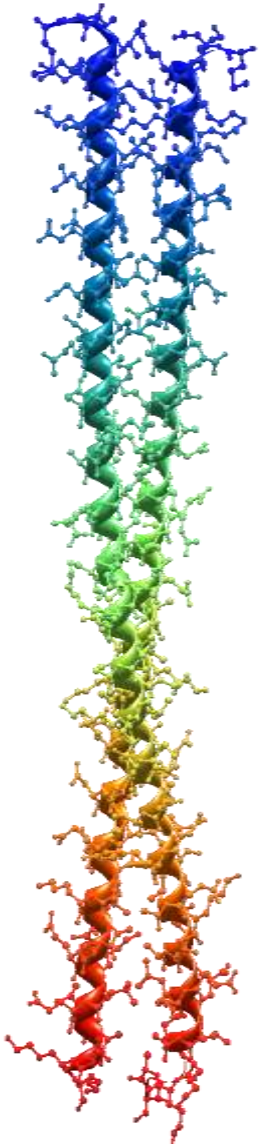
# Struktura polimerów i biopolimerów (1)



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Pracownia Teorii Biopolimerów

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http://www.biocomp.chem.uw.edu.pl

1. Struktura polimerów, elementy statystyki konformacyjnej i termodynamiki
    - polimery syntetyczne i naturalne, izomerie polimerów
    - konformacje polimerów liniowych, pojęcie kłębka statystycznego
    - przejście od kłębka losowego do formy globularnej
    - dyfuzja polimerów
    - proste modele obliczeniowe układów polimerowych i co z nich wynika
2. Polimery naturalne – czym się różnią od syntetycznych?
3. Białka globularne
    - struktura chemiczna, konformacje łańcucha polipeptydowego
    - poziomy organizacji struktury białek globularnych
    - klasyfikacje strukturalne białek globularnych
    - sekwencja, struktura, funkcja biologiczna (relacje ewolucyjne)
4. Dynamika i termodynamika białek
5. Inne biomakromolekuły (białka membranowe, membrany, biopolimery strukturalne)
6. Kwasy nukleinowe
    - DNA, struktura chemiczna i kod genetyczny
    - DNA, struktura przestrzenna i jej rola
    - RNA, różne formy i funkcje, struktura przestrzenna tRNA
7. Oddziaływania miedzymakromolekularne

# Przykładowa literatura:

http://www.biocomp.chem.uw.edu.pl (przykłady, filmy, prezentacje)

P. G. de Gennes, „Scaling concepts in polymer physics”, Cornell University Press, Ithaca, New York, 1979 (i nowsze wydania)

C. Branden, J. Tooze, „Introduction to protein structure”, Garland Pub, New York, 1999 (i nowsze wydania)

T. E. Creighton, „Proteins, structures and molecular properties”, W. H. Freeman, New York, 1993

K. Binder, D. W. Heermann, „Monte Carlo simulations in statistical physics” , Springer, New York, 2002.

D. Frenkel, B. Smit, „Understanding molecular simulations. From algorithms to applications”, Academic Press, San Diego, California, 1996.

# Polymers

- Macromolecule that is formed by linking of repeating units through covalent bonds in the main backbone
- Properties are determined by molecular weight, length, backbone structure, side chains, crystallinity
- Resulting macromolecules have huge molecular weights

H. Staudinger

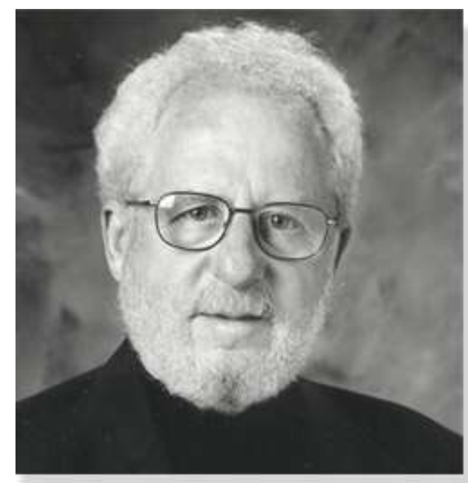
G. Natta & K. Ziegler

# NOBEL PRIZES IN POLYMERS

P. Flory

B. Merrifield

P. G. DeGennes



A. Heeger

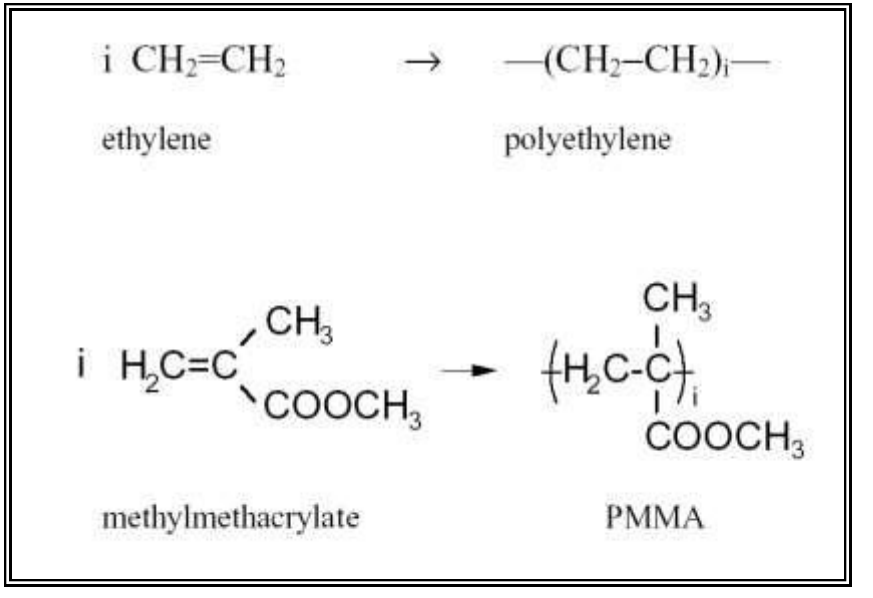
**One more scientist (Nobel Prize in 1921) whose contributions concerning Brownian motion, viscosity of solutions, and light scattering are essential to polymer science.**


for *"the development*
*of multiscale models*
*for complex chemical systems"*

# Polymers

- Terminology:
  - mer: a unit
  - monomer: one unit
  - dimer: two units
  - trimer: three units
  - tetramer: four units
  - polymer: many units
  - pre-polymer: growing towards being a polymer
  - oligomer: few units fixed in size
  - homopolymer: polymer of fixed mer type

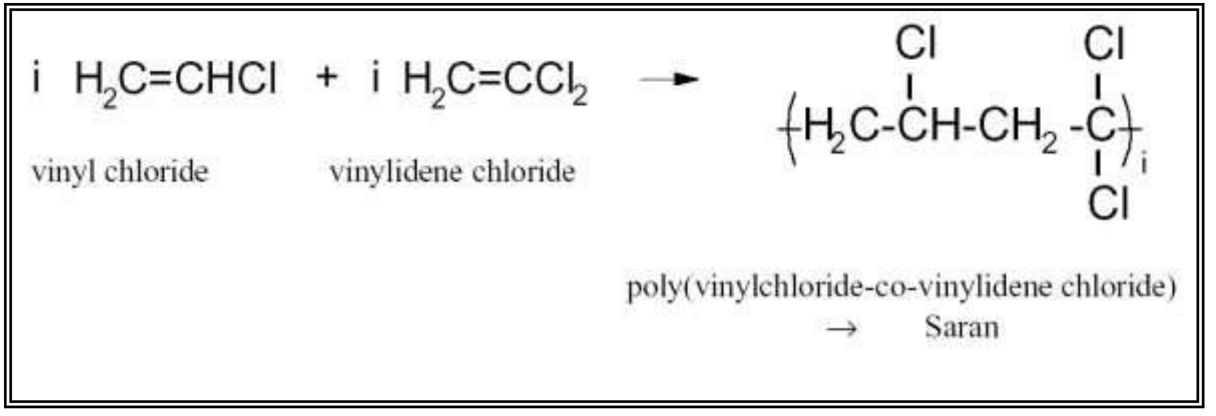
HOMOPOLYMER



# Polymers

- Terminology (contn):
  - copolymer: polymers of two mer types
    - random · · ·-B-A-B-A-B-B-A-· · ·
    - alternating· · ·-A-B-A-B-A-B-A-· · ·
    - block · · ·-A-A-A-A-B-B-B-· · ·
  - heteropolymer: polymers of many mer types

COPOLYMER



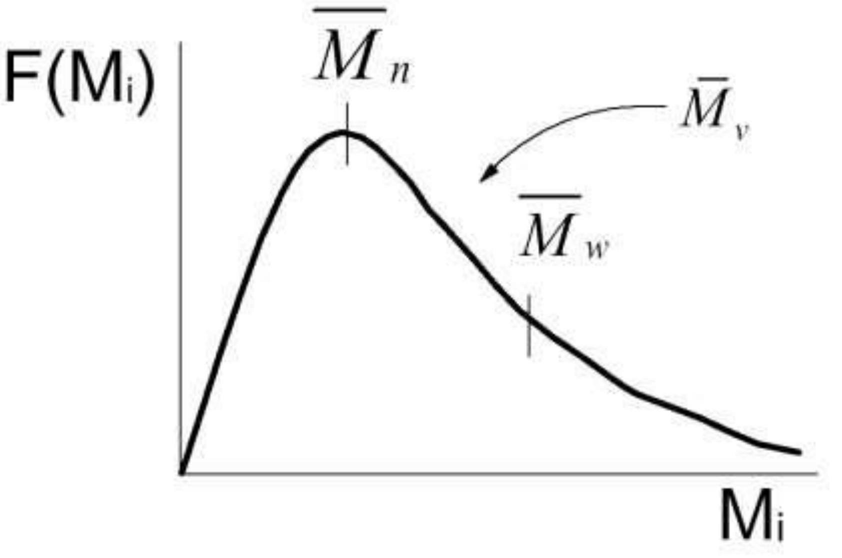
# Polymers: Molecular Weight

- number average, $M_n$

$$\overline{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

- weight average, $M_w$

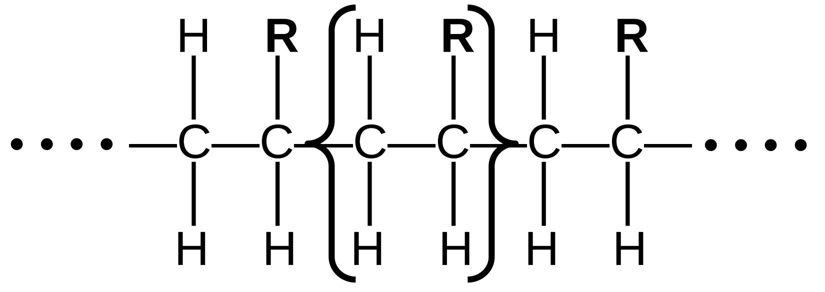
$$\overline{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$




$N_i$: # of molecules with degree of polymerization of i

$M_i$: molecular weight of i

# Polymers

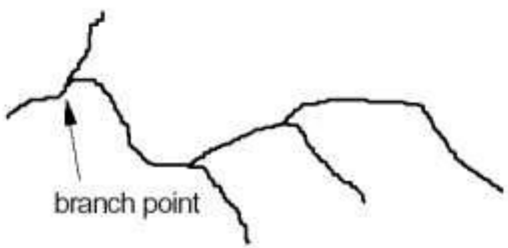



| Structure | Source-Based Name | Application |
|---|---|---|
| R = -H | Polyethylene | Plastic |
| R = $-CH_3$ | Polypropylene | Rope |
| R = -Cl | Poly(vinyl chloride) | "Vinyl" |
| X = -H, R = $-C_2H_5$ | Poly(ethyl acrylate) | Latex paints |
| X = $-CH_3$, R = $-CH_3$ | Poly(methyl methacrylate) | Plastic |
| R = -H | Polybutadiene | Tires |
| R = $-CH_3$ | Polyisoprene | Tires |
| X = -F, R = -F | Polytetrafluoroethylene | Teflon® |

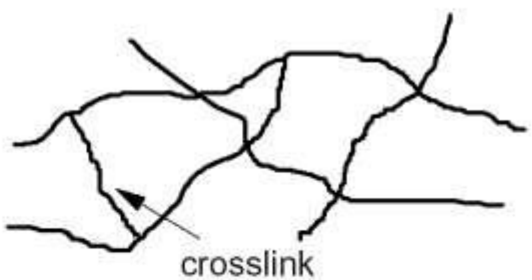
# Polymers

***Structural characteristics*** – Closely related to material properties

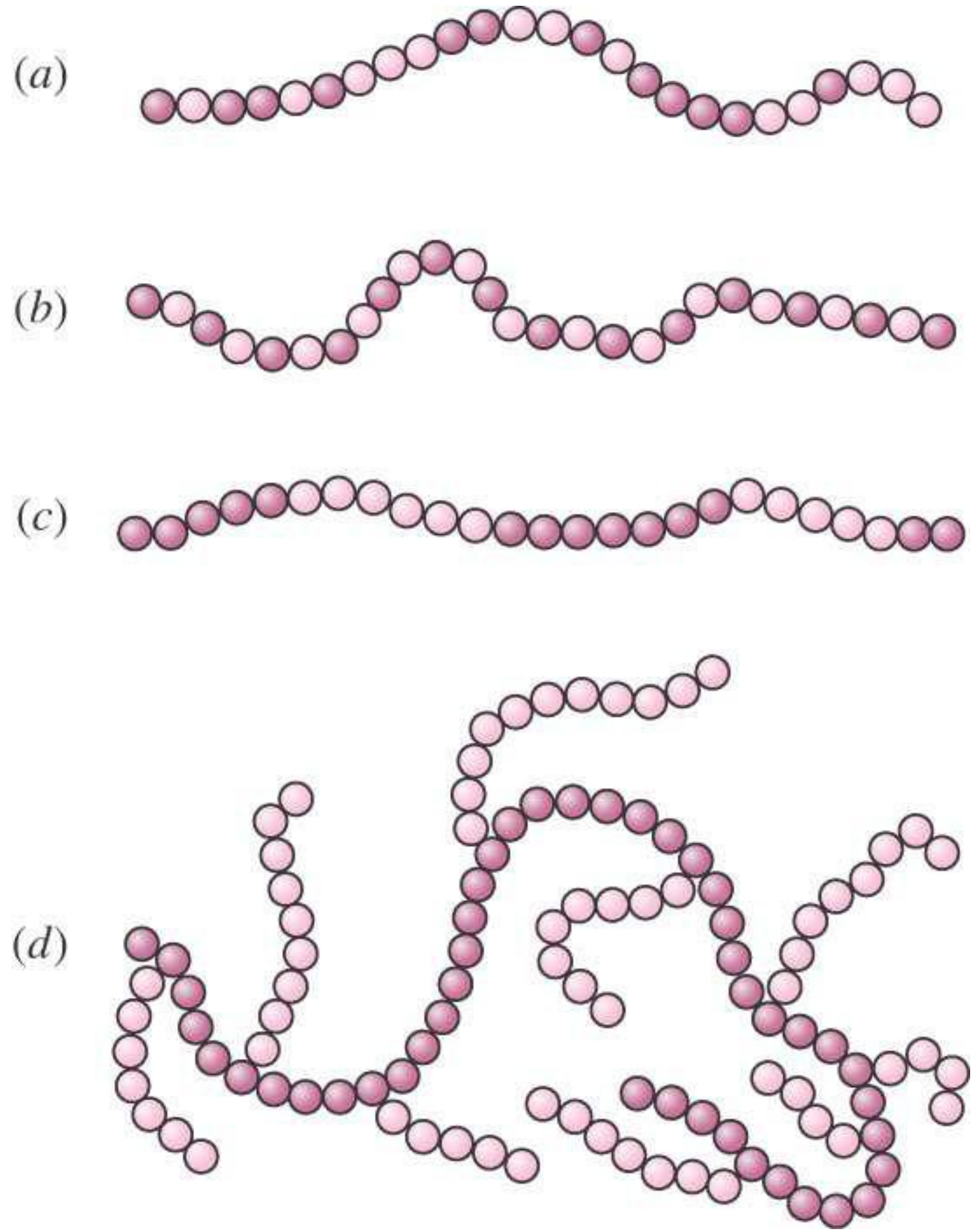
**linear** (uninterrupted straight chain)




**branched** (occasional branches off longer chain)



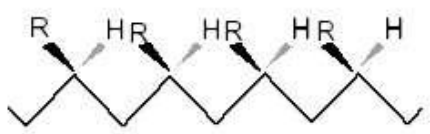

**networked** (many interconnected linear chains; one giant molecule)


(a)
(b)
(c)
(d)

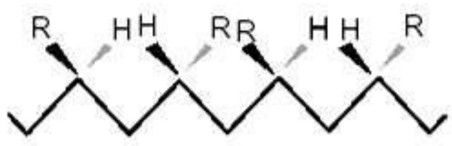
# Polymers

- Polymers can be either amorphous or semi-crystalline
- Tacticity, i.e. arrangements of substituents around the backbone, determines the degree of crystallinity
- Atactic polymers are amorphous
- Isotactic and syndiotactic may crystallize
- Crytallinity depends on:
  - –size of side groups (smaller, ↑crystallinity)
  - –regularity of chain
- Increased crystallinity enhances mechanical properties

***Stereochemistry of Linkages***




**ISOTACTIC** – R groups on same side of backbone




**SYNDIOTACTIC** – R groups on alternating sides of backbone

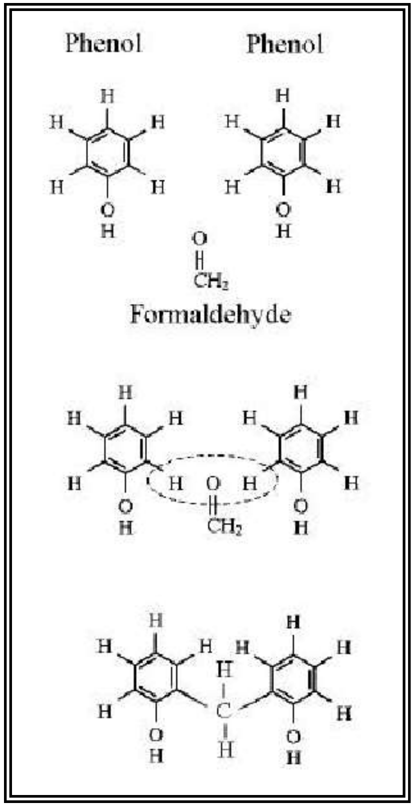
**ATACTIC** — Random (most common)

# Polymer Synthesis

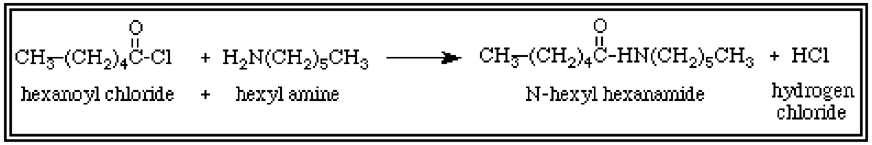
- Two common methods of polymerization
  - Condensation polymerization (or stepwise addition)
  - Addition reaction (or chain polymerization)
- Condensation: Two monomers react to form a covalent bond usually with elimination of a small molecule such as water, HCl, methanol, or $CO_2$. Reaction continues until one type of reactant is used up.
- Addition: Monomers react through stages of initiation, propagation, and termination.
  - initiators such as free radicals, cations, anions opens the double bond of the monomer which becomes active and bonds with other such monomers
  - rapid chain reaction propagates in this fashion
  - reaction is terminated by another free radical or another polymer

# Polymer Synthesis: Condensation

- phenol-formaldehyde: results in condensation of a water molecule

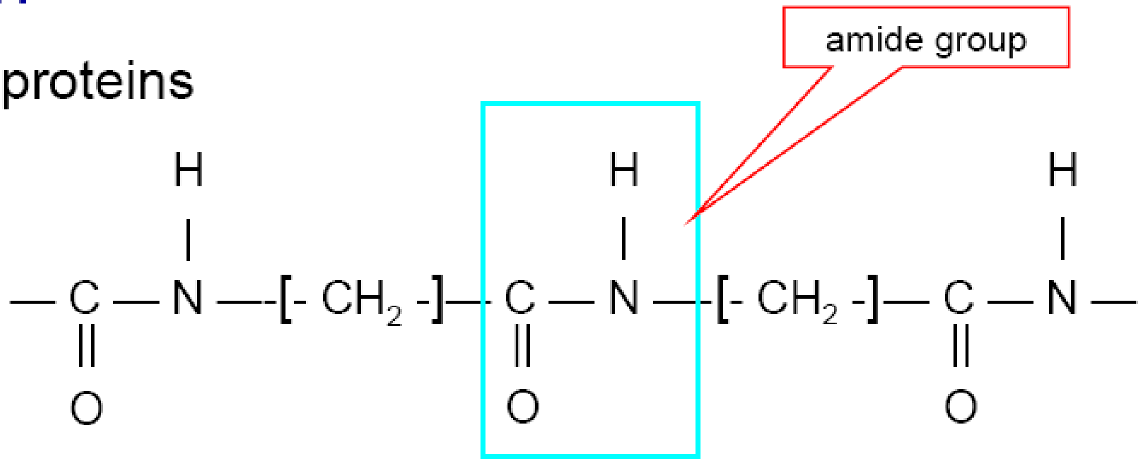



- nylon (polyamide): an organic acid reacts with an amine to form an amide. HCl condenses

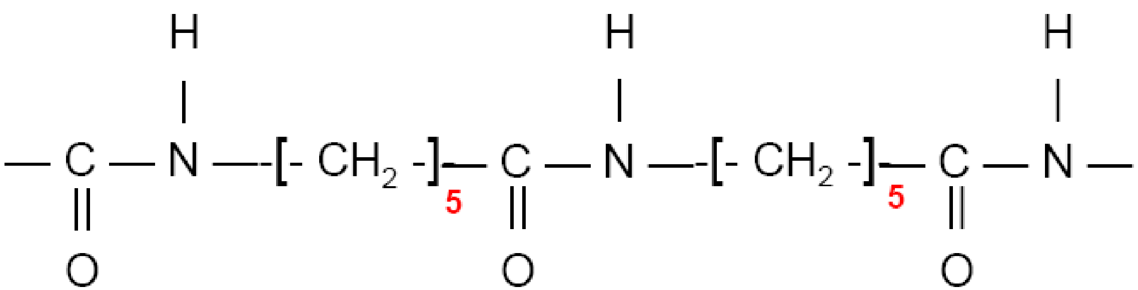


# Introduction

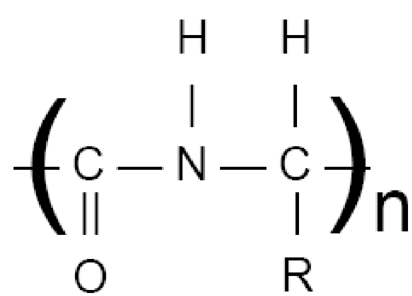
- Nylons and proteins
  - nylon 2



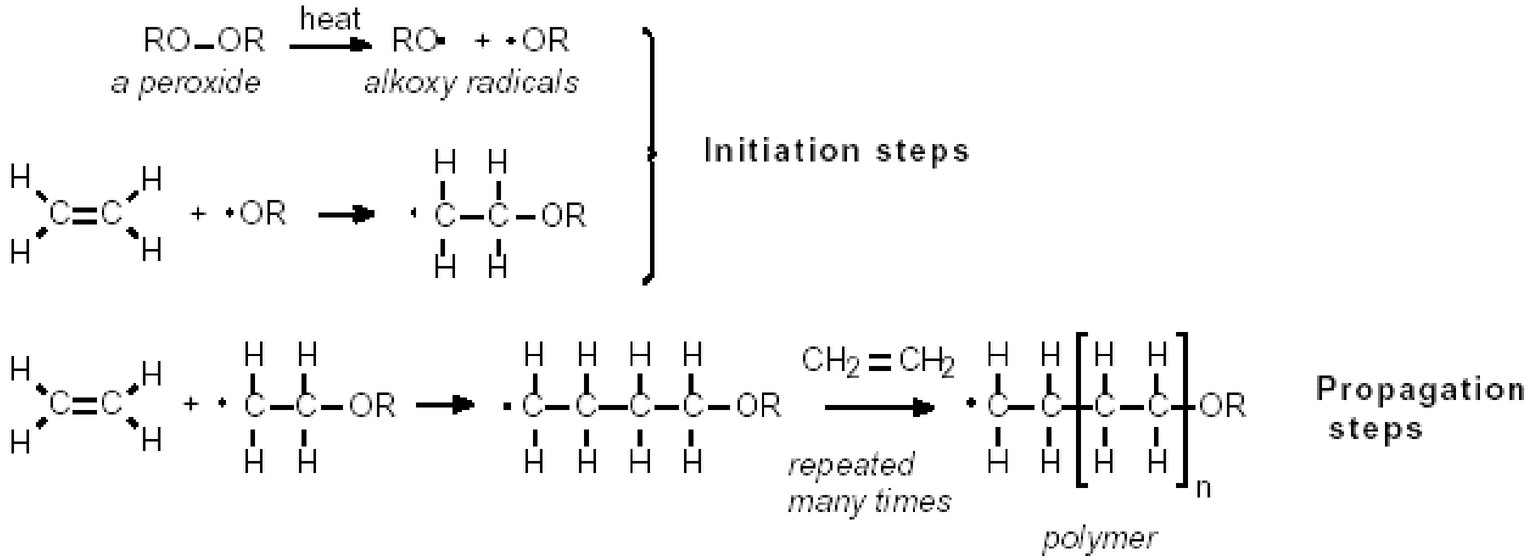

  - nylon 6



  - proteins are "decorated" nylon 2
    - R one of 20 amino acids
    - R : H $\rightarrow$ glycine, CH3 $\rightarrow$ alanine, etc



# Polymers Synthesis: Addition

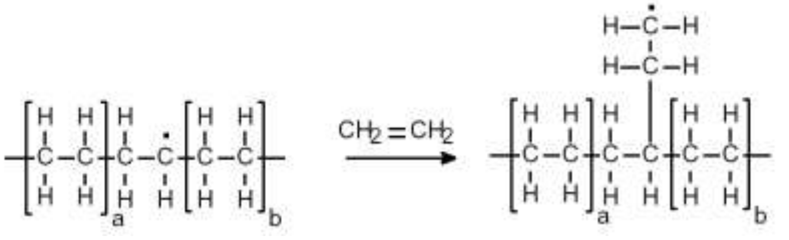



Termination may occur by:

- two radicalized polymers reacting
- another radicalized monomer
- one initiator (alkoxy radical, •OR, in this case)

# Condensation vs. Addition

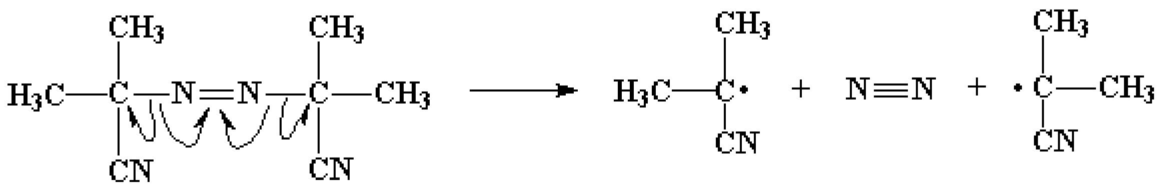
- Addition:
  - Difficult to control molecular weight
  - Undesirable branching products



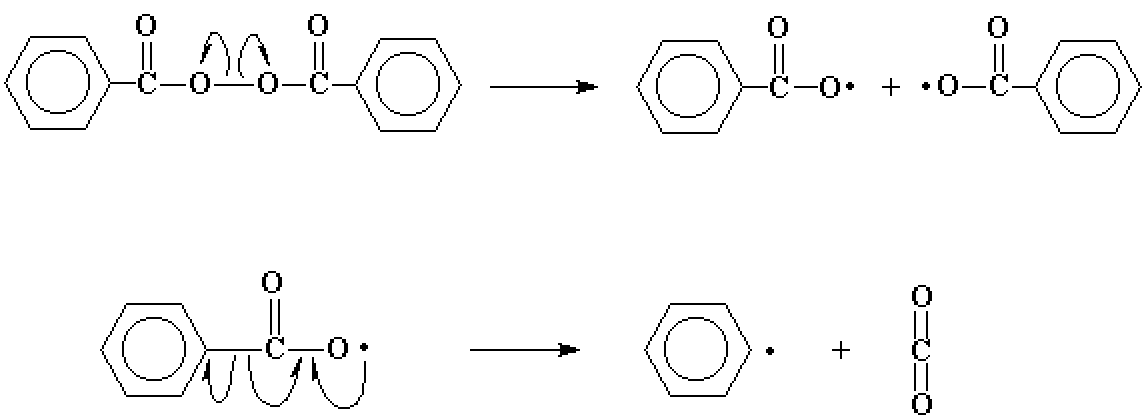

- Condensation:
  - Molecular weight closely controlled
  - Polydispersity ratios close to unity can be obtained

# Classical Free-Radical Polymerization

# Initiator Decomposition

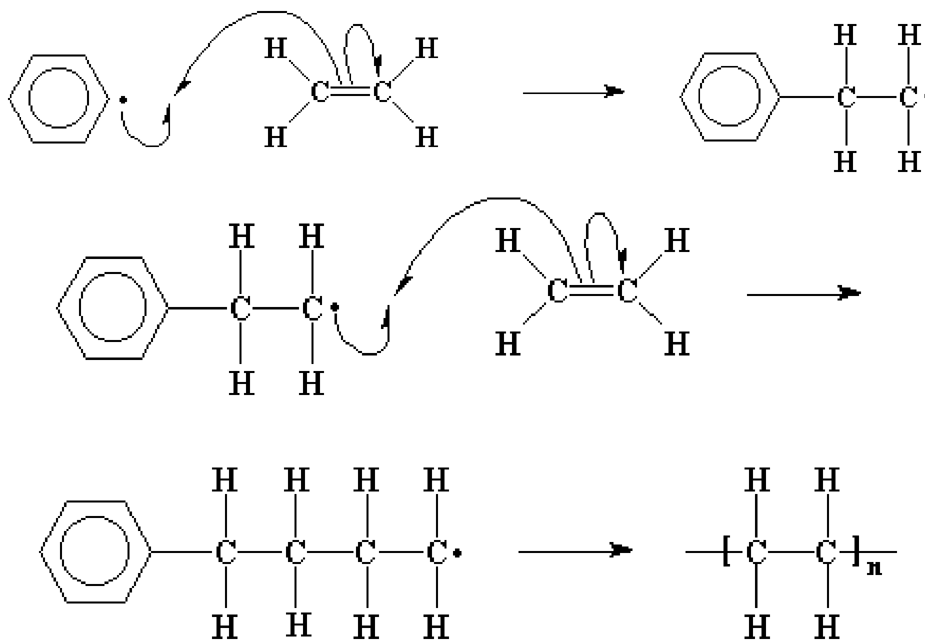


2,2`-azo-*bis*-isobutyrylnitrile(AIBN)



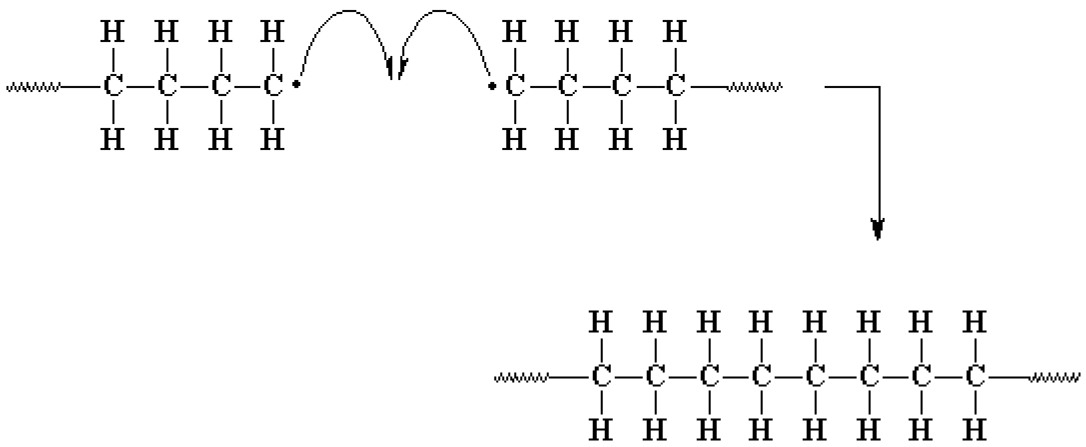
Benzoyl peroxide

# Initiation and Propagation

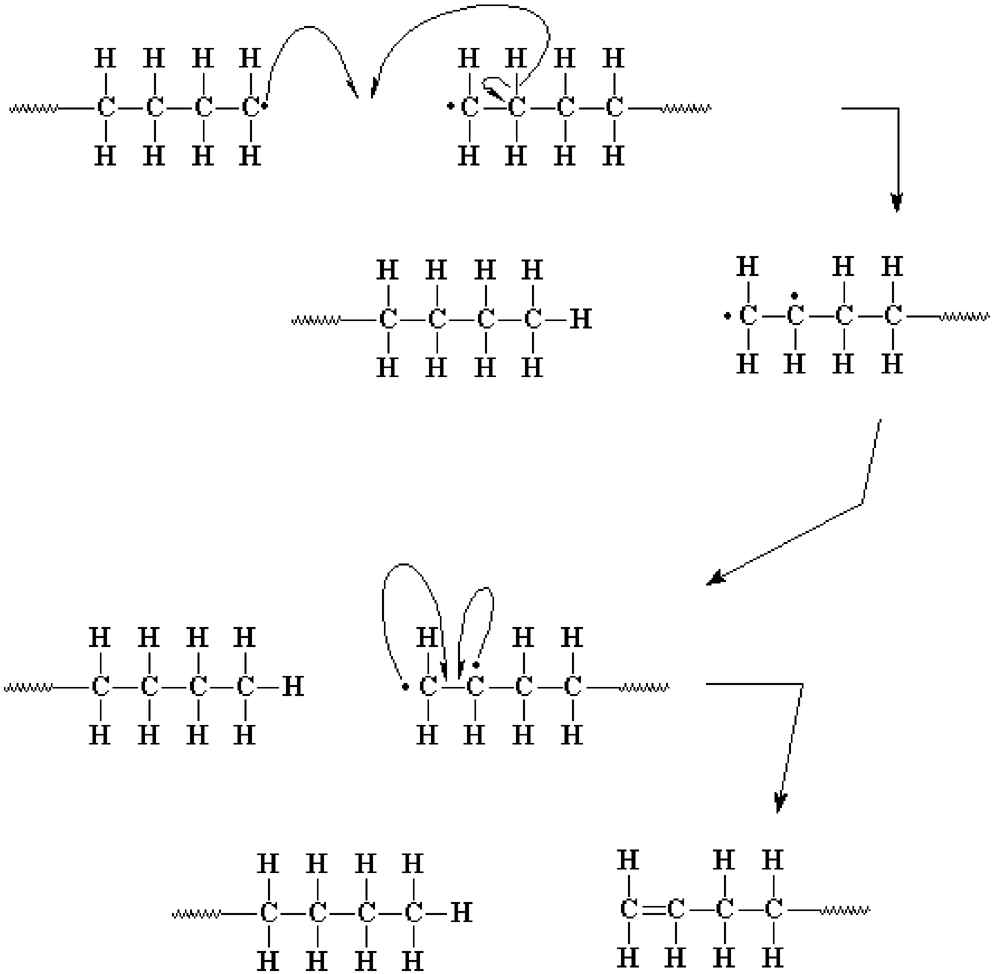



Note: The termination steps are not shown

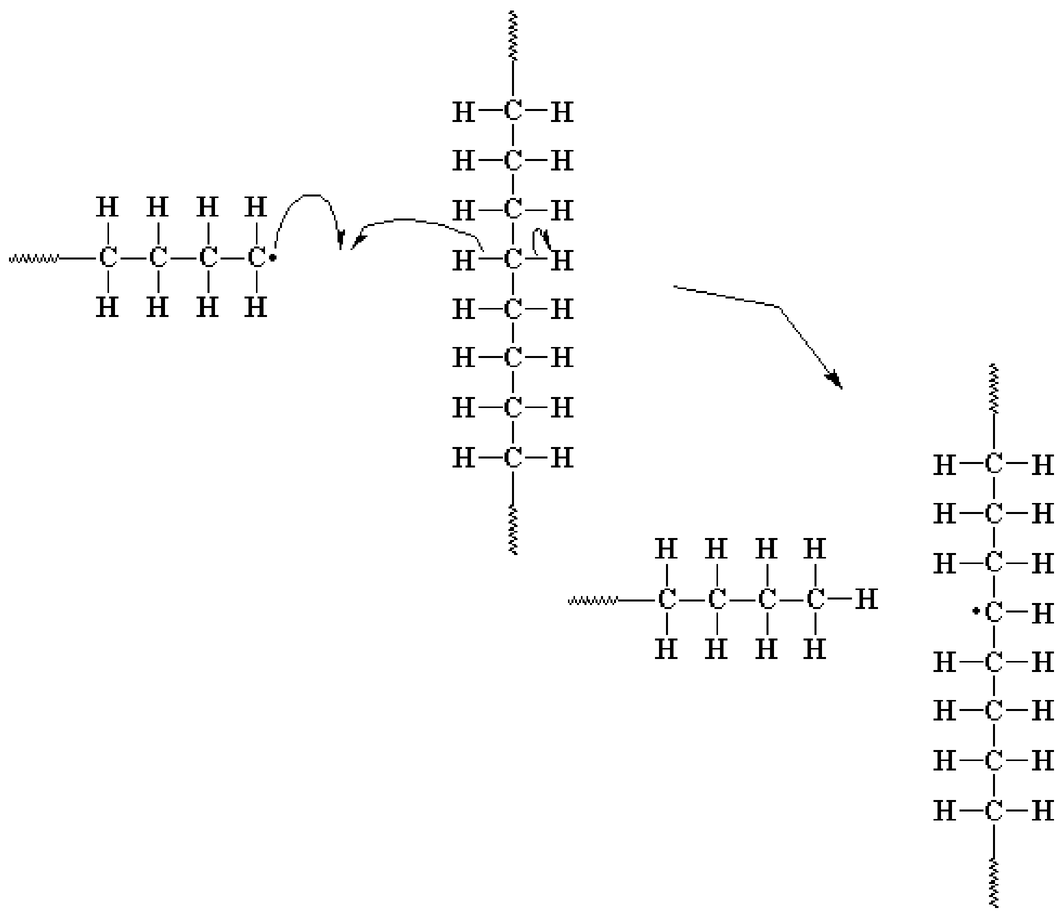
# Termination by Coupling



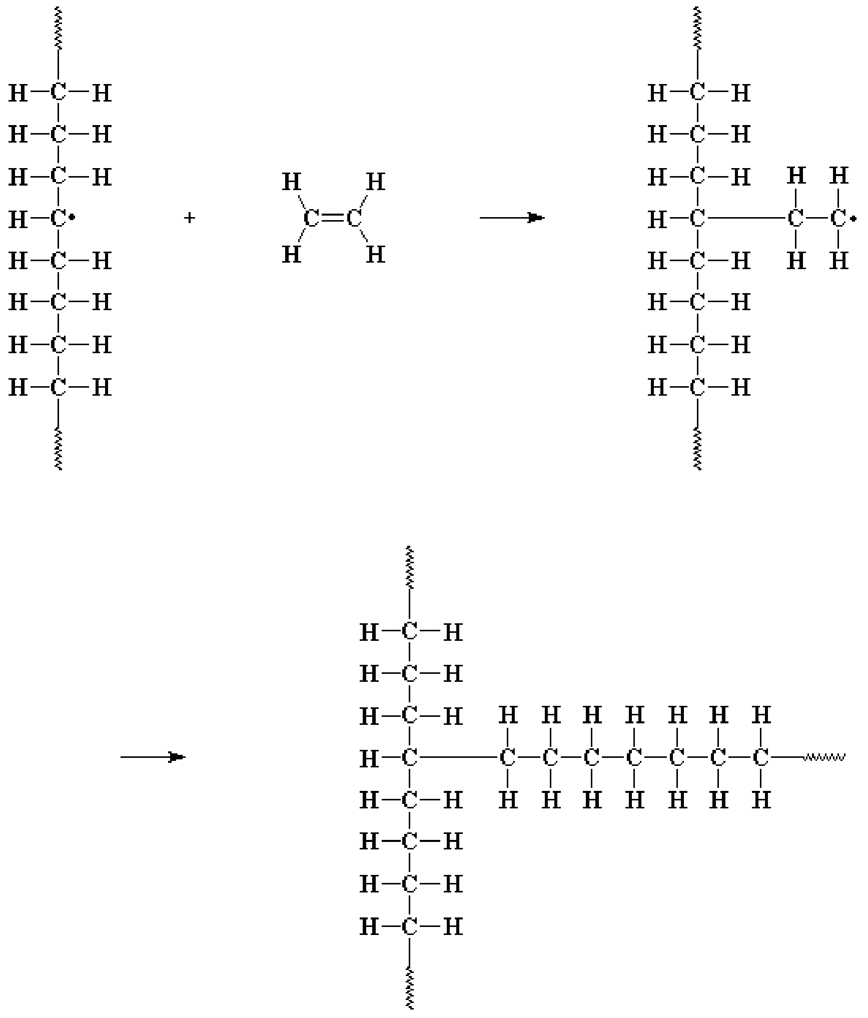
# Termination by Disproportionation



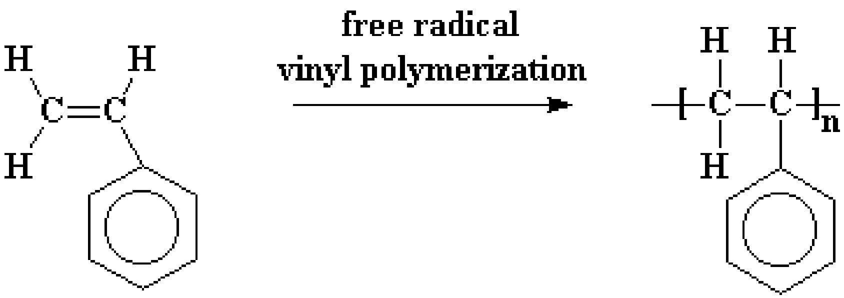
# Branching



# Branching – Cont'd

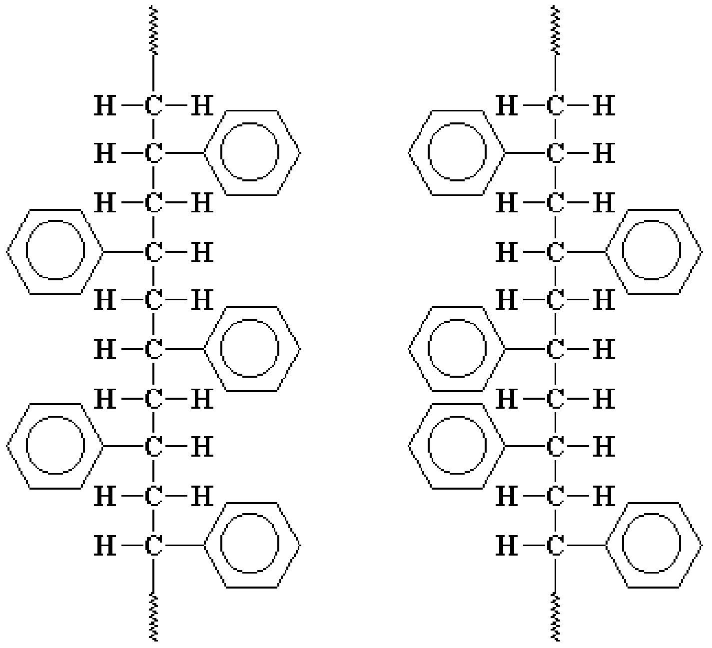


# Polystyrene




styrene

polystyrene



syndiotactic polystyrene

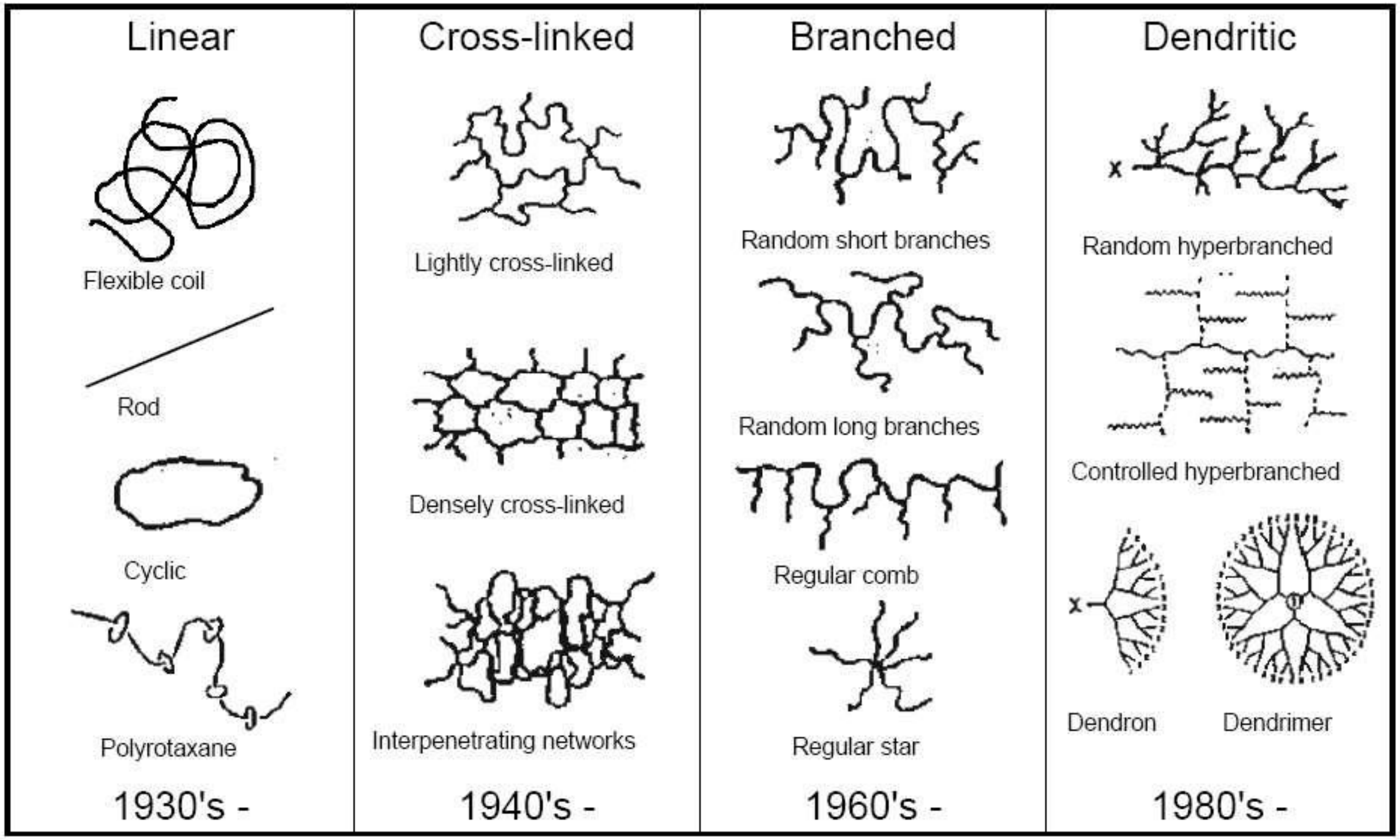
atactic polystyrene

Syndiotactic polystyrene has a regular structure, so it can pack into crystal structures. The irregular atactic polystyrene can't.

- Chain structure

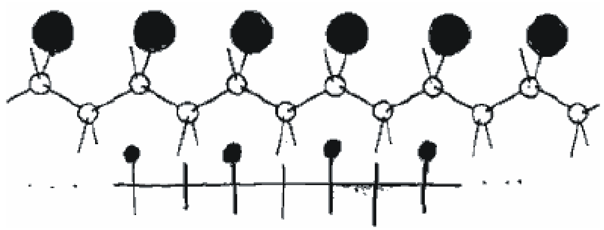
# Introduction

- Structures

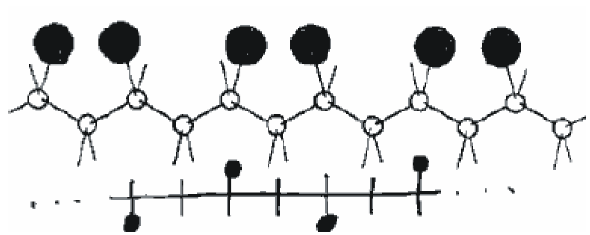


# Introduction

- Tacticity = stereochemical handedness
  - isotactic



  - syndiotactic



  - atactic