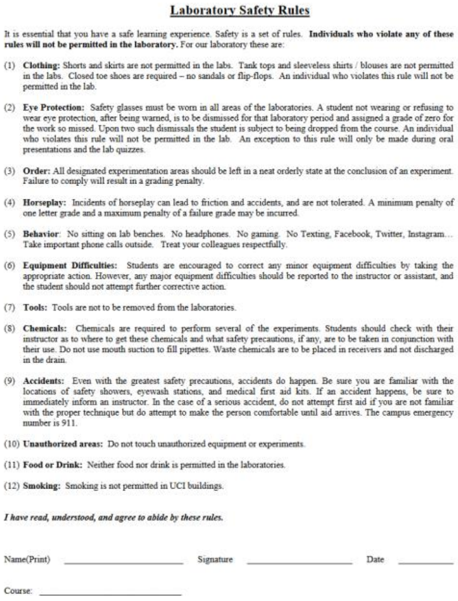
MSE 160 – Polymer synthesis and characterization

MSE 160 Laboratory Safety Rules form posted on class page (bowmanlab.eng.uci.edu/class)

Lab Manager Steve Weinstock will give a safety introduction during your first lab session



Laboratory Safety Rules

It is essential that you have a safe learning experience. Safety is a set of rules. **Individuals who violate any of these rules will not be permitted in the laboratory.** For our laboratory these are:

(1) **Clothing:** Shorts and skirts are not permitted in the labs. Tank tops and sleeveless shirts / blouses are not permitted in the labs. Closed toe shoes are required – no sandals or flip-flops. An individual who violates this rule will not be permitted in the lab.

(2) **Eye Protection:** Safety glasses must be worn in all areas of the laboratories. A student not wearing or refusing to wear eye protection, after being warned, is to be dismissed for that laboratory period and assigned a grade of zero for the work so missed. Upon two such dismissals the student is subject to being dropped from the course. An individual who violates this rule will not be permitted in the lab. An exception to this rule will only be made during oral presentations and the lab quizzes.

(3) **Order:** All designated experimentation areas should be left in a neat orderly state at the conclusion of an experiment. Failure to comply will result in a grading penalty.

(4) **Horseplay:** Incidents of horseplay can lead to friction and accidents, and are not tolerated. A minimum penalty of one letter grade and a maximum penalty of a failure grade may be incurred.

(5) **Behavior**: No sitting on lab benches. No headphones. No gaming. No Texting, Facebook, Twitter, Instagram… Take important phone calls outside. Treat your colleagues respectfully.

(6) **Equipment Difficulties:** Students are encouraged to correct any minor equipment difficulties by taking the appropriate action. However, any major equipment difficulties should be reported to the instructor or assistant, and the student should not attempt further corrective action.

(7) **Tools:** Tools are not to be removed from the laboratories.

(8) **Chemicals:** Chemicals are required to perform several of the experiments. Students should check with their instructor as to where to get these chemicals and what safety precautions, if any, are to be taken in conjunction with their use. Do not use mouth suction to fill pipettes. Waste chemicals are to be placed in receivers and not discharged in the drain.

(9) **Accidents:** Even with the greatest safety precautions, accidents do happen. Be sure you are familiar with the locations of safety showers, eyewash stations, and medical first aid kits. If an accident happens, be sure to immediately inform an instructor. In the case of a serious accident, do not attempt first aid if you are not familiar with the proper technique but do attempt to make the person comfortable until aid arrives. The campus emergency number is 911.

(10) **Unauthorized areas:** Do not touch unauthorized equipment or experiments.

(11) **Food or Drink:** Neither food nor drink is permitted in the laboratories.

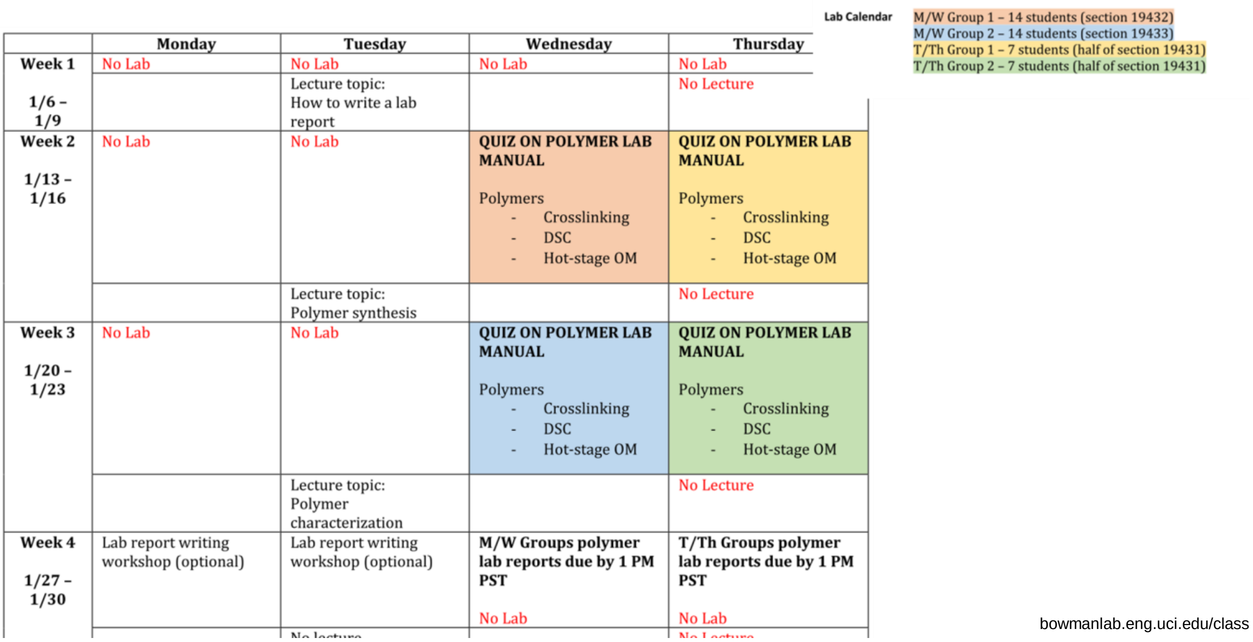
(12) **Smoking:** Smoking is not permitted in UCI buildings.

I have read, understood, and agree to abide by these rules.

Name(Print) ____________________ Signature __________________ Date _________

Course: ________________________

Labs this week



Lab Calendar

M/W Group 1 – 14 students (section 19432)
M/W Group 2 – 14 students (section 19433)
T/Th Group 1 – 7 students (half of section 19431)
T/Th Group 2 – 7 students (half of section 19431)

	Monday	Tuesday	Wednesday	Thursday
Week 1 **1/6 – 1/9**	No Lab	No Lab	No Lab	No Lab
		Lecture topic: How to write a lab report		No Lecture
Week 2 **1/13 – 1/16**	No Lab	No Lab	**QUIZ ON POLYMER LAB MANUAL** Polymers - Crosslinking - DSC - Hot-stage OM	**QUIZ ON POLYMER LAB MANUAL** Polymers - Crosslinking - DSC - Hot-stage OM
		Lecture topic: Polymer synthesis		No Lecture
Week 3 **1/20 – 1/23**	No Lab	No Lab	**QUIZ ON POLYMER LAB MANUAL** Polymers - Crosslinking - DSC - Hot-stage OM	**QUIZ ON POLYMER LAB MANUAL** Polymers - Crosslinking - DSC - Hot-stage OM
		Lecture topic: Polymer characterization		No Lecture
Week 4 **1/27 – 1/30**	Lab report writing workshop (optional)	Lab report writing workshop (optional)	**M/W Groups polymer lab reports due by 1 PM PST** No Lab	**T/Th Groups polymer lab reports due by 1 PM PST** No Lab
		No lecture		No Lecture

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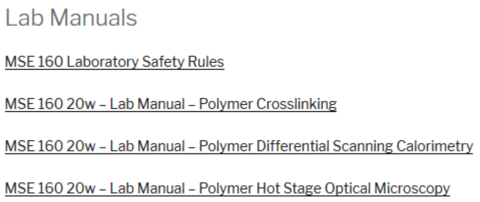
Labs this week



Lab Manuals

MSE 160 Laboratory Safety Rules

MSE 160 20w – Lab Manual – Polymer Crosslinking

MSE 160 20w – Lab Manual – Polymer Differential Scanning Calorimetry

MSE 160 20w – Lab Manual – Polymer Hot Stage Optical Microscopy

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From last lecture…

Quizzes will happen on your first lab session of each module; they are 5 questions, will take 10 mins.

I added a document on Error Analysis to the Class page. Measurements are uncertain, and errors arise from propagating these uncertainties through calculations.

Everyone has 2.5 weeks to write the lab report, appendix is not required.

Lecture outline

Outline

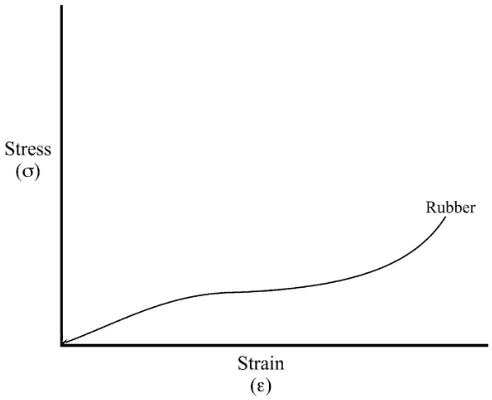
- Synthesis
  - Thermoplastics and thermosets
  - Epoxy cross-linking
  - Polymer structure
  - Polymerization mechanisms

- Characterization

No other material is as heavily utilized in our society as organic-based polymers

Organic-based materials are generally associated with “soft” characteristics

relatively low-melting and facile plastic deformation



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Organic-based materials are generally associated with “soft” characteristics

relatively low-melting and facile plastic deformation

numerous polymer classes exhibit hardness and thermal stabilities that rival inorganic ceramics

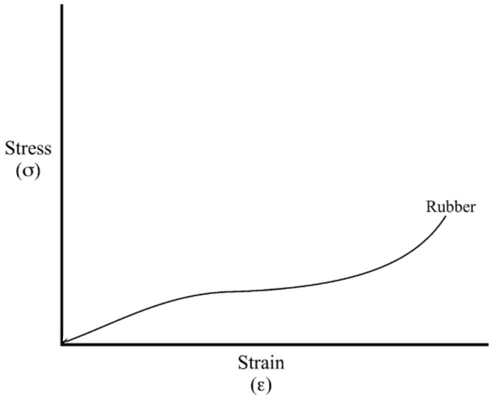
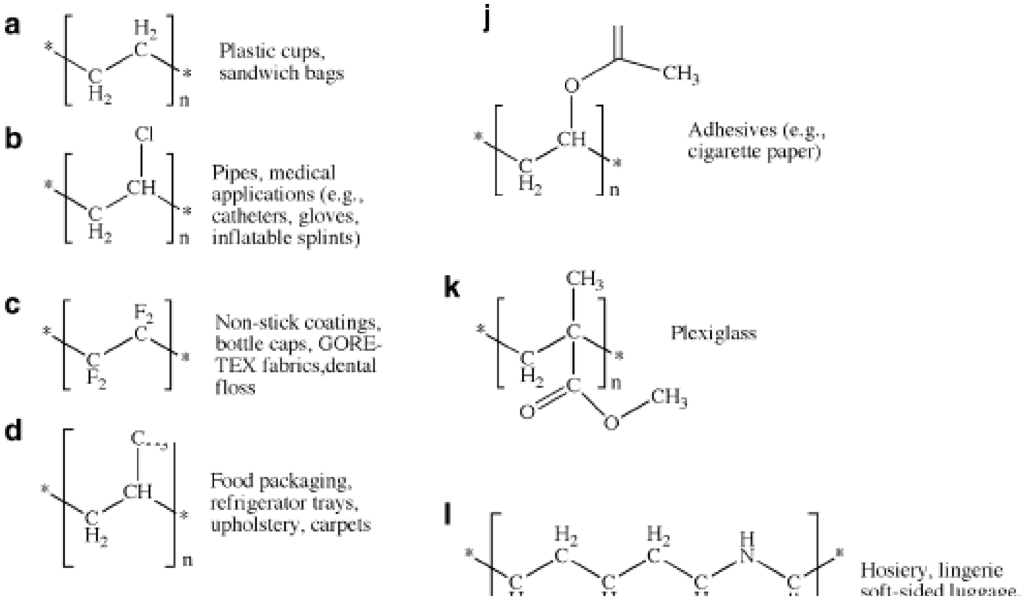


Figure 5.2. Stress *vs.* strain curves for various polymers around its glass-transition temperature. The maximum in the curve that occurs at T_g is referred to as the *yield point* (onset of plastic deformation).

Polymers are made of multiple monomers



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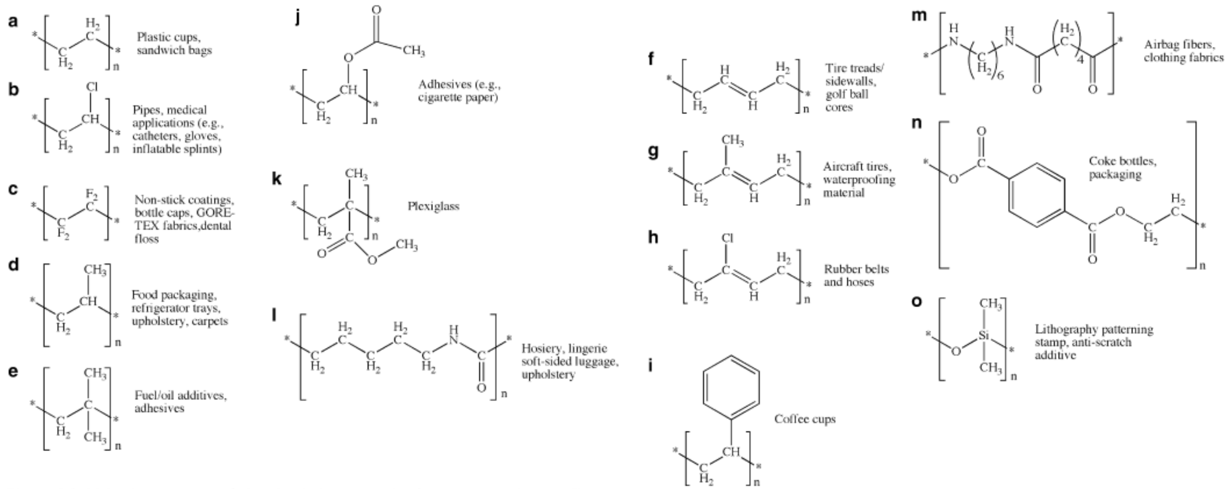


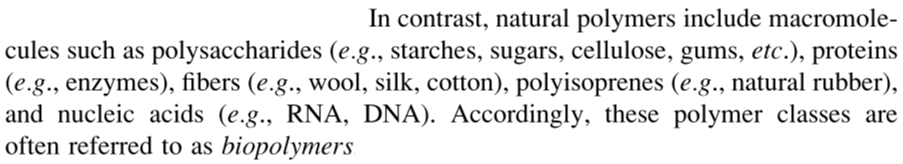
Figure 5.1. Molecular structures of the chemical repeat units for common polymers. Shown are (a) polyethylene (PE), (b) poly(vinyl chloride) (PVC), (c) polytetrafluoroethylene (PTFE), (d) polypropylene (PP), (e) polyisobutylene (PIB), (f) polybutadiene (PBD), (g) *cis*-polyisoprene (natural rubber), (h) *trans*-polychloroprene (Neoprene® rubber), (i) polystyrene (PS), (j) poly(vinyl acetate) (PVAc), (k) poly(methyl methacrylate) (PMMA), (1) polycaprolactam (polyamide – nylon 6), (m) nylon 6,6, (n) poly(ethylene teraphthalate), (o) poly(dimethyl siloxane) (PDMS).

The most fundamental classification of polymers is whether they are synthetic or naturally-occurring

Let’s name some naturally-occurring polymers

The most fundamental classification of polymers is whether they are synthetic or **naturally-occurring**

Let’s name some naturally-occurring polymers



In contrast, natural polymers include macromolecules such as polysaccharides (*e.g.*, starches, sugars, cellulose, gums, *etc.*), proteins (*e.g.*, enzymes), fibers (*e.g.*, wool, silk, cotton), polyisoprenes (*e.g.*, natural rubber), and nucleic acids (*e.g.*, RNA, DNA). Accordingly, these polymer classes are often referred to as *biopolymers*

The most fundamental classification of polymers is whether they are **synthetic** or naturally-occurring

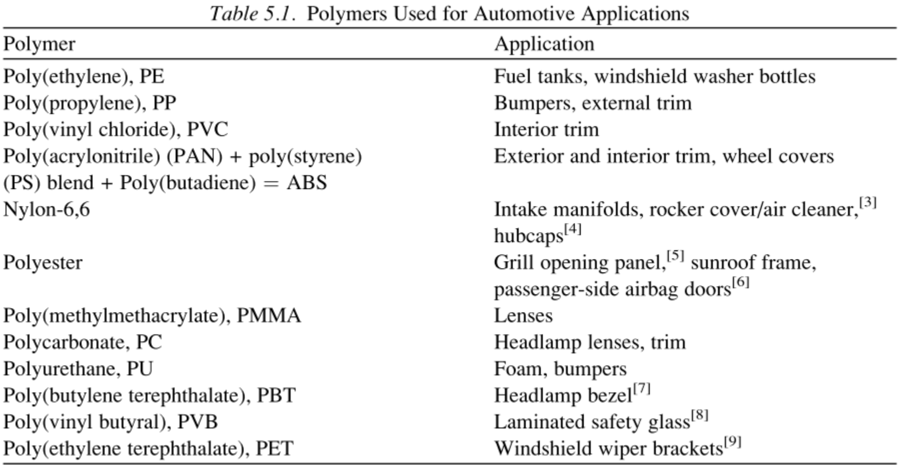


Table 5.1. Polymers Used for Automotive Applications

Polymer	Application
Poly(ethylene), PE	Fuel tanks, windshield washer bottles
Poly(propylene), PP	Bumpers, external trim
Poly(vinyl chloride), PVC	Interior trim
Poly(acrylonitrile) (PAN) + poly(styrene) (PS) blend + Poly(butadiene) = ABS	Exterior and interior trim, wheel covers
Nylon-6,6	Intake manifolds, rocker cover/air cleaner,[3] hubcaps[4]
Polyester	Grill opening panel,[5] sunroof frame, passenger-side airbag doors[6]
Poly(methylmethacrylate), PMMA	Lenses
Polycarbonate, PC	Headlamp lenses, trim
Polyurethane, PU	Foam, bumpers
Poly(butylene terephthalate), PBT	Headlamp bezel[7]
Poly(vinyl butyral), PVB	Laminated safety glass[8]
Poly(ethylene terephthalate), PET	Windshield wiper brackets[9]

Thermoplastics and thermosets

Synthetic polymers may be classified under two general umbrellas: thermoplastics and thermosets

Thermoplastics comprise long molecules with side chains or groups that are not connected to neighboring molecules (i.e., not crosslinked).

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What do the names suggest about their higher T behavior?

Thermosets are initially liquids and become hardened by a thermally induced crosslinking process known as curing.

Thermoplastics comprise long molecules with side chains or groups that are not connected to neighboring molecules (i.e., not crosslinked).

They transform to a rubbery elastomer or flexible plastic at an elevated temperature.

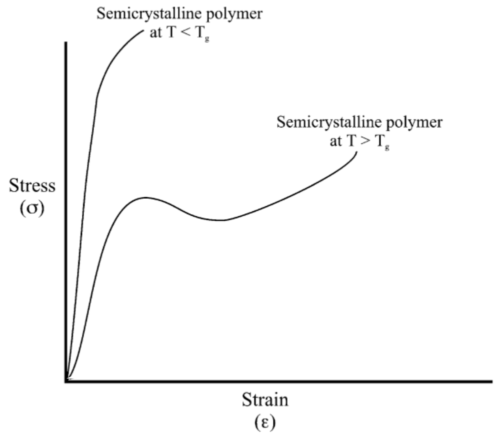
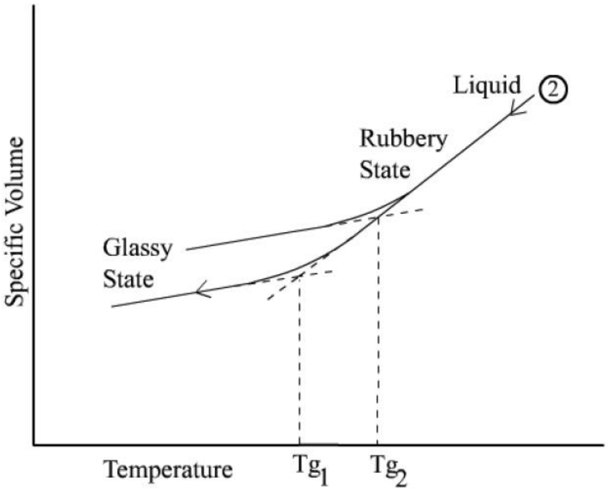


Figure 5.2. Stress *vs*. strain curves for various polymers around its glass-transition temperature. The maximum in the curve that occurs at T_g is referred to as the *yield point* (onset of plastic deformation).

The glass-transition temperature (T_g) is the most important property of polymers

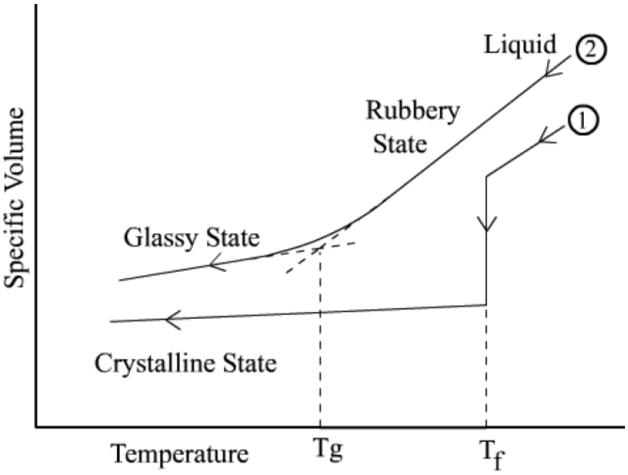
T_g and volume depend on the cooling rate, conformations will vary

Glass transition is “kinetically limited”, so volume will spontaneously decrease with time



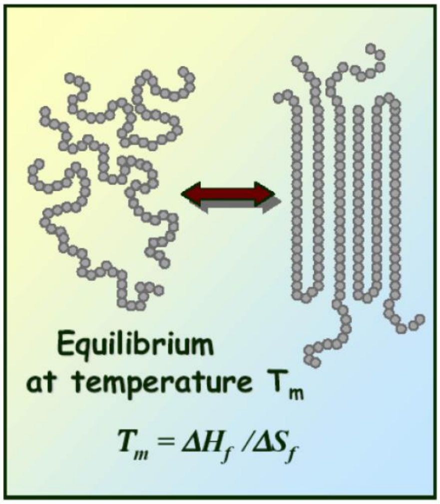
Polymers can also crystallize during cooling

Discontinuous volume change at crystallization temperature, T_f



Polymers can also crystallize during cooling

System is in equilibrium at T_m



The subscript “f” stands for fusion

Polymers can also crystallize during cooling

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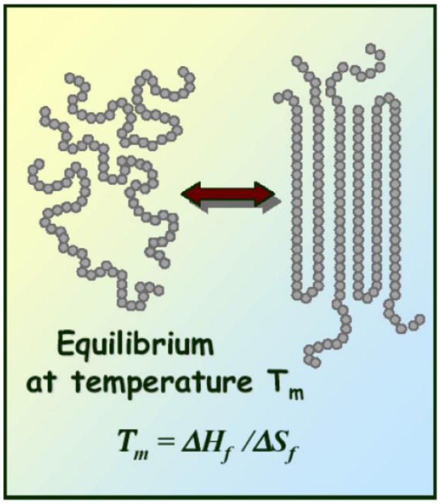

$$\Delta G_f = \Delta H_f - T\Delta S_f$$

And at Equilibrium

$$\Delta G_f = 0$$

Hence $\boxed{T_m = \Delta H_f / \Delta S_f}$

The subscript “f” stands for fusion

For melting ΔS_f is positive

Polymers can also crystallize during cooling

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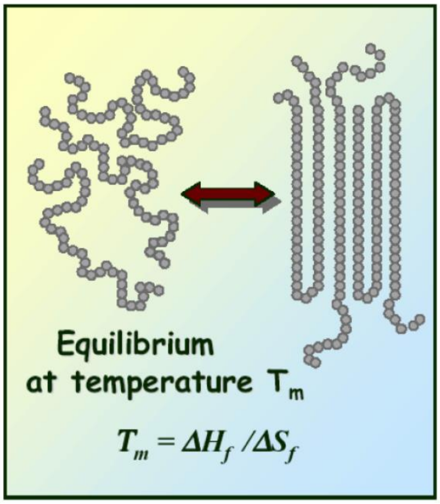

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The subscript “f” stands for fusion

Surface energy osf the nucleus is neglected!!

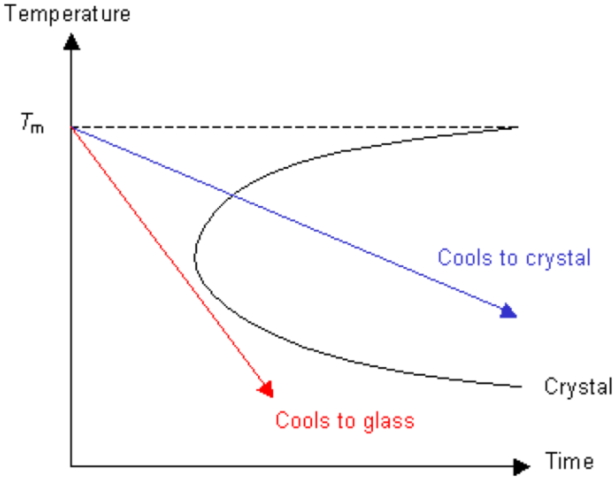
For melting ΔS_f is positive

Polymers can also crystallize during cooling

High cooling rate can yield a glass

Seed nucleation is favored by low temperature

Nuclei growth is favored by high temperature



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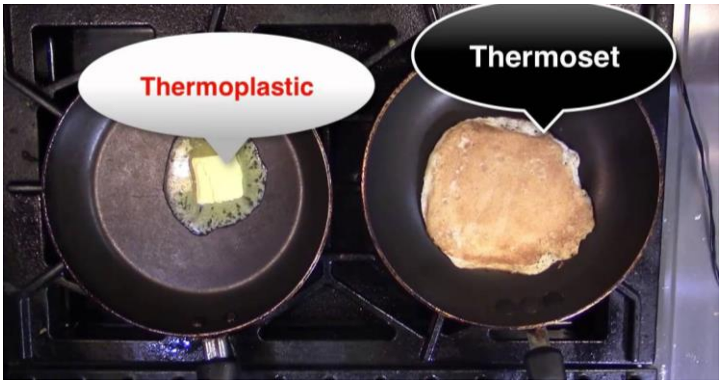
The crosslinking process yields a stable 3D network



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Most common type of thermosetting polymer is epoxy resin (adhesives and paints/coatings)

Epoxy cross-linking

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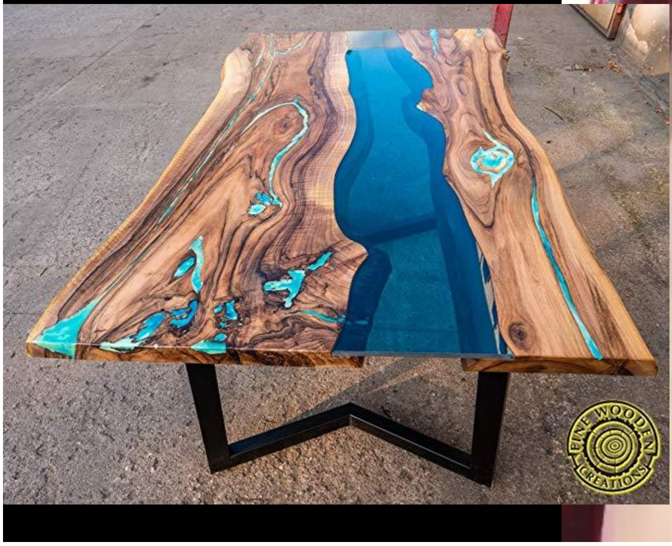
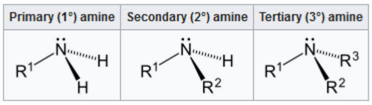


Epoxy resin harden through crosslinking reactions with a curing agent called polyamine

Primary and secondary polyamines contain reactive —NH_2 groups



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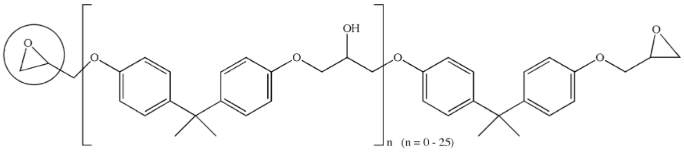
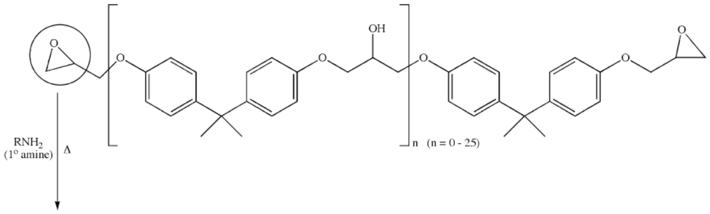


Epoxy resin monomer

Epoxy resin harden through crosslinking reactions with a curing agent called polyamine

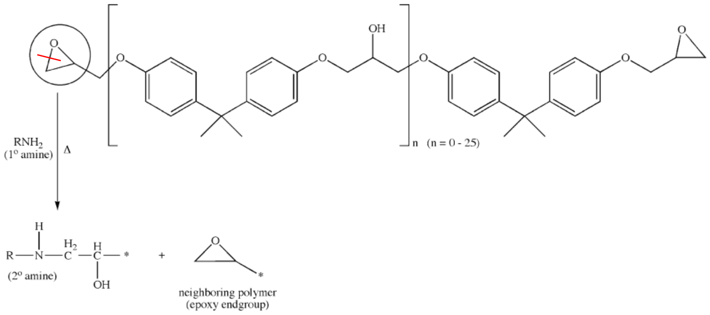
Primary and secondary polyamines contain reactive —NH_2 groups



Reaction with primary amine

Epoxy resin harden through crosslinking reactions with a curing agent called polyamine

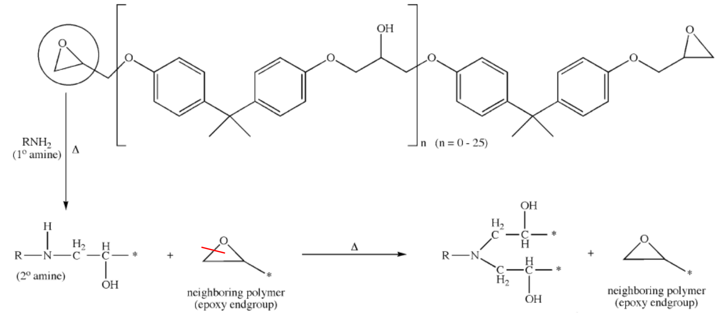
Primary and secondary polyamines contain reactive —NH_2 groups



Forms reactive secondary amine

Epoxy resin harden through crosslinking reactions with a curing agent called polyamine

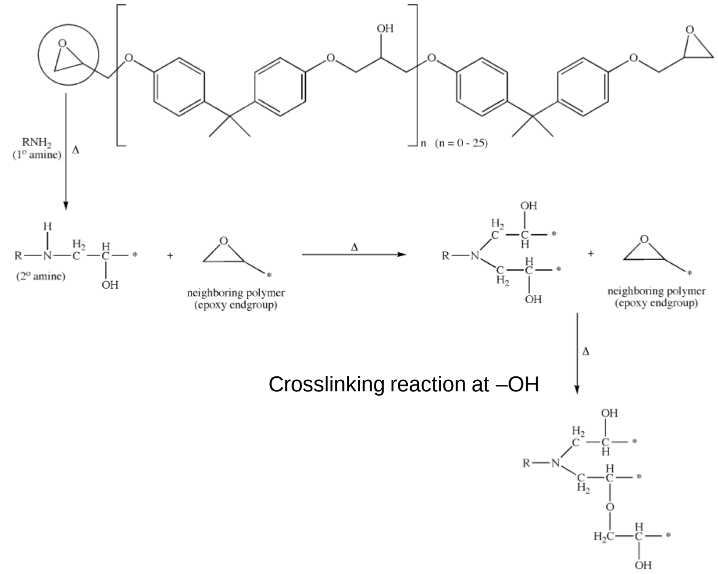
Primary and secondary polyamines contain reactive —NH_2 groups



Reactive ternary amine formed

Epoxy resin harden through crosslinking reactions with a curing agent called polyamine

Primary and secondary polyamines contain reactive —NH_2 groups



Crosslinking reaction at –OH

Epoxy resin harden through crosslinking reactions with a curing agent called polyamine

Primary and secondary polyamines contain reactive —NH_2 groups

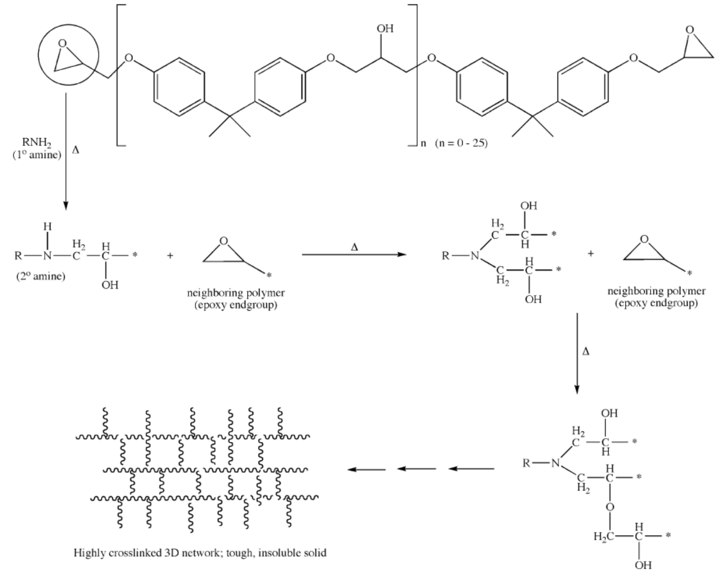
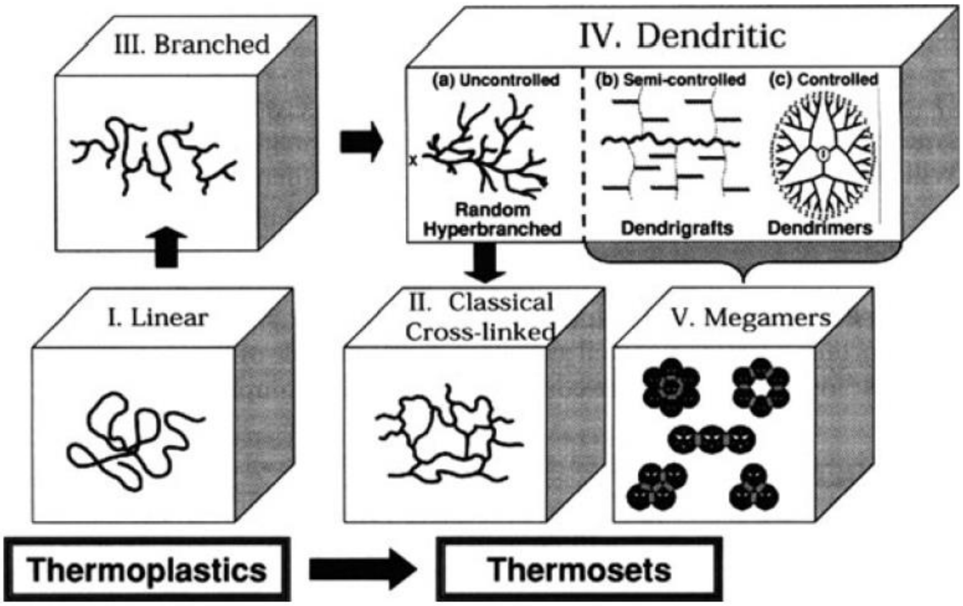


Figure 5.3. Illustration of a hardening mechanism responsible for epoxy resin curing.

Polymer structure

There are five classes of macromolecular architectures



There are five classes of macromolecular architectures

Linear chains are best able to pack into a regular crystalline array

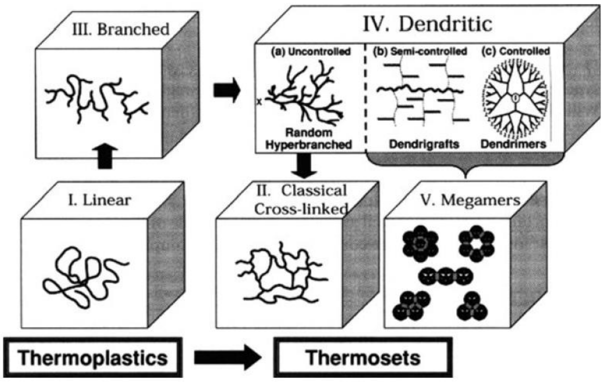


Figure 5.4. The five major structural classes of polymers. Reproduced with permission from Frechet, J. M. J.; Tomalia, D. A. *Dendrimers and Dendritic Polymers*, Wiley: New York, 2001.

There are five classes of macromolecular architectures

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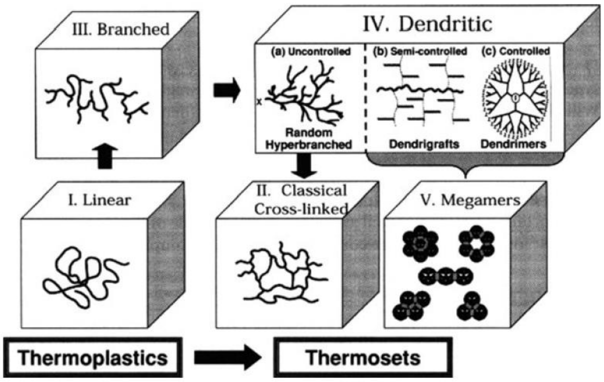
As the degree of chain branching increases, only amorphous phases are formed



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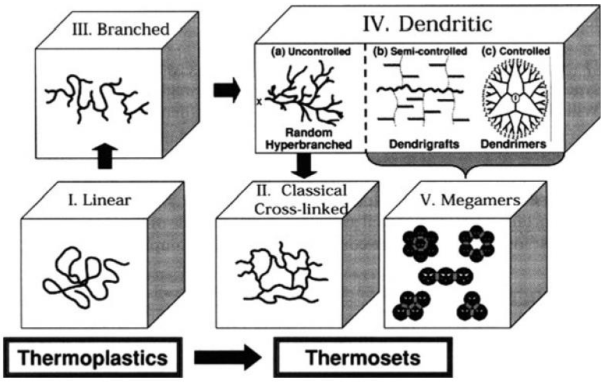
There are five classes of macromolecular architectures

Linear chains are best able to pack into a regular crystalline array

As the degree of chain branching increases, only amorphous phases are formed

Crystalline regions generally form where the polymer chains are regularly organized, while others remain disordered



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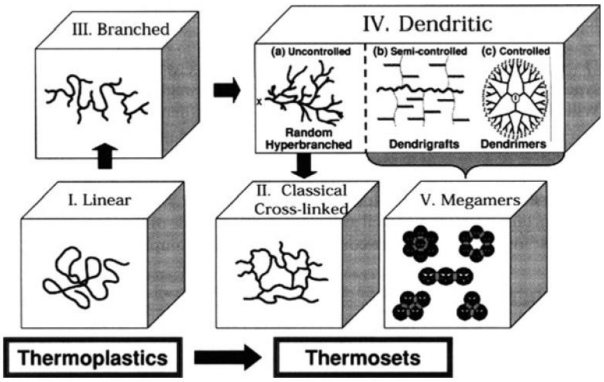
There are five classes of macromolecular architectures

Structure directly affects physical properties of the polymer, e.g. tensile strength, flexibility, and opaqueness



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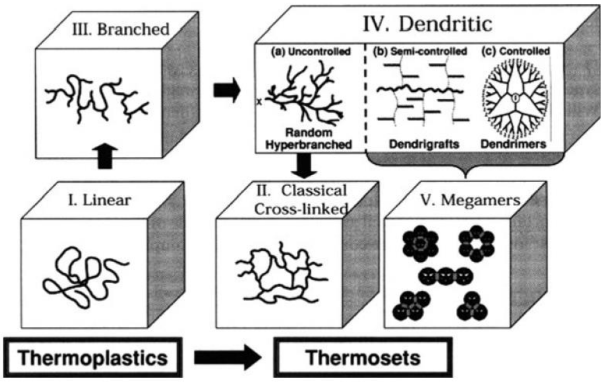
A “homopolymer” is synthesized from only one type of monomer

A “copolymer” polymer is synthesized from > 1 type of monomer



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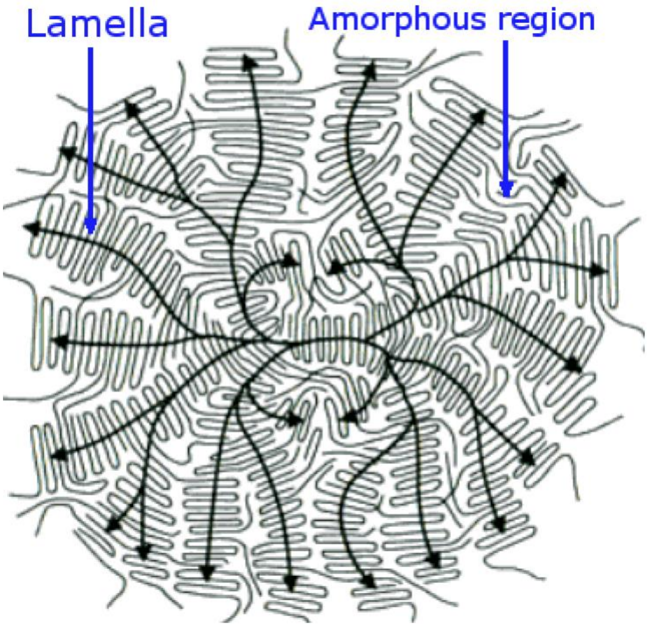
Crystallinity forms where polymer chains are regularly organized



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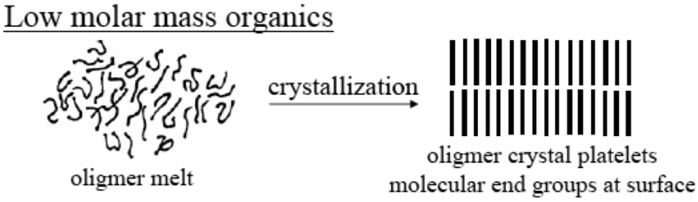

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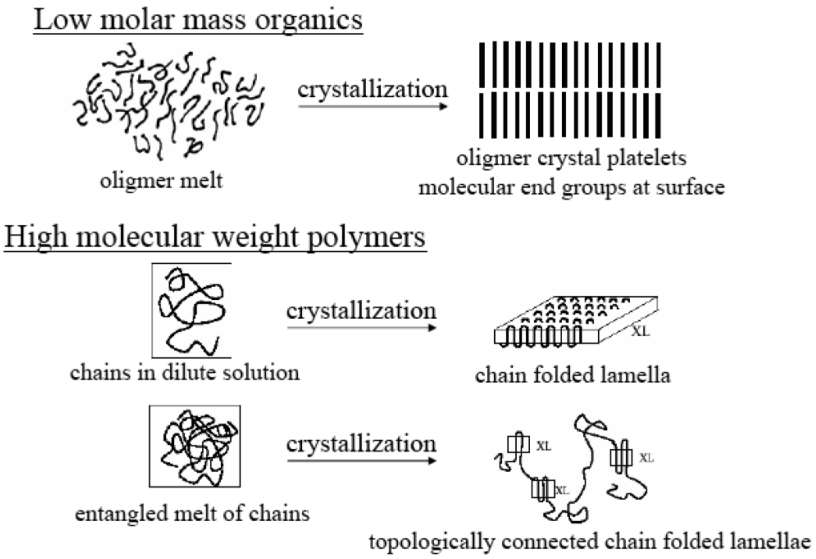
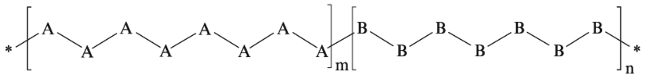


There are four types of copolymers

Block copolymers contain long adjacent sequences of A and B monomers



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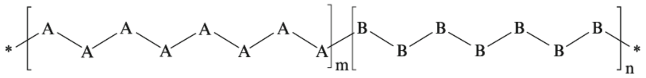

Alternating copolymers comprise sequence (— A — B —)$_n$

Random copolymer has random linkages, e.g. — AAABBABBAABB —

There are four types of copolymers

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Graft copolymers have monomer chain with offshoots

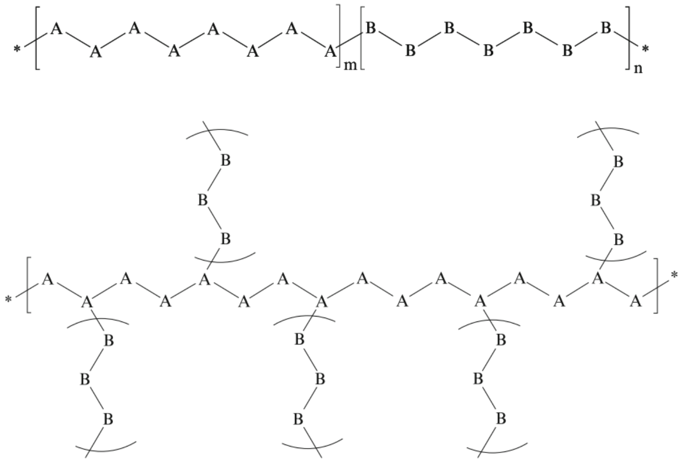

Figure 5.5. Illustration of (a) block copolymers and (b) graft copolymers.

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Graft copolymers have monomer chain with offshoots

Structure, length, and placement of copolymer units affects properties, e.g. crystallinity, density, strength, brittleness, melting point, and electrical conductivity

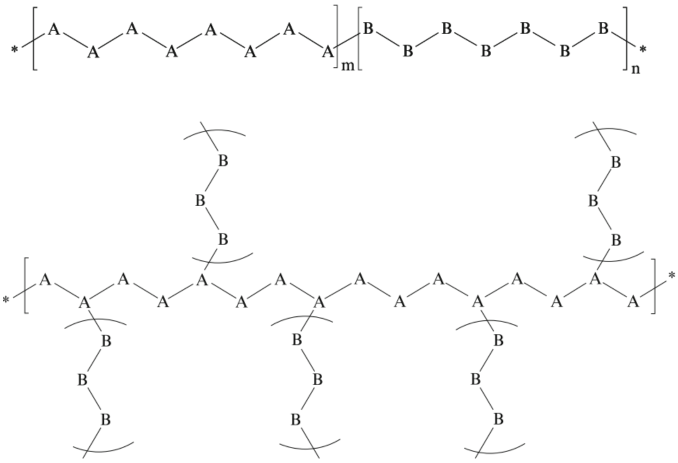

Figure 5.5. Illustration of (a) block copolymers and (b) graft copolymers.

Properties are strongly affected by intermolecular forces between individual polymer chains

The main polymer chain made of covalently bonded neighboring carbons

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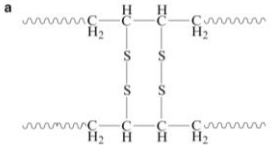
Crosslinking via covalent bond formation is responsible for vulcanization of rubber



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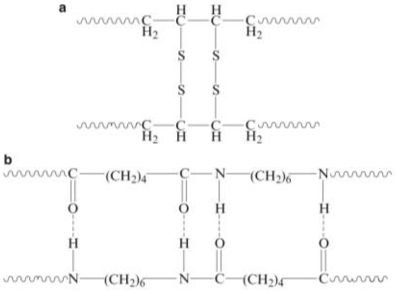
Flexibility of nylon is due to relatively weaker interchain hydrogen bonding interactions



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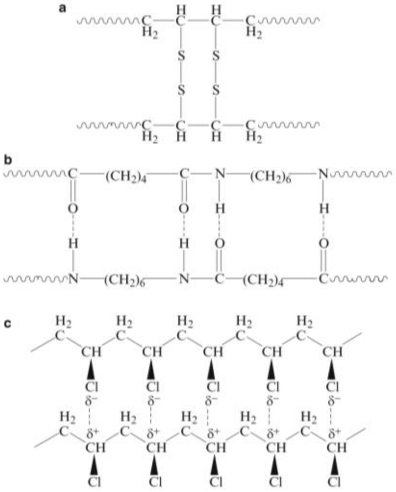

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…and van der Waals forces (induced dipole)

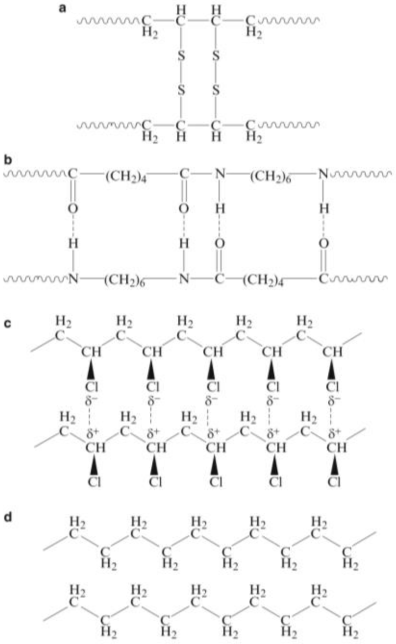

Figure 5.8. The intermolecular forces involved in adjacent polymer chains. Shown are (a) covalent crosslinking (vulcanized rubber), (b) hydrogen bonding (nylon 6,6), (c) dipole–dipole (PVC), and (d) van der Waal interactions (polyethylene).

Polymerization mechanisms

Polymers may be synthesized by two general mechanisms

Step-growth (condensation) polymerization relies on reactions of **functionalized** monomers to build up polymer chains

Chain (addition) polymerization involves the activation/addition of **unsaturated** monomers

Step-growth relies on reactions of functionalized monomers to build up polymer chains

Builds up polymer chains through dimers, trimers, etc., to form oligomers and polymers

Proceeds through reaction of neighboring complementary functional groups

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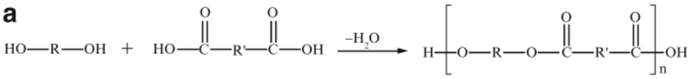
Small molecular byproducts such as HX, H_2O, etc. are generated

$$n\,\mathrm{XRX} + n\,\mathrm{HYR'YH} \rightarrow \mathrm{X(RYR')}_n\mathrm{YH} + n\,\mathrm{HX},$$
$$\text{where } \mathrm{X} = \mathrm{OH, Cl}, \textit{etc.};\ \mathrm{Y} = \mathrm{NH, O}$$



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E.g. acid/base-catalyzed synthesis of SiO_2 networks by sol–gel

Polydispersivity index (PDI) values of ~2 - 3

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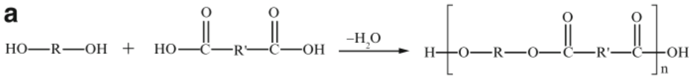

$$\mathrm{HO{-}R{-}OH} + \mathrm{HO{-}\overset{O}{\overset{\|}{C}}{-}R'{-}\overset{O}{\overset{\|}{C}}{-}OH} \xrightarrow{-H_2O} \mathrm{H{-}\left[O{-}R{-}O{-}\overset{O}{\overset{\|}{C}}{-}R'{-}\overset{O}{\overset{\|}{C}}\right]_n{-}OH}$$

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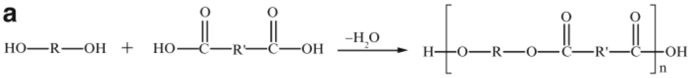

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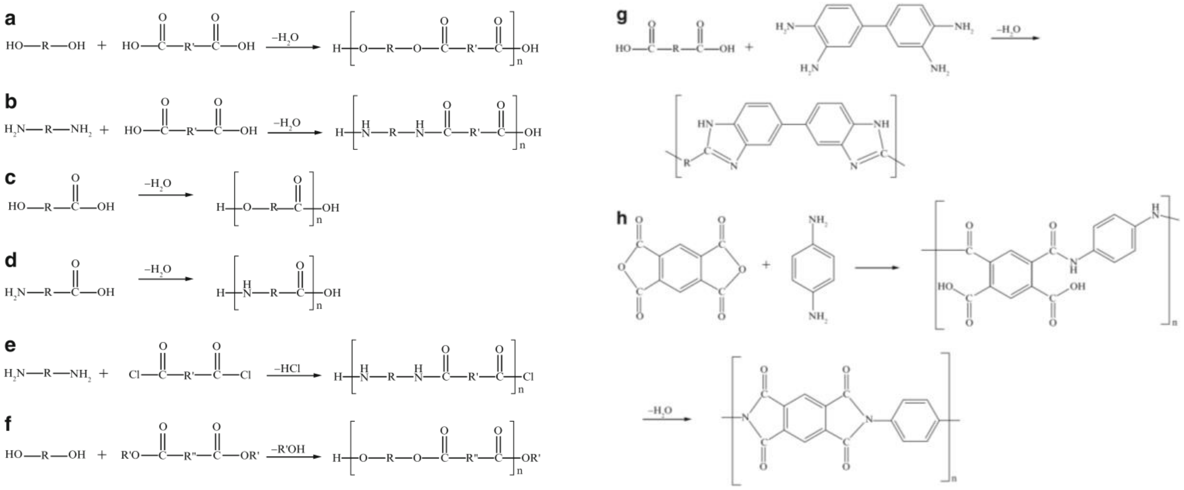

Figure 5.24. Reaction schemes for the most common types of step-growth polymerization. Shown are (a/c) polyester formation, (b/d) polyamide formation, (e) polyamide formation through reaction of an acid chloride with a diamine, (f) transesterification involving a carboxylic acid ester and an alcohol, (g) polybenzimidazole formation through condensation of a dicarboxylic acid and aromatic tetramines, and (h) polyimide formation from the reaction of dianhydrides and diamines.

Addition polymerization involves the activation/addition of unsaturated monomers

Yields a much higher MW polymer in a relatively short period of time

Small molecular byproducts are not generated

PDI values of ca. 10–20

Addition polymerization involves the activation/addition of unsaturated monomers

Involves three steps: initiation, propagation, and termination

---

Addition polymerization involves the activation/addition of unsaturated monomers

Involves three steps: initiation, propagation, and termination

During initiation, radicals or ionic species are made from controlled decomposition of initiator molecule.

$$H_2C{=}CH_2 + \cdot R \xrightarrow{\text{"Initiation"}} H_2\dot{C}{-}\overset{H_2}{C}{-}R$$

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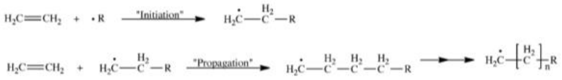
Involves three steps: initiation, propagation, and termination

During initiation, radicals or ionic species are made from controlled decomposition of initiator molecule.

Intermediates are added to the C ═ C bonds of monomers to propagate growth



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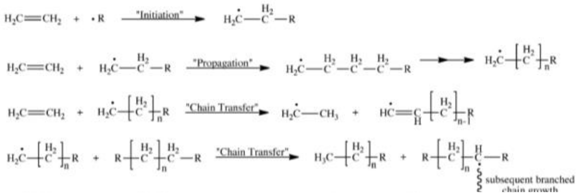
facile chain-transfer may occur, where the radical end of the growing chain abstracts an atom from another molecule/chain, stopping primary chain growth.



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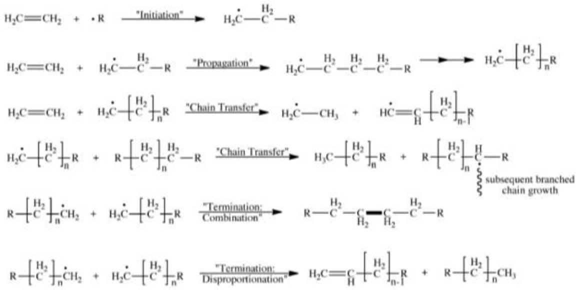
Termination of polymer growth occurs through either combination or disproportionation (simultaneous redox)



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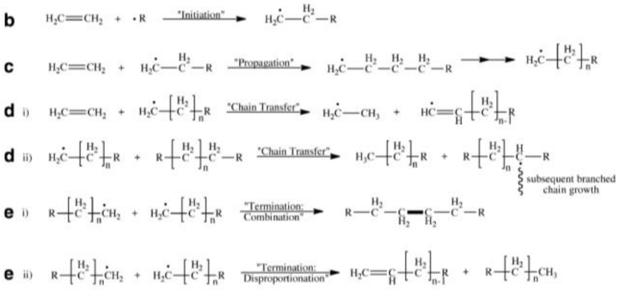

Figure 5.9. Reactions involved in free-radical addition polymerization. Shown are (a) (i)–(iii) generation of free radicals from a variety of initiators, (b) initiation of polymer chain growth through the combination of a free radical and unsaturated monomer, (c) propagation of the polymer chain through the combination of growing radical chains, (d) chain-transfer of free radicals between the primary and neighboring chains, and (e) termination of the polymer growth through either combination (i) or disproportionation (ii) routes.

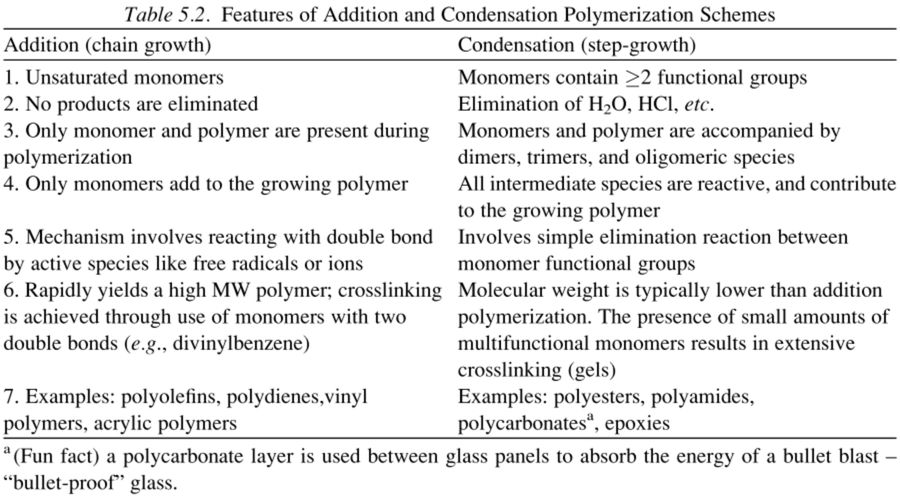

Table 5.2. Features of Addition and Condensation Polymerization Schemes

Addition (chain growth)	Condensation (step-growth)
1. Unsaturated monomers	Monomers contain ≥2 functional groups
2. No products are eliminated	Elimination of H_2O, HCl, *etc*.
3. Only monomer and polymer are present during polymerization	Monomers and polymer are accompanied by dimers, trimers, and oligomeric species
4. Only monomers add to the growing polymer	All intermediate species are reactive, and contribute to the growing polymer
5. Mechanism involves reacting with double bond by active species like free radicals or ions	Involves simple elimination reaction between monomer functional groups
6. Rapidly yields a high MW polymer; crosslinking is achieved through use of monomers with two double bonds (*e.g.*, divinylbenzene)	Molecular weight is typically lower than addition polymerization. The presence of small amounts of multifunctional monomers results in extensive crosslinking (gels)
7. Examples: polyolefins, polydienes,vinyl polymers, acrylic polymers	Examples: polyesters, polyamides, polycarbonates[a], epoxies

[a] (Fun fact) a polycarbonate layer is used between glass panels to absorb the energy of a bullet blast – "bullet-proof" glass.

Molecular weight (MW) of a polymer is MW of the monomer(s) multiplied by the degree of polymerization

Degree of polymerization (DoP)

$$\mathrm{DoP} = \frac{M_r}{M_R}$$

where M_r = relative molar mass of the polymer, and MR = relative molar mass of the monomer

Polydispersity is the range of the molecular weight distribution

The polydispersity index (PDI)

$$\mathrm{PDI} = \frac{\overline{M}_w}{\overline{M}_n}$$

where M_W is the weight average molecular weight, M_n is the number average molecular weight

The PDI for synthetic polymers is always >1.0; as chains approach a uniform length, the PDI will approach unity

Biopolymers (e.g., polypeptides) have PDI values ≈ or = 1, indicating that only one length of polymer is present

References (see Class page)

Fahlman (2011) Polymeric Materials chapter in Materials Chemistry, *Springer*