Introduction to Polymers

16:160:509 – Polymer Chemistry

Lecture 1 & 2

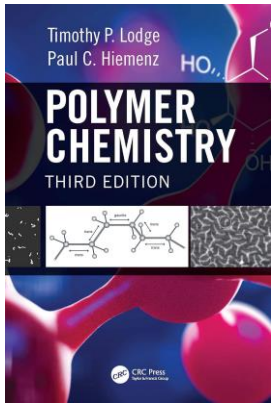
RUTGERS
School of Arts and Sciences
DEPARTMENT OF CHEMISTRY
AND CHEMICAL BIOLOGY

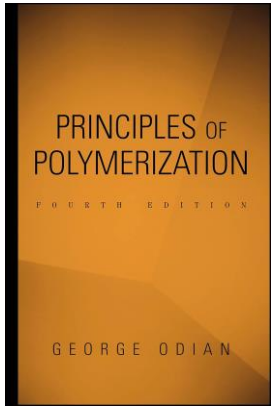
Course Logistics

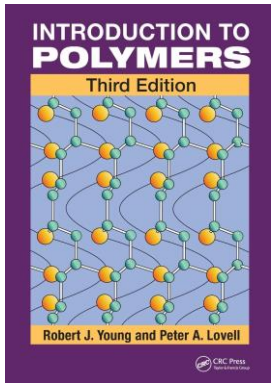
- **Grading:**
  1. Lecture Participation: 10%
  2. Midterm Exams 1 & 2: 50% (the higher score will count for 35% and the lower for 15%)
  3. Final Presentation: 40%
- **Final Presentation:** On October 14th, 20 papers will be posted on Canvas. These papers are selected from recent journals and cover a broad range of topics discussed in the course. You will need to choose one paper to give a 20-minute presentation during the final three classes of the semester.
- **Practice Problems:** There is no graded homework in this course, but practice problems and solutions will be posted periodically throughout the semester. These practice problems mirror what you should expect on the midterm exams.
- **Textbooks:**

1. *Polymer Chemistry* by Timothy P. Lodge, Paul C. Hiemenz, 3rd Edition (2020) (required)
2. *Principles of Polymerization* by George Odian, 4th Edition (2004) (required)
3. *Introduction to Polymers* by Robert J. Young, Peter A. Lovell, 3rd Edition (2011) (optional)

- **Office Hours:** Friday 1:00–2:00 pm (my office CCB 3202)







Course Schedule

Chemistry 409/509 Fall 2024 Course Schedule			
09/05 (Thu.)	Lecture 1	Introduction of Polymers I: History, Structural Isomerism	Lodge 1.1-1.6 Odian 1.1-1.3
09/09 (Mon.)	Lecture 2	Introduction of Polymers II: Properties, Molecular Weight Distribution, GPC	Lodge 1.7-1.10 Odian 1.4-1.6
09/12 (Thu.)	Lecture 3	Step-Growth Polymerization I: Introduction, MWD, Kinetics	Lodge 2.1-2.4, 2.8 Odian 2.1-2.7
09/16 (Mon.)	Lecture 4	Step-Growth Polymerization II: Process Conditions	Lodge 2.5-2.7 Odian 2.8, 2.14
09/19 (Thu.)	Lecture 5	Chain-Growth Radical Polymerization I: Introduction, Kinetics	Lodge 3.1-3.6 Odian 3.1-3.5
09/23 (Mon.)	Lecture 6	Chain-Growth Radical Polymerization II: MWD, Thermodynamics, Chain Transfer	Lodge 3.7-3.9, 4.7 Odian 3.6-3.12
09/26 (Thu.)	Lecture 7	Chain-Growth Radical Polymerization III: Process Conditions, Copolymerization	Lodge 5.1-5.3 Odian 3.13-3.14, 4.1-4.3
09/30 (Mon.)	Lecture 8	Chain-Growth Radical Polymerization IV: Copolymerization	Lodge 5.4-5.6 Odian 6.1-6.3
10/03 (Thu.)	Lecture 9	Controlled Polymerization I: Introduction, Poisson Distribution, Anionic Polymerization	Lodge 4.1-4.3 Odian 5.1, 5.3
10/07 (Mon.)	Lecture 10	Controlled Polymerization II: Anionic Polymerization, Cationic Polymerization	Lodge 4.3, 4.5 Odian 5.2, 5.3, 5.6
10/10 (Thu.)	Lecture 11	Controlled Polymerization III: Reversible Deactivation Radical Polymerization	Lodge 4.6 Odian 3.15
10/14 (Mon.)	Midterm Exam I (Lecture 1 through Lecture 10) (Paper choice for the final presentation will be posted after the lecture)		
10/17 (Thu.)	Lecture 12	Controlled Polymerization IV: Block Copolymer Synthesis	Lodge 4.4 Odian 5.4
10/21 (Mon.)	Lecture 13	Ring-Opening Polymerization I: Cyclic Ethers/Acetals, Lactams, NCA, Lactones (Choice of paper for the final presentation is due)	Lodge 4.8 Odian 7.1-7.3, 7.5
10/24 (Thu.)	Lecture 14	Ring-Opening Polymerization II: ROMP, Radical ROP, Inorganic Polymers	Lodge 4.8 Odian 7.4, 7.8-7.11
10/28 (Mon.)	Lecture 15	Stereochemistry of Polymerization I: Stereoregularity, Stereoregulation in Polymerization	Lodge 5.7-5.9 Odian 8.1-8.3
10/31 (Thu.)	Lecture 16	Stereochemistry of Polymerization II: Ziegler–Natta Polymerization, Metallocene Polymerization	Lodge 5.11-5.12 Odian 8.4-8.12
11/04 (Mon.)	Lecture 17	Polymer Topology I: Cyclic/Star/Bottlebrush Polymers, Surface Brushes	Lodge 4.4 Odian 9.9
11/07 (Thu.)	Lecture 18	Polymer Topology II: Crosslinked Polymer Networks	Lodge 10.1-10.2 Odian 9.2, 2.10-2.12
11/11 (Mon.)	Lecture 19	Polymer Topology III: Hyperbranched Polymers, Dendrimers	Lodge 4.9 Odian 2.16
11/14 (Thu.)	Lecture 20	Special Topic I: Semiconducting Polymers	
11/18 (Mon.)	Midterm Exam II (Lecture 11 through Lecture 19)		
11/21 (Thu.)	Lecture 21	Special Topic II: Synthesis of Biopolymers	
11/25 (Mon.)	Lecture 22	Special Topic III: Polymeric Biomaterials	
11/26 (Tue.) (Thu. Classes)	Lecture 23	Special Topic IV: Polymer Sustainability	
12/02 (Mon.)	Final Presentation of Literature by Students		
12/05 (Thu.)	Final Presentation of Literature by Students		
12/09 (Mon.)	Final Presentation of Literature by Students		

Prerequisites

Organic Chemistry:

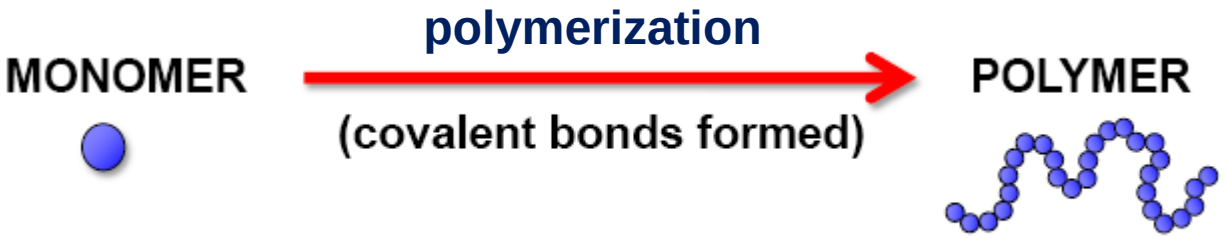
- Basic Nomenclature
- Resonance Structures and Arrow Pushing
- Nucleophiles and Electrophiles
- Reaction Energy Landscape
- Stereochemistry and Chirality
- Major Types of Reactive Intermediates: Carbanions, Carbocations, Free Radicals
- Nucleophilic Substitution/Addition of Carbonyl Compounds
- Conjugate Addition

Physical Chemistry:

- Basic Definitions of Enthalpy and Entropy
- Expression of Gibbs Free Energy
- Chemical Equilibrium and Equilibrium Constant
- Arrhenius Equation
- Chemical Kinetics: Rate and Reaction Order
- Rate Equations (including the integral forms for simple zero-, first-, second-, and third-order kinetics)

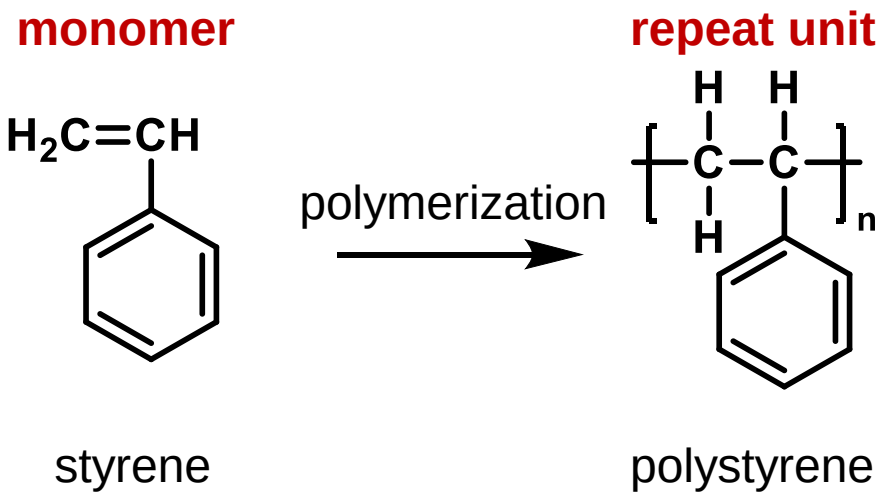
What Is a Polymer?

Definition: Many units of monomers (or repeating units) covalently bonded together to form a long chain.



From the Greek words:
'poly' meaning 'many'
'mers' meaning 'parts'

In chemistry literature, the words 'polymer' and 'macromolecule' are often used interchangeably.



n: degree of polymerization (DP)

Calculate the molar mass of a polystyrene molecule with a DP of 150.

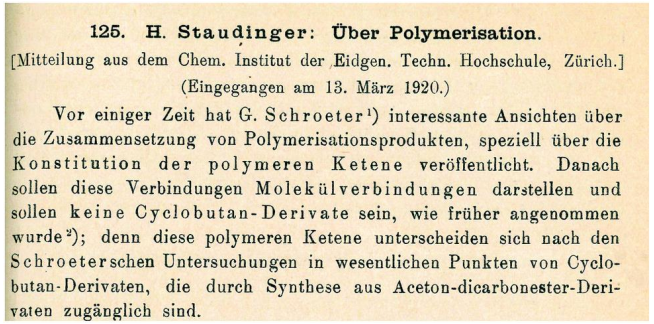
M_0 (molar mass of repeat unit) = 104 g/mol

$M = M_0 \times n = 104 \times 150 = 15600$ g/mol

A Brief History of Polymer Science/Technology

- 1839 Vulcanization of natural rubber (Goodyear)
- 1868 Celluloid – made by nitration of cellulose
- 1907 Bakelite – first truly synthetic polymer invented by Baekeland

Herman Staudinger
1953 Nobel Prize



125. H. Staudinger: Über Polymerisation.

[Mitteilung aus dem Chem. Institut der Eidgen. Techn. Hochschule, Zürich.]

(Eingegangen am 13. März 1920.)

Vor einiger Zeit hat G. Schroeter[1]) interessante Ansichten über die Zusammensetzung von Polymerisationsprodukten, speziell über die Konstitution der polymeren Ketene veröffentlicht. Danach sollen diese Verbindungen Molekülverbindungen darstellen und sollen keine Cyclobutan-Derivate sein, wie früher angenommen wurde[2]); denn diese polymeren Ketene unterscheiden sich nach den Schroeterschen Untersuchungen in wesentlichen Punkten von Cyclobutan-Derivaten, die durch Synthese aus Aceton-dicarbonester-Derivaten zugänglich sind.

Macromolecular hypothesis

Wallace Carothers

Inventor of Nylon

- 1920 Staudinger – first to recognize the long-chain nature of polymers
- 1929 Carothers – invented condensation (or step) polymerization
- 1935 Nylon was synthesized by Carothers at DuPont and achieved great commercial success shortly afterward

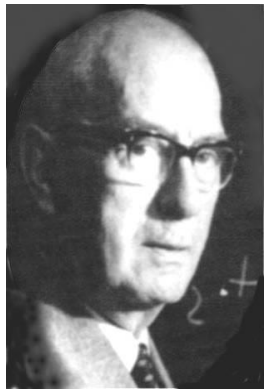
A Brief History of Polymer Science/Technology

- 1937 Synthesis of polystyrene by Dow Chemical
- 1939 Commercial production of polyethylene by Imperial Chemical Industries
- 1940-50 P. J. Flory introduced a statistical approach to describe polymerization kinetics

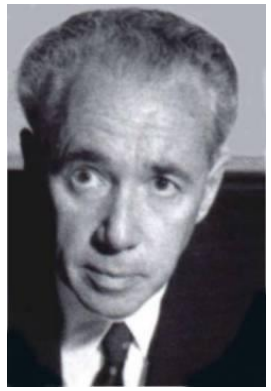
Paul J. Flory

Physical chemistry of macromolecules

1974 Nobel Prize



Karl Ziegler



Giulio Natta

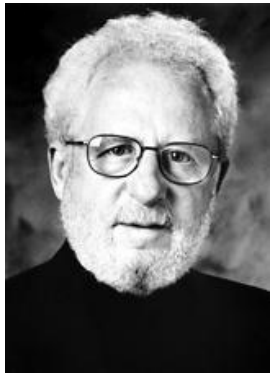
Coordination polymerization

1963 Nobel Prize

- 1953-60 Karl Ziegler and Giulio Natta: coordination polymerization
- 1955-60 Michael Szwarc proposed the idea of living polymerization and demonstrated it using anionic polymerization

A Brief History of Polymer Science/Technology

- 1960's Development of gel permeation chromatography (GPC)
- 1966 Stephanie Kwolek invented Kevlar at DuPont
- 1977 Hideki Shirakawa, Alan Heeger, and Alan MacDiarmid discovered conductive polymers



Conductive polymer

2000 Nobel Prize

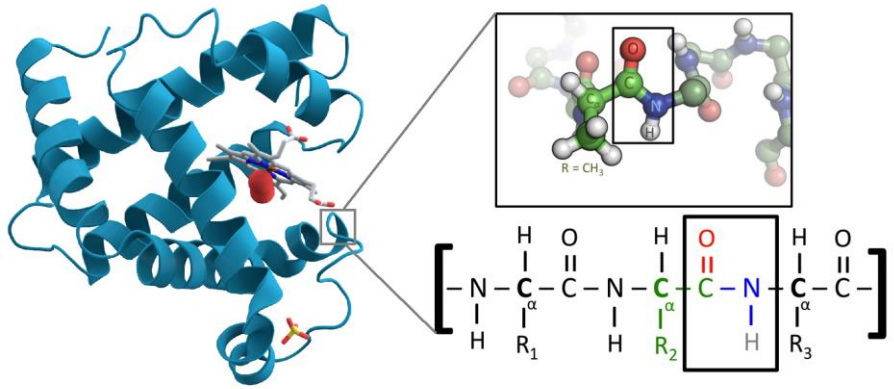
Olefin metathesis

2005 Nobel Prize

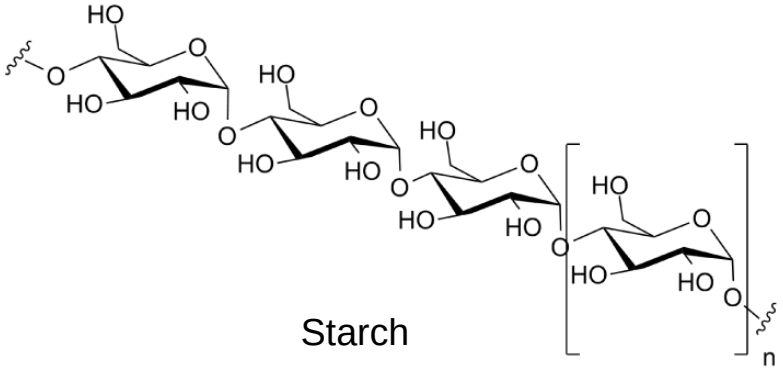
Alan Heeger Alan MacDiarmid Hideki Shirakawa **Robert Grubbs Richard Schrock**

- 1977 Frank Davis developed PEGylation to extend blood life of proteins
- 1980-2000 Development of new living polymerization methods based on cationic, free radical, and olefin metathesis polymerization
- 1990's - present Many specialty (high value) applications developed for polymers

Natural Polymer Materials

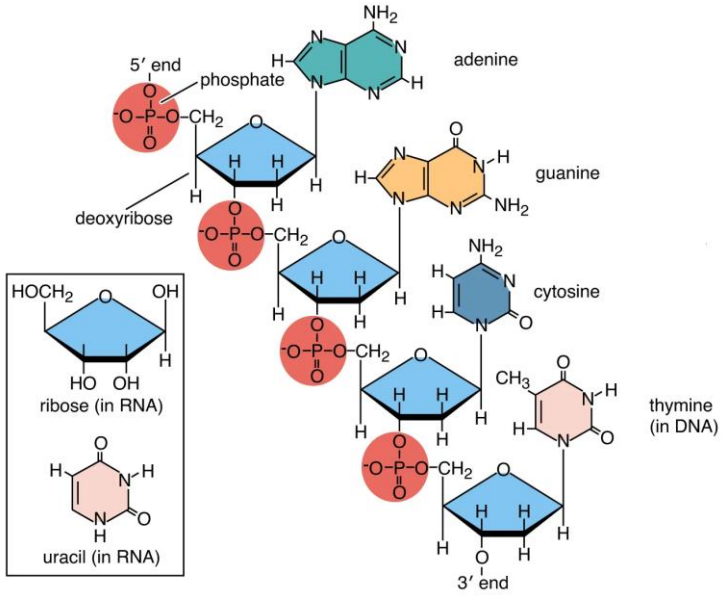


Proteins



Starch

Carbohydrates



Nucleic acids

Silk

Hides

Wood

Latex

Shells

Muscles

Synthetic Polymers Are Ubiquitous in Modern Society

Packaging materials

Containers

Appliances

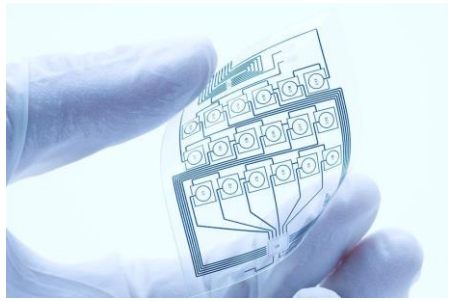
Furniture

Automobile parts

Paint

Coating

Rubber tires



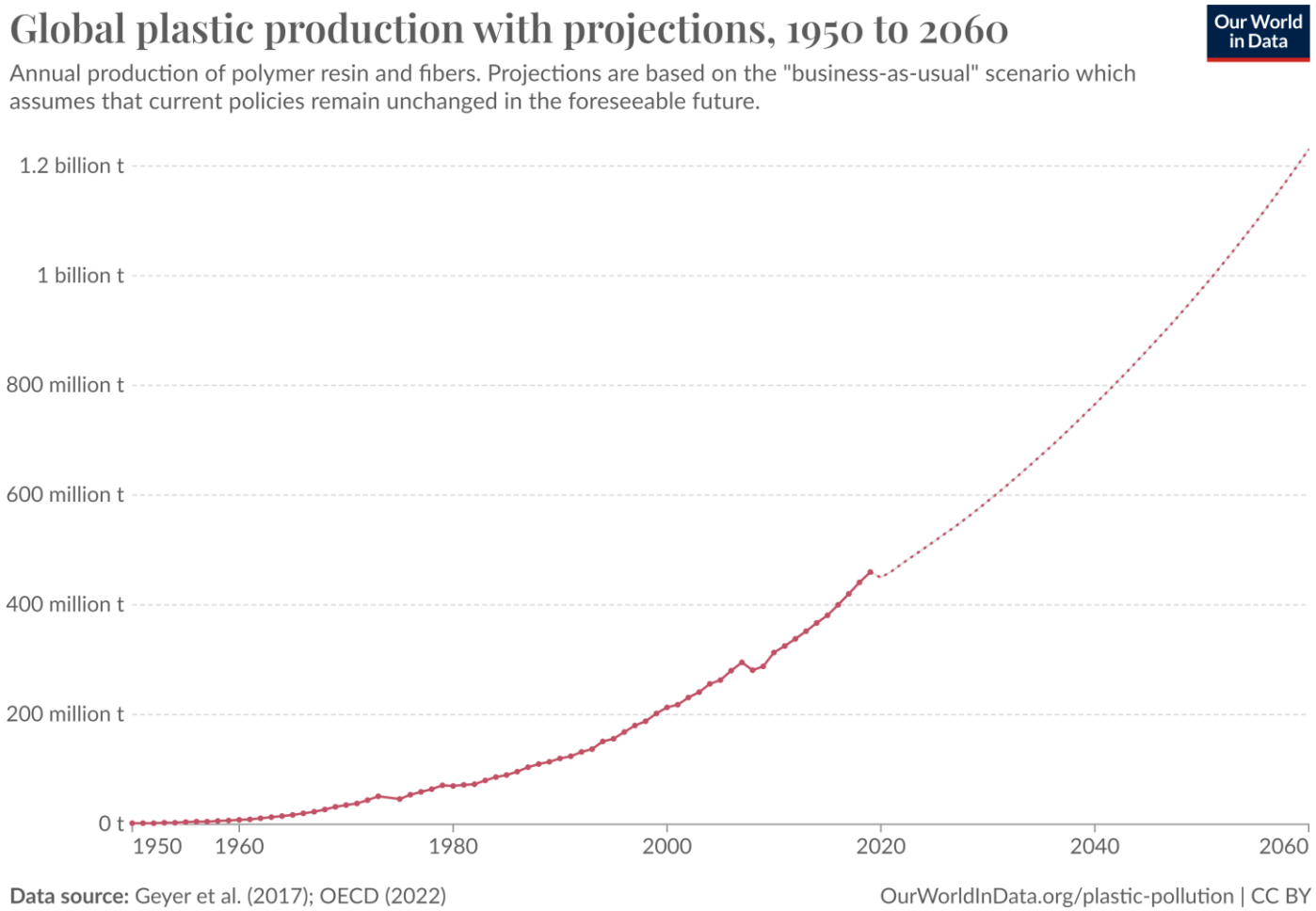
Flexible electronics

Fabrics

Pipes

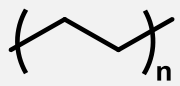
Lubricant

Why Do We Study Polymer Chemistry?

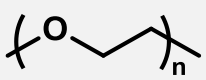


- The annual production of polymers is 400 million tons, significantly surpassing the combined output of all other synthetic chemicals.
- Over 60% of industrial chemists are engaged in polymer-related projects.
- Polymers continue to find applications far beyond commodity products, such as in photolithography for chip production, drug carriers, medical implants, and flexible electronics.
- As the world demands a more sustainable future for the polymer industry, numerous opportunities emerge at the chemistry level to benefit future generations.

Chemical Structures Dictate the Properties of Polymers



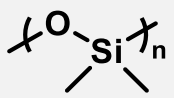
Polyethylene (PE)



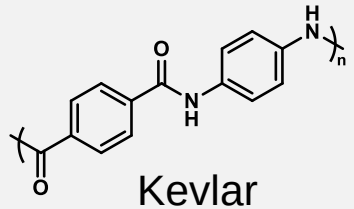
Polyethylene glycol (PEG)

Hydrophobic

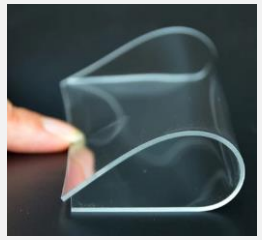
Water-soluble



Polydimethylsiloxane (PDMS)

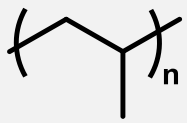


Kevlar

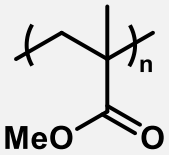


Soft and flexible

Bulletproof



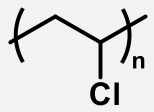
Polypropylene (PP)



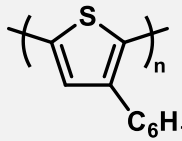
Poly(methyl methacrylate) (PMMA)

Highly opaque

Transparent (“acrylic glass”)

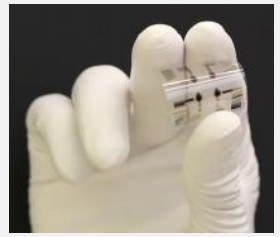


Polyvinyl chloride (PVC)



Poly(3-hexylthiophene) (P3HT)

Insulating



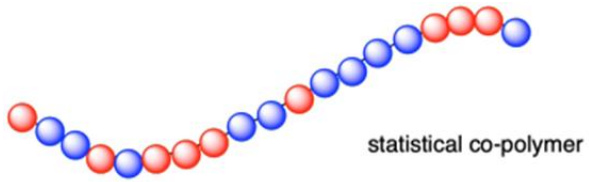
Semiconducting

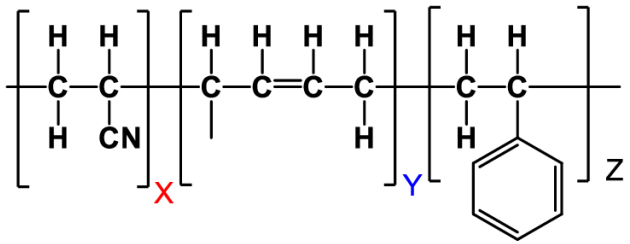
Copolymers

Among synthetic polymers, those with a single kind of repeat unit are called **homopolymers**, and those containing at least two kinds of *repeat unit* are **copolymers**.

Statistical Copolymers

–AAABABAABBABBB–

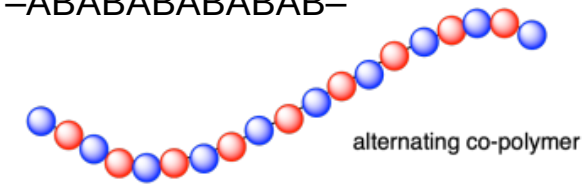


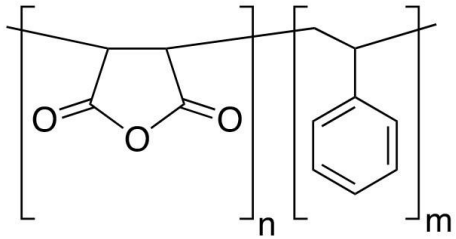


Acrylonitrile butadiene styrene (ABS)

Alternating Copolymers

–ABABABABABAB–

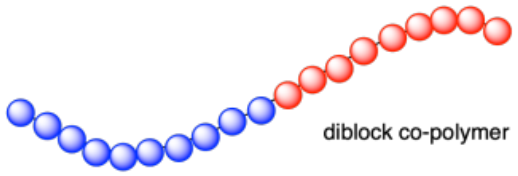


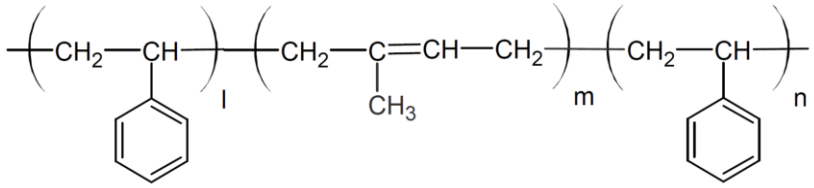


Styrene maleic anhydride (SMA)

Block Copolymers

–AAAAAAAAAAAABBBBBBBBBB–

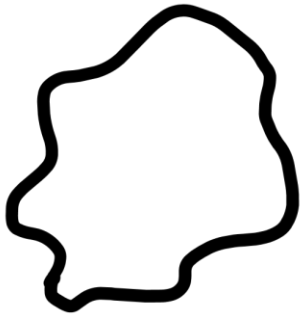




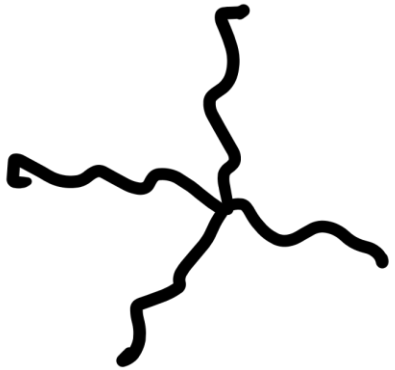
Styrene-isoprene-styrene (SIS)

Polymer Architecture (Topology)

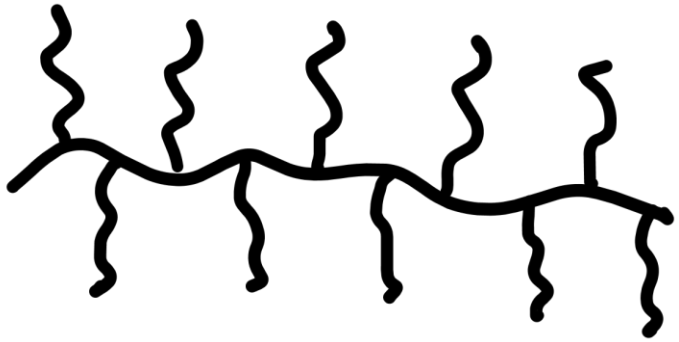
Linear polymer



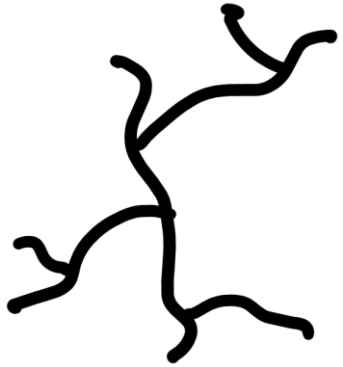
Cyclic polymer



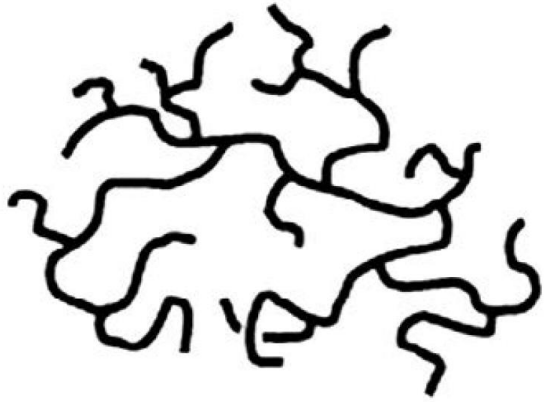
Star polymer



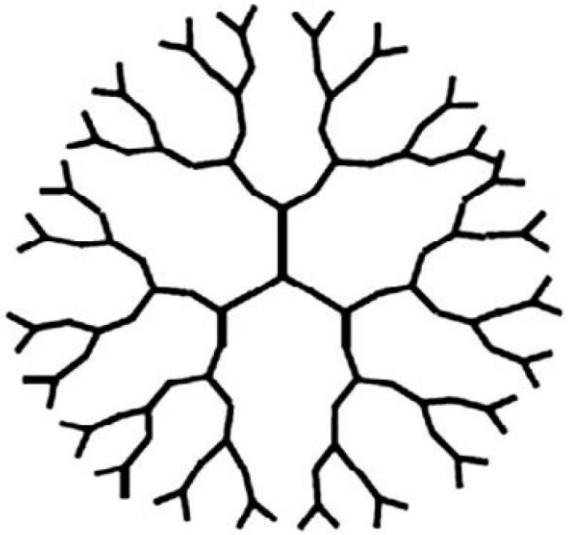
Bottlebrush polymer



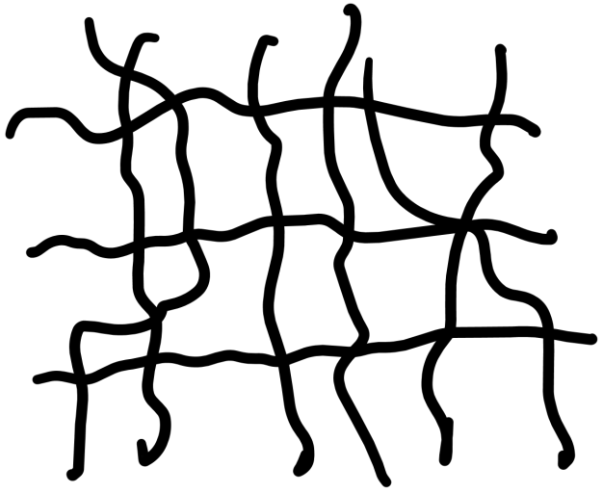
Branched polymer



Hyperbranched polymer



Dendrimer

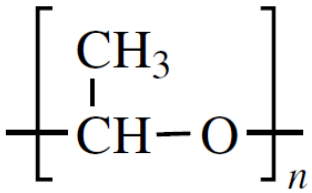


Crosslinked network

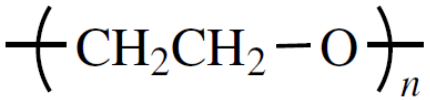
Structural Isomerism

1. Constitutional isomerism

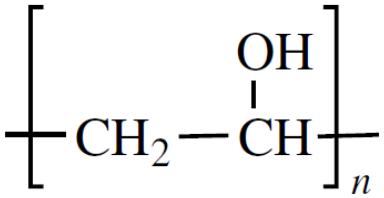
Polymers have the same overall chemical composition (i.e., same molecular formula) but differ in connectivity.



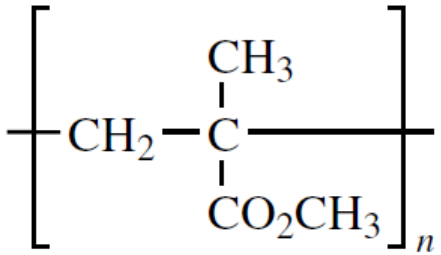
Polyacetaldehyde



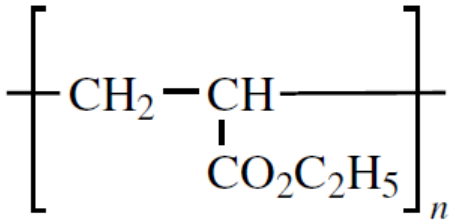
Poly(ethylene oxide)



Poly(vinyl alcohol)



Poly (methyl methacrylate)

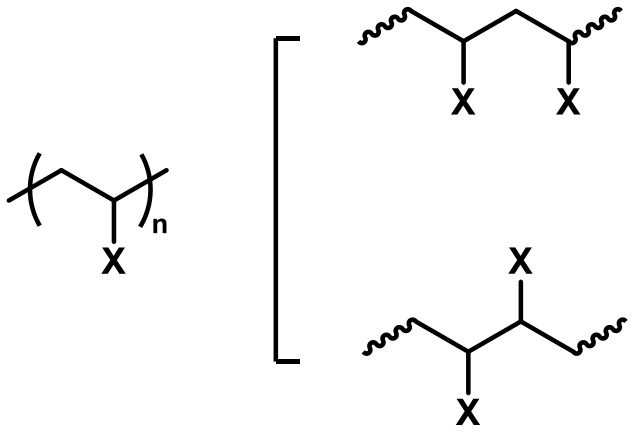


Poly (ethyl acrylate)

Structural Isomerism

2. Positional isomerism

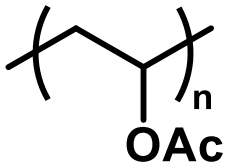
The relative positions of substituents along the polymer backbone may differ.



head-to-tail (HT)

head-to-head (HH)

Head-to-tail placement is usually the predominant mode in synthetic polymers due to the underlying chemical mechanisms, as we will see later.

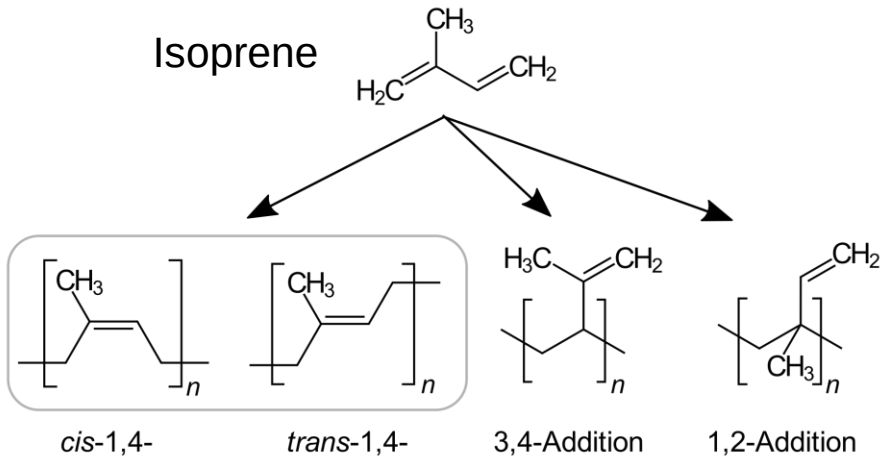


>98–99% repeat units in polyvinyl acetate (PVAc) exist in HT placement

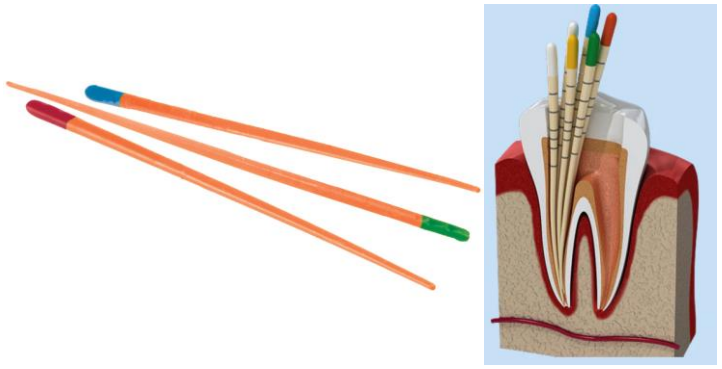
Structural Isomerism

3. Geometrical isomerism

Monomers with two polymerizable groups can yield isomeric polymers if one or the other of the alternate polymerization routes is favored.



Natural Rubber (*cis*-1,4-)



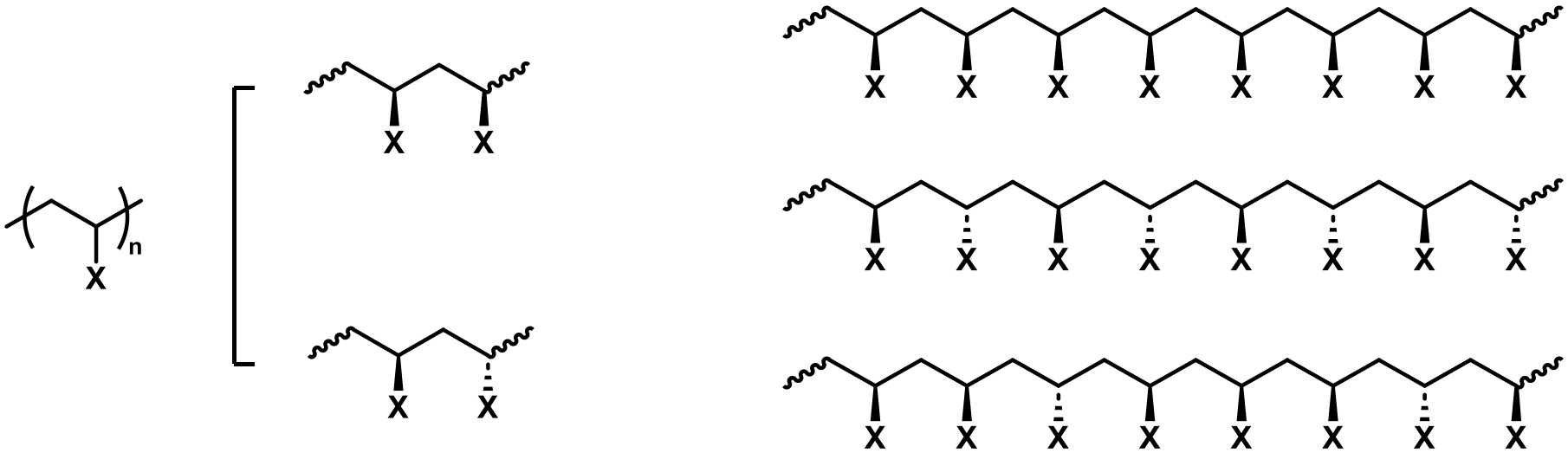
Gutta Percha (*trans*-1,4-)

The physical properties of polyisoprene highly depend on the double bond geometry.

Structural Isomerism

4. Stereo isomerism

Polymers that differ in the configuration of stereogenic centers



- Amorphous (cannot crystallize)
- Very gooey and waxy
- No commercial application

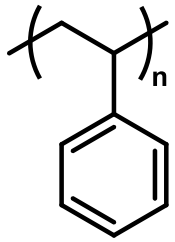
Atactic polypropylene

- Semi-crystalline
- Superior properties
- 74 million tonnes annually

Isotactic polypropylene

Synthetic Polymers Are Heterogeneous

Suppose you have just ordered 10 tonnes of polystyrene. By some miracle, all the polymers in the sample you received have M = 50,000 g/mol (which is on the lower end of polystyrene available commercially). Assuming each stereogenic center has no effect on the configuration of the other stereogenic centers on the chain, what are the chances that any two molecules in this sample have exactly the same chemical structure?



Polystyrene (PS)

Molar mass of each repeat unit: 104 g/mol

Each chain has $\frac{50{,}000}{104} \approx 480$ repeat units

Each stereogenic center on the chain has 50% chance to be R, and 50% chance to be S. The total # of possible configuration is $2^{480} \approx 3 \times 10^{144}$.

The total # of molecules in your sample is $\frac{10 \times 10^3 \times 10^3}{50{,}000} \times 6.02 \times 10^{23} \approx 1.2 \times 10^{26}$

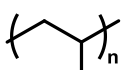
Clearly, there is essentially no chance that any two molecules have the identical structure, even without taking other factors into account (e.g., positional isomerism, molecular weight distribution).

Glass Transition and Chain Flexibility

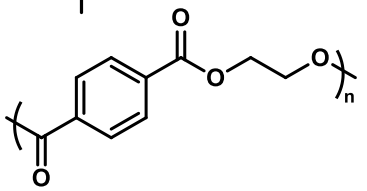
Polymer chains are flexible even in bulk, but the chain/segmental motion becomes slower as temperature decreases. At a certain temperature (i.e., the glass-transition temperature T_g), segmental motion ceases and chains become "frozen". This is reflected macroscopically as the material transitions from a viscous, "rubbery" state to a hard, "glassy" state when it is cooled. T_g is highly correlated with the flexibility of polymer backbones.

Polymer	T_g (°C)
Poly(dimethylsiloxane)	–123
Polyethylene	–120
1,4-Polybutadiene (*cis*)	–112
Polyisobutylene	–75
1,4-Polyisoprene (*cis*)	–70
Poly(ethylene oxide)	–70
Polypropylene	–10
Poly(vinyl acetate)	30
Poly(hexamethylene adipamide)	50
Poly(ethylene terephthalate)	70
Poly(vinyl alcohol)	90
Poly(vinyl chloride)	90
Polystyrene	100
Poly(methyl methacrylate)	110
Poly(tetrafluoroethylene)	130
Polycarbonate of bisphenol A	150
Poly(oxy-2,6-dimethyl-1,4-phenylene)	210
Poly(*p*-phenylene terephthalamide)	240

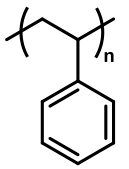
PE



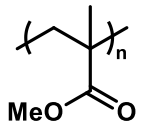
PP



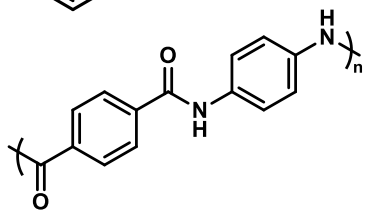
PET



PS



PMMA



Kevlar

Polymer Crystallinity and Chain Packing

- Polymers with regular or stereoregular structures may crystallize by packing their chains periodically by cooling the sample to a certain temperature (i.e., the melting temperature T_m).
- Polymers that cannot crystallize are called "amorphous".
- Unlike small molecules, a bulk polymer sample never becomes 100% crystalline. Therefore, such polymers are considered semi-crystalline, with crystalline domains interspersed with amorphous regions. For example, the degree of crystallinity in industrial polypropylene ranges from 30% to 60%.

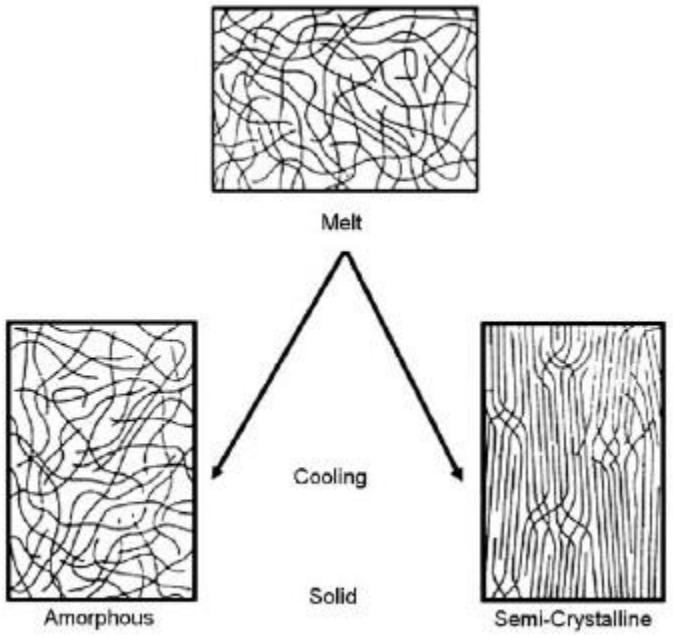
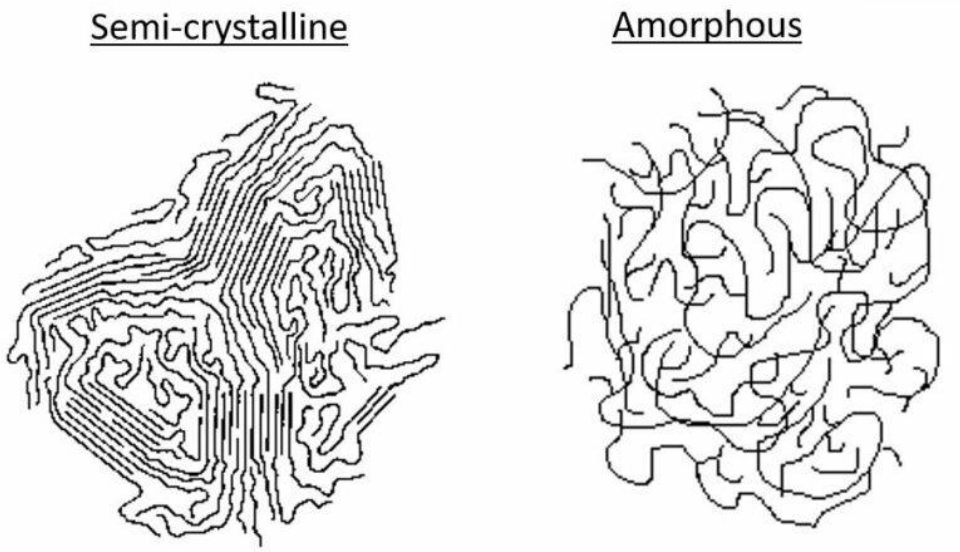
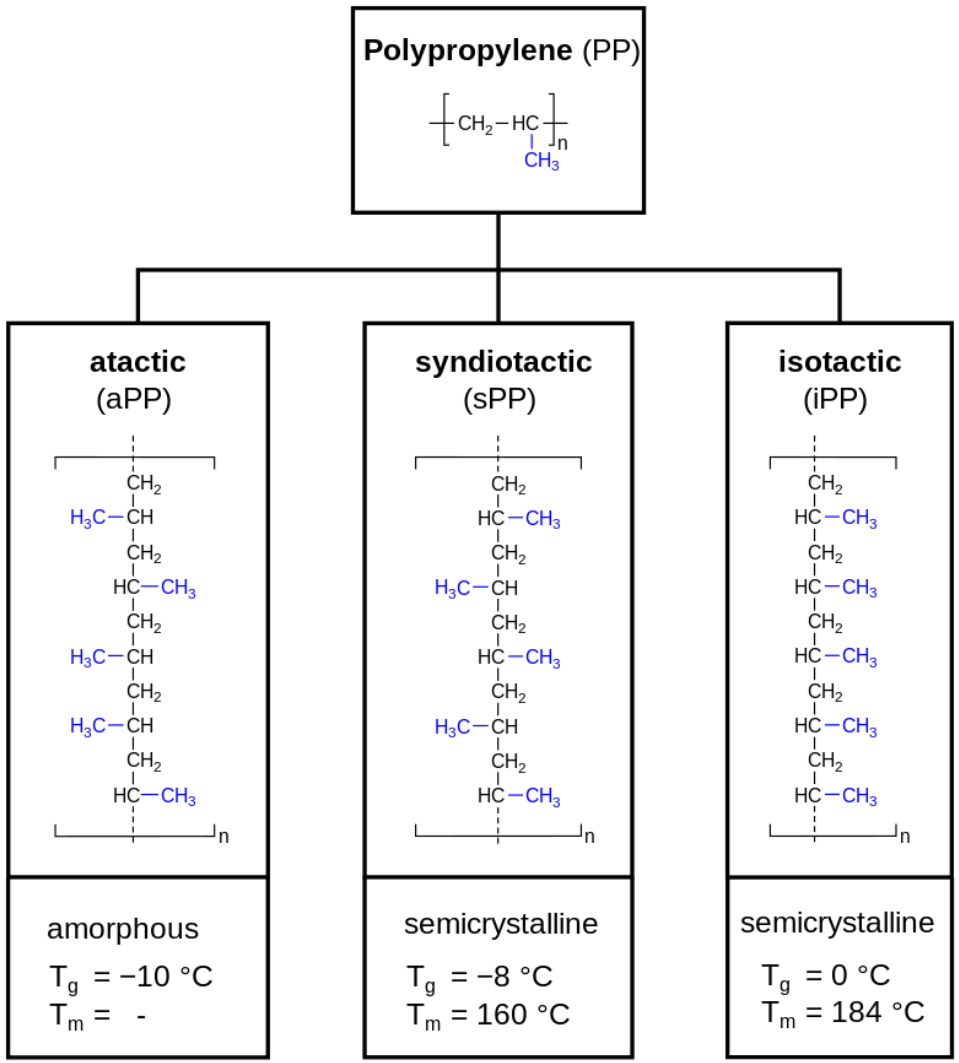


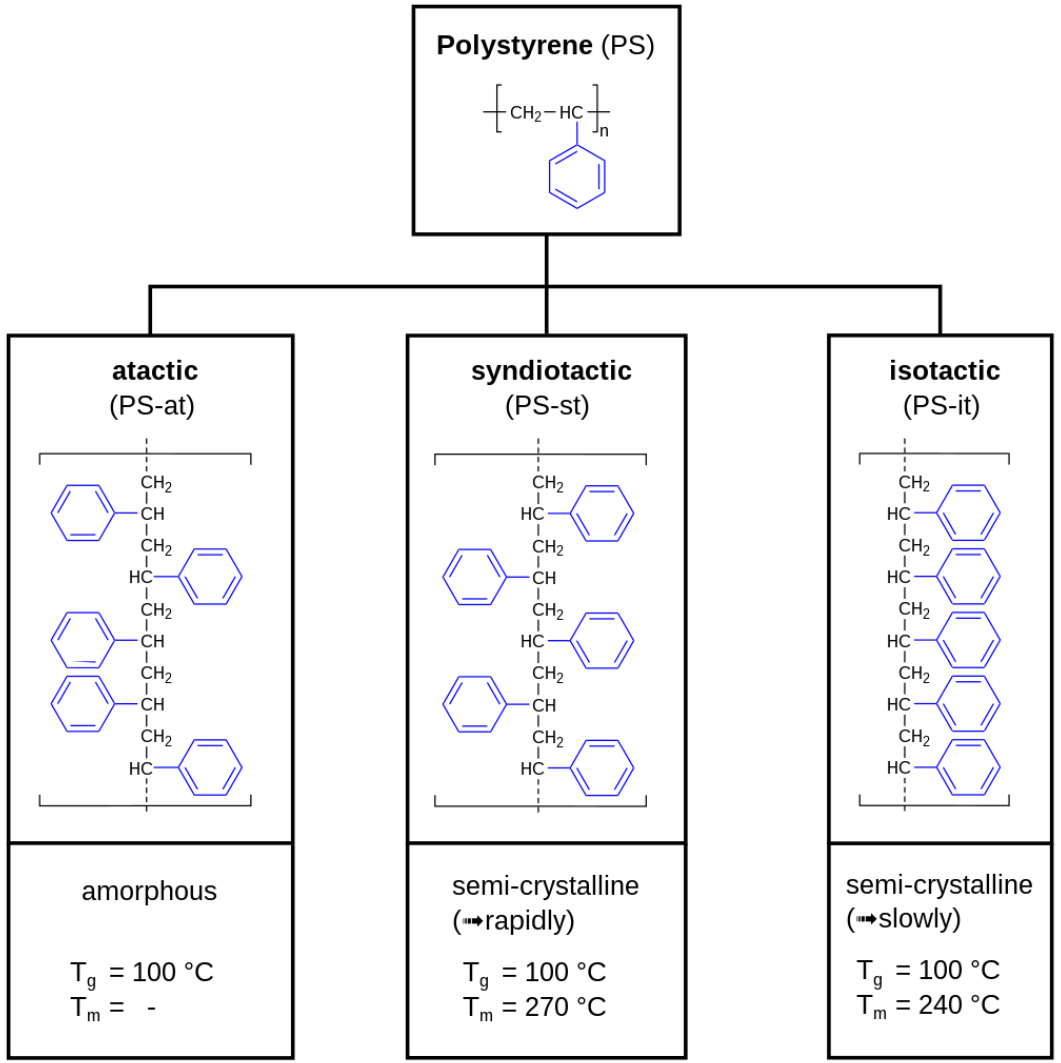
Figure 3.4 Cooling behaviour of materials



Polymer Crystallinity and Chain Packing



This one is used in everyday products



This one is used in everyday products

Classification of Polymers Based on Processing Behavior

Thermoplastic polymers: **Hard** $\underset{\text{cool}}{\overset{\text{heat}}{\rightleftharpoons}}$ **Soft**

Thermoplastic polymers are *melt-processable* above its T_g (amorphous) or T_m (semicrystalline)

This is a physical + reversible change

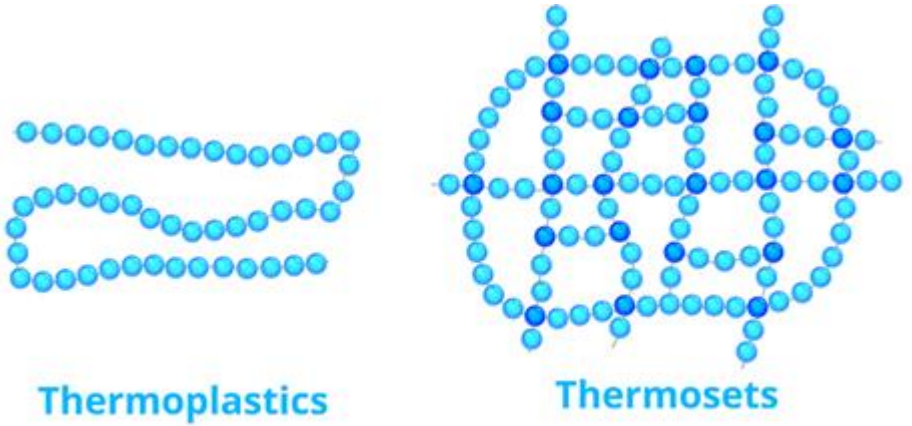
polystyrene, polyethylene, polypropylene, poly(vinyl chloride), etc.

Thermoset polymers: **Soft** $\xrightarrow{\text{curing}}$ **Hard**

Thermoset polymers become hard and rigid on heating due to inter-chain cross-linking reactions (known as “curing”).

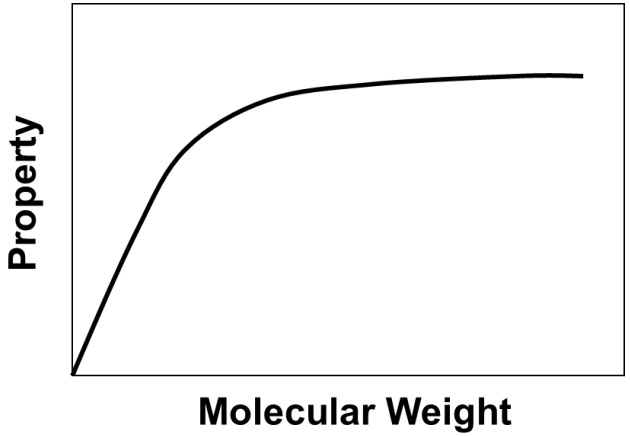
This is a chemical, irreversible change

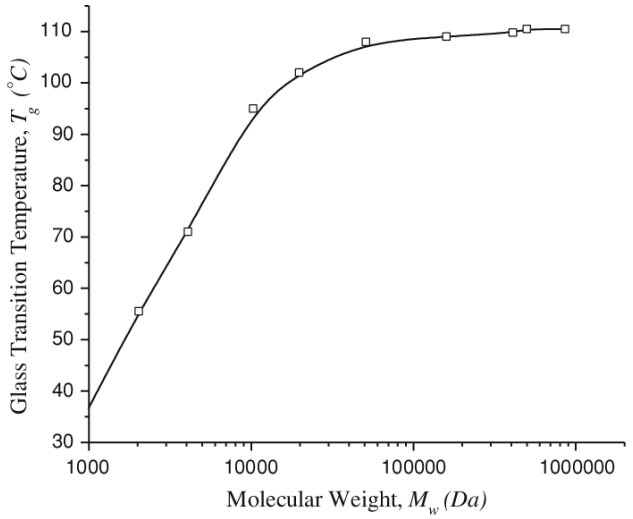
epoxy resins, phenol-formaldehyde resins (Bakelite), synthetic rubber, etc.

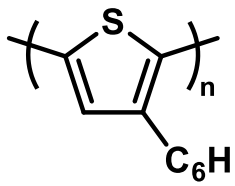


How Big Is Big?

We often say that polymers have high molecular weights, but how large does a molecule need to be to qualify as a polymer?

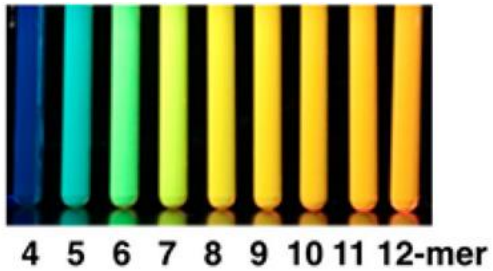




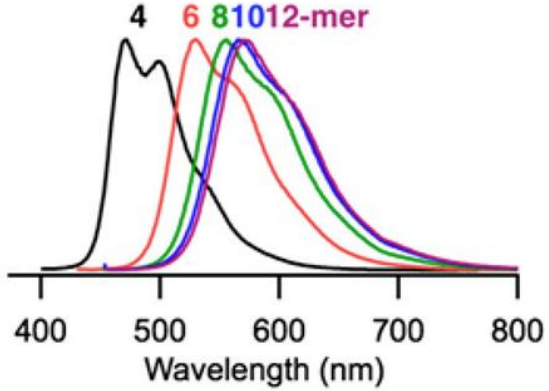


M_0 = 166

Poly(3-hexylthiophene)
(P3HT)



"oligomer"



It is hard to define a definitive molecular weight cutoff for polymers, but many people (especially academic chemists) agree that M = 1000 is a reasonable cutoff for polymers.

Lawrence, J.; Goto, E.; Ren, J. M.; McDearmon, B.; Kim, D. S.; Ochiai, Y.; Clark, P. G.; Laitar, D.; Higashihara, T.; Hawker, C. J., *J. Am. Chem. Soc.* **2017,** *139*, 13735-13739.

Molecular Weight Average

Almost every synthetic polymer sample contains molecules with various degrees of polymerization (i.e., polymer shows dispersity with respect to molecular weight). How should we describe the molecular weight of a specific polymer sample?

i-mer : a molecule with degree of polymerization i

n_i : the number of i-mers

Molar mass of i-mer : $M_i = i \cdot M_0$

Q1: If we choose a molecule at random from our sample, what is the probability of obtaining an i-mer?

Probability $x_i = \frac{n_i}{\sum n_i}$ => This probability is number (or mole) fraction of i-mer

Let's define an average molecular weight using this probability

number-average molecular weight $M_n = \sum M_i x_i = \frac{\sum n_i \cdot M_i}{\sum n_i} = M_0 \cdot \frac{\sum i \cdot n_i}{\sum n_i}$

Physical meaning of M_n: If we choose a molecule at random from our sample, what is its average molecular weight?

Molecular Weight Average

Q2: If we choose a repeat unit at random, what is the probability that the chosen repeat unit is from an i-mer?

- Suppose we have a 10-mer and a 20-mer.
- If we choose a **molecule** at random, there is a 50% chance we will get a 10-mer and a 50% chance we will get a 20-mer.
- If we choose a **repeat unit** at random, there is a 1/3 chance the chosen repeat unit will be from the 10-mer and a 2/3 chance the chosen repeat unit will be from the 20-mer.

Clearly, a different probability applies. We can calculate it as:

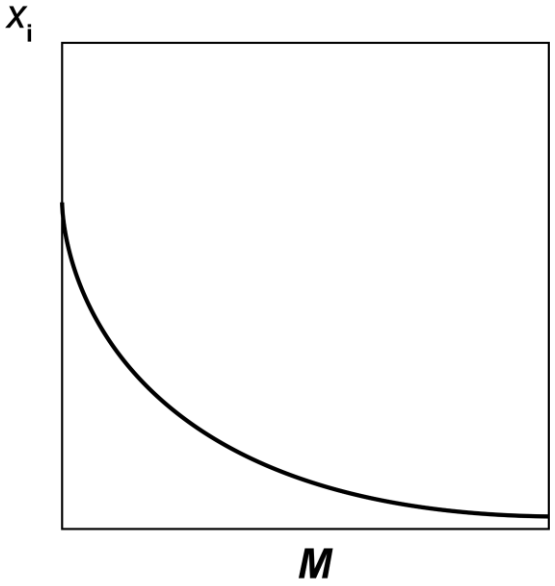
$w_i = \frac{i \cdot n_i}{\sum i \cdot n_i}$ => This probability is weight (or mass) fraction of i-mer

Let's define another average molecular weight using this probability

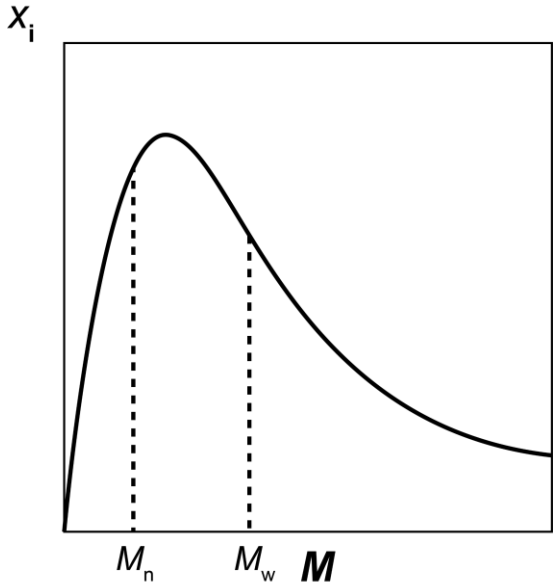
weight-average molecular weight $M_w = \sum M_i \cdot w_i = \frac{\sum i \cdot n_i \cdot M_i}{\sum i \cdot n_i} = M_0 \frac{\sum i^2 \cdot n_i}{\sum i \cdot n_i}$

Physical meaning of M_w: If we choose a repeat unit at random, what is the average molecular weight of the molecule containing that chosen repeat unit?

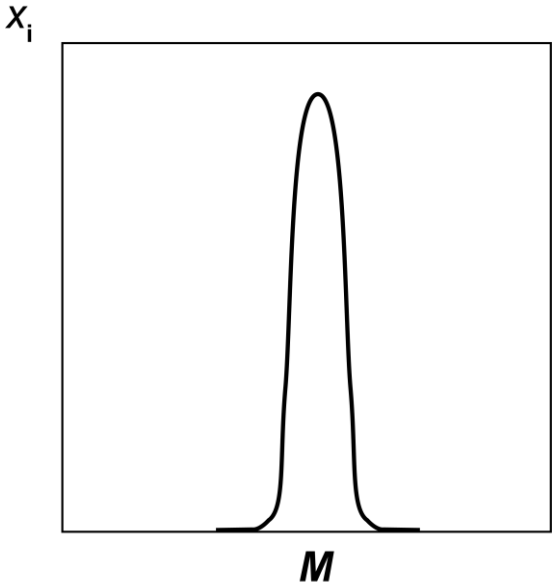
Molecular Weight Distribution



Step-growth polymerization



Free radical polymerization



Living polymerization

In statistics, we use the standard deviation σ to describe how dispersed the data is in relation to the mean. However, in polymer chemistry, we prefer to use dispersity $Đ$, which is defined as:

$$Đ = \frac{M_w}{M_n}$$

A larger $Đ$ indicates a wider distribution, while a smaller (closer to 1) $Đ$ indicates a narrower distribution. There is a simple mathematical relationship between $Đ$ and σ (see derivation on page 28 in Lodge).

$$\sigma = M_n \sqrt{Đ - 1}$$

An Example Distribution

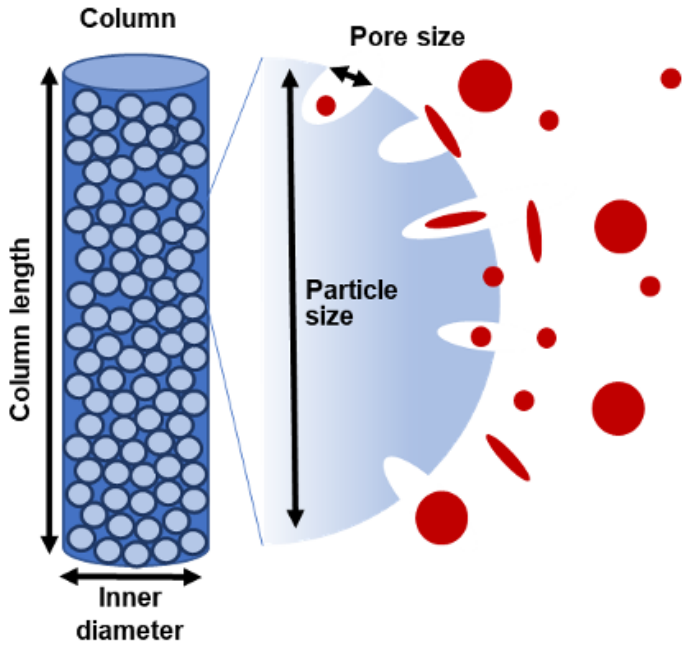
n_i (mol)	M_i (g/mol)	$M_i \cdot n_i$	$M_i^2 \cdot n_i$
0.003	10,000	30	300,000
0.008	12,000	96	1,152,000
0.011	14,000	154	2,156,000
0.017	16,000	272	4,352,000
0.009	18,000	162	2,916,000
0.001	20,000	20	400,000
$\Sigma = 0.049$		$\Sigma = 734$	$\Sigma = 11,276,000$

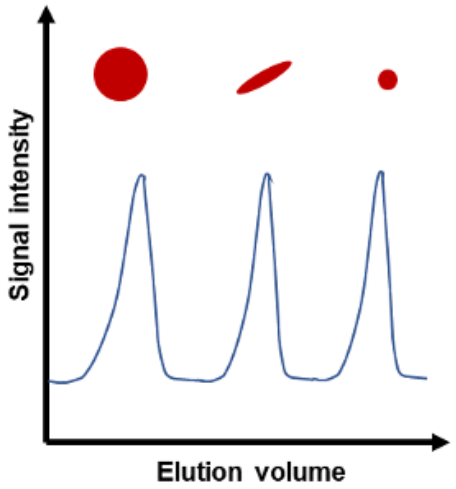
$$M_n = \frac{\sum n_i \cdot M_i}{\sum n_i} = \frac{734}{0.049} = 14,980 \text{ g/mol}$$

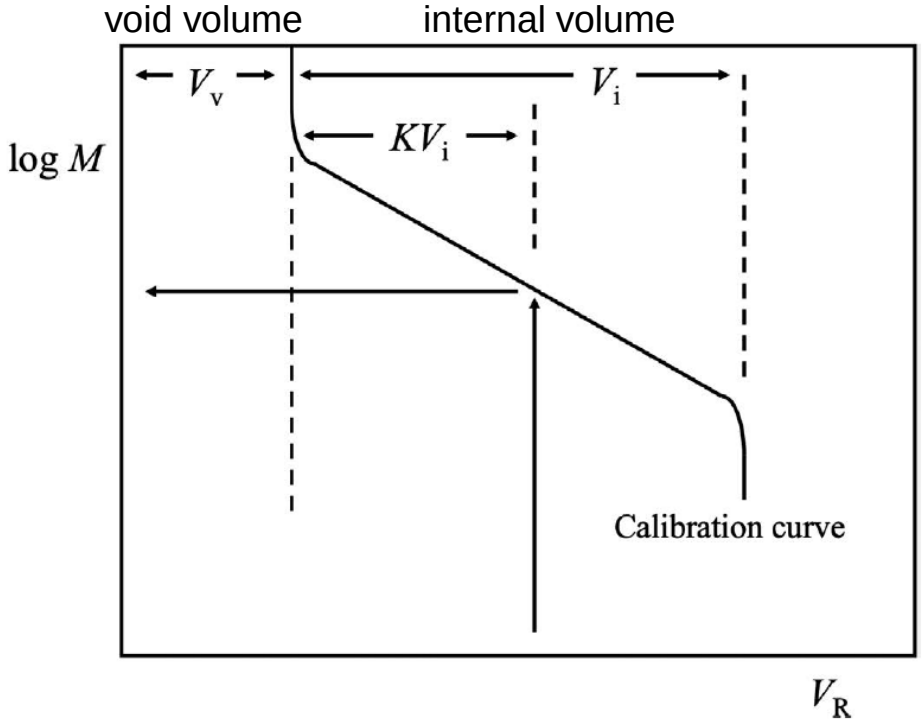
$$M_w = \frac{\sum i \cdot n_i \cdot M_i}{\sum i \cdot n_i} = \frac{\sum \frac{M_i}{M_{i=0}} \cdot n_i \cdot M_i}{\sum \frac{M_i}{M_{i=0}} \cdot n_i} = \frac{\sum M_i^2 \cdot n_i}{\sum M_i \cdot n_i} = \frac{11,276,000}{734} = 15,362 \text{ g/mol}$$

$$Đ = \frac{M_w}{M_n} = \frac{15,362}{14,980} = 1.026$$

Size Exclusion Chromatography (SEC)

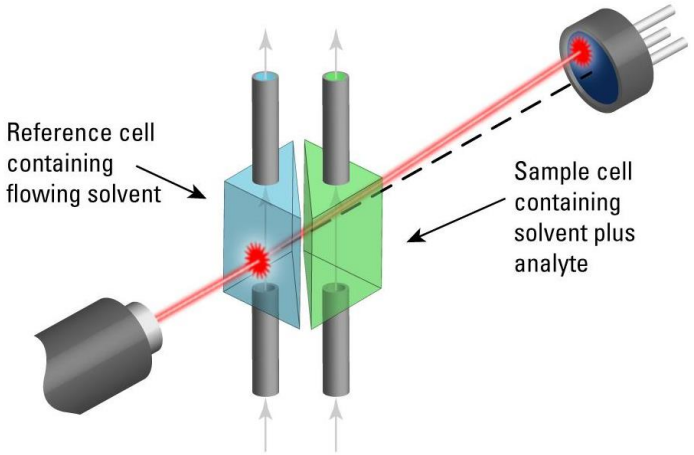




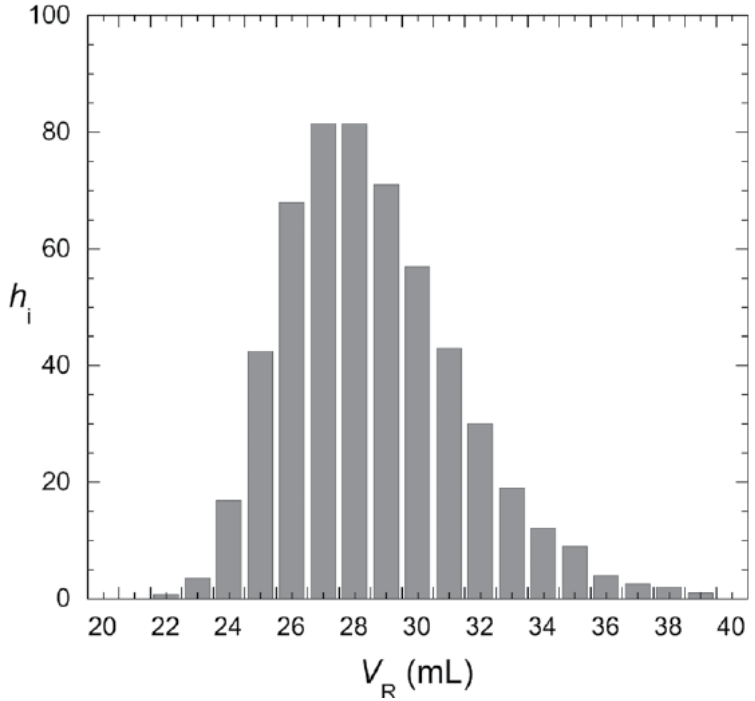


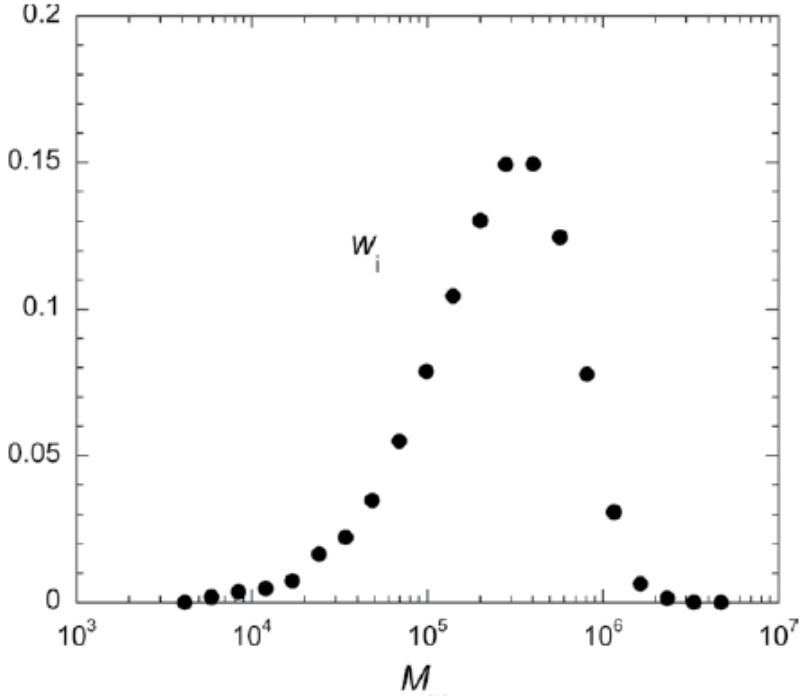
- Also known as gel permeation chromatography (GPC), SEC separates molecules based on their size: larger molecules elute first, while smaller molecules elute more slowly.
- Molecular weight can be determined from the elution volume using calibration curves of polymer standards.
- Note that SEC separates molecules based on their hydrodynamic size; polymers of different compositions have different molecular weight dependence of their size. For example, a more rigid polymer will have a larger size compared to a flexible polymer of equal molecular weight. Therefore, it is important to use polymer standards of identical compositions (to the ones you want to measure) to generate calibration curves.

Size Exclusion Chromatography (SEC)



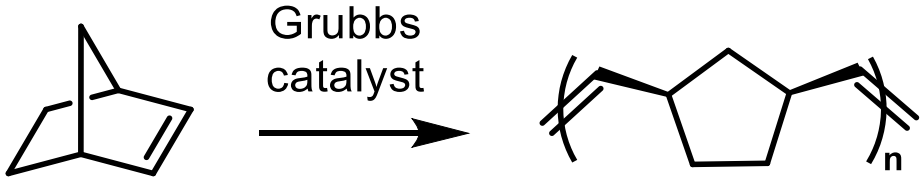
$$n(c) = n_s + (\mathrm{d}n/\mathrm{d}c)c$$





- The most common detector for SEC is the refractive index (RI) detector. It measures the refractive index of the eluent to determine the polymer concentration in real time.
- There are other types of detectors available (e.g., UV-Vis, light scattering, viscometer), some of which allow for calibration-free measurement of molecular weight (see details on page 423 in Lodge).
- When using SEC, it is important to make sure the polymers you wish to measure are compatible with the liquid phase the SEC is running in. Common liquid phases include THF, toluene, chloroform, DMF, and aqueous solutions.

What Polymer Chemistry Is About



Reactions (organic chemistry)

initiation

$A_2 \xrightarrow{k_d} 2\,A\cdot$ $\quad R_i=2k_d f_i[A_2]$

$A\cdot + M \xrightarrow{k_i} P_1\cdot$ $\quad k_i >> k_p$

propagation

$P_n\cdot + M \xrightarrow{k_p} P_{n+1}\cdot$ $\quad R_p=k_p[M][P\cdot]$

termination by disproportionation

$P_n\cdot + P_m\cdot \xrightarrow{k_{td}} P_n^H + P_m^=$ $\quad R_{td}=2k_{td}[P\cdot]^2$ $\quad R_t=R_{tc}+R_{td}$

termination by combination

$P_n\cdot + P_m\cdot \xrightarrow{k_{tc}} P_{n+m}$ $\quad R_{tc}=2k_{tc}[P\cdot]^2$

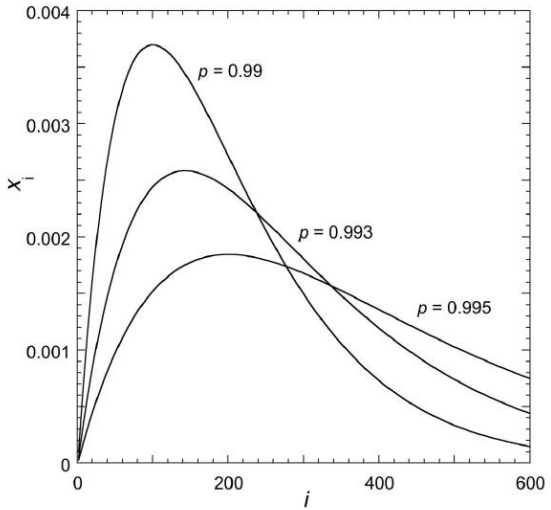
Kinetics (physical chemistry)

$$\left(\frac{n_i}{n}\right)_c = \frac{k_{t,c}\sum_{j=1}^{i-1}(1-p)p^{i-j-1}[P\bullet](1-p)p^{j-1}[P\bullet]}{k_{t,c}[P\bullet]^2}$$

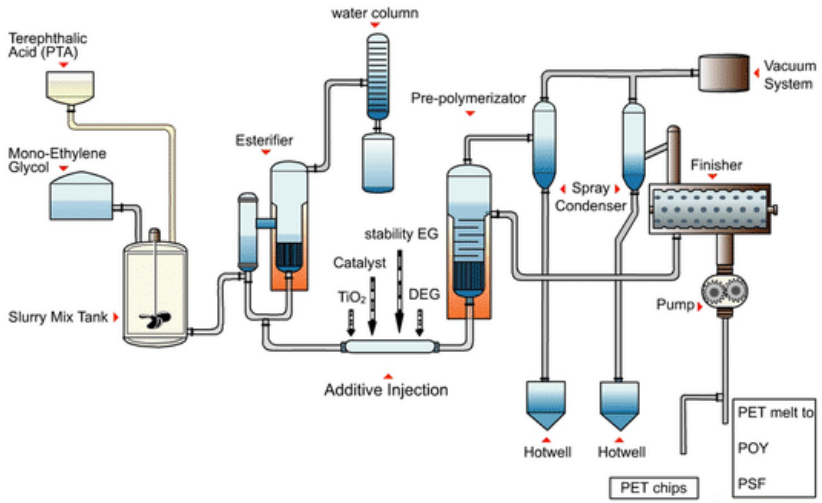
$$= \sum_{j=1}^{i-1}(1-p)^2 p^{i-2}$$

$$(N_n)_c = \frac{2}{1-p}$$

$$(N_w)_c = \frac{2+p}{1-p}$$



Distribution and average (statistics)



Processing (engineering)