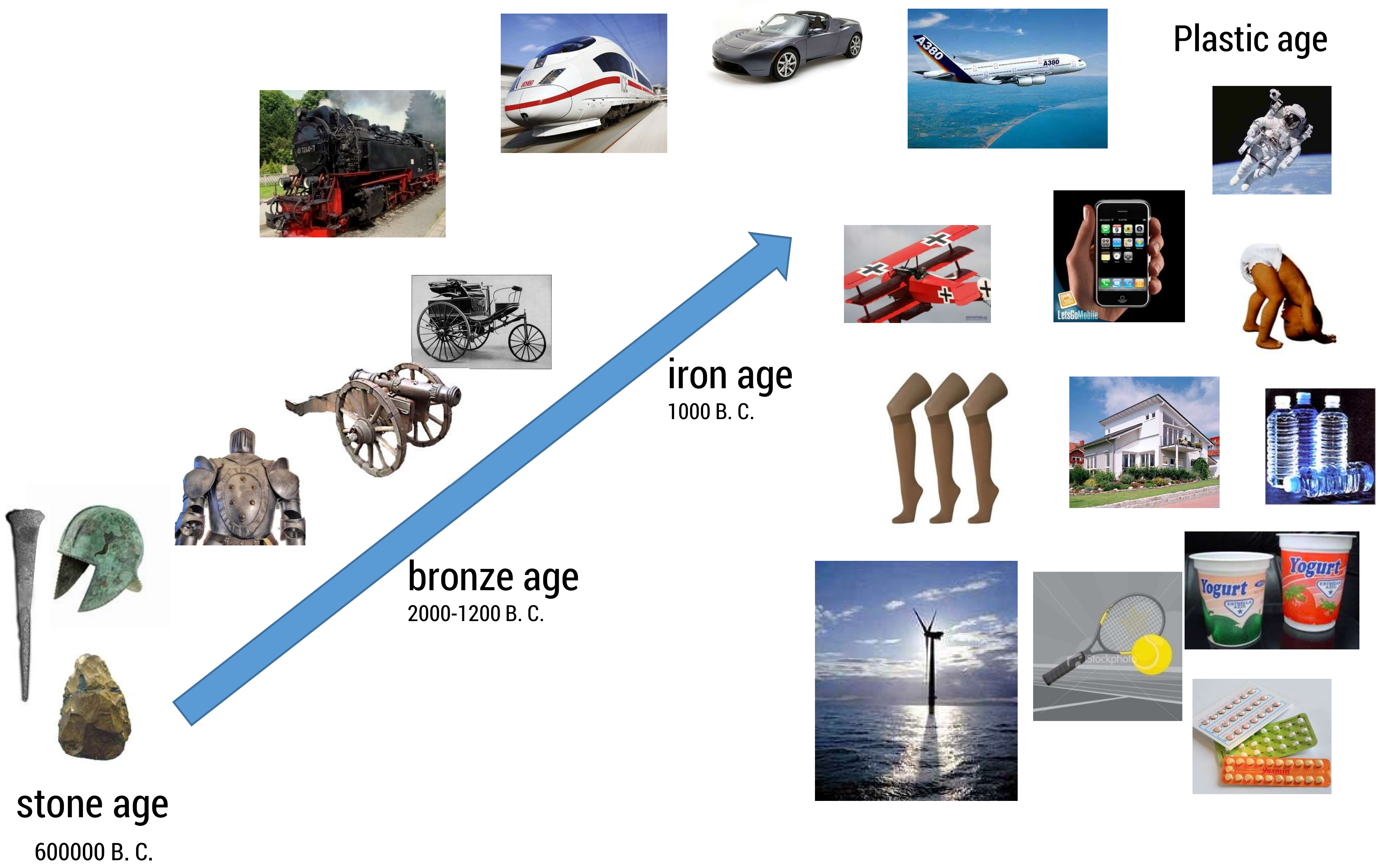
bronze age

2000-1200 B. C.

stone age

600000 B. C.

We live in the Plastic age



We live in the Plastic age

Energy

Mobility

Health

Living

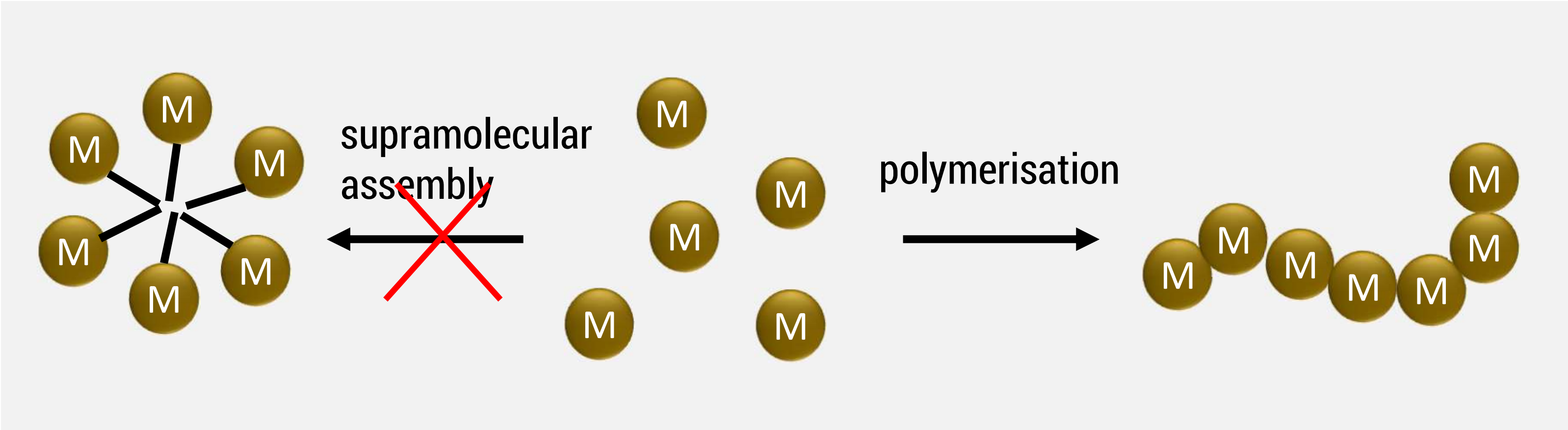
Communication

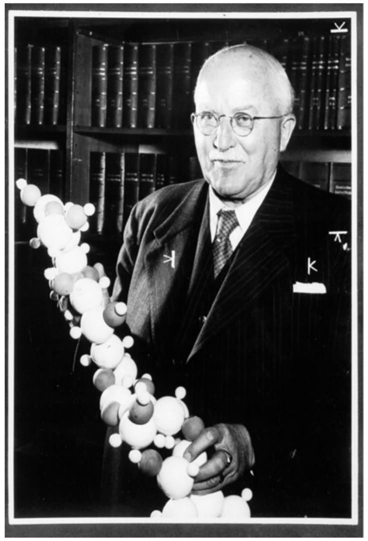
Protection

1900
Substitutes for silk, natural rubber and ivory

2010
High Tech materials

Staudinger´s concept of macromolecules (1920)

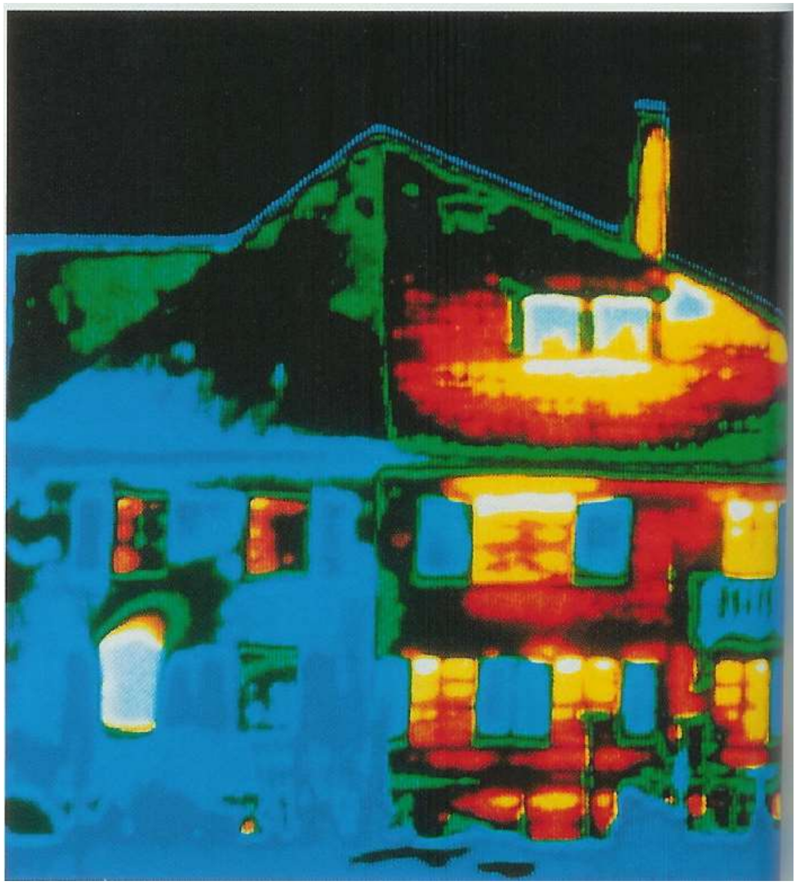




Hermann Staudinger
(1881-1965)

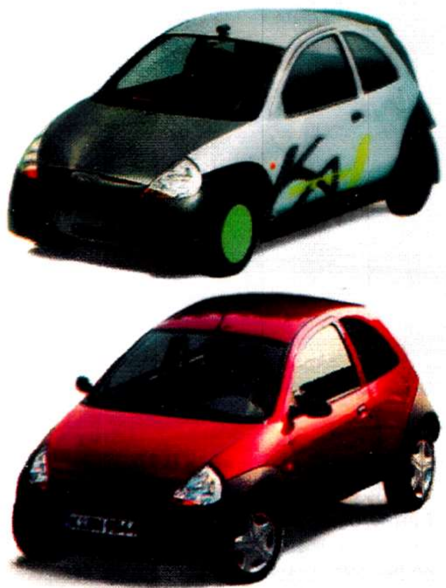
- 1920 postulation of large, chain-like molecules with > 100.000 atoms
- 1922 Term „Macromolecules“
- 1940 Institute for Macromolecular Chemistry Freiburg
- 1953 Nobel prize for chemistry

Polymers help saving fuel → eco efficiency



Insulation

Light-weight structures

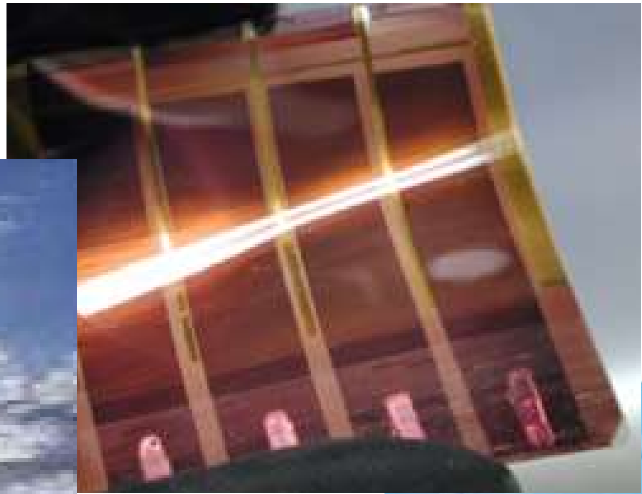


LEICHTER FAHREN
Mit aerodynamischer Verkleidung und leichten Materialien wird der 871 Kilo schwere Ford Ka (unten) zum 610 Kilo leichten Prototyp Step One. Verbrauch: 3,3 l/100 km

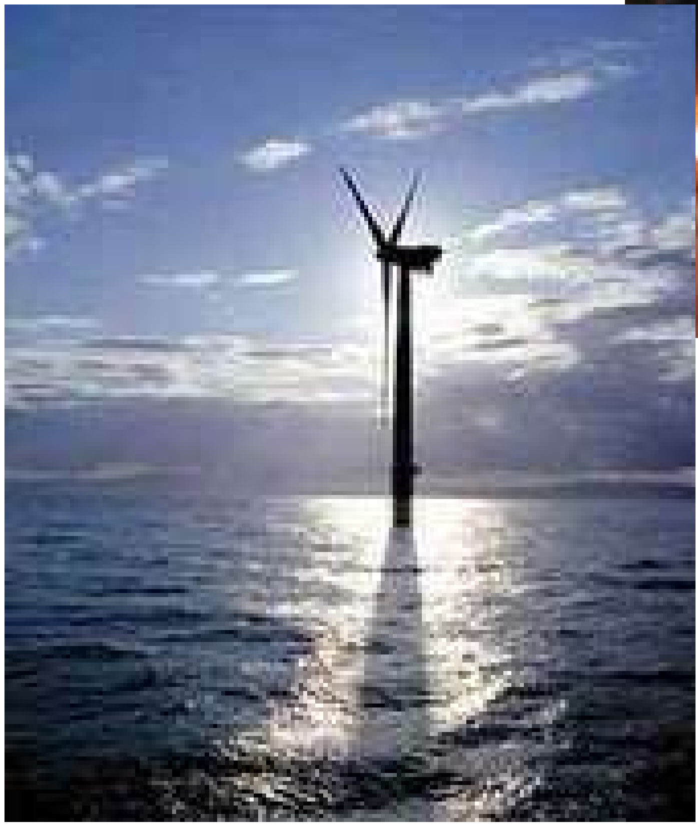
100 kg Gewichtsreduktion
= 0.6 L/100 km Treibstoffeinsparung

Polymers and energy

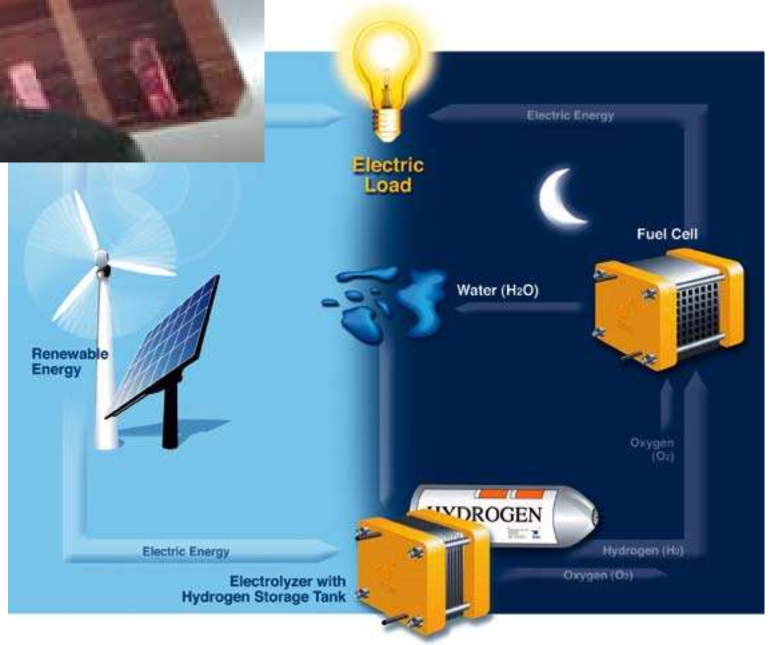
Polymer solar cells



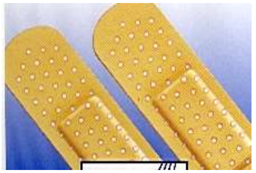
Off-shore Windpark

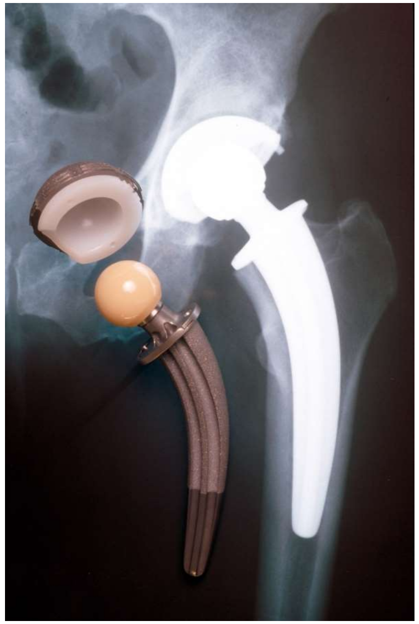


Fuel cell
membranes



Polymer materials increase quality of life





Polymer materials offer many advantages…

- High value for society (high-tec for all!)
- Attractive price/performance ratio
- No corrosion and light weight
- Versatility: tailor-made properties, applications and flexible feed stocks
- Can be brought into shape easily (extrusion, fibers etc)
- High eco efficiency and sustainability
- High energy efficiency (energy content of crude oil, light weight structures insulation)

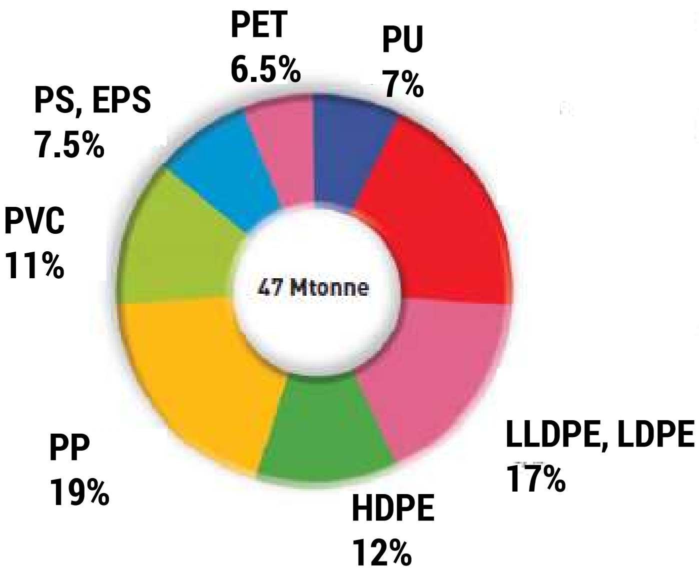
Global production of plastics

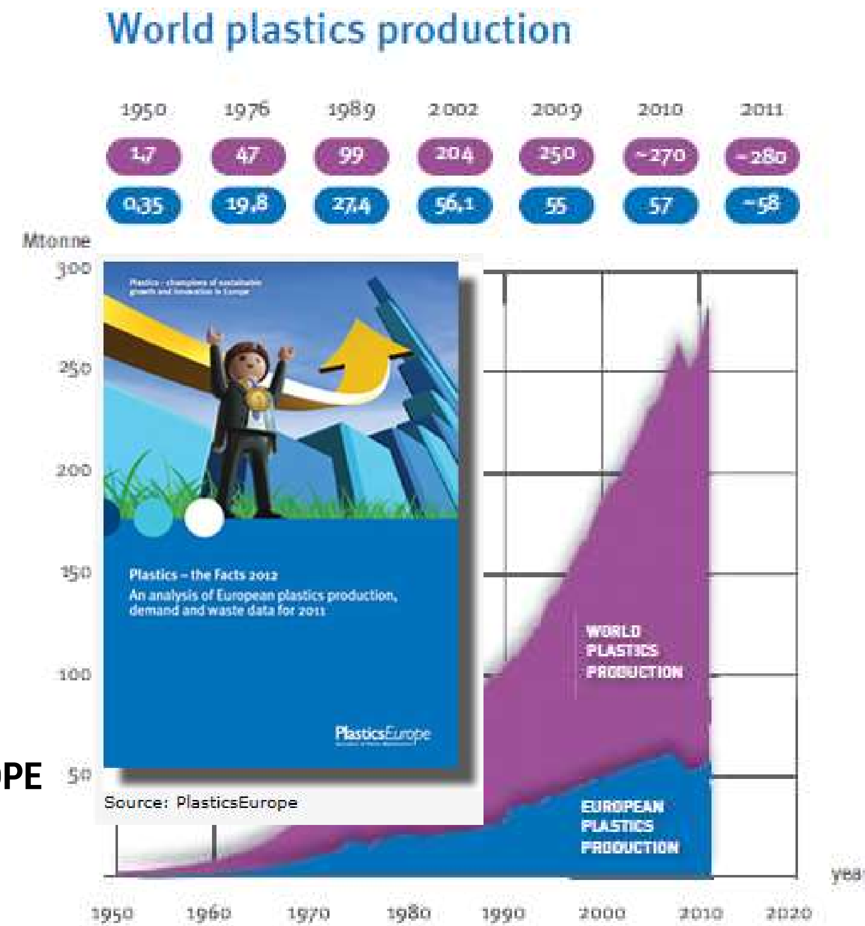
PLASTICS:

39 % Packaging
21 % Building & Construction
8 % Automotive
5 % Electrical & Electronics
5 % Appliances
4 % Furniture
2 % Farming

Global production 2013:
300 Mio Tons!

European Plastics Demand





http://www.plasticseurope.org/Document/plastics-the-facts-2012.aspx

Use of plastics in europe

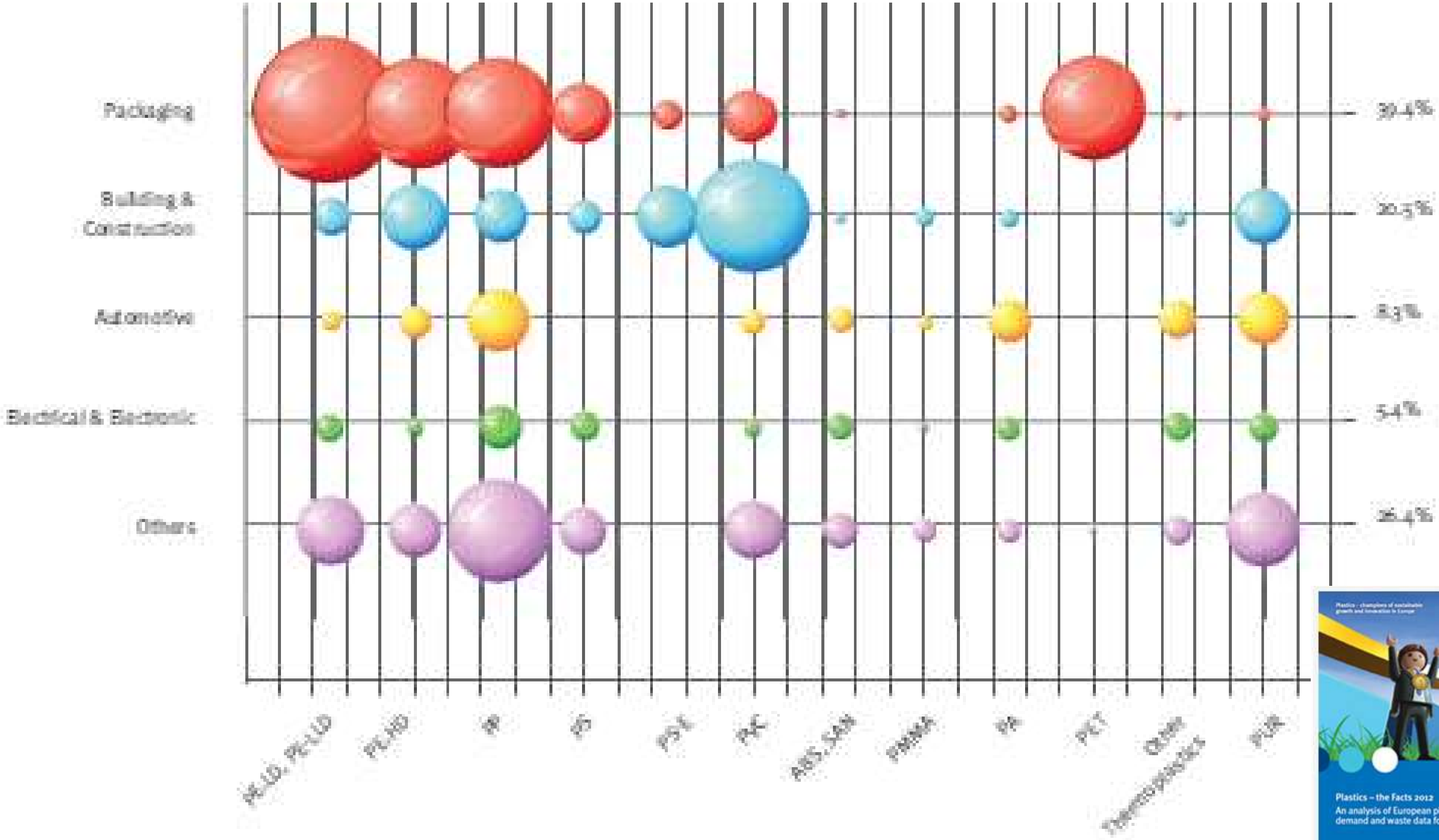


Figure 6: European Plastics Demand* by Segment and Resin Type 2011
Source: PlasticsEurope Market Research Group (PEMRG)
* EU-27+N/CH incl. Other Plastics (~5.7 Mtonne)

Source: PlasticsEurope

Use of plastics in europe

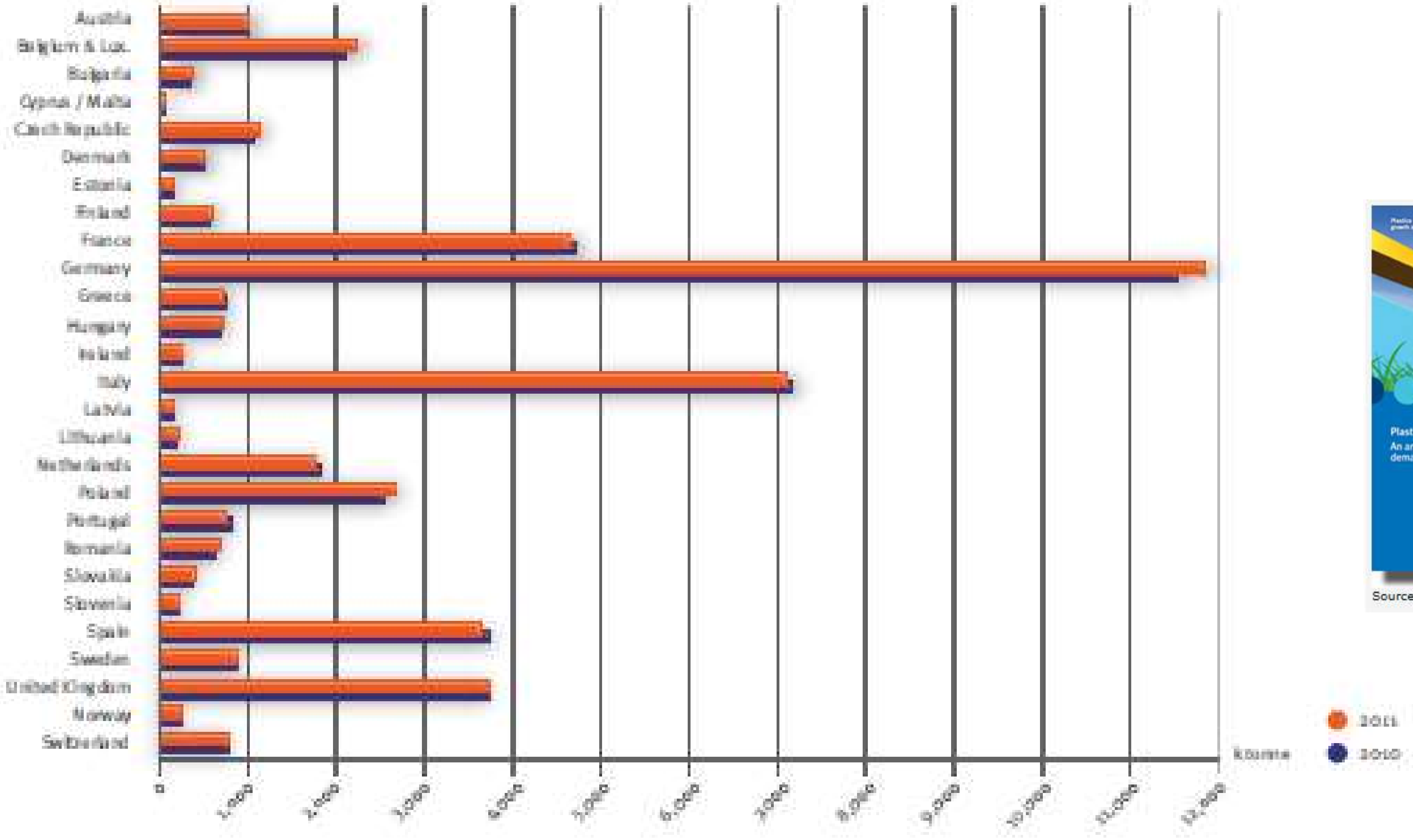


Figure 4: European Plastics Demand by Country (k tonne/year)

Source: PlasticsEurope Market Research Group (PEMRG)

6

Source: PlasticsEurope

But: plastics are everywhere…

Great pacific garbage patch

http://yourmedia.at/blog/2006/05/masala-thema-mull-karussell-im-pazifik/

Beach in Mumbai, India

http://www.tt.com/panorama/natur/9372598-91/5.250.000.000.000-plastikteilchen-schwimmen-in-den-meeren.csp

http://www.spektrum.de/news/muellstrudel-der-menschheit/999508

… in the ocean
… in inland waters

Problems:

- Most polymers are hydrophobic and act as sponges for pestizides
- Grinding leads to simplified intake
- Microplastics

Nobel prizes for polymer-related discoveries

2000: A. J. Heeger, A. G. MacDiarmid, H. Shirakawa

- Electrically conducting polymers (discovery 1976)

1991: P.-G. de Gennes (physics)

- Ordering processes in liquid crystals and polymer solutions

1974: P. J. Flory

- Fundamental achievements in physical chemistry of macromolecules

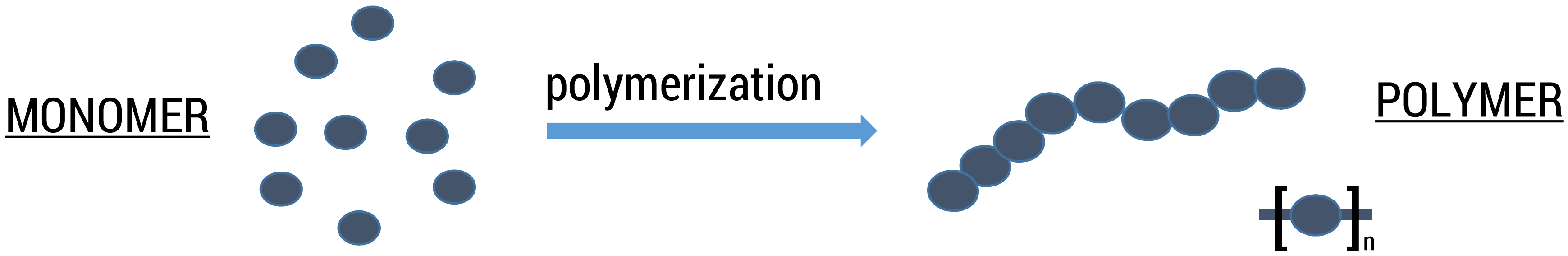
1963: K. Ziegler, G. Natta

- Catalytic polyolefine synthesis

1953: H. Staudinger

- concept of macromolecules (1920)

IUPAC Definitions

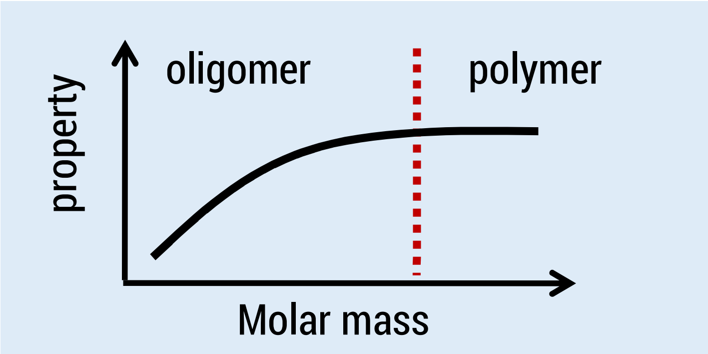


Repeat unit n: degree of polymerization (DP)

<u>Monomer:</u>
A molecule which can undergo polymerization
<u>Polymer:</u>
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
<u>Oligomer:</u>
A molecule of intermediate relative molecular mass, the structure of which essentially comprises a small plurality of units derived, actually or conceptually, from molecules of lower relative molecular mass.

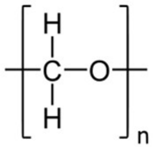
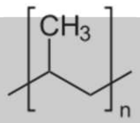
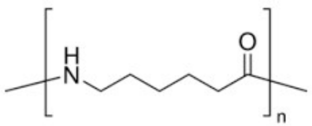
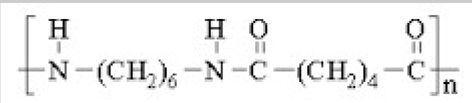
polymer ? macromolecule

When is a polymer a polymer ?



$$n\,M \longrightarrow -\!\!\left[\!-M-\!\right]_n\!\!-$$

Poly(repeat unit)

Polymer	Nomenclature	Repeat unit
$[-CH_2-CH_2-]_n$	Polyethylene (PE)	$[CH_2]_n \equiv [CH_2CH_2]_n$
	Polyoxymethylene (POM) Polyacetal, Polyformaldehyde	$[CHO]_n$
	Polyproylene (PP)	$[CHCH_3\text{-}CH_2]_n$
	Polyamide-6 (PA-6, Perlon, e-Caprolactame)	$[NH(CH_2)_5CO]_n$
	Polyamide-6,6 (PA-66, Nylon, Adipic acid and hexamethylenediamine)	$[NH(CH_2)_6NHCO(CH_2)_4CO]_n$

Some common abbreviations

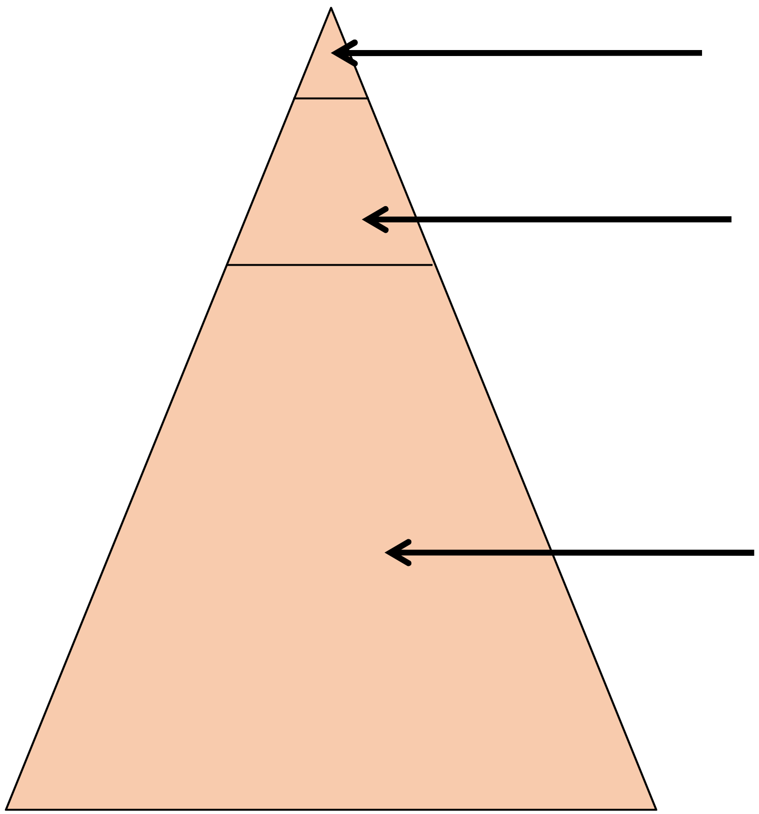
A1 Kurzzeichen für Kunststoffe

Tabelle A1

Kurzzeichen	Bezeichnung
ABS	Acrylnitril-Butadien-Styrol
AES	Acrylnitril-Ethylen-Propylen-Dien-Styrol
ASA	Acrylnitril-Styrol-Acrylat
CA	Celluloseacetat
CAB	Celluloseacetobutyrat
CAP	Celluloseacetopropionat
COC	Cycloolefin-Copolymer
EP	Epoxidharz
EVAC	Ethylen-Vinylacetat-Copolymer
EVOH	Ethylen-Vinylalkohol-Copolymer
LCP	Flüssigkristall-Polymer (Liquid-Crystal-Polymer)
MF	Melamin-Formaldehyd-Harz
PA	Polyamid
PAEK	Polyaryletherketon
PAI	Polyamidimid
PBT	Polybutylenterephthalat
PC	Polycarbonat
PE	Polyethylen
PEEK	Polyetheretherketon
PEEKEK	Polyetheretherketonetherketon
PEI	Polyetherimid
PEK	Polyetherketon
PES	Polyethersulfon
PET	Polyethylenterephthalat
PF	Phenol-Formaldehyd-Harz
PHB	Polyhydroxybutyrat
PI	Polyimid
PLA	Polylactid
PMMA	Polymethylmethacrylat
POM	Polyoxymethylen
PP	Polypropylen
PPE	Polyphenylenether
PPS	Polyphenylensulfid
PPSU	Polyphenylensulfon
PS	Polystyrol
PSU	Polyarylsulfon
PTFE	Polytetrafluorethylen
PUR	Polyurethan
PVC	Polyvinylchlorid
PVCVAC	Vinylchlorid-Vinylacetat
PVDC	Polyvinylidenchlorid
PVDF	Polyvinylidenfluorid
SAN	Styrol-Acrylnitril
SBS	Styrol-Butadien-Styrol-Block-Copolymer
TPE	thermoplastisches Elastomer
UF	Harnstoff-Formaldehyd-Harz
UP	ungesättigtes Polyesterharz

G. Abts, "Kunststoff-Wissen für Einsteiger", Hanser-Verlag 2010

Classifications of polymers: price and production



< 1% <u>High performance polymers</u>
PEEK, F-Polymere, LCP, PPS, PEI, PES

ca. 16% <u>Engineering plastics</u>
PC, ABS, SAN, HIPS, PP, PMMA, PA, PBT

84 % <u>Commodity plastics</u>
Polyethylene PE (HDPE, LDPE, LLDPE)
Polypropylene PP
Polystyrene PS
Polyvinylchloride PVC
Polyethyleneterephthalate PET

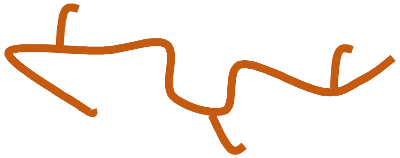
Classifications of polymers: processing and thermal properties

Thermoplasts

-linear chains:

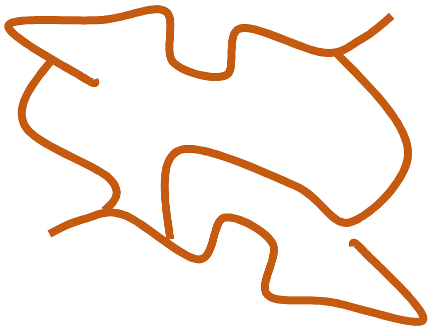
-branched: long chain branches

Short chain branches



Elastomers

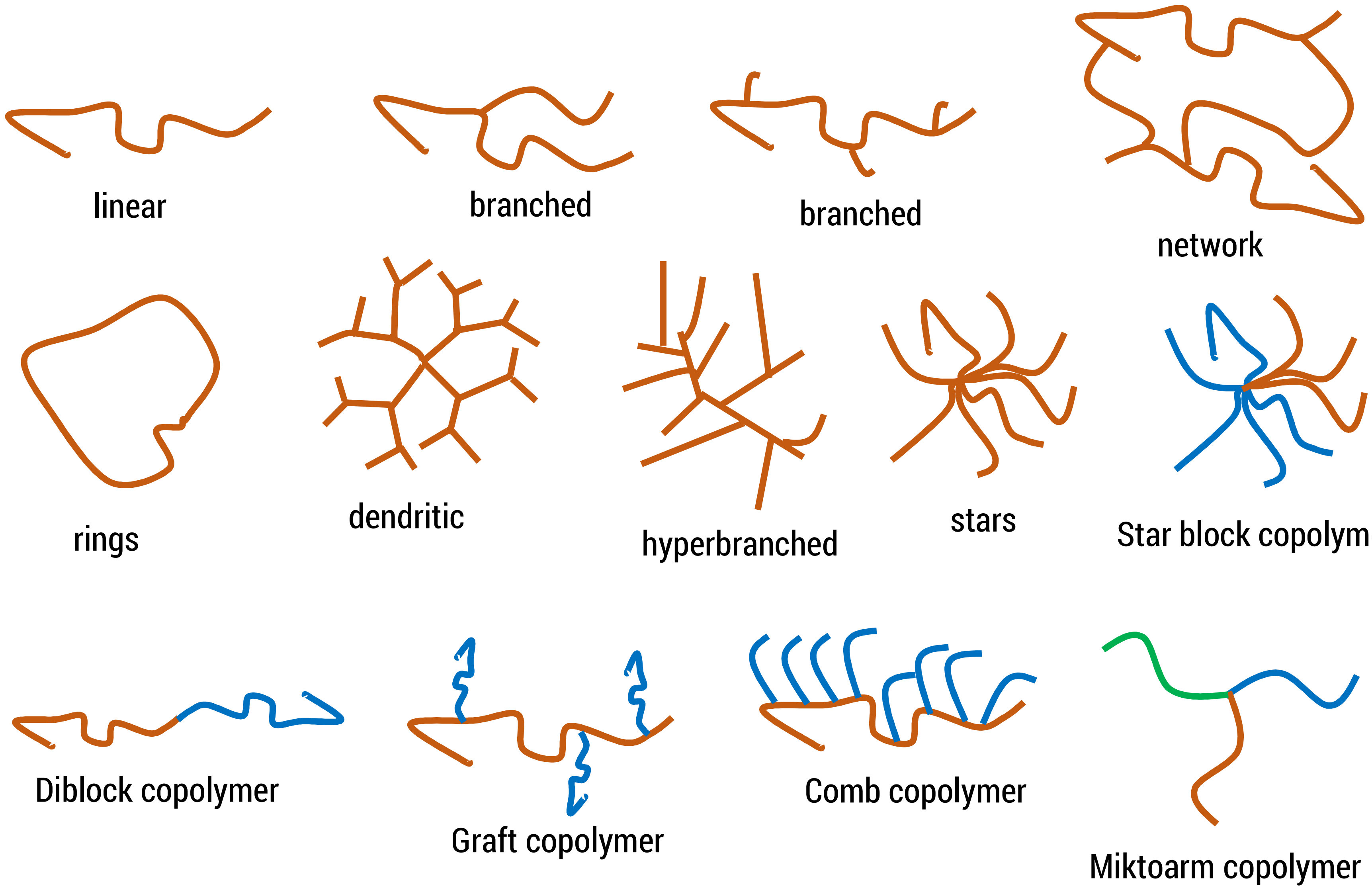
-weakly linked network
-physical or covalent cross links
-Glass transition temperature T_g < RT



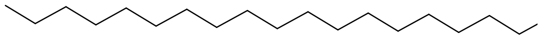
Thermosets

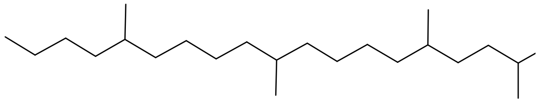
-strongly linked network
-often covalent cross links
- Glass transition temperature T_g typically > RT

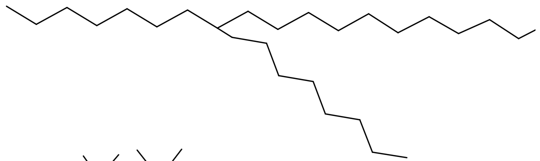
Classifications of polymers: topology and architecture

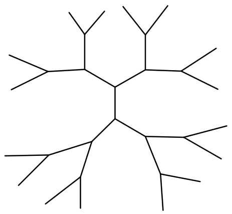


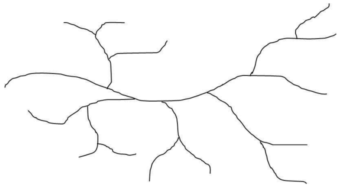
<u>Constitution:</u> how are atoms and monomers linked together ?
→ chain length, branching, crosslinking, end groups, regioselectivity, monomer sequence, etc

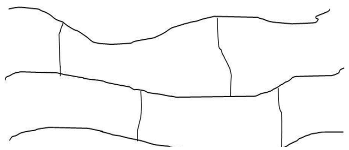

Linear

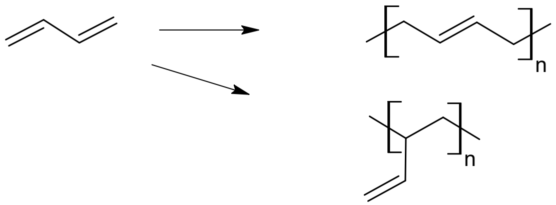

Short chain Branching

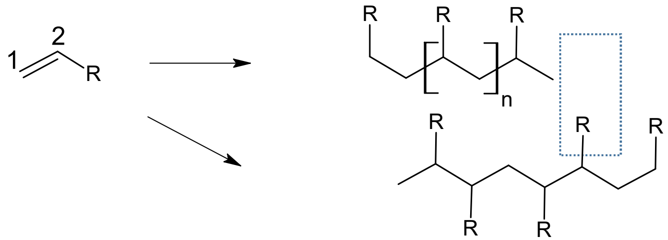

Long chain branching


Dendritic


hyperbranched


networks


1,4
1,2

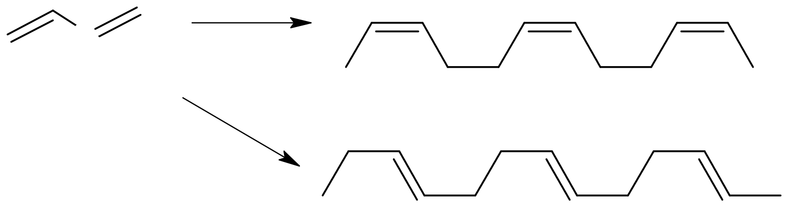


Head-to-tail
Head-to-head

A, B →	AABAAAABBABB	Random copolymer
Poly(A-alt-B)	ABABABABABAB	Alternating copolymer
Poly(A-block-B)	AAAAAABBBBBB	Block copolymer
Poly(A-g-B)	AAAAAAAAAAAA | BBBBBBBB	Graft copolymer

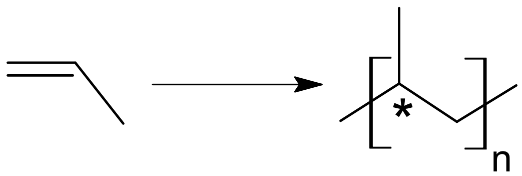
Constitution, Configuration and Conformation

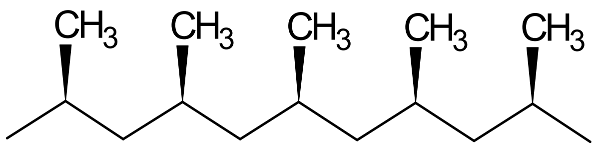
<u>Configuration</u> = stereochemistry, tacticity, stereoregularity



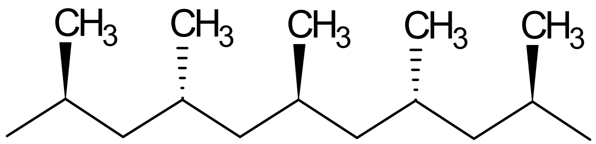
cis-1,4 Polybutadien

trans-1,4 Polybutadien





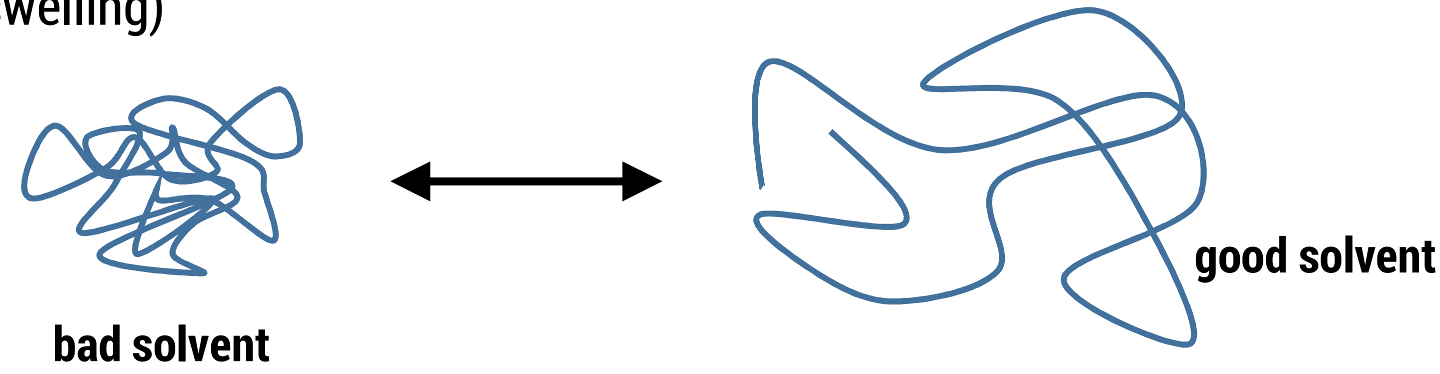
isotactic



syndiotactic

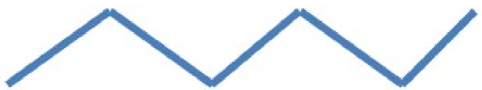
Configurational isomers have the same constitution!

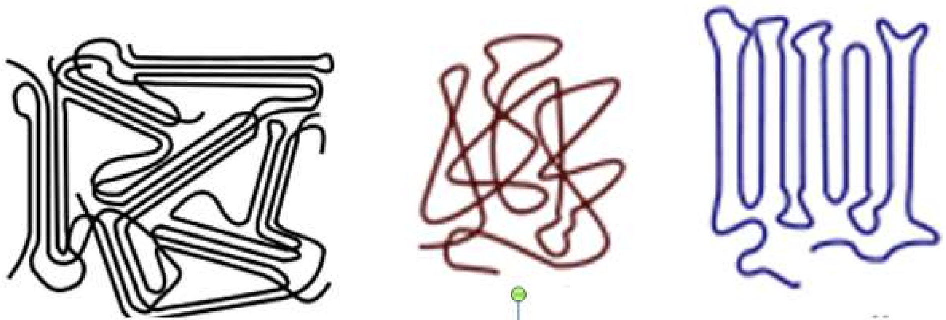
<u>Conformation</u> <u>in solution</u>: chain flexibility and stiffness, solvent effects (degree of swelling)



<u>Conformation</u> <u>in the solid state</u>: random coil (amorphous), ordered (crystalline structures)

Polyethylene = all trans
(Zig-zag –chain)

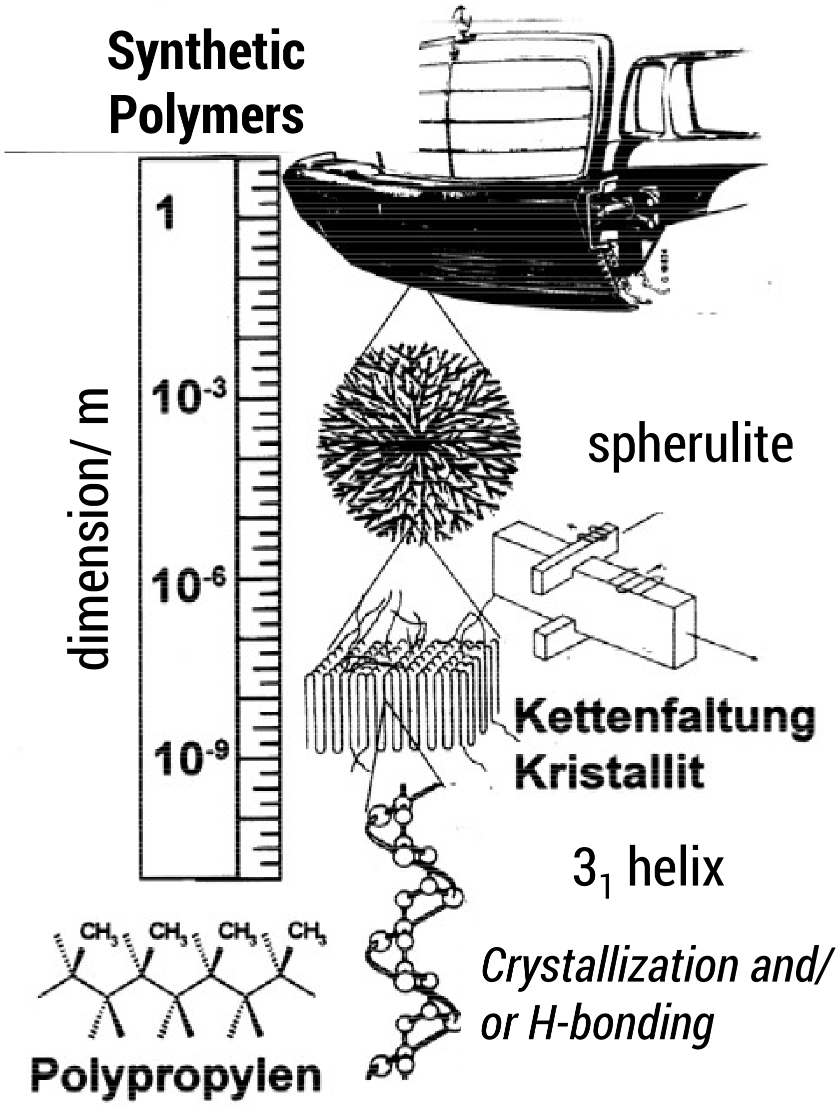




Fringed micelle   random coil   lamella

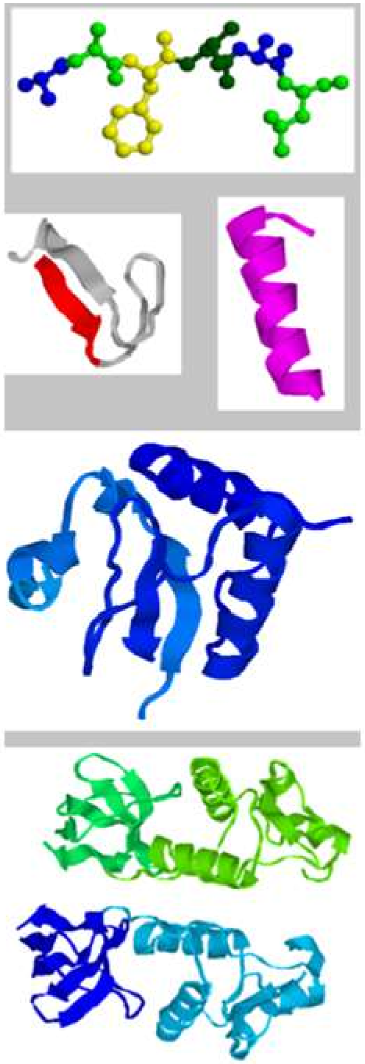
Conformation is important for structure formation

Synthetic Polymers



Crystallization and/ or H-bonding

Biopolymers: Proteins



Primary structure

secondary structure

tertiary structure

quaternary structure

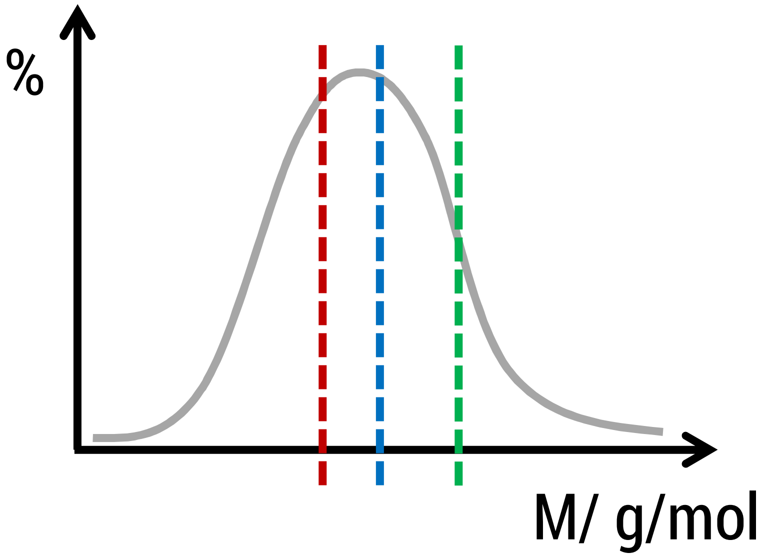
H-bonding stabilizes secondary and higher structures

Molecular weight and molecular weight determination

- **Synthetic polymers are dispers!** („polydispers“ outdated)

(except step-by-step syntheses → no polymerization!)

- **Only natures does monodispers systems** (proteins)
- **Synthetic polymers are characterized by the distribution of chain lengths**:



number average molecular weight:

$$\overline{M_n} = \frac{\sum_i n_i M_i}{\sum_i n_i}$$

weight average molecular weight:

$$\overline{M_w} = \frac{\sum_i n_i {M_i}^2}{\sum_i n_i M_i}$$

centrifuge average molecular weight:

$$\overline{M_z} = \frac{\sum_i n_i {M_i}^3}{\sum_i n_i {M_i}^2}$$

Molecular weight determination is central in polymer science!

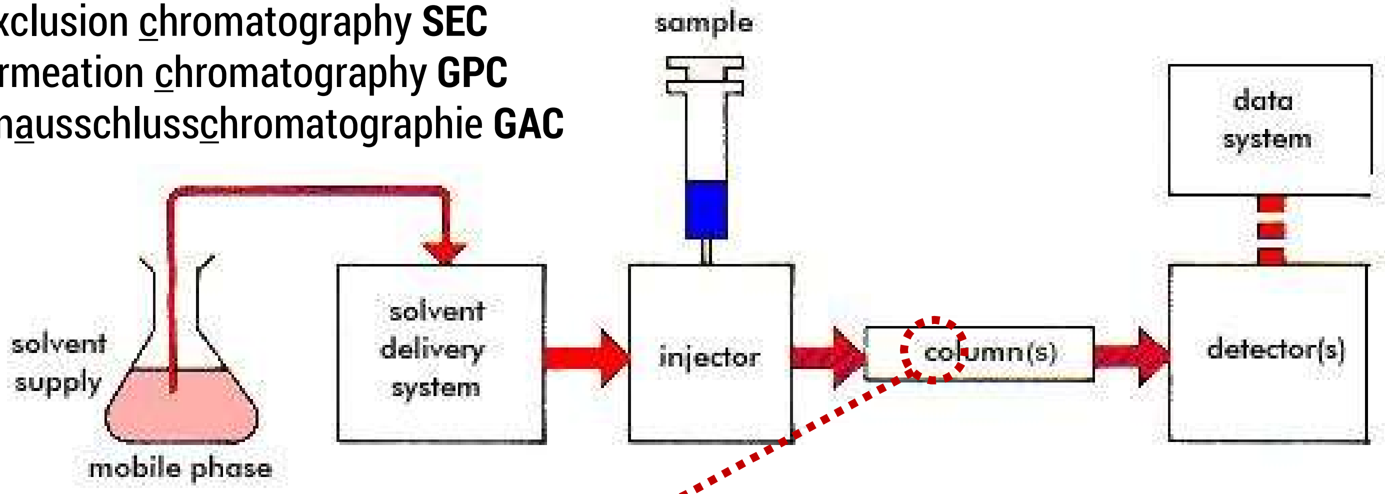
- Many methods exist all with advantages and disadvantages.
- Some of them give average molecular weights (M_n or M_w), some with of them the entire distribution
- Some of them are relative and some of them are absolute methods
- Most important is size exclusion chromatography (SEC) or gel permeation chromatography (GPC) → distribution, relative
- Absolute values for M_n: Membrane osmosis, MALDI-ToF, ^{1}H NMR

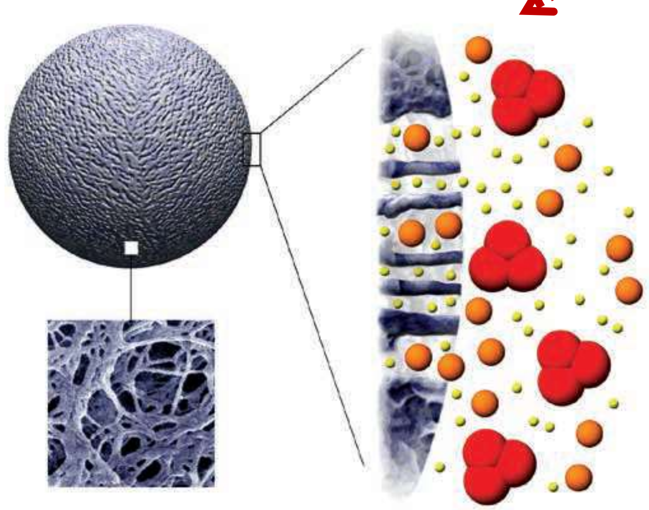
Overview of common methods for molecular weight determination

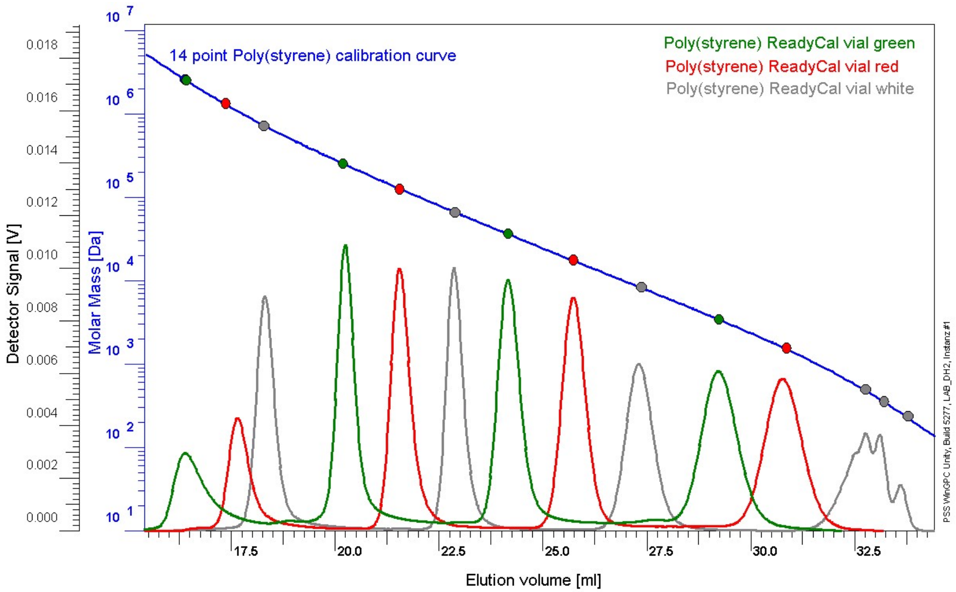
method	mean values	distribution	range g/mol
Absolute methods			
Membrane osmosis	M_n	No	$10^4 < M < 10^6$
Ultracentrifugation	M_n, M_w, M_z	No	$M > 10^2$
Static light scattering	M_w	No	$M > 5*10^3$
Small angle X-ray scattering	M_w	No	$M > 5*10^3$
Small angle neutron scattering	M_w	No	$M > 5*10^3$
MALDI-ToF	M_n, M_w, M_z	Yes	$M < 5*10^5$
End group analysis (NMR, titration)	M_n	No	$M < 10^5$
Relative methods			
Viscosimetry	M_η	No	$M > 10^2$
Size exclusion chromatography	M_n, M_w, M_z	Yes	$M < 5*10^6$
Field flow fractionation	M_n, M_w, M_z	yes	$M > 10^2$

Size exclusion chromatography SEC

<u>S</u>ize <u>e</u>xclusion <u>c</u>hromatography **SEC**
<u>G</u>el <u>p</u>ermeation <u>c</u>hromatography **GPC**
<u>G</u>rößen<u>a</u>usschluss<u>c</u>hromatographie **GAC**







Properties of polymers: molecular weight

molecular weight of e.g. PE

1‘000 10‘000 100‘000 1‘000‘000 g/mol

„Low“ molar mass

- low viscosity
- Extended chain crystal
- Fast crystallization
- High crystallinity
- High stiffness

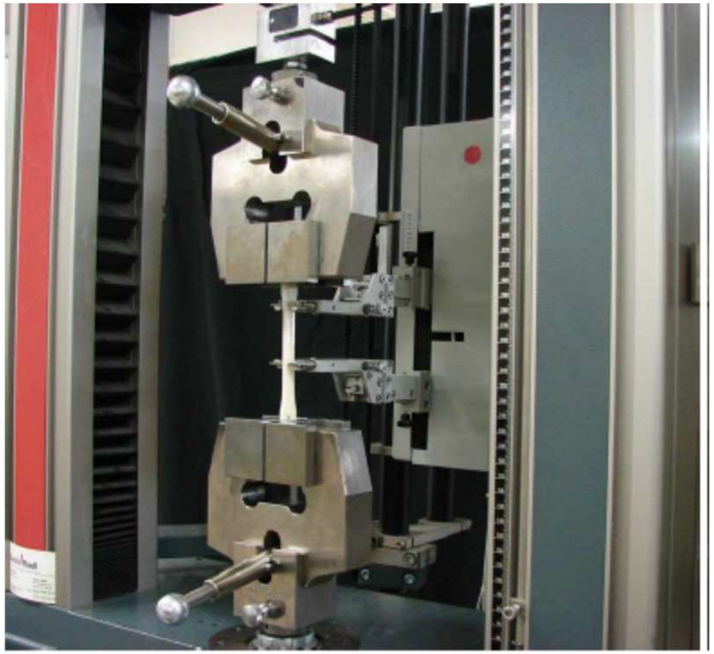
„high“ molar mass

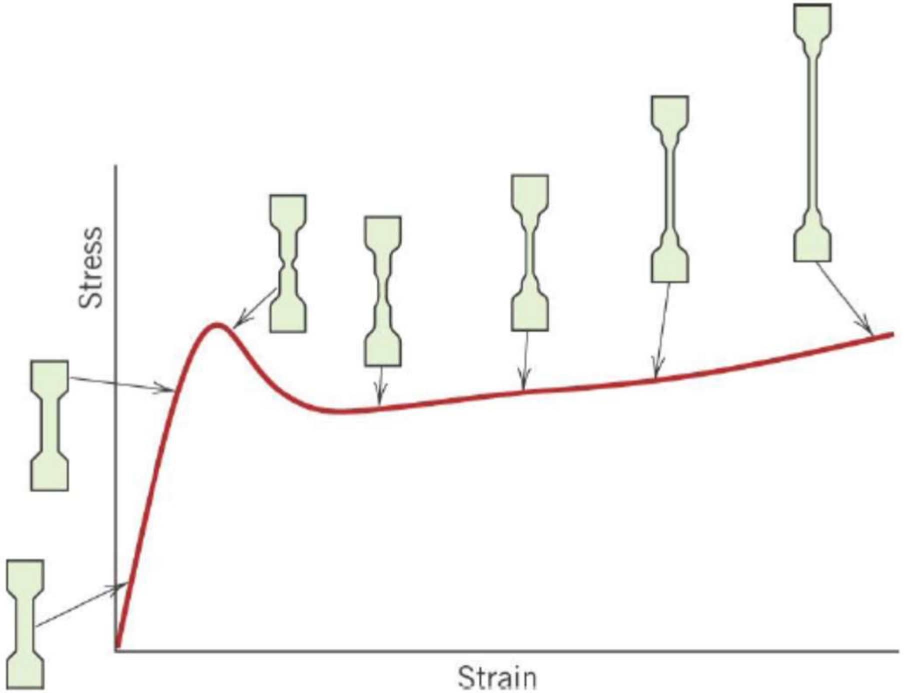
- high viscosity
- entanglements
- slow crystallization
- lower crystallinity
- High toughness

Molecular weight distributions with tailored content of low, medium and high molecular weight chains allows to fine-tune properties!

Properties of polymers: mechanical properties

Stress-strain experiment



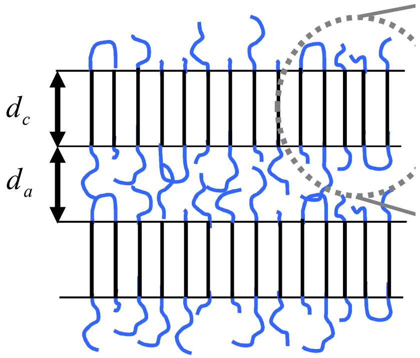


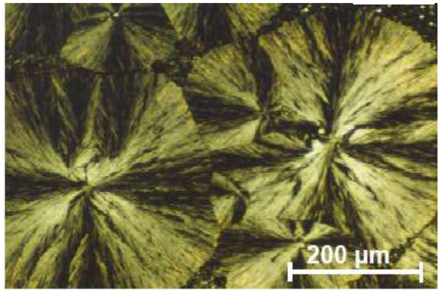
Other mechanical experiments: shear experiments, dynamic mechanical analysis, bending, notch impact test

Properties of polymers: morphology

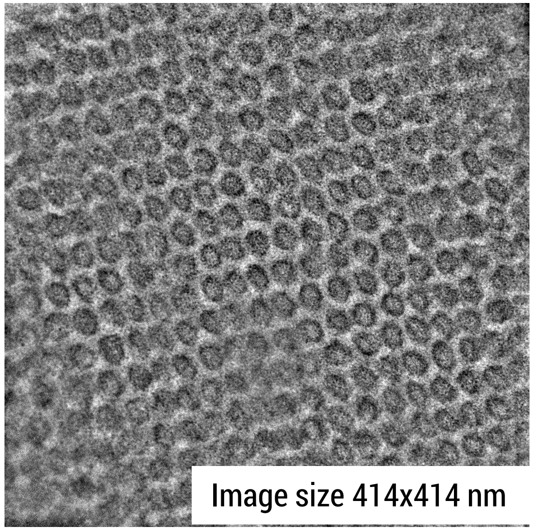
Most polymeric materials are structured on the nanometer and/ or micrometer scale

semicrystalline homopolymers
-lamellar crystals ~ 10 nm
-spherulites ~ 1-1000 µm



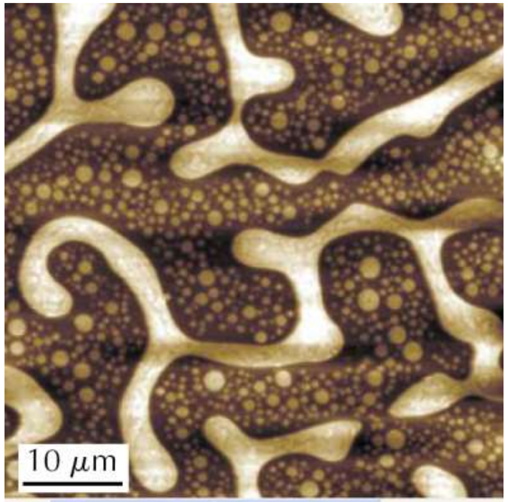


Block copolymers
-Microphase separation
~ 5-50 nm



Polymer blends
- 100 nm – 1 mm

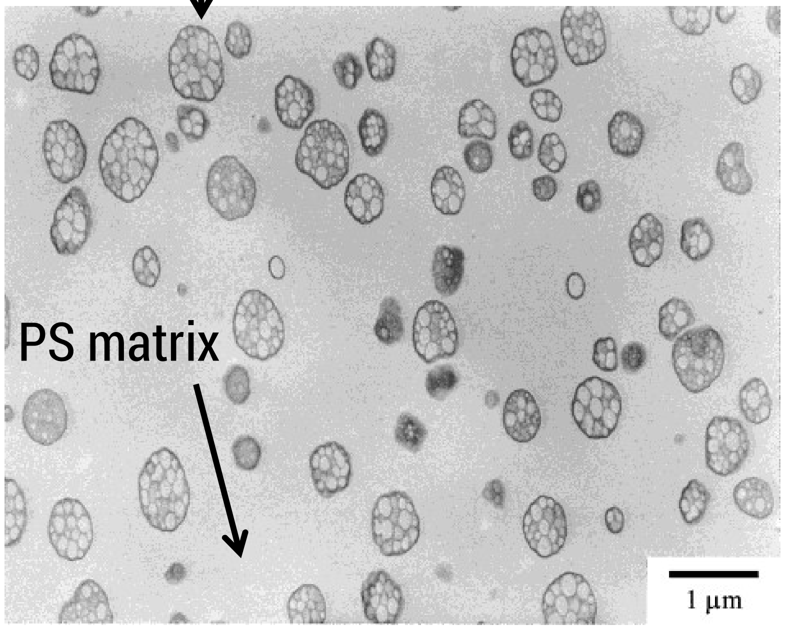
Malliaras and Friend,
Phys. Today, 58, 53 (2005)



HIPS: high impact polystyrene

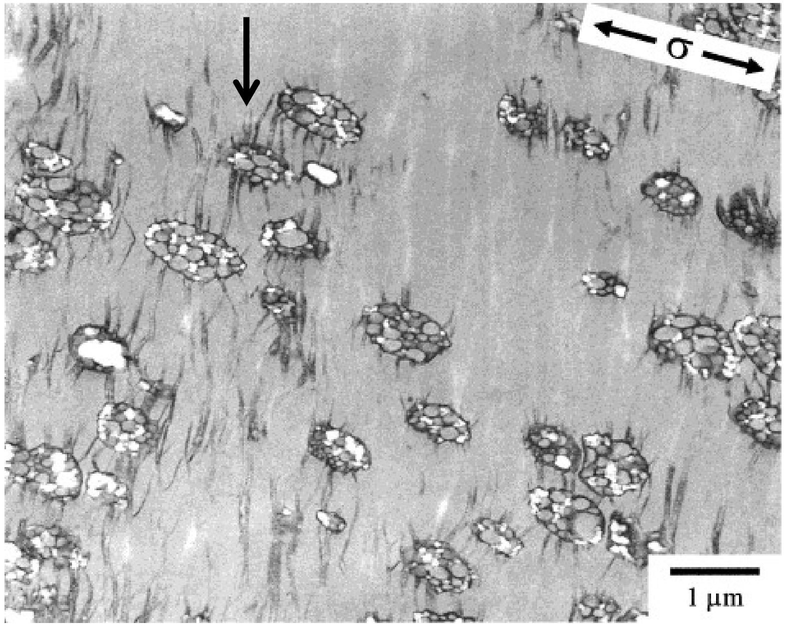
PB rubber particle

PS matrix



before deformation

crazes (Mikrorisse)



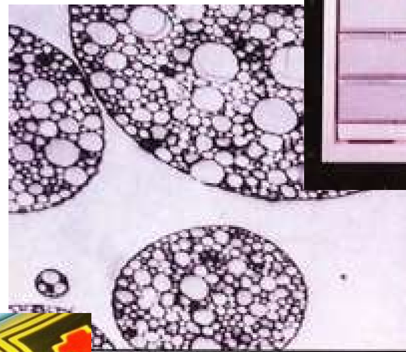
after deformation

Macromolecules **2000,** *33,* 5740-5742

Polymeric materials are multi-component systems

…and may contain:

+ Additives (> 1 %):
  Antioxidants, light protectors, bio-stabilizers, lubricants, biocides, processing agents,…)
+ Polymers (→Blends)
+ fillers
+ fiber reinforcement (→ composites)
+ colorants
+ foaming agents
+ plasticizer
+ cross-linker
+…….



HIPS

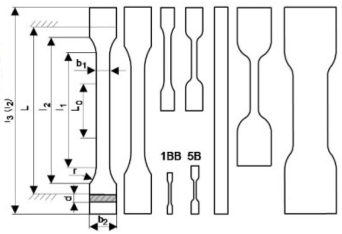
Many parameters determine material properties

Testing method (DIN, ISO)
Geometry
kind of loading
conditioning

Monomers, reaction engineering

Polymer Synthesis

Method of testing



Material Properties

Structure Formation

Processing

Material combination (blends, composites, formulation, additives)