Polymer Chemistry and Macromolecular Engineering

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Image credit: The Ocean Cleanup

Plastic Waste Enters the Food Chain

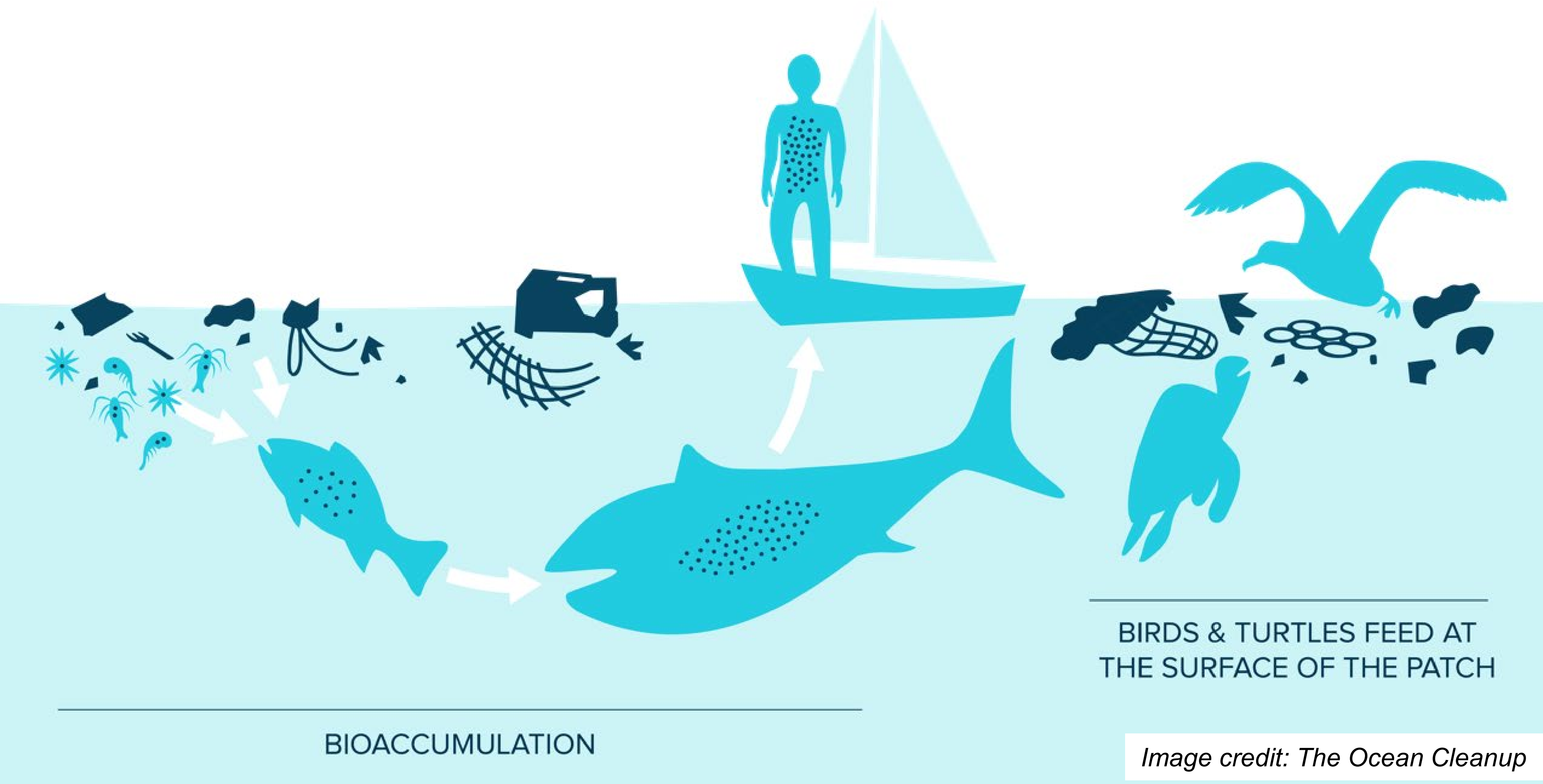


Image credit: The Ocean Cleanup

Polymers for Good

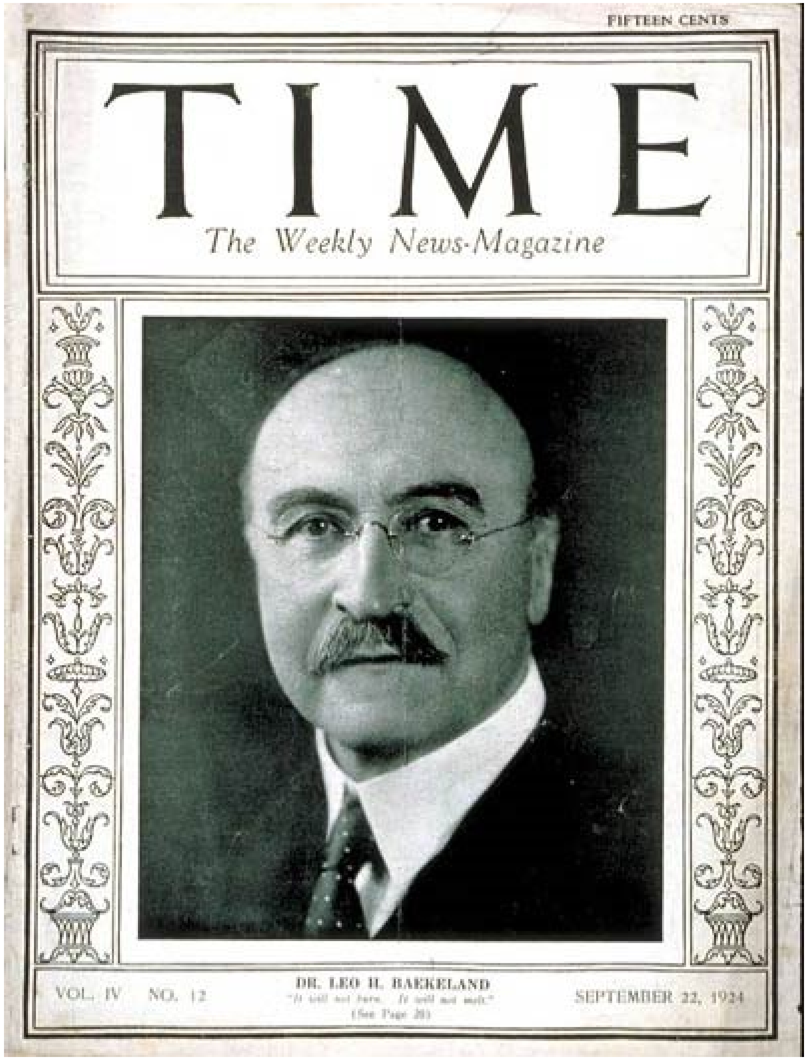
Materials are key towards a sustainable future

https://www.un.org/sustainabledevelopment/

Plastics have Revolutionarized the World

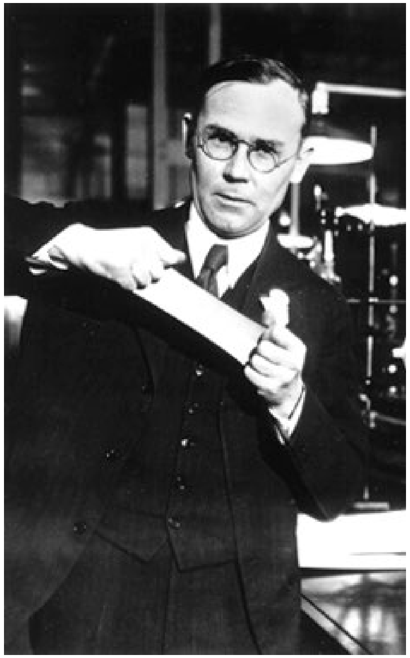
(and will continue to do so)

Phenol - Formaldehyde Resins

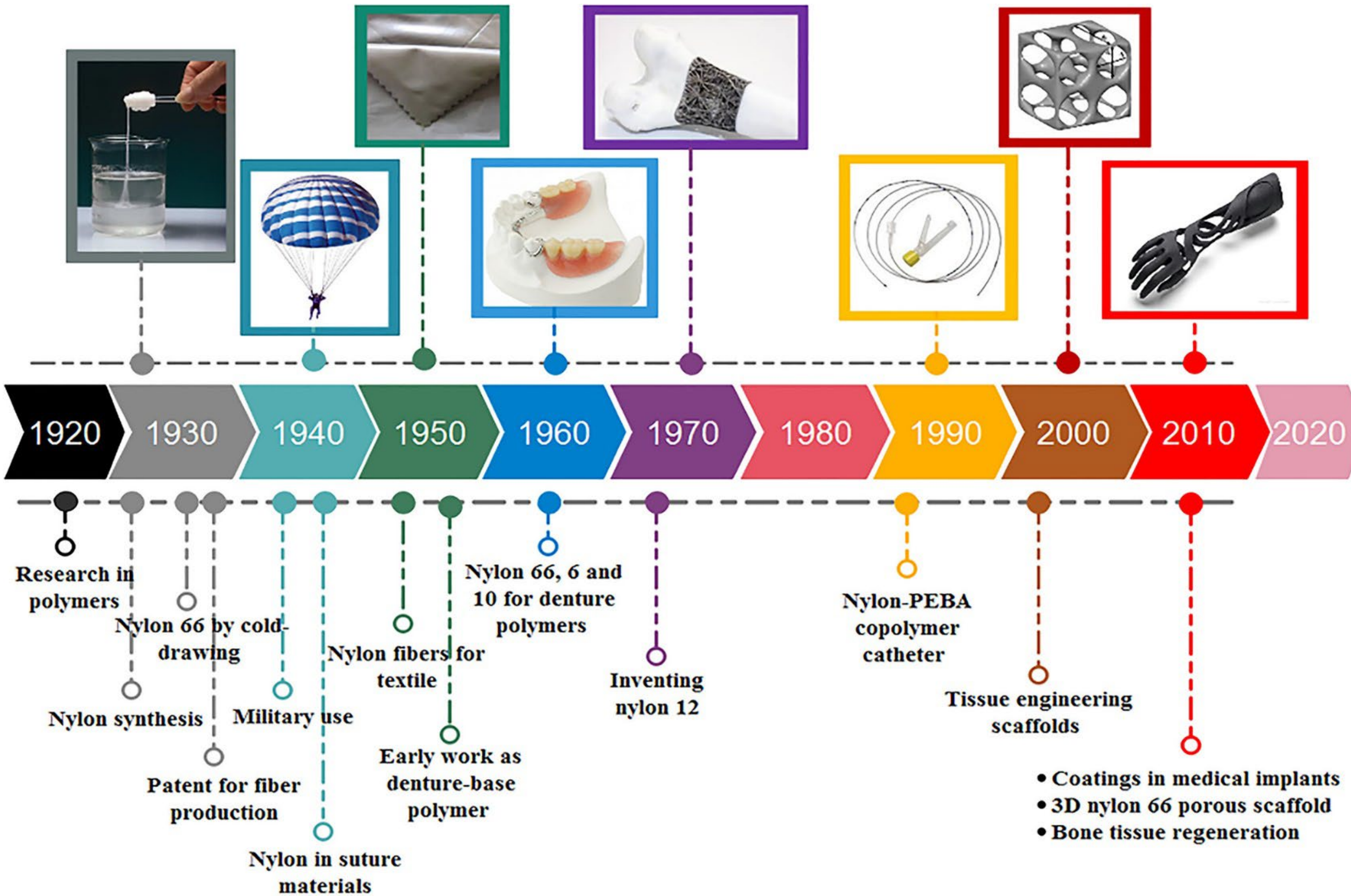


Leo Baekeland
Bakelite® (1907)

Nylon

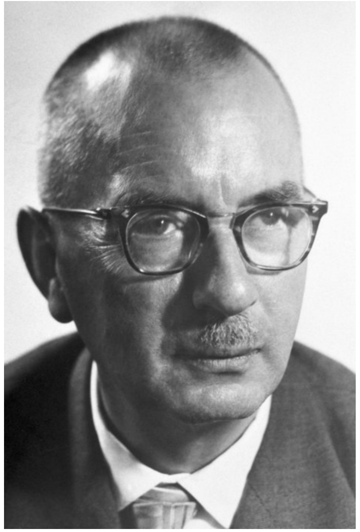


Wallace Carothers (DuPont) (1935)



M. Shakiba, E. R. Ghomi, F. Khosravi, S. Jouybar, A. Bigham, M. Zare, M. Abdouss, R. Moaref, S. Ramakrishna, *Polym. Adv. Technol.* **2021**, *32*, 3368-3383

Polyolefins



Karl Ziegler **Giulio Natta**

Nobel Prize in chemistry (1963)

Catalytic Polymerization of Olefins

Conductive Polymers

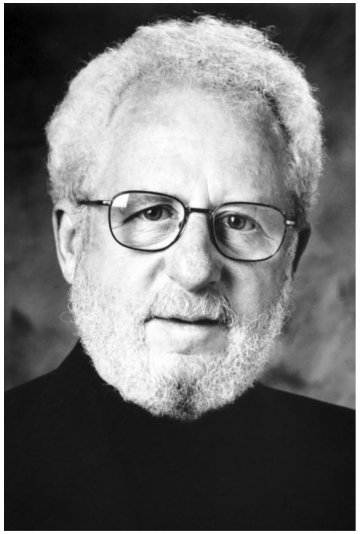


Photo from the Nobel Foundation archive.
Alan J. Heeger


Photo from the Nobel Foundation archive.
Alan G. MacDiarmid


Photo from the Nobel Foundation archive.
Hideki Shirakawa

The Nobel Prize in Chemistry 2000 was awarded jointly to Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa "for the discovery and development of conductive polymers"

Plastics that harvest Energy

Renewed Prospects for Organic Photovoltaics

Guichuan Zhang,† Francis R. Lin,† Feng Qi, Thomas Heumüller, Andreas Distler, Hans-Joachim Egelhaaf, Ning Li, Philip C. Y. Chow,* Christoph J. Brabec,* Alex K.-Y. Jen,* and Hin-Lap Yip*

Cite This: *Chem. Rev.* 2022, 122, 14180–14274 Read Online

Plastics for Energy Storage

ESSAY

ADVANCED ENERGY MATERIALS

10th Anniversary Article

www.advenergymat.de

Enabling Deformable and Stretchable Batteries

David G. Mackanic, Michael Kao, and Zhenan Bao**

Plastics that can Interrogate the Human Body

Cite This: *ACS Cent. Sci.* 2019, 5, 1884–1891

http://pubs.acs.org/journal/acscii

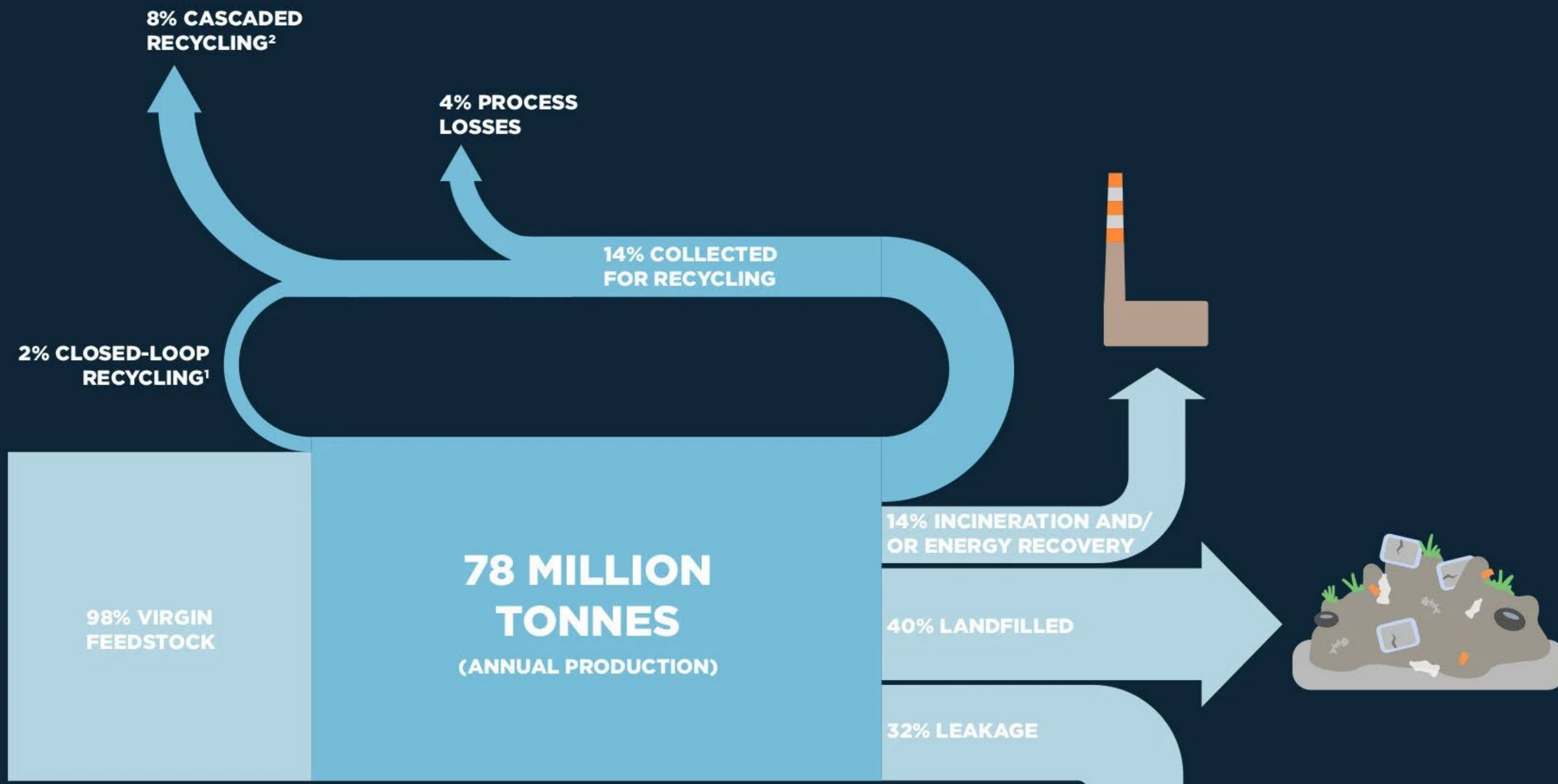
Stretchable and Fully Degradable Semiconductors for Transient Electronics

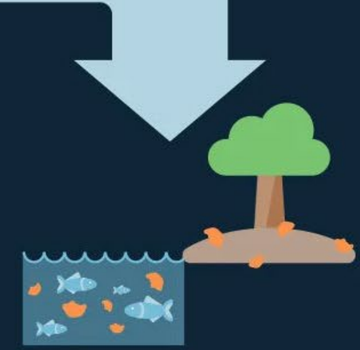
Helen Tran,† Vivian Rachel Feig,‡ Kathy Liu,‡ Hung-Chin Wu,† Ritchie Chen,§ Jie Xu,†,# Karl Deisseroth,†,§,||,⊥ and Zhenan Bao*,†

The Problem And How to Move Forward

Image credit: The Ocean Cleanup

TODAY, PLASTIC PACKAGING MATERIAL FLOWS ARE LARGELY LINEAR





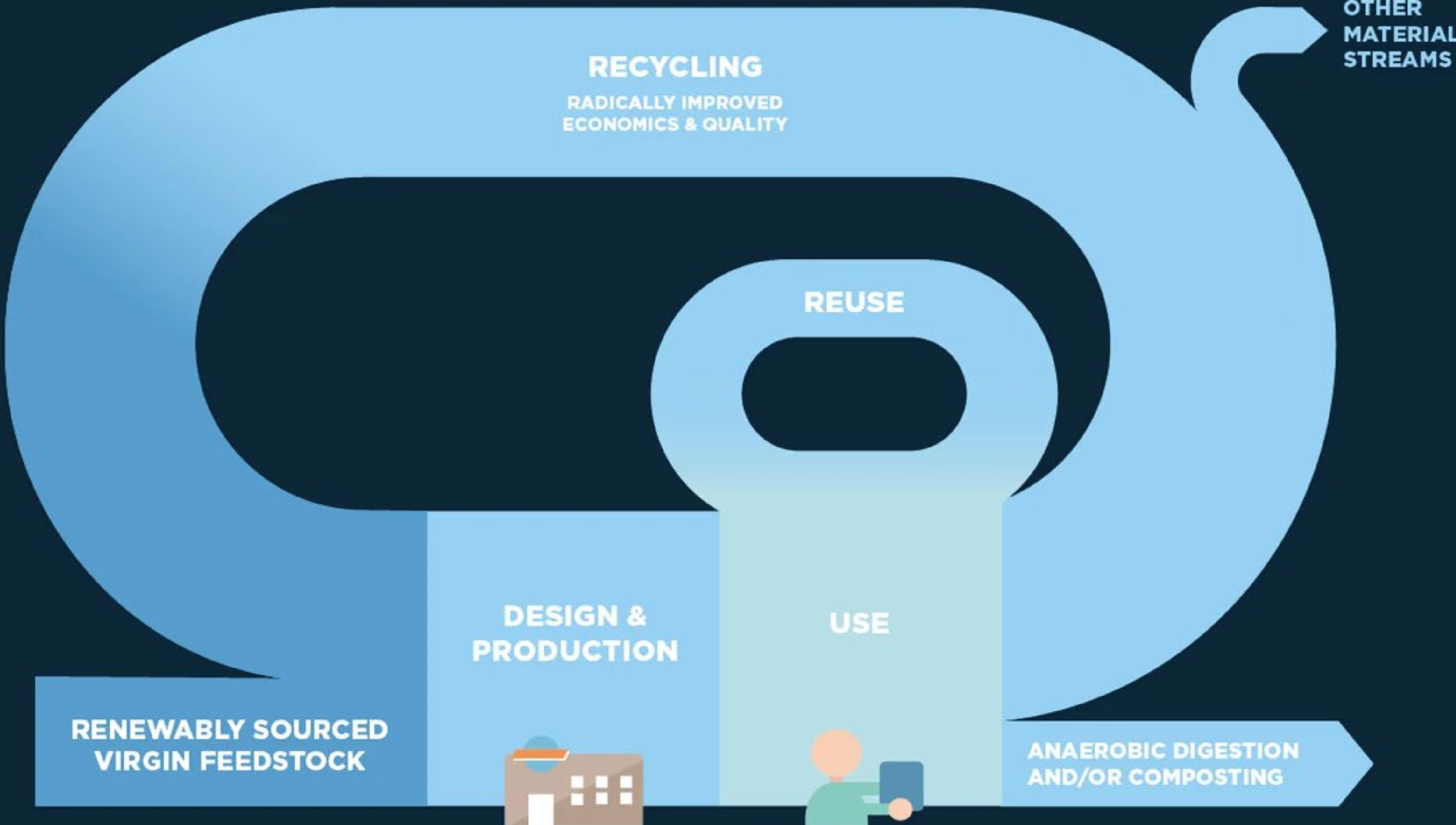
ELLEN MACARTHUR FOUNDATION

WORLD ECONOMIC FORUM, ELLEN MACARTHUR FOUNDATION, MCKINSEY & COMPANY, A NEW PLASTICS ECONOMY: RETHINKING THE FUTURE OF PLASTICS (2016)
ELLENMACARTHURFOUNDATION.ORG/PUBLICATIONS

1 Closed-loop recycling: Recycling of plastics into the same or similar-quality application
2 Cascaded recycling: Recycling of plastics into other, lower-value applications

Source: Project Mainstream analysis – for details please refer to the extended version of the report available on the website of the Ellen MacArthur Foundation: www.ellenmacarthurfoundation.org

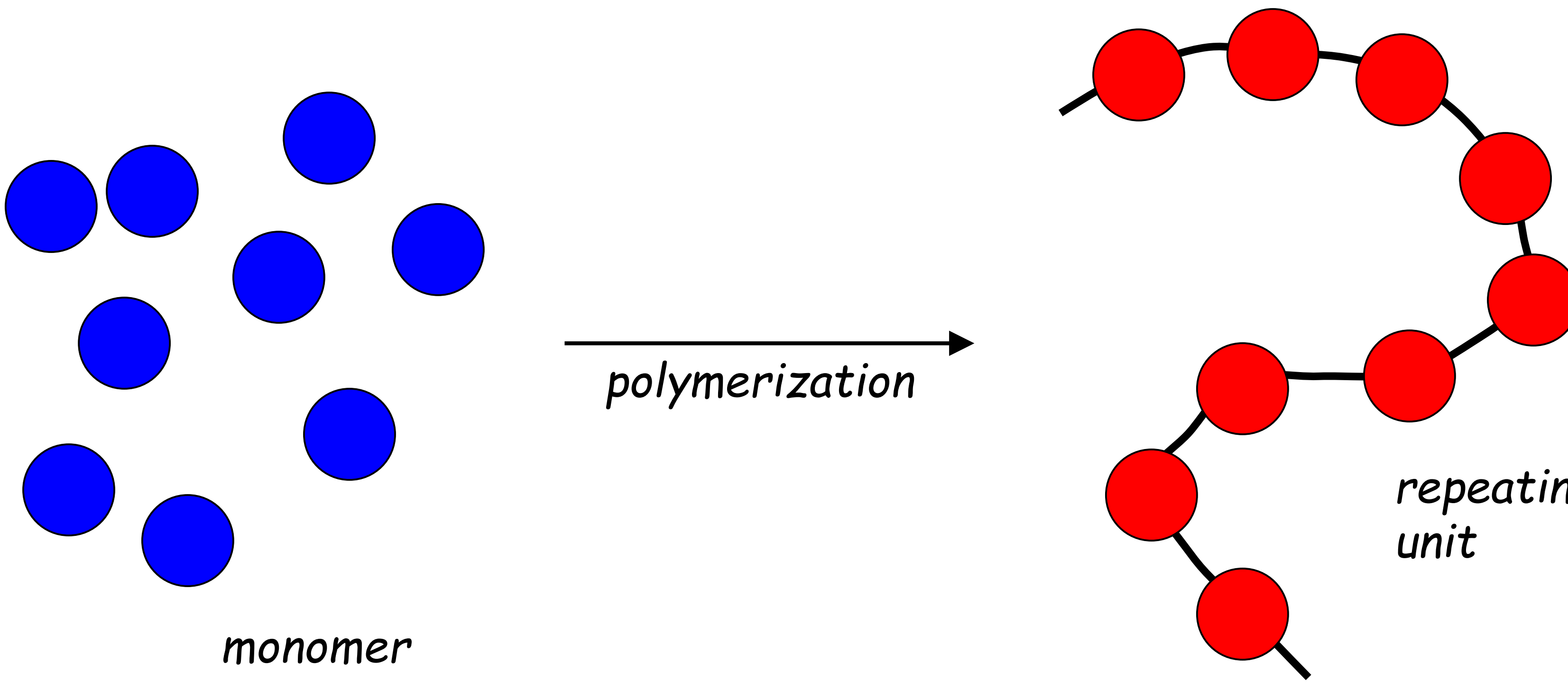
A CIRCULAR ECONOMY FOR PLASTIC



(Some of Many) Polymer Chemistry Challenges

- Synthesis of polymers from renewable, non-fossil based feedstocks
- “Green” synthesis and processing
- Recycling / upcycling of polymers
- Degradable / compostable polymers

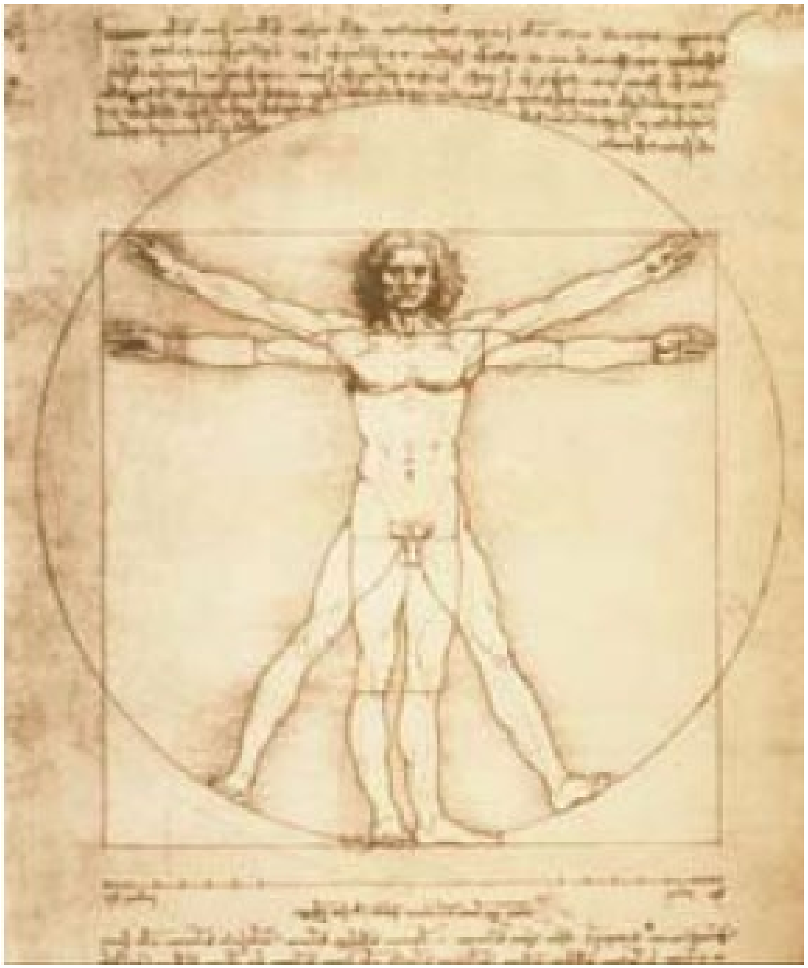
What are Polymers?



degree of polymerization

molecular weight

We are all made up of Polymers !



- DNA
- Proteins
- Polysaccharides

Polymers are Everywhere !

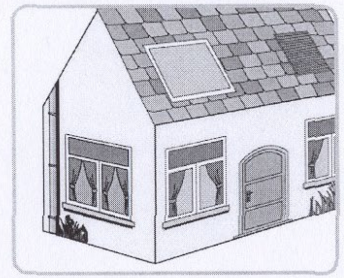
Some examples to illustrate the dramatic impact of using this 'material of choice' to conserve energy during use

• *Better fuel consumption in vehicles:*

Increasingly lighter, stronger plastics are helping automotive designers meet the twin challenges of increasing performance and minimising environmental impact. It is estimated that 100 kilograms of plastics have typically replaced 200-300 kilograms of conventional materials in today's vehicles saving around 12 million tonnes of oil and reducing CO_2 emissions by 30 million tonnes per year across Europe. Hybrid fuel systems, powered by dual petrol and electric systems, are already coming onto the market. Plastics' strength, durability and lightweight properties make them the ideal material for these fuel saving second generation vehicles.

• *Improving energy efficiency in the home:*

In northern European countries almost one quarter of all energy consumed is used in domestic heating. Plastics foam insulation in housing typically saves the energy that is required to produce it within a year. Over the lifetime of the building, the energy savings rise to 40-60 times that required to produce the insulation. The CO_2 reduction over the lifetime is 10-40 times that used to produce the insulation.

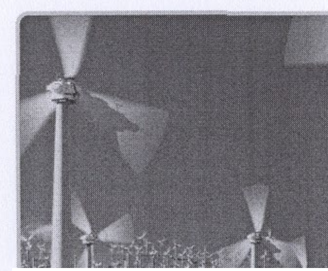


• *Contribution to new energy sources:*

An integral component of plastics' environmental credentials is their contribution to the design of renewable or alternative energy technologies such as solar, wave and wind power.

Photovoltaic solar cells, which help convert the sun's energy into usable energy, rely on plastics' resistance to extremes of temperature and light to work efficiently. Innovations in plastics mean that the cost of generating usable domestic electricity from solar radiation has been reduced. This, added to the fact that solar power is a clean source of energy, means that the increased use of solar energy in the future looks likely, reducing our dependence on fossil fuel energy. Furthermore, it is essential that the energy equivalent to that used in the production of the plastics for fuel cells will be recovered by the active solar cell within two to three years.

In the future, hydrogen fuel cell technology may radically alter the way we power our vehicles. Fuel cells use hydrogen as an energy source. No carbon dioxide is emitted during the chemical process that converts hydrogen into electrical energy. The weight of the fuel cell systems is a crucial part of the fuel cell design and plastics play a vital role in enhancing their performance. The thermoplastics plates reduce overall weight as they replace plates made from milled graphite or stainless steel coated with gold. Plastics are involved in the construction of efficient, affordable automotive fuel cells and unlike other materials are corrosion proof and *retain their shape, even at* temperatures up to 240 degrees Celsius. Fuel cell technology has the versatility to be used in a range of applications including cell phones, lap tops and building and home automation.



http://www.apme.org/

Goals of this Course

Polymer Synthesis

1. Become acquainted with the most common techniques that are used to make synthetic polymers

   $\Rightarrow$ Polymer Chemistry

2. Understand the influence of various reaction parameters on molecular characteristics such as molecular weight (distribution), topology and microstructure

   $\Rightarrow$ Macromolecular Engineering

Prerequisites (*)

Learning Prerequisites

Recommended courses

General chemistry, Inorganic chemistry, Organic and polymer chemistry

This course assumes that you are familiar with:

- Functional groups in organic molecules (alcohols, amines, carboxylic acids, etc) and their reactivity
- Basic organic functional group transformations (most notably ester and amide bond formation)
- Basic radical chemistry

(*) https://edu.epfl.ch/coursebook/en/polymer-chemistry-and-macromolecular-engineering-MSE-437

Study Material & Course Format

1. G. Odian, *Principles of Polymerization*, 4th Ed., **2004**, John Wiley & Sons
   Online avalable at: https://onlinelibrary.wiley.com/doi/pdf/10.1002/047147875X

2. Lecture notes (moodle.epfl.ch)

3. Short videos (moodle.epfl.ch)

Course Organization:

The **lecture notes** summarize the core knowledge that needs to be acquired in order to achieve the learning outcomes of the course.

The **book** provides further background and places the course material in a broader context. Reading of the indicated parts of the textbook is strongly recommended before studying the lecture notes.

Short videos provide further explanation to some of the topics that are covered by the lecture notes.

Questions and Exercises sessions provide opportunities to discuss questions about the course material, and to work on exercises

Course Organization and Assessment

Course organization:

• Study material: book, lecture notes and pre-recorded videos will be made available online

• Lectures: **Thursday 08:15 – 10:00**. Discussion of fundamental principles as well as contemporary problems and challenges in polymer science (see weekly planner for specific dates).

• Questions and Exercise sessions: **Thursday 10:15 – 11:00** according to the course schedule. These sessions serve to (i) discuss questions related to the study material and (ii) to work on exercises (see weekly planner for specific dates).

Course assessment:

• Three tests during the semester (25 % each). One sheet (front and back) with handwritten key equations and definitions is allowed (bring a pocket calculator)

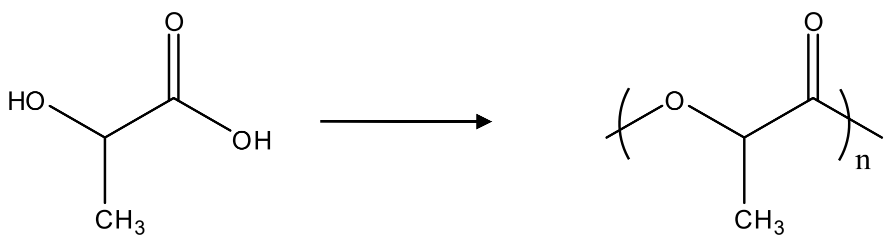
• Individual mini project (during the semester) – analysis of a scientific paper related to the course following a series of pre-defined questions (25 %)

Weekly Planner

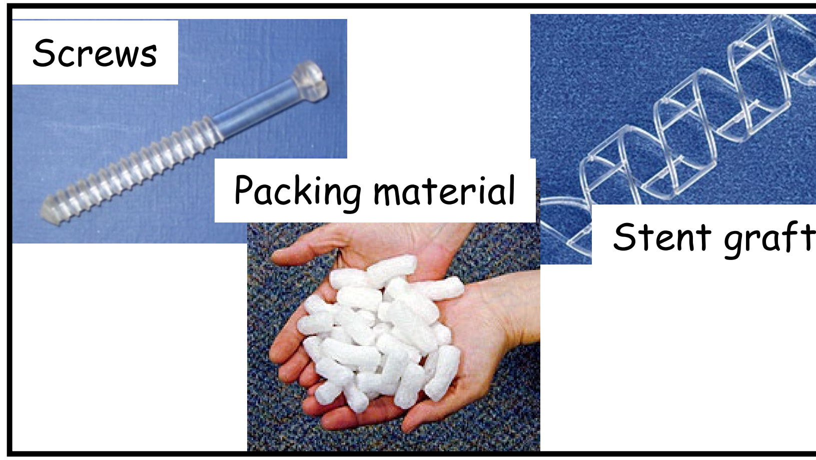
DATE	TOPIC	STUDY MATERIAL	08.15 – 10:00 (BS260)	10:15 – 11:00 (BS260)
11.09.2025	**Course overview & introduction**	Odian, Chapter 1 Video's, lecture notes and exercises on Moodle	**Lecture:** Course overview; introduction	**/**
18.09.2025	**NO CLASS**			
25.09.2025	**Step polymerization**	Odian, Chapter 2: § 2-1 – 2-8, 2-13. **Not:** 2-2a-2, 2-2d, 2-4c, 2-7d, 2-7e. Video's, lecture notes and exercises on Moodle.	**Lecture:** Step polymerization	**Recitations:** Introduction; Step polymerization
02.10.2025		**Test I (Introduction & Step Polymerization) [10:15 – 11:00]**	**/**	**TEST I**
09.10.2025	**Controlling dispersity; Living step growth polymerization**		**Lecture:** Controlling dispersity; Living step growth polymerization	/
16.10.2025	**Radical chain, and controlled free radical polymerization**	Odian, Chapter 3: § 3-1 – 3-11 and § 3-15. Video's, lecture notes and exercises on Moodle	**Lecture:** Radical chain, and controlled free radical polymerization	**Lecture:** Radical chain, and controlled free radical polymerization
23.10.2025	**NO CLASS**	**FALL BREAK**		
30.10.2025	**NO CLASS**			
06.11.2025	**Metal free ATRP**		**Lecture:** Metal free ATRP	**Recitations:** Radical chain; controlled free radical polymerization
13.11.2025		**Articles and report template for mini projects available on Moodle**		
13.11.2025		**Test II (Controlling dispersity; Living step growth polymerization; Radical chain, and controlled free radical polymerization; Metal free ATRP) [10:15 – 11:00]**	**/**	**TEST II**
20.11.2025	**Ionic chain polymerization**	Odian, Chapter 5: Odian: § 5-1 – 5-5. Video's, lecture notes and exercises on Moodle	**Lecture:** Ionic chain polymerization	**/**
27.11.2025	**Chain copolymerization**	Odian, Chapter 6: § 6-1 – 6-4. Video's, lecture notes and exercises on Moodle	**Lecture:** Chain copolymerization	**Recitations:** Ionic chain polymerization
04.12.2025	**NO CLASS**			
11.12.2025	**Sequence control**		**Lecture:** Sequence control	**Recitations:** Chain copolymerization
18.12.2025		**Test III (Ionic chain polymerization and chain copolymerization, Sequence control) [10:15 – 11:00]**	**/**	**TEST III**
18.12.2025		**Deadline (23:59 h) to submit mini project reports (via Moodle)**		

Step Polymerization

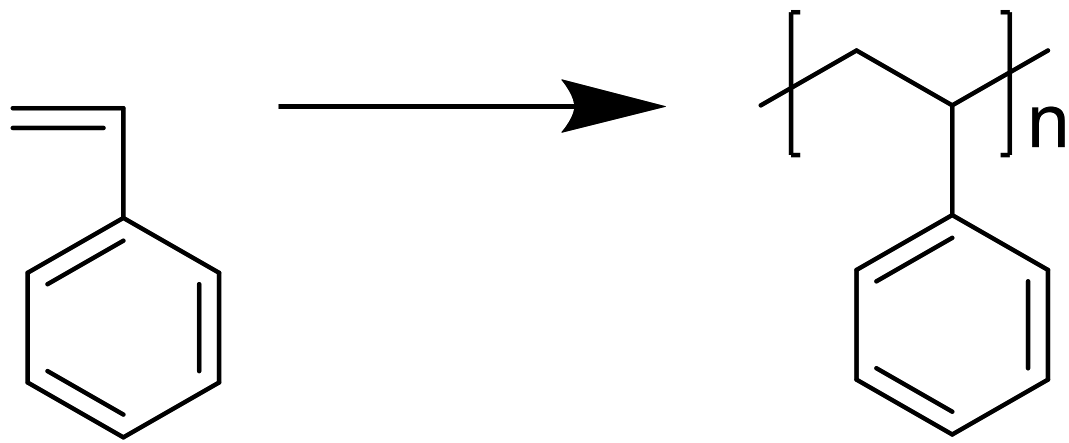
Synthesis of biodegradable polymers



Further, recommended reading:
M. Ajioka, K. Enomoto, K. Suzuki, A. Yamaguchi, *J. Environm. Polym. Degrad.* **1995**, *3*, 225



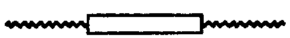
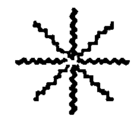
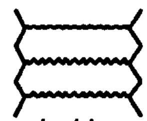
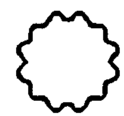
Radical Chain Polymerization



Living Free Radical Polymerization & Macromolecular Engineering

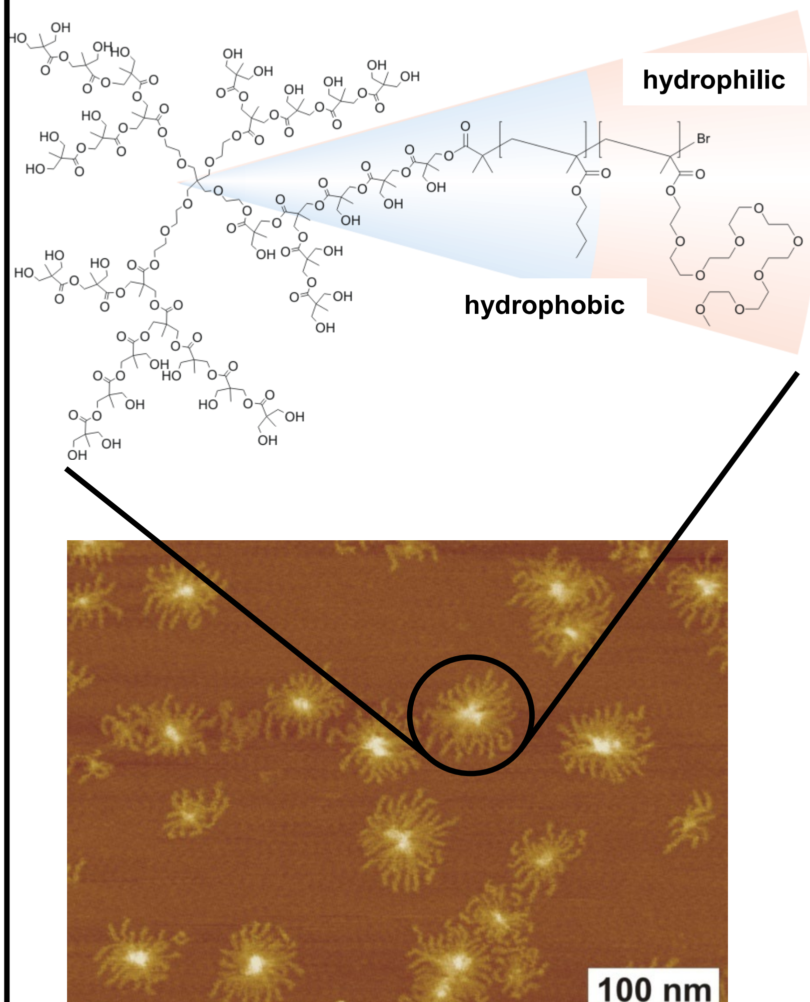
Synthesis of polymers with precise control over molecular weight, composition and topology

Table 1. Architectural forms of polymers available by living polymerization techniques.

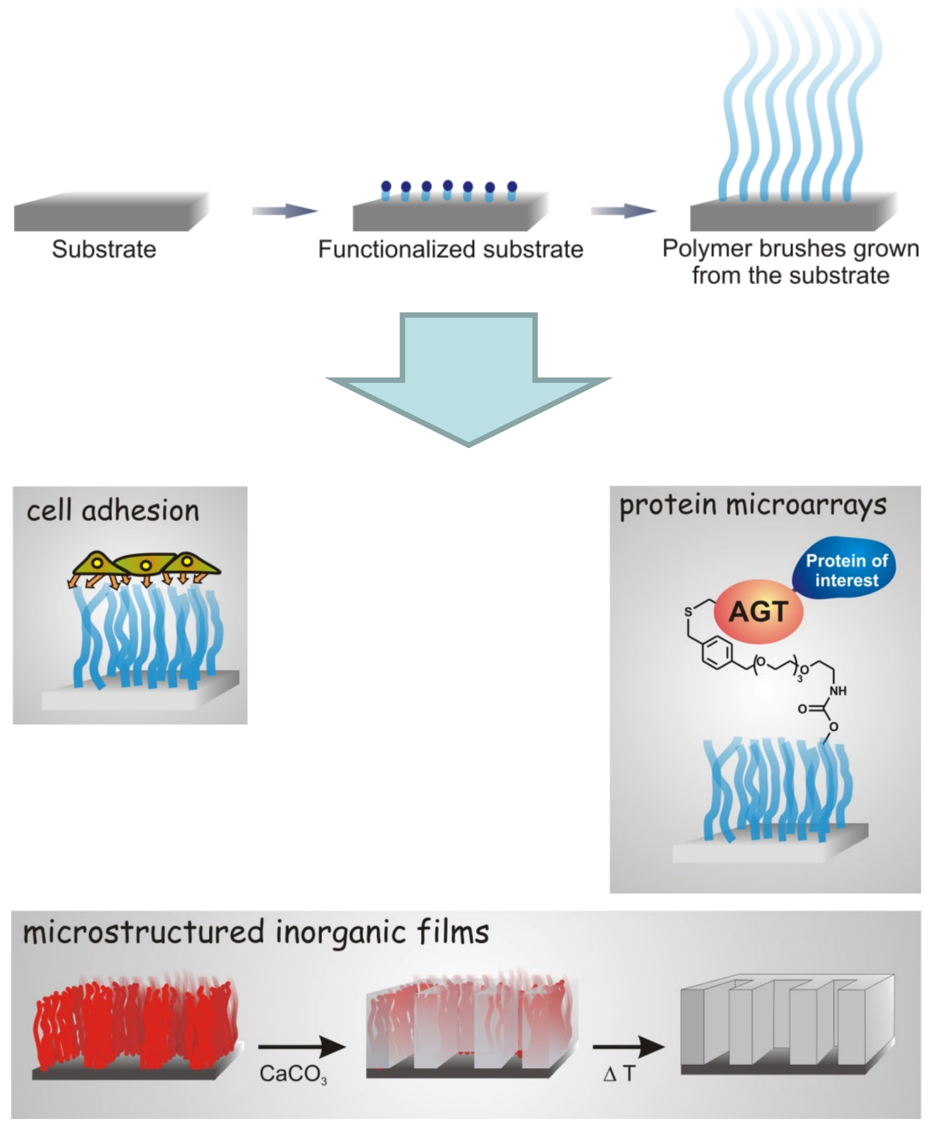
	Polymer	Application
1	 *Functional ended*	Dispersing agents Synthesis of macromonomers
2	 *α,ω-difunctional*	Elastomers synthesis Chain extension Cross-linking agents
3	 *AB Block*	Dispersing agents Compatibilizers for polymer blending
4	 *ABA Block*	Thermoplastic elastomers
5	 *Graft*	Elastomers Adhesives
6	 *Comb*	Elastomers Adhesives
7	 *Star*	Rheology control Strengthening agents
8	 *Ladder*	High-temperature plastics Membranes Elastomers
9	 *Cyclic*	Rheology control
10	 *Amphiphilic network*	Biocompatible polymers

Macromolecular Engineering

Unimolecular Nanocontainers



Polymer Brushes: Functional Coatings



Ionic Chain Polymerization: How to Make Synthetic Rubber ?!

Natural Rubber:

Isolation

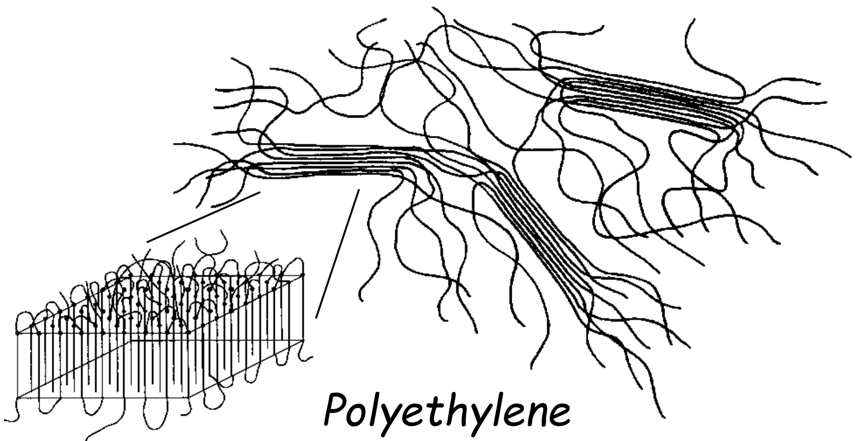
Synthetic Rubber:

1. Cationic polymerization of isobutylene

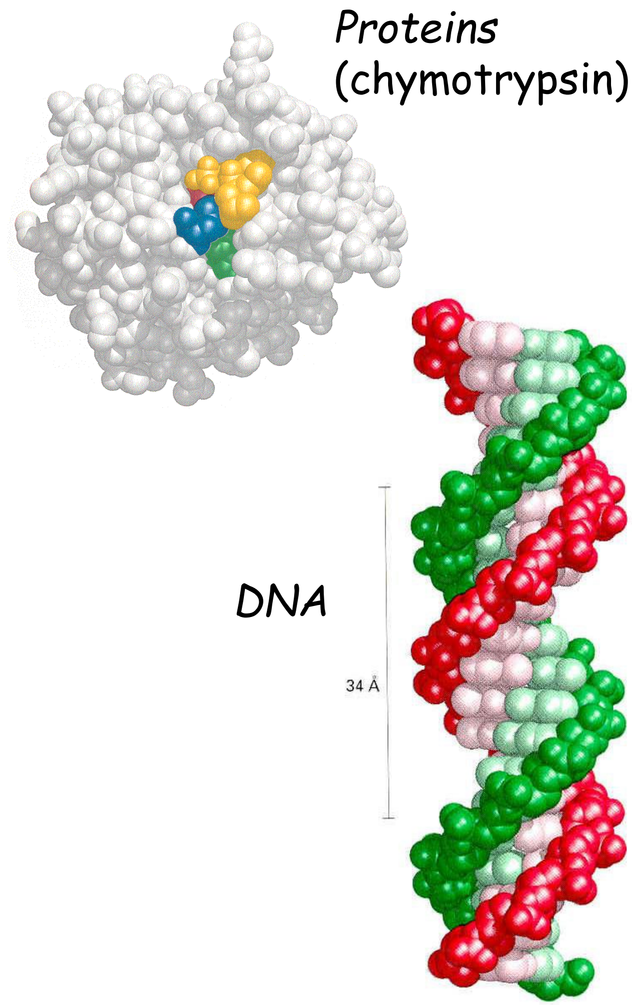
2. Anionic polymerization:
   Thermoplastic elastomers

Today's Outline

Synthetic Polymers



Biological Polymers



1. Classification of polymers
   - Chemical structure
   - Polymerization mechanism

2. Properties of polymer chains
   - Molecular weight

3. Nomenclature of polymers

Classification of Polymers

- Based on composition and architecture
- Based on chemical structure
- Based on polymerization mechanism
- Based on physical and mechanical properties

There is no single generally accepted classification that is unambiguous!

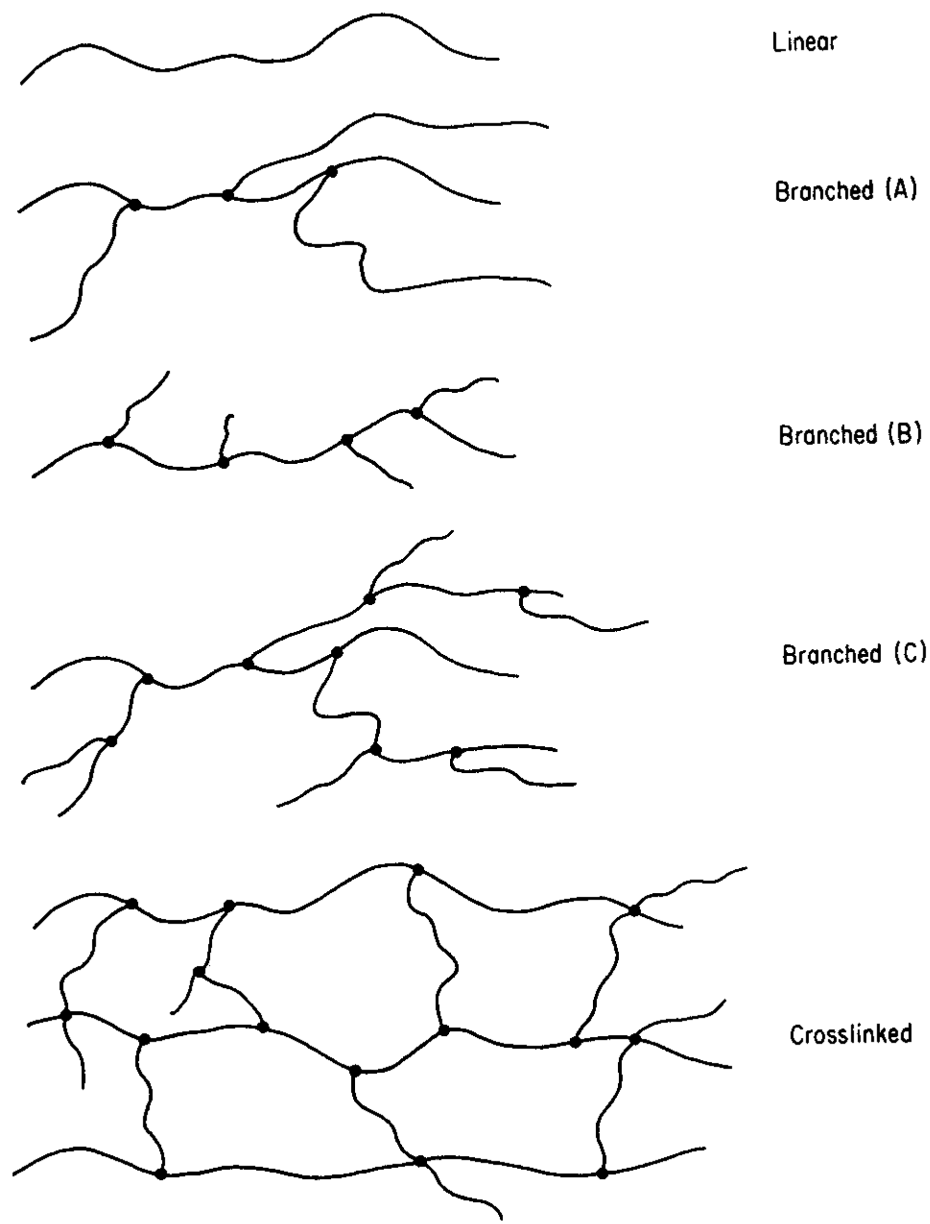
1. Polymer Composition and Architecture

Composition:

Homopolymers:	polymers prepared from a single monomer (A)
Copolymers:	polymers prepared from ≥ 2 monomers (A and B)

random:	AABABBAAABAB
alternating:	ABABABABABABA
block:	AAAABBBB
	AAAABBBBAAAA
	AAAABBBBCCCC
graft:	AAAAAAAAAAAA
	BBBBBB (grafted to the sixth A)

Architecture:



Classification of Polymers

- Based on composition and architecture
- Based on chemical structure
- Based on polymerization mechanism
- Based on physical and mechanical properties

There is no single generally accepted classification that is unambiguous!

2. Chemical Structure

(A) Condensation polymers

(B) Addition polymers

Definitions

A polymer is classified as a condensation polymer:

(i) if its synthesis involves the elimination of small molecules
(ii) if it contains functional groups as part of the polymer main chain
(iii) if its repeating unit lacks certain atoms that are present in the hypothetical monomer it is made of

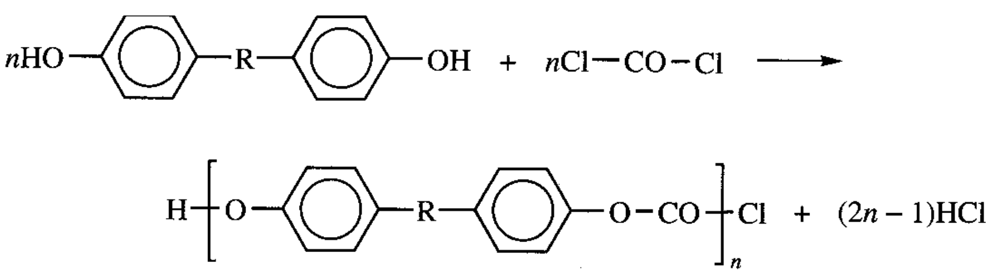
A polymer that does not fulfill any of the above requirements is classified as an addition polymer

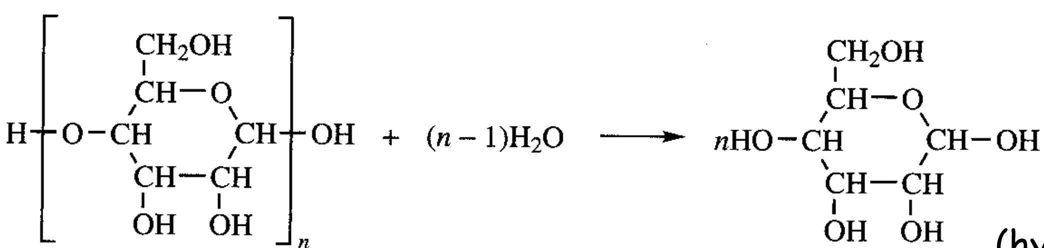
Condensation Polymers

- Polymer formation is accompanied by elimination of a small molecule
- Composition of repeat unit ≠ composition monomer

$$n\mathrm{H_2N{-}R{-}NH_2} + n\mathrm{HO_2C{-}R'{-}CO_2H} \longrightarrow \mathrm{H{+}NH{-}R{-}NHCO{-}R'{-}CO{+}_{\mathit{n}}OH} + (2n-1)\mathrm{H_2O}$$

$$n\mathrm{HO{-}R{-}OH} + n\mathrm{HO_2C{-}R'{-}CO_2H} \longrightarrow \mathrm{H{+}O{-}R{-}OCO{-}R'{-}CO{+}_{\mathit{n}}OH} + (2n-1)\mathrm{H_2O}$$





Cellulose

Glucose

(hypothetical reaction)

Condensation Polymers

$$n\mathrm{HO{-}R{-}OH} \;+\; n\mathrm{OCN{-}R'{-}NCO} \longrightarrow$$

$$\mathrm{HO}\left(\mathrm{R{-}OCONH{-}R'{-}NHCO{-}O}\right)_{(n-1)}\mathrm{R{-}OCONH{-}R'{-}NCO}$$

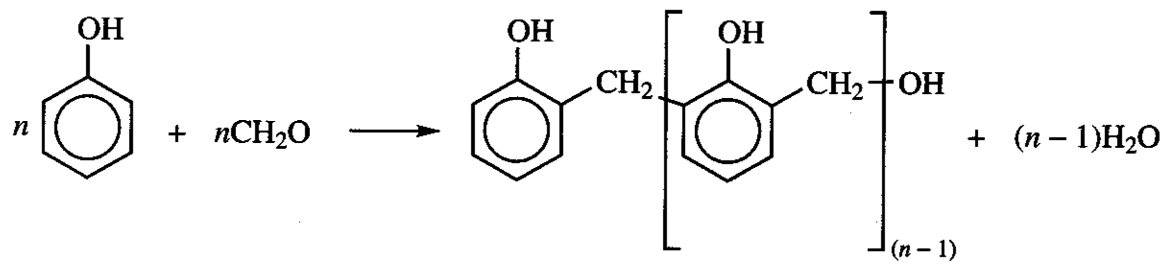
- Condensation polymers contain repeating units that are joined by functional units of one kind to another (e.g. ester, amide, urethane, sulfide, ether)
- Addition polymers do not contain functional groups as part of the polymer main chain

General structure of a condensation polymer:

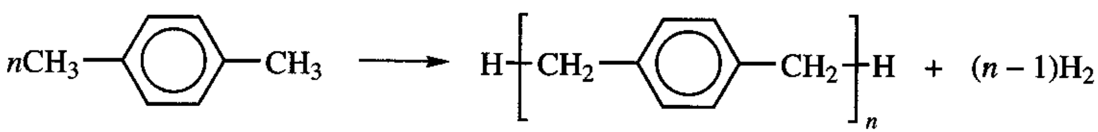
-R-Z-R-Z-R-Z-R-Z-R-

with R = aliphatic or aromatic group and
Z = -OCO-, -NHCO-, -OCONH-, -O-, -OCOO-, $-SO_2-$

Other Examples



phenol-formaldehyde polymers



poly(p-xylene)

Addition Polymers

- Composition of repeat unit = composition monomer
- Polymer formation is <u>not</u> accompanied by elimination of a small molecule

$$n\mathrm{CH_2{=}CHY} \longrightarrow \mathrm{-\!\!\left(CH_2-CHY\right)\!\!-}_n$$

TABLE 1-1 Typical Condensation Polymers

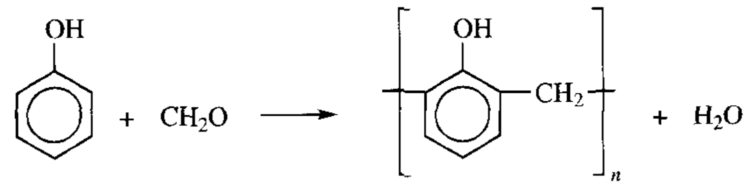
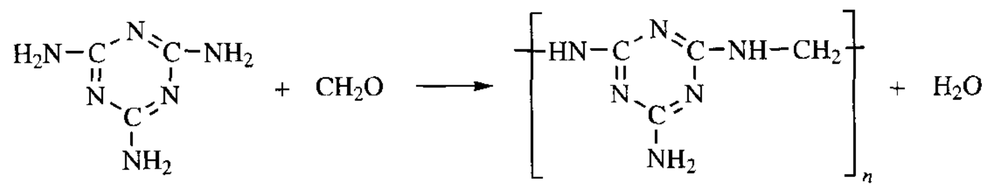
Type	Characteristic Linkage	Polymerization Reaction
Polyamide	—NH—CO—	$H_2N{-}R{-}NH_2 + HO_2C{-}R'{-}CO_2H \longrightarrow H(NH{-}R{-}NHCO{-}R'{-}CO)_nOH + H_2O$
		$H_2N{-}R{-}NH_2 + ClCO{-}R'{-}COCl \longrightarrow H(NH{-}R{-}NHCO{-}R'{-}CO)_nCl + HCl$
		$H_2N{-}R{-}CO_2H \longrightarrow H(NH{-}R{-}CO)_nOH + H_2O$
Protein, wool, silk	—NH—CO—	Naturally occurring polypeptide polymers; degradable to mixtures of different amino acids.
		$H(NH{-}R{-}CONH{-}R'{-}CO)_nOH + H_2O \longrightarrow H_2N{-}R{-}CO_2H + H_2N{-}R'{-}CO_2H$
Polyester	—CO—O—	$HO{-}R{-}OH + HO_2C{-}R'{-}CO_2H \longrightarrow H(O{-}R{-}OCO{-}R'{-}CO)_nOH + H_2O$
		$HO{-}R{-}OH + R''O_2C{-}R'{-}CO_2R'' \longrightarrow H(O{-}R{-}OCO{-}R'{-}CO)_nOH + R''OH$
		$HO{-}R{-}CO_2H \longrightarrow H(O{-}R{-}CO)_nOH + H_2O$
Polyurethane	—O—CO—NH—	$HO{-}R{-}OH + OCN{-}R'{-}NCO \longrightarrow (O{-}R{-}OCO{-}NH{-}R'{-}NH{-}CO)_n$
Polysiloxane	—Si—O—	$Cl{-}SiR_2{-}Cl \xrightarrow[-HCl]{H_2O} HO{-}SiR_2{-}OH \longrightarrow H(O{-}SiR_2)_nOH + H_2O$
Phenol–formaldehyde	$—Ar—CH_2—$	
Urea–formaldehyde	$—NH—CH_2—$	$H_2N{-}CO{-}NH_2 + CH_2O \longrightarrow (HN{-}CO{-}NH{-}CH_2)_n + H_2O$
Melamine–formaldehyde	$—NH—CH_2—$	
Polysulfide	$—S_m—$	$Cl{-}R{-}Cl + Na_2S_m \longrightarrow (S_m{-}R)_n + NaCl$
Polyacetal	$—O{-}\underset{\displaystyle R}{CH}{-}O—$	$R{-}CHO + HO{-}R'{-}OH \longrightarrow (O{-}R'{-}OCHR)_n + H_2O$

TABLE 1-2 Typical Addition Polymers

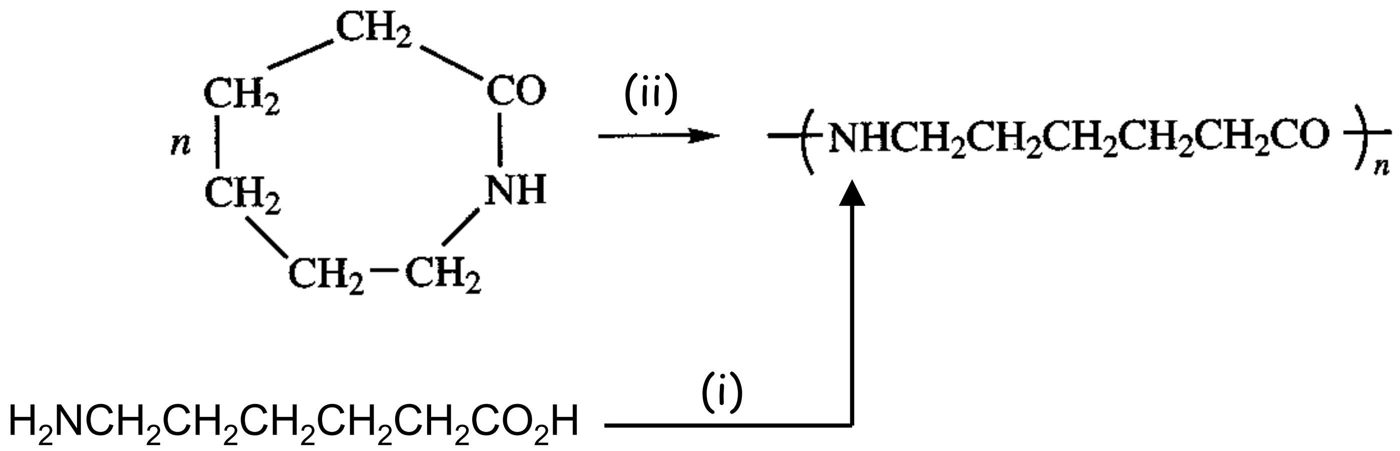
Polymer	Monomer	Repeating Unit
Polyethylene	$CH_2{=}CH_2$	$-CH_2-CH_2-$
Polyisobutylene	$CH_2{=}C(CH_3)_2$	$-CH_2-C(CH_3)_2-$
Polyacrylonitrile	$CH_2{=}CH-CN$	$-CH_2-CH(CN)-$
Poly(vinyl chloride)	$CH_2{=}CH-Cl$	$-CH_2-CH(Cl)-$
Polystyrene	$CH_2{=}CH-\phi$	$-CH_2-CH(\phi)-$
Poly(methyl methacrylate)	$CH_2{=}C(CH_3)(CO_2CH_3)$	$-CH_2-C(CH_3)(CO_2CH_3)-$
Poly(vinyl acetate)	$CH_2{=}CH-OCOCH_3$	$-CH_2-CH(OCOCH_3)-$
Poly(vinylidene chloride)	$CH_2{=}CCl_2$	$-CH_2-CCl_2-$
Polytetrafluoroethylene	$CF_2{=}CF_2$	$-CF_2-CF_2-$
Polyisoprene (natural rubber)	$CH_2{=}C(CH_3)-CH{=}CH_2$	$-CH_2-C(CH_3){=}CH-CH_2-$

Problem

Classification based on polymer structure is not unambiguous!

Many polymers can be synthesized via different routes and materials properties may depend on the synthetic strategy used.

Nylon 6, poly(ε-caprolactam), poly(6-amino caproic acid)



Classification of Polymers

- Based on composition and architecture
- Based on chemical structure
- Based on polymerization mechanism
- Based on physical and mechanical properties

There is no single generally accepted classification that is unambiguous!

3. Polymerization Mechanism

(A) Step polymerization

(B) Chain polymerization

Step versus Chain Polymerization

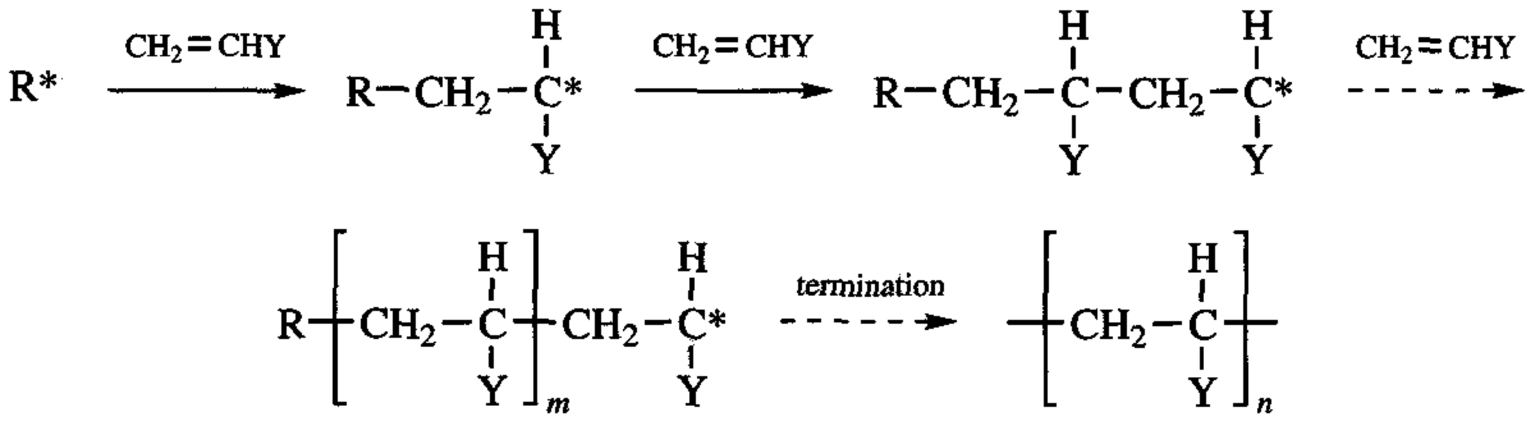
- Identities of the species that can react with each other
- Relationship between polymer molecular weight and monomer conversion

Step Polymerization

monomer + monomer	→	dimer
dimer + monomer	→	trimer
dimer + dimer	→	tetramer
trimer + monomer	→	tetramer
trimer + dimer	→	pentamer
trimer + trimer	→	hexamer
tetramer + monomer	→	pentamer
tetramer + dimer	→	hexamer
tetramer + trimer	→	heptamer
tetramer + tetramer	→	octamer
etc.		

- Reaction occurs between any of the different sized species present in the reaction system
- Molecular weight increases relatively slowly with conversion

Chain Polymerization

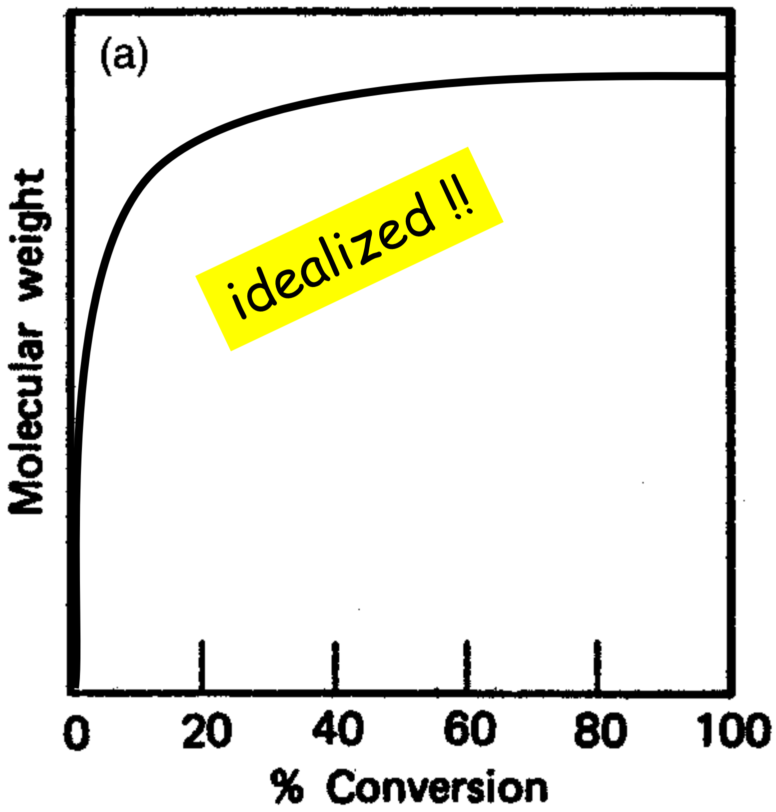


R* can be a free radical, cation or anion

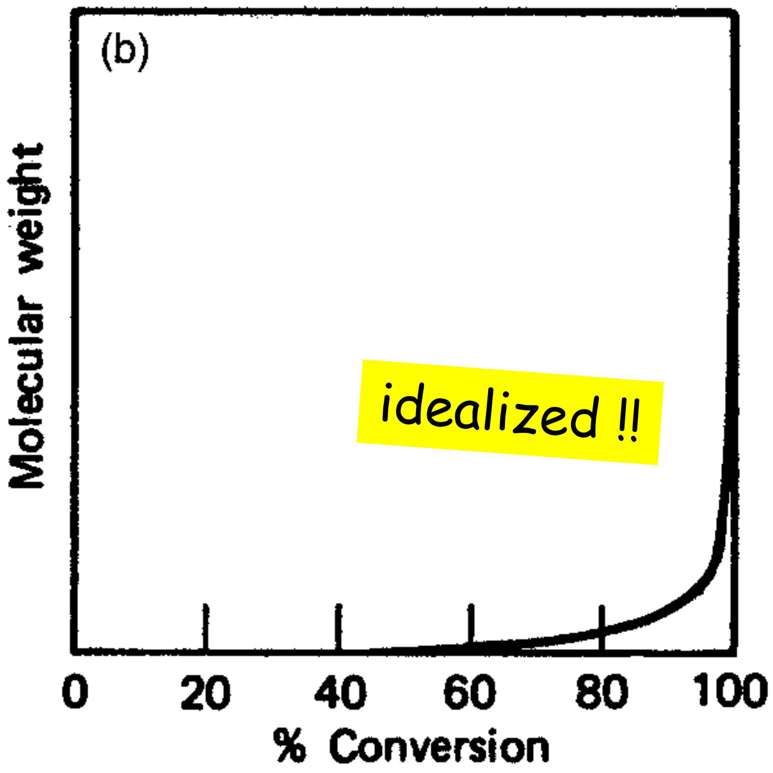
- Monomer only reacts with the reactive center
- Chain growth is very rapid
- Monomer concentration decreases throughout the polymerization, while the number of high molecular weight polymer molecules increases
- The molecular weight of the polymer is relatively independent on monomer conversion (compared to a step polymerization)

Schematic Development of Molecular Weight

chain polymerization



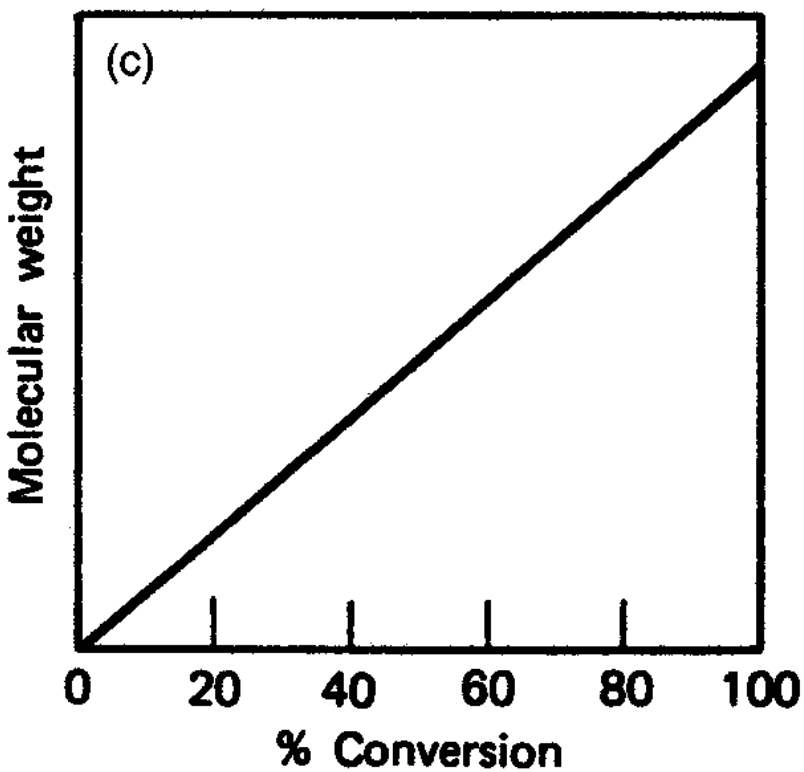
step polymerization



Ambiguities & Problems I.

- **Nonterminating chain polymerization**:
  Fast initiation process in combination with the absence of reactions that can terminate the propagating reactive centers („living" polymerization): linear increase of molecular weight with conversion

- **Protein biosynthesis** also shows this behaviour

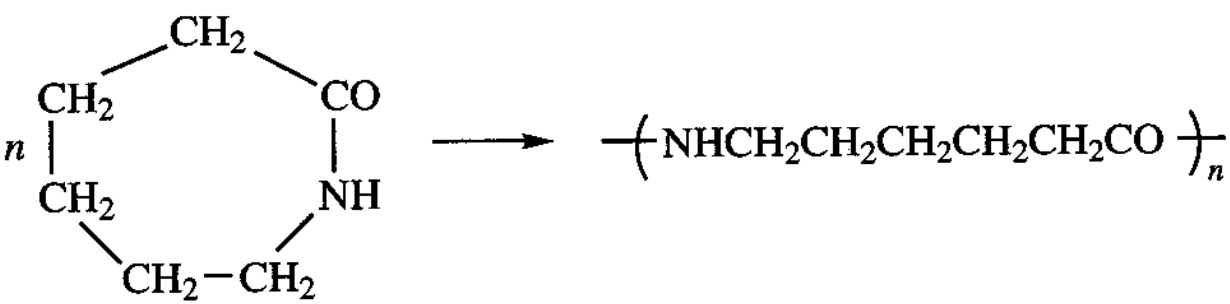


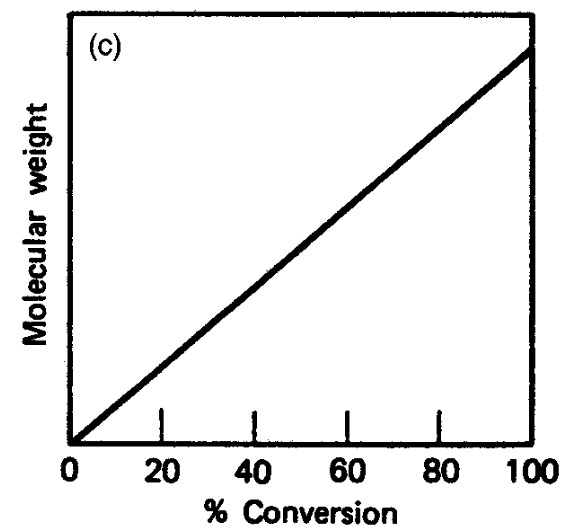
Ambiguities & Problems II.

Ring-opening polymerization:

Poly(propylene oxide)

Nylon 6, poly(ε-caprolactam), poly(6-amino caproic acid)

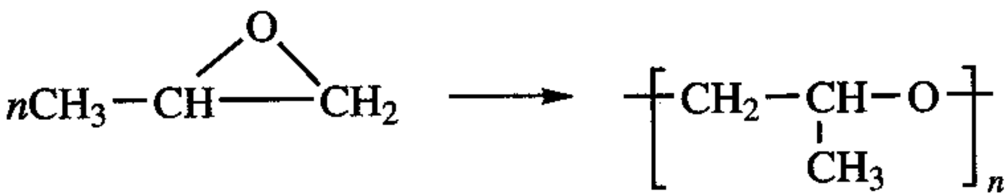


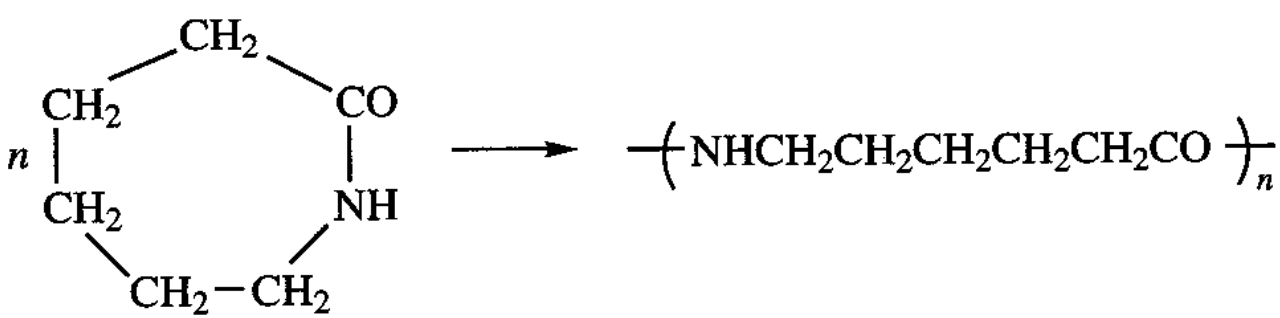


Ring-opening polymerizations often show a linear increase in molecular weight with monomer conversion

Conclusions

Both structure and mechanism are usually needed in order to clearly classify a polymer !!





Classification of Polymers

- Based on composition and architecture
- Based on chemical structure
- Based on polymerization mechanism
- Based on physical and mechanical properties

There is no single generally accepted classification that is unambiguous!

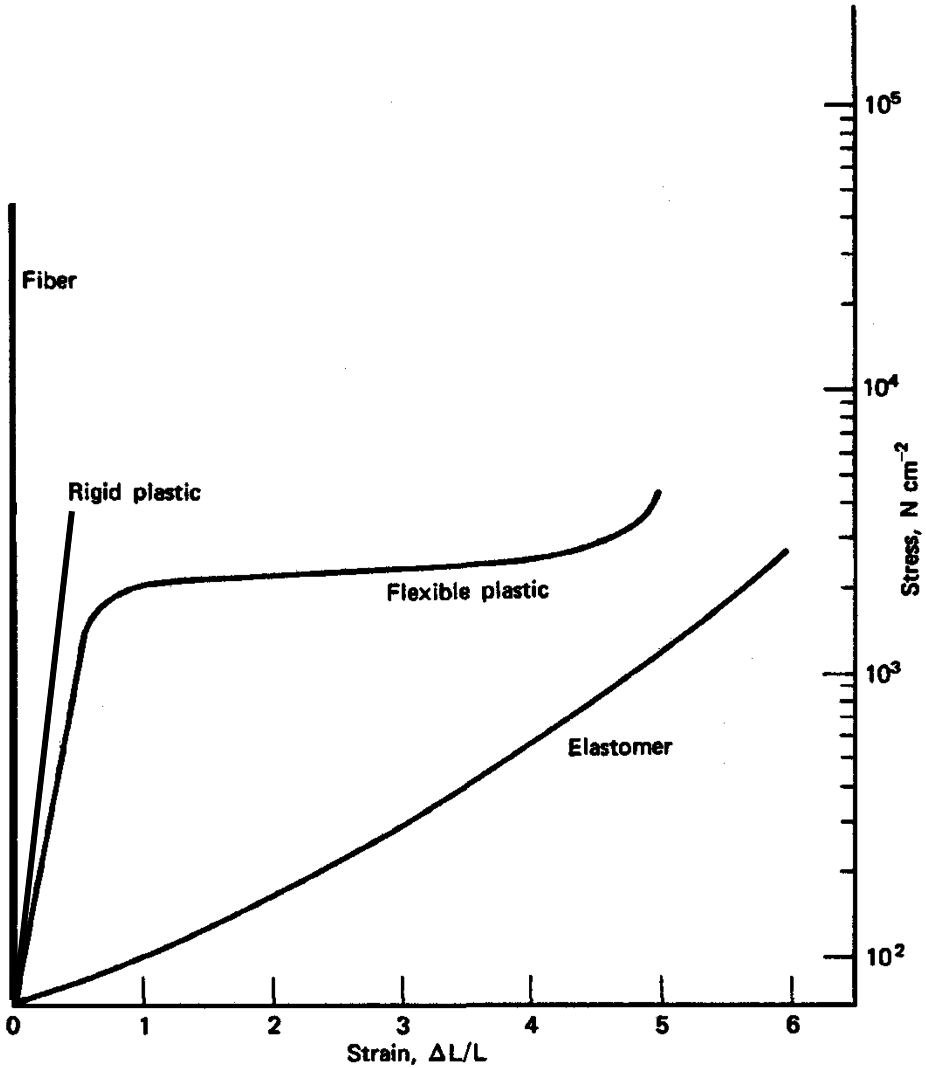
4. Physical and Mechanical Properties

- Classification by mechanical properties: modulus (E) $\sigma = E\,\varepsilon$

stress   strain

E: resistance to deformation/ stiffness

$E_{fiber} > E_{plastic} > E_{rubber}$



- Classification by end-use:
  1. Plastics
  2. Fibers
  3. Rubbers (elastomers)
  4. Adhesives
  5. Coatings

<table>
<tr><th>Elastomers</th><th>Plastics</th><th>Fibers</th></tr>
<tr><td>Polyisoprene</td><td>Polyethylene</td><td></td></tr>
<tr><td>Polyisobutylene</td><td>Polytetrafluoroethylene</td><td></td></tr>
<tr><td></td><td>Poly(methyl methacrylate)</td><td></td></tr>
<tr><td></td><td>Phenol–formaldehyde</td><td></td></tr>
<tr><td></td><td>Urea–formaldehyde</td><td></td></tr>
<tr><td></td><td>Melamine–formaldehyde</td><td></td></tr>
<tr><td colspan="2">←——Polystyrene——→</td><td></td></tr>
<tr><td colspan="2">←——Poly(vinyl chloride)——→</td><td></td></tr>
<tr><td colspan="2">←——Polyurethane——→</td><td></td></tr>
<tr><td colspan="2">←——Polysiloxane——→</td><td></td></tr>
<tr><td></td><td colspan="2">←——Polyamide——→</td></tr>
<tr><td></td><td colspan="2">←——Polyester——→</td></tr>
<tr><td></td><td colspan="2">←——Cellulosics——→</td></tr>
<tr><td></td><td colspan="2">←——Polypropene——→</td></tr>
<tr><td></td><td></td><td>Polyacrylonitrile</td></tr>
</table>

A given polymer may fall into more than one category !

Plastics

Commodity plastics	• High volume, low cost • Often used for disposable items • Polyethylene, polypropylene, poly(vinyl chloride), polystyrene
Engineering plastics	• Higher costs, lower volume • Superior mechanical properties and greater durability • Examples: polyamides, polyesters, polycarbonate • Applications: transportation, construction, electrical and electronic goods
Thermoplasts	• Polymers that soften and flow upon heating
Thermosets	• Polymers that do not flow upon heating

Commodity Plastics

Type	Abbreviation	Major Uses
Low-density polyethylene	LDPE	Packaging film, wire and cable insulation, toys, flexible bottles, housewares, coatings
High-density polyethylene	HDPE	Bottles, drums, pipe, conduit, sheet, film, wire and cable insulation
Polypropylene	PP	Automobile and appliance parts, furniture, cordage, webbing, carpeting, film packaging
Poly(vinyl chloride)	PVC	Construction, rigid pipe, flooring, wire and cable insulation, film and sheet
Polystyrene	PS	Packaging (foam and film), foam insulation, appliances, housewares, toys

Principal Engineering Plastics

Type	Abbreviation
Acetal[a]	POM
Polyamide[b]	—
Polyamideimide	PAI
Polyarylate	—
Polybenzimidazole	PBI
Polycarbonate	PC
Polyester[c]	—
Polyetheretherketone	PEEK
Polyetherimide	PEI
Polyimide	PI
Poly(phenylene oxide)	PPO
Poly(phenylene sulfide)	PPS
Polysulfone[d]	—

[a]Common name for polyformaldehyde. Abbreviation refers to poly(oxymethylene).

[b]Principally nylons 6 and 66.

[c]Principally poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT).

[d]Several types marketed.

Principal Thermosetting Plastics

Type	Abbreviation	Typical Uses
Phenol–formaldehyde	PF	Electrical and electronic equipment, automobile parts, utensil handles, plywood adhesives, particle board binder
Urea–formaldehyde	UF	Similar to PF polymers; also treatment of textiles, coatings
Unsaturated polyester	UP	Construction, automobile parts, boat hulls, marine accessories, corrosion-resistant ducting, pipe, tanks, etc., business equipment
Epoxy		Protective coatings, adhesives, electrical and electronics applications, industrial flooring, highway paving materials, composites
Melamine–formaldehyde	MF	Similar to UF polymers; decorative panels, counter and table tops, dinnerware

Fibers

Some characteristics:
- High strength and modulus
- Good elongation (stretchability)
- Good thermal stability (-> ironing)
- Spinnability
- ......

Natural fibers: Cotton (= polysaccharide)
Wool (= protein (keratin))
Silk (= protein)

Synthetic fibers:

Type	*Description*
Cellulosic	
Acetate rayon	Cellulose acetate
Viscose rayon	Regenerated cellulose
Noncellulosic	
Polyester	Principally poly(ethylene terephthalate)
Nylon	Includes nylon 66, nylon 6, and a variety of other aliphatic and aromatic polyamides
Olefin	Includes polypropylene and copolymers of vinyl chloride, with lesser amounts of acrylonitrile, vinyl acetate, or vinylidene chloride (copolymers consisting of more than 85% vinyl chloride are called *vinyon* fibers)
Acrylic	Contain at least 80% acrylonitrile; included are *modacrylic* fibers comprising acrylonitrile and about 20% vinyl chloride or vinylidene chloride

Rubbers / Elastomers

Rubber: natural polymer
Elastomer: synthetic material

} Usually both are used interchangeably

- Easily undergo very large reversible elongations ($\leq$ 500-1000 %) at relatively low stresses
- Are covalently crosslinked, three dimensional networks

Principal Types of Synthetic Rubber

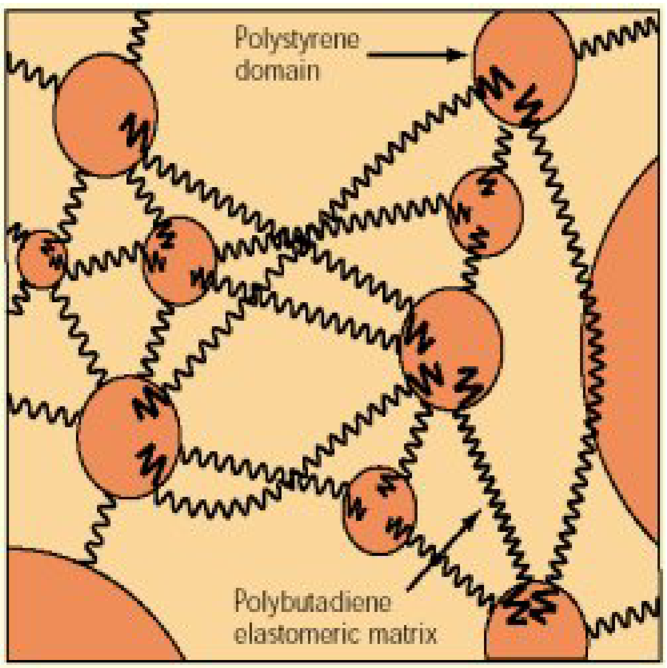
Type	*Description*
Styrene–butadiene	Copolymer of the two monomers in various proportions depending on properties desired; called SBR for styrene–butadiene rubber
Polybutadiene	Consists almost entirely of the *cis*-1,4 polymer
Ethylene–propylene	Often abbreviated EPDM for ethylene–propylene–diene monomer; made up principally of ethylene and propylene units with small amounts of a diene to provide unsaturation
Polychloroprene	Principally the *trans*-1,4 polymer, but also some *cis*-1,4 and 1,2 polymer; also known as *neoprene* rubber
Polyisoprene	Mainly the *cis*-1,4 polymer; sometimes called "synthetic natural rubber"
Nitrile	Copolymer of acrylonitrile and butadiene, mainly the latter
Butyl	Copolymer of isobutylene and isoprene, with only small amounts of the latter
Silicone	Contains inorganic backbone of alternating oxygen and methylated silicon atoms; also called polysiloxane
Urethane	Elastomers prepared by linking polyethers through urethane groups

Thermoplastic elastomers: behave as rubbers, but can be melt processed

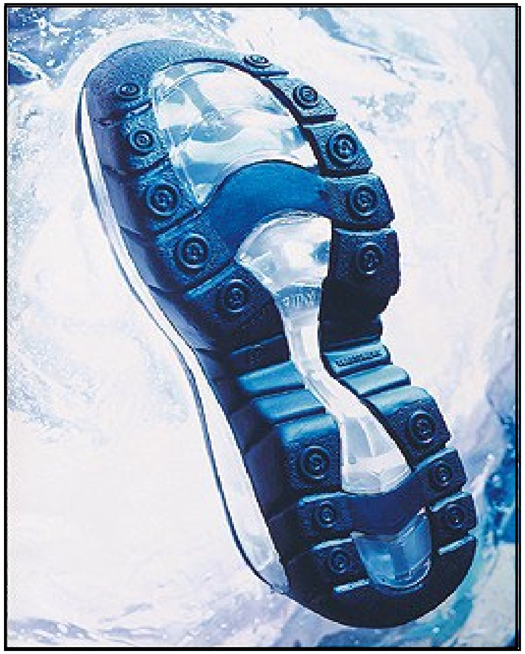
Thermoplastic Elastomers

Styrene-isoprene-styrene and styrene-1,2-butadiene-styrene ABA triblock copolymers with short styrene blocks are useful as thermoplastic elastomers (*Cariflex*, *Kraton*, *Soloprene*, *Stereon*)

Thermoplastic elastomers behave as elastomers at ambient temperatures but are thermoplastic at elevated temperatures ($T > T_{g,PS}$), where they can be molded and remolded



The polystyrene blocks aggregate to form glassy (hard) domains that physically crosslink the rubbery (soft) polydiene blocks



http://www.kraton.com/

Adhesives and Coatings

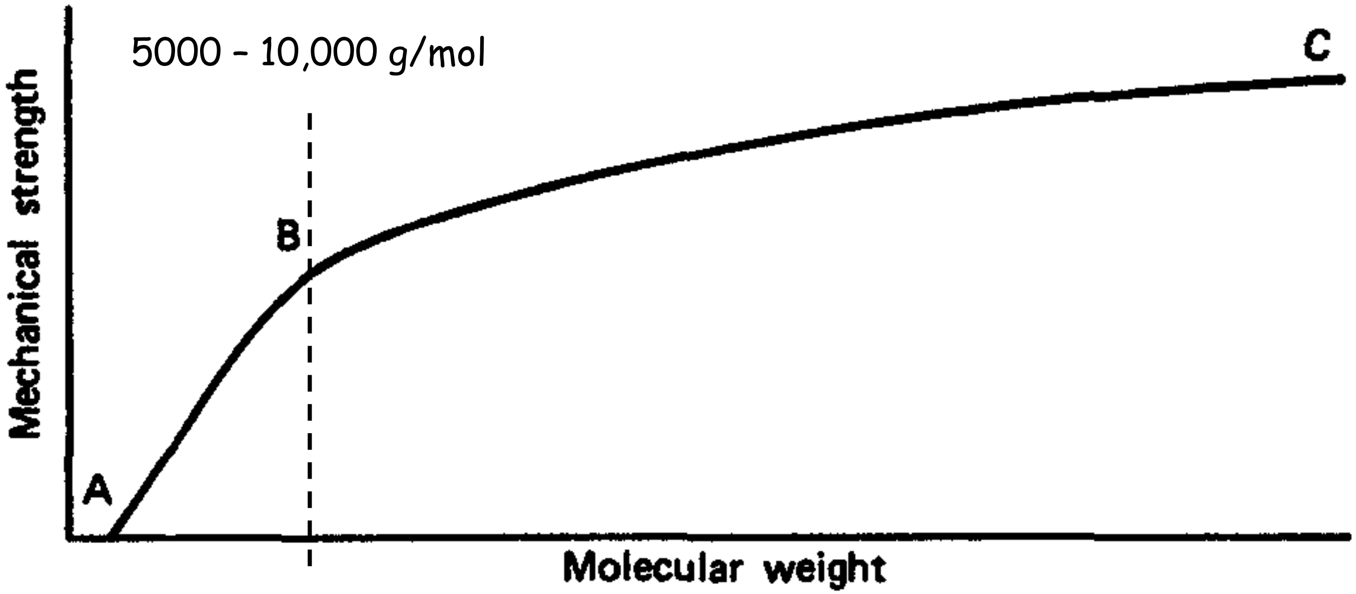
- Coatings: Protection, decoration
- Adhesives

} Usually not a single polymer, but complex formulations including solvents, fillers, pigments, ...

Properties of Polymer Chains

Molecular weight and molecular weight distribution

Molecular Weight



A: There is a minimum molecular weight required for a polymer to have a certain property
B: Critical molecular weight; strength increases fast until this point; minimum useful molecular weight typically 5.000 – 10.000
C: Limiting value

The desired polymer molecular weight is often a compromise in order to meet particular materials demands without overly sacrifying other properties

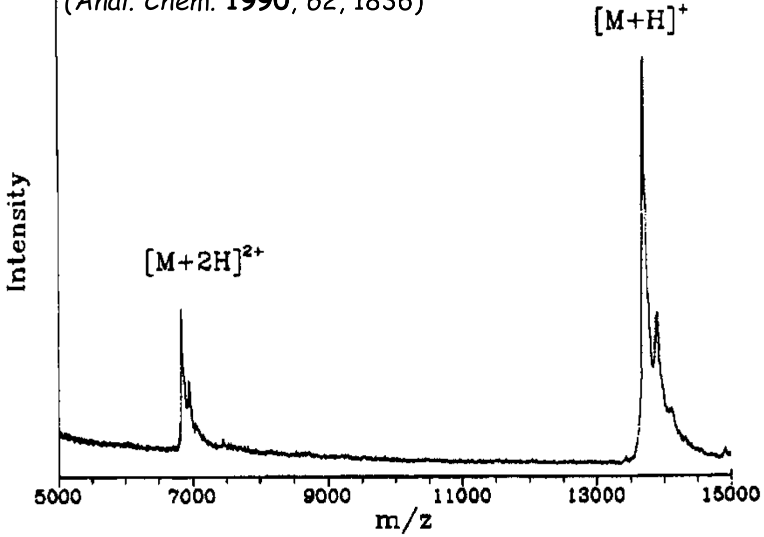
Synthetic Polymers are Mixtures!

- Due to statistical variations in the polymerization process, polymers even in their purest form, are usually mixtures of molecules of different molecular weights
- Both the average molecular weight and the molecular weight distribution are needed to fully characterize a polymer

MALDI TOF mass spectra of a natural polymer (protein) vs. that of a synthetic polymer

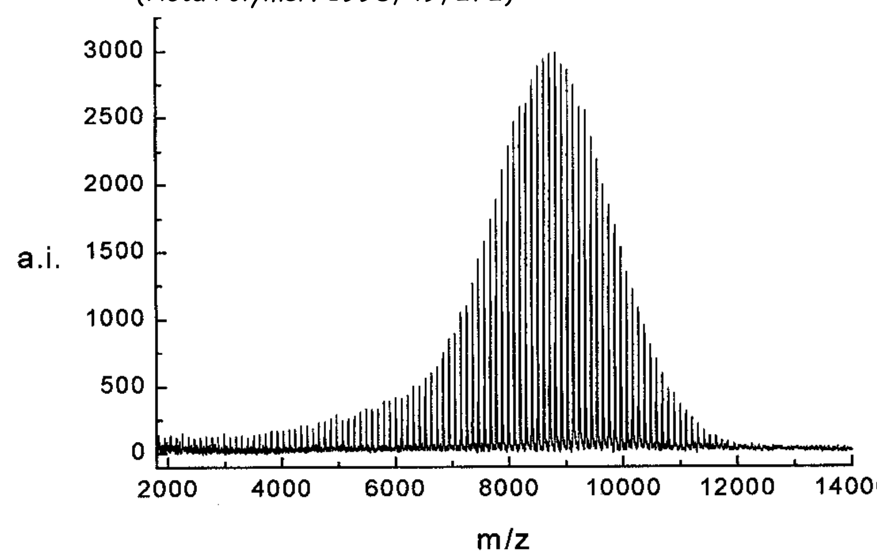
Ribonuclease A:

(Anal. Chem. **1990**, *62*, 1836)



Polystyrene (M_n = 9000 Da):

(Acta Polymer. **1998**, *49*, 272)



Measuring Polymer Molecular Weights

Problem: different techniques yield different molecular weights

1. Number-average molecular weight (M_n)

   M_n determined by methods that count the number of polymer molecules in a sample. Methods rely on colligative properties such as vapor pressure lowering, freezing point depression etc.

   Defined as: $$\overline{M}_n = \frac{w}{\sum N_x} = \frac{\sum N_x M_x}{\sum N_x} = \sum \underline{N}_x M_x$$

   i.e. the total weight (w) of all the molecules in a polymer sample divided by the total number of moles present. N_x is the number of moles whose weight is M_x. $\underline{N}_x$ *is the mole fraction of molecules of size* M_x

2. Weight-average molecular weight (M_w)

M_w is obtained from light scattering, which is greater for larger-sized molecules than for smaller sized molecules.

Defined as:

$$\overline{M}_w = \sum w_x M_x$$

where w_x is the weight fraction of molecules whose weight is M_x

Alternatively:

$$\overline{M}_w = \frac{\sum c_x M_x}{\sum c_x} = \frac{\sum c_x M_x}{c} = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

where c_x is the weight concentration of M_x molecules, c is the total weight concentration of all the polymer molecules, and:

$$w_x = \frac{c_x}{c}$$

$$c_x = N_x M_x$$

$$c = \sum c_x = \sum N_x M_x$$

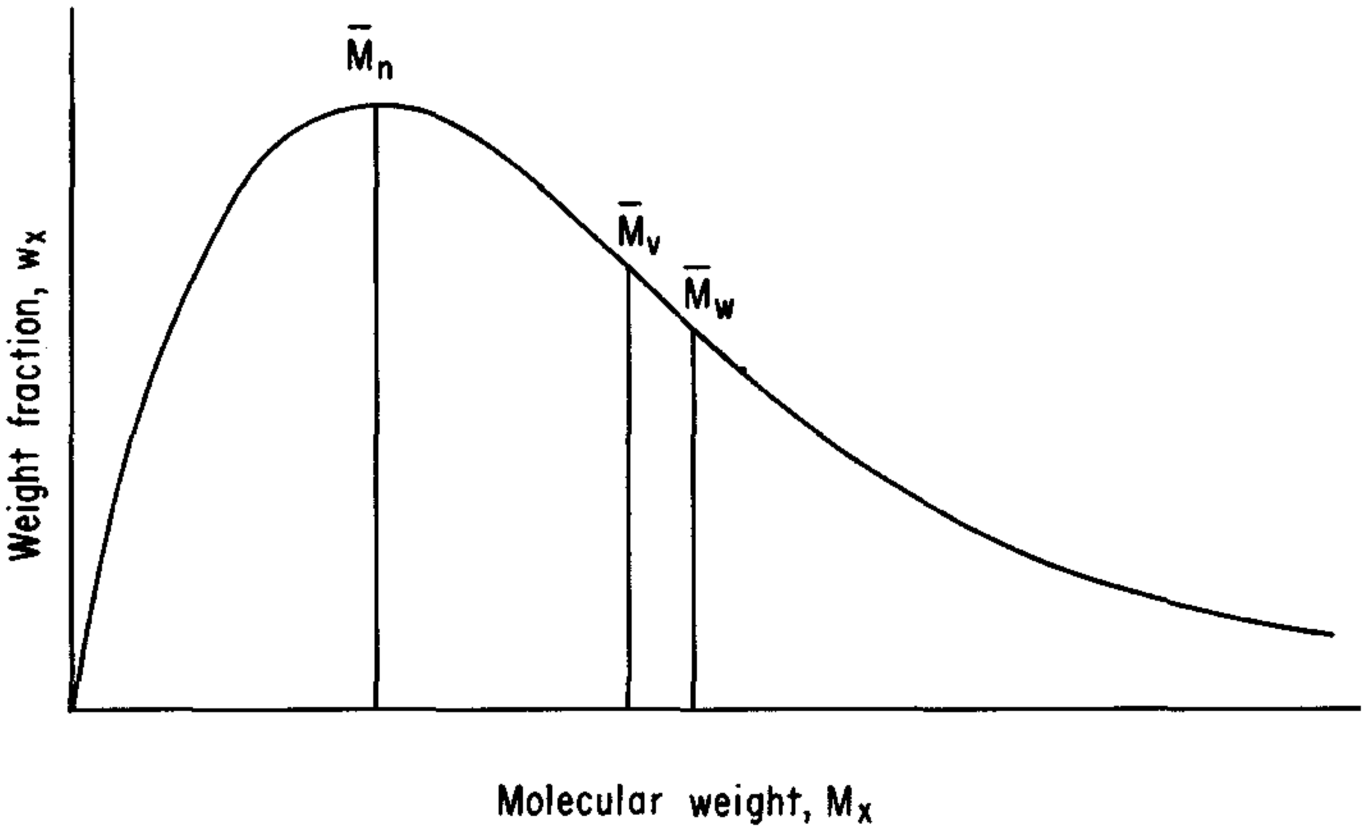
3. Viscosity-average molecular weight (M_v)

Solution viscosity does not measure M_w since the exact dependence of solution viscosity is different from light scattering

Defined as: $$\overline{M}_v = \left[\sum w_x M_x^a\right]^{1/a} = \left[\frac{\sum N_x M_x^{a+1}}{\sum N_x M_x}\right]^{1/a}$$

with a = 0.5-0.9. The constant a depends on the hydrodynamic volume of the polymer and the effective volume of the solvated polymer molecule in solution, and varies with polymer, solvent and temperature

M_n, M_v and M_w

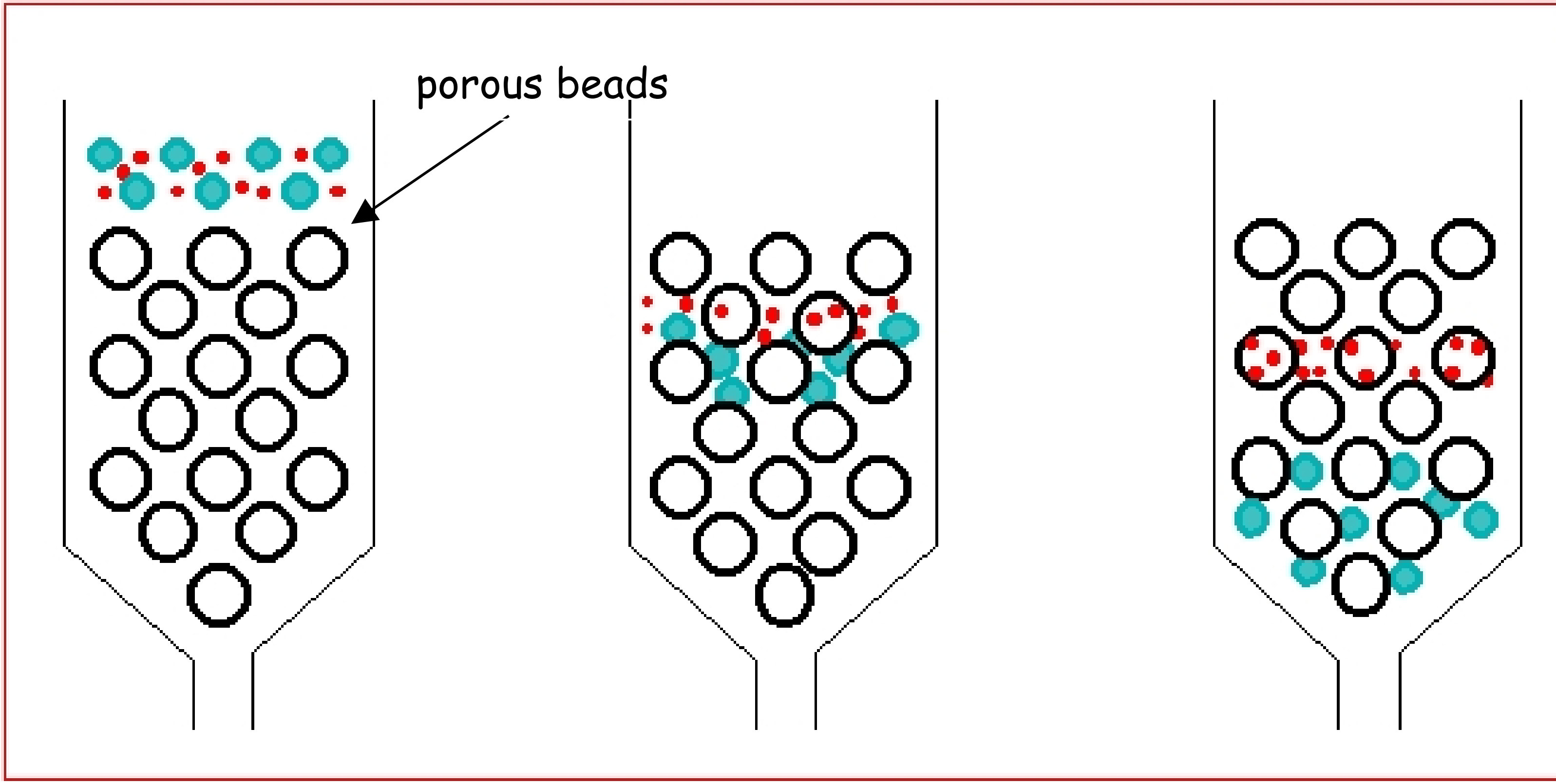


Distribution of molecular weights in a typical polymer sample.

- M_v and M_w are usually quite close (within 10-20%)
- M_n is biased towards the low molecular weight fraction
- M_w is biased towards the higher molecular weight fraction
- M_w/M_n (= *Đ = dispersity*) depends on the breadth of the distribution curve and is used as a measure of chain length heterogeneity

Measuring Molecular Weight Distributions

Gel Permeation Chromatography



Gel Permeation Chromatography

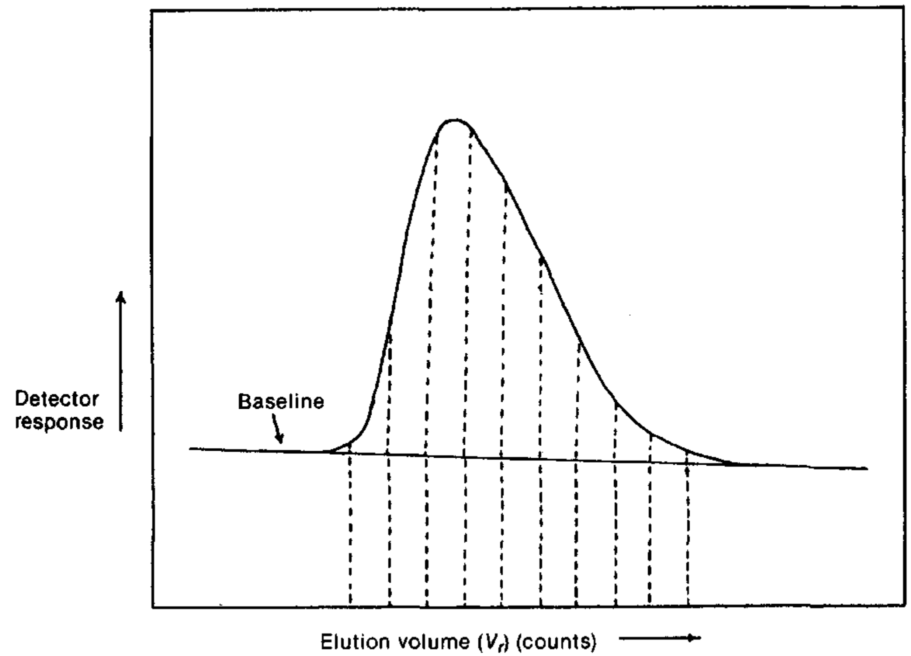


FIGURE 2.10. Typical gel permeation chromatogram. Dotted lines represent volume "counts."

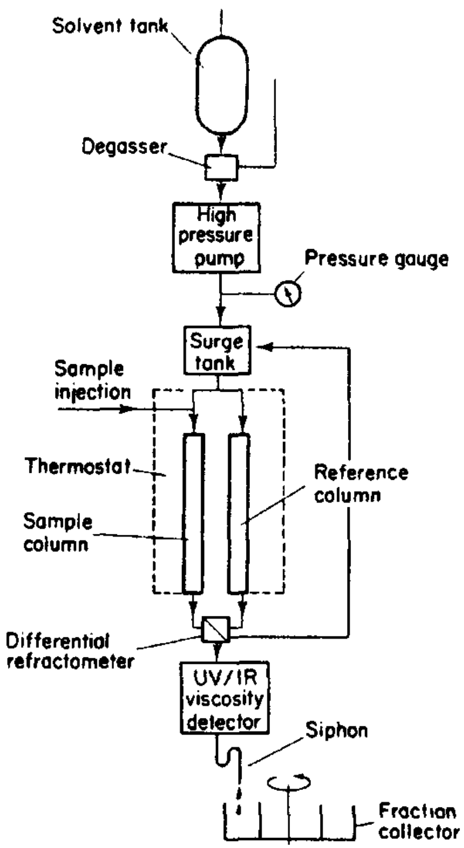


FIGURE 2.9. Schematic representation of a gel permeation chromatograph. [From Rabek,[9g] copyright 1980. Reprinted by permission of John Wiley & Sons, Ltd.]

Nomenclature of Polymers

Polymer nomenclature leaves much to be desired .....

Different nomenclature systems:

1. Nomenclature based on source
2. Nomenclature based on structure (non-IUPAC)
3. IUPAC structure-based nomenclature system
4. Tradenames and nonnames

Nomenclature based on Source

- Polymers synthesized from a single monomer as in addition and ring-opening polymerizations
- Prefix „poly“ + name of the monomer without a space or hyphen

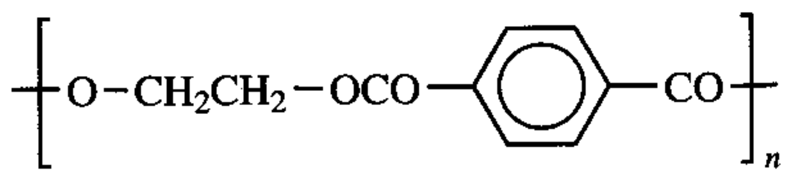
ethylene	→	polyethylene	
acetaldehyde	→	polyacetaldehyde	
3-methyl-1-pentene	→	poly(3-methyl-1-pentene)	Multiworded names or abnormally long names
vinyl chloride	→	poly(vinyl chloride)	
propylene oxide	→	poly(propylene oxide)	
chlorotrifluoroethylene	→	poly(chlorotrifluoroethylene)	
ε-caprolactam	→	poly(ε-caprolactam)	

Nomenclature based on structure (non-IUPAC)

- Polymers synthesized from two different monomers
- Prefix „poly" followed without a space or hyphen by parentheses enclosing the name of the structural group attached to the parent compound (= ester amide, urethane, etc.)

Poly(hexamethylene sebacamide)

IV



Poly(ethylene terephthalate)

V

Poly(trimethylene ethyleneurethane)

VI

IUPAC Structure-based Nomenclature System

- Single-strand organic polymers
- Based on the selection of a preferred constitutional repeating unit (CRU)
- The CRU (also referred to as structural repeating unit) is the smallest possible repeating unit of the polymer
- Polymer name = poly(CRU) or poly[CRU]

IUPAC rules for naming single-strand organic polymers:

1. The name of a polymer is the prefix *poly* followed in parentheses or brackets by the name of the CRU. The CRU is named by naming its subunits. Subunits are defined as the largest subunits that can be named by the IPUAC rules for small organic compounds.

2. The CRU is written from left to right beginning with the subunit of highest seniority and proceeding in the direction involving the shortest route to the subunit next in seniority.

3. The seniority of different types of subunits is heterocyclic rings > heteroatoms or acyclic subunits containing heteroatoms > carbocyclic rings > acyclic subunits containing only carbon. The presence of various types of atoms, groups of atoms, or rings that are not part of the main polymer chain but are substituents on the CRU do not affect this order of seniority.

4. For heterocyclic rings the seniority is a ring system having nitrogen in the ring > a ring system having a heteroatom other than nitrogen in the order of seniority defined by rule 5 below > a ring system having the greatest number of heteroatoms > a ring system having the largest individual ring > a ring system having the greatest variety of heteroatoms > a ring system having the greatest number of heteroatoms highest in the order given in rule 5.

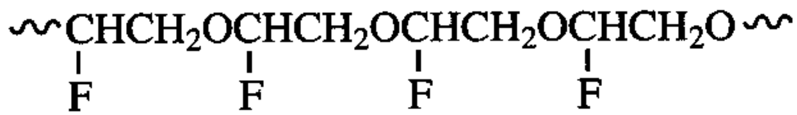
5. For heteroatom(s) or acyclic subunits containing heteroatom(s), the order of decreasing priority is O, S, Se, Te, N, P, As, Sb, Bi, Si, Ge, Sn, Pb, B, Hg. (Any heteroatom has higher seniority than carbon—rule 3.) The seniority of other heteroatoms within this order is determined from their positions in the periodic table.

6. For carbocyclic rings the seniority is a ring system having the greatest number of rings > the ring system having the largest individual ring > the ring system having the greatest number of atoms common to its rings.

7. For a given carbocyclic or heterocyclic ring system: (a) when rings differ only in degree of unsaturation, seniority increases with degree of unsaturation; (b) for the same ring system, seniority is higher for the ring system having the lowest location number (referred to as *locant*), which designates the first point of difference for ring junctions.

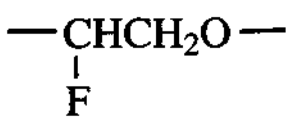
8. These orders of seniority are superseded by the requirement of minimizing the number of free valences in the CRU, that is, the CRU should be a bivalent unit wherever possible.

9. Where there is a choice subunits should be oriented so that the lowest locant results for substituents.

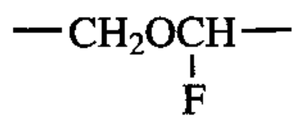


VIII

the possible CRUs are

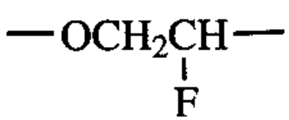


IX



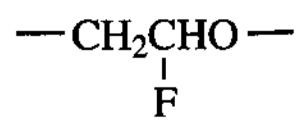
X

XI



XII

XIII



XIV

XI: poly[oxy(1-fluoroethylene)]
XII: poly[oxy(2-fluoroethylene)]

Tradenames and nonnames

Nylon: Polyamides from unsubstituted, nonbranched aliphatic monomers

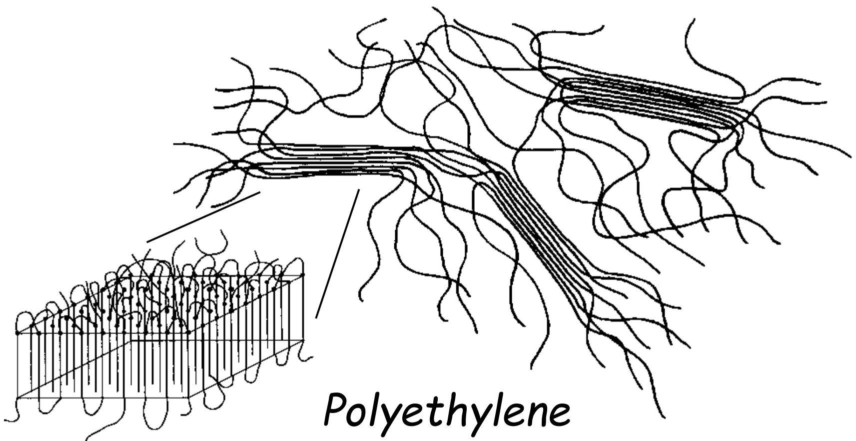
nylon 6,6	poly(hexamethylene adipamide)
nylon 6,10	poly(hexamethylene sebacamide)

first number: number of methylene groups in diamine portion
second number: number of carbon atoms in diacyl portion

Polyamides from single monomers are denoted by a single number representing the number of carbon atoms in the repeating unit e.g. nylon 6, poly(ε-caprolactam) or poly(6-amino caproic acid)

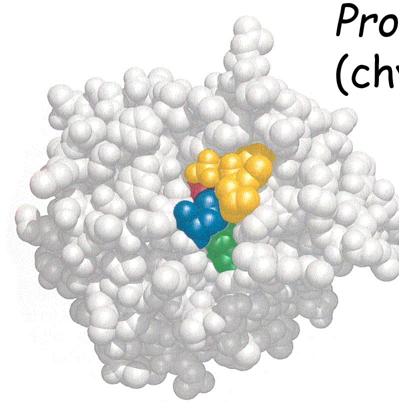
Summary

Synthetic Polymers



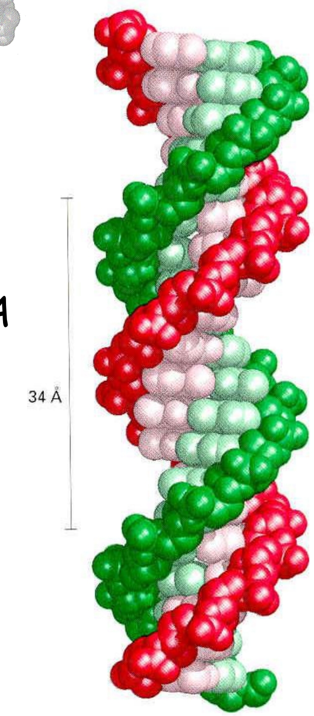
Polyethylene
(semi-crystalline)

Biological Polymers



Proteins
(chymotrypsin)

DNA



1. Classification of polymers
    - Chemical structure
    - Polymerization mechanism

2. Properties of polymer chains
    - Molecular weight

3. Nomenclature of polymers

Summary of Important Points

- Monomer; Polymerization; Polymer; Repeating unit; Degree of polymerization; Molecular weight

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- A polymer is classified as a **condensation polymer** if its synthesis involves the *elimination of small molecules*, or it contains *functional groups as part of the polymer main chain* or its *repeating unit lacks certain atoms* that are present in the hypothetical monomer it is made of.
- A polymer that does not fulfill any of these requirements is classified as an **addition polymer**.

- **Step polymerization**:
  - Reaction occurs between any of the different sized species present in the reaction system
  - Molecular weight increases relatively slowly with conversion

- **Chain polymerization**:
  - Monomer only reacts with the reactive center
  - Chain growth is very rapid
  - Monomer concentration decreases throughout the polymerization, while the number of high molecular weight polymer molecules increases
  - The molecular weight of the polymer is relatively independent on monomer conversion (compared to a step polymerization)

- Synthetic Polymers are Mixtures!

$$\overline{M}_n = \frac{w}{\sum N_x} = \frac{\sum N_x M_x}{\sum N_x} = \sum \underline{N}_x M_x$$

$$\overline{M}_w = \sum w_x M_x = \frac{\sum c_x M_x}{\sum c_x} = \frac{\sum c_x M_x}{c} = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$
