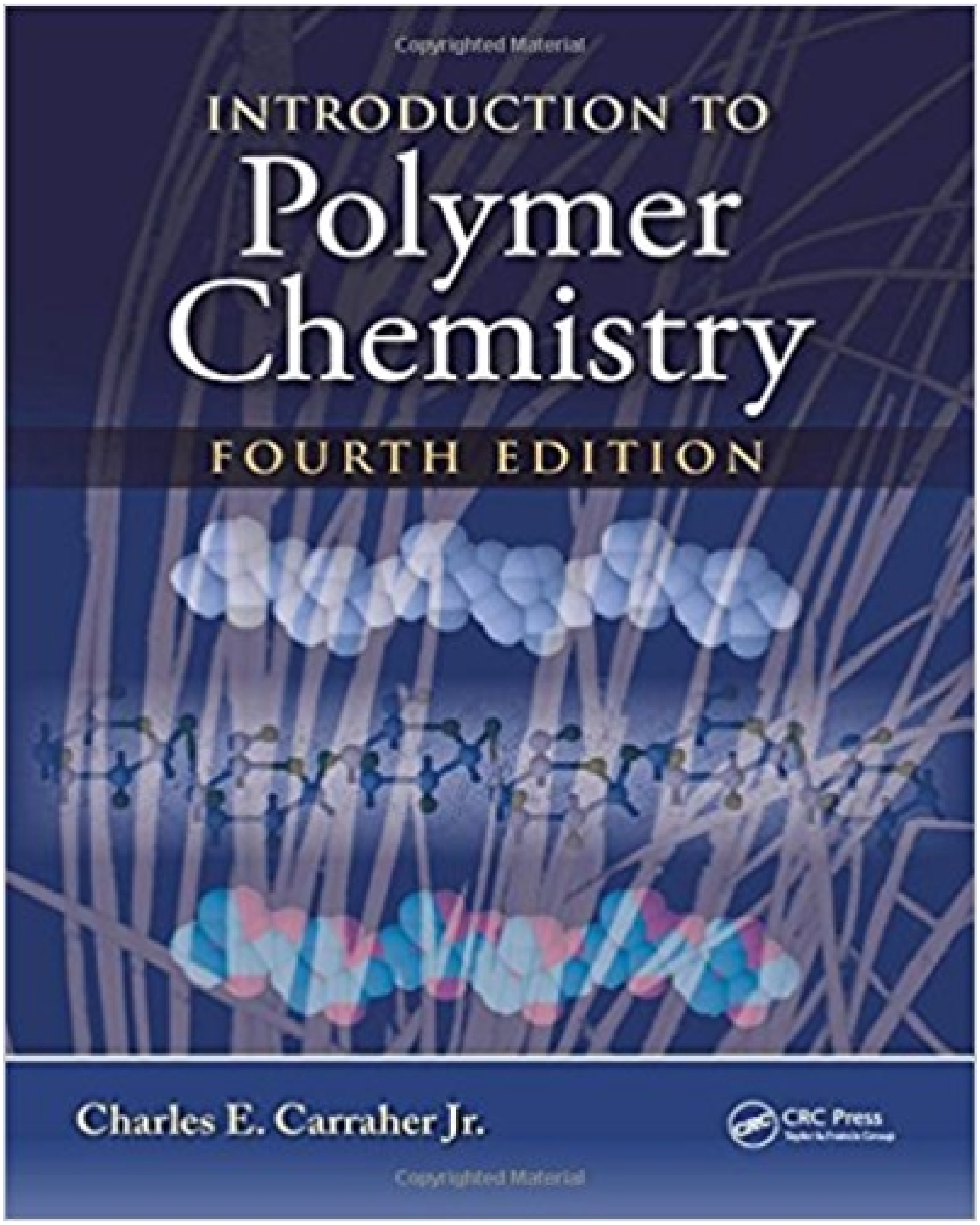
Solutions for Introduction to Polymer Chemistry 4th Edition by Carraher Jr






# Solutions

# Chapter 2

**EXERCISES**

*(To answer some of these questions you may need to look at other parts in the book for structures and specific details.)*

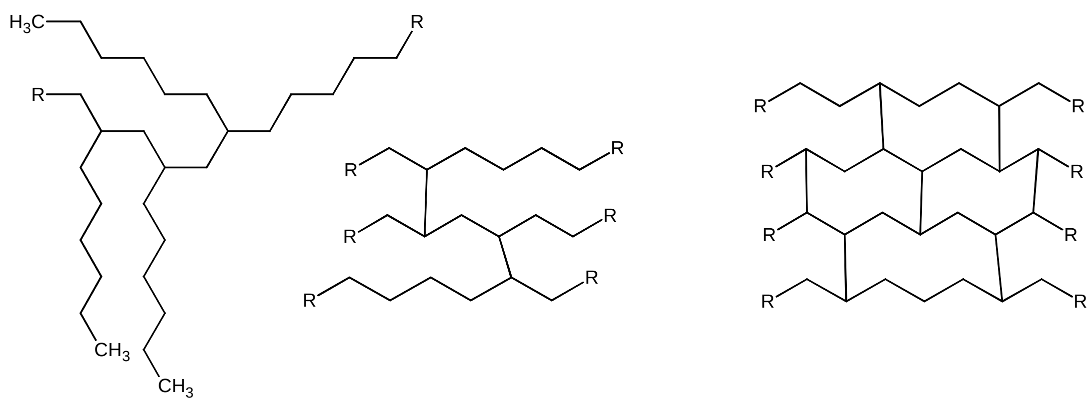
1. Make sketches or diagrams showing (a) a linear polymer, (b) a polymer with pendant groups, (c) a polymer with short branches, (d) a polymer with long branches, and crosslinked polymers with (e) low and (f) high crosslinked density.
2. Which has (a) the greater volume for the same weight of material and (b) the lower softening point: HDPEC or LDPE?
3. What is the approximate bond length of the carbon atoms in (a) a linear and (b) a crosslinked polymer.
4. What is the approximate contour length of a HDPE chain with an average degree of polymerization (chain length) of n = 2000 and of a PVC chain of the same number of repeating units?
5. Which of the following are monodisperse polymers with respect to chain length? (A) heva rubber, (b) corn starch, (c) cellulose from cotton, (d) an enzyme, (e) HDPE, (f) PVC, (g) a specific DNA, (h) nylon 66, (i) a specific RNA?
6. What is the average degree of polymerization of LDPE having an average molecular weight of 28,000?
7. What is the structure of the repeating unit in (a) polypropylene, (b) poly(vinyl chloride, (c) hevea rubber?
8. Which of the following is a branched chain polymer: (a) HDPE, (b) Isotactic PP, (c) LDPE, (d) amylose starch?
9. Which of the following is a thermoplastic: (a) ebonite, (b) Bakelite, (c) vulcanized rubber, (d) HDPE, (e) celluloid, (f) PVC, (g) LDPE?
10. Which has the higher crosslinked density, (a) ebonite or (b) soft vulcanized rubber?
11. Do HDPE and LDPE differ in (a) configuration or (b) conformation?
12. Which is a trans isomer: (a) gutta percha or (b) hevea rubber?
13. Which will have the higher softening point: (a) gutta percha or (b) hevea rubber?
14. Show (a) a heat-to-tail, and (b) a head-to-head configuration for PVC.
15. Show the structure of a typical portion of the chain of (a) s-PVC, (b) i-PVC.
16. Show Newman projections of the gauche forms of HDPE.
17. Name polymers whose intermolecular forces are principally (a) London forces, (b) dipole-dipole forces, (c) hydrogen bonding.
18. Which will be more flexible: (a) poly(ethylene terephthate), or (b) poly(butylene terephthalate)?
19. Which will hve the higher glass transition temperature: (a) poly(methylene methacrylate) or (b) poly(butyl methacrylate)?
20. Which will have the higher $T_g$ : (a) i-PP or (b) a-PP?
21. Which will be more permeable to a gas at room temperature: (a) i-PP or (b) a-PP?
22. Under what kind of physical conditions are you more apt to form spherulites.
23. What is the full contour length of a molecule of HDPE with a DP of 1,500?
24. Which would be more flexible: (a) poly(methyl acrylate) or (b) poly(methyl methacrylate?
25. Which would you expect to form “better” helical structures (a) i-polypropylene or (b) a-

polypropylene?
26. Which would you expect to have a higher melting point (a) nylon-66, or (b) an aramide?
27. What type of hydrogen bonds are present in the internal structure of a globular protein?
28. Which would have the greater tendency to "cold flow" at room temperature: (a) poly(vinyl acetate) ($T_g$ = 301 K) or (b) polystyrene ($T_g$ = 375 K)?
29. Which would be least transparent: (a) combination of amorphous and crystalline PS, (b) entirely crystalline PS, or (c) entirely amorphous PS?
30. Which would be more apt to produce crystallites: (a) HDPE or (b) poly(butyl methacrylate)?
31. Which of the following would you expect to provide strong fibers (a) nylon-66, (b) a-polypropylene, (c) wool.
32. Which would tend to be more crystalline when stretched: (a) unvulcanized rubber or (b) ebonite?
33. Which would be more apt to exhibit side chain crystallization (a) poly(metnyl methacrylate) or (b) poly(dodecyl methacrylate)?

**ANSWERS**

1. (a) -MMMMMMMMMMMMM-, (b) -CCCCCCCCCCCCC-, (c) -CCCCCCCCC-

| | | | | | | |     | |
X X X X X X X     M M
M M

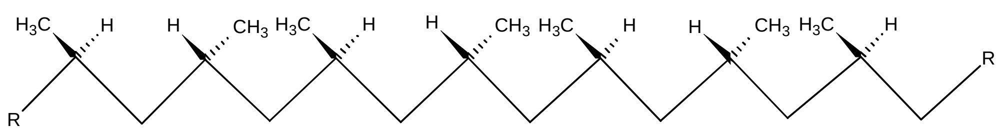



(d) (e) (f)

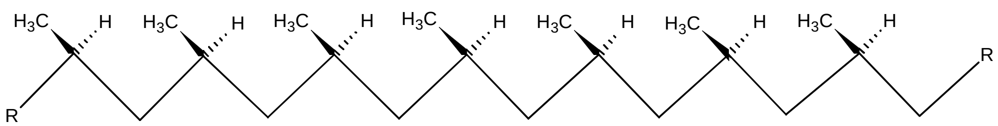
2. (a) LDPE, (b) LDPE.
3. (a) about 109.5; (b) about 109.5 ; zigzag chains characteristic of alkanes
4. Contour length are both about the same since the backbone for each is composed entirely of carbon atoms. Given a C-C bond length of 0.126 nm this means the effective length for each unit is 2 x 0.126 nm = 0.252 nm. Thus the contour length is 0.252 nm times 2000 units = 504 nm.
5. d,g,i.
6. 1,000

7. (a) $-CH_2-CH(CH_3)-$,
(b) $-CH_2-CHCl-$,
(c) $-CH_2-CH(CH_3)=CH-CH_2-$
8. c.
9. d,e,f,g.
10. a.
11. a.
12. a.
13. a.
14. (a) $-CH_2-CH(OH)-CH_2-CH(OH)-$,
(b) $-CH_2-CH(OH)-CH(OH)-CH_2-$

15.
(a) syndiotactic-polypropylene or simply sPP.




(b) isotactic-polypropylene or simply iPP.




16. See Figure 2.7; simply extend the end methyl groups making them methylene groups.
17. (a) HDPE, LDPE, hevea rubber, etc., (b) PVC, etc., (c) nylon-66, cellulose, silk, etc.
18. b.
19. a.
20. a.
21. b.
22. Low or no flow; slow cooling rate; linear polymers.
23. 378 nm
24. a.
25. (a) because of a more regular structure.
26. b.
27. Intramolecular hydrogen bonds.
28. a.
29. Being transparent depends of having a homogeneous structure so (a) is the least homogeneous and thus has varying refractive indexes causing it to appear hazy.
30. a
31. a and c.
32. a.

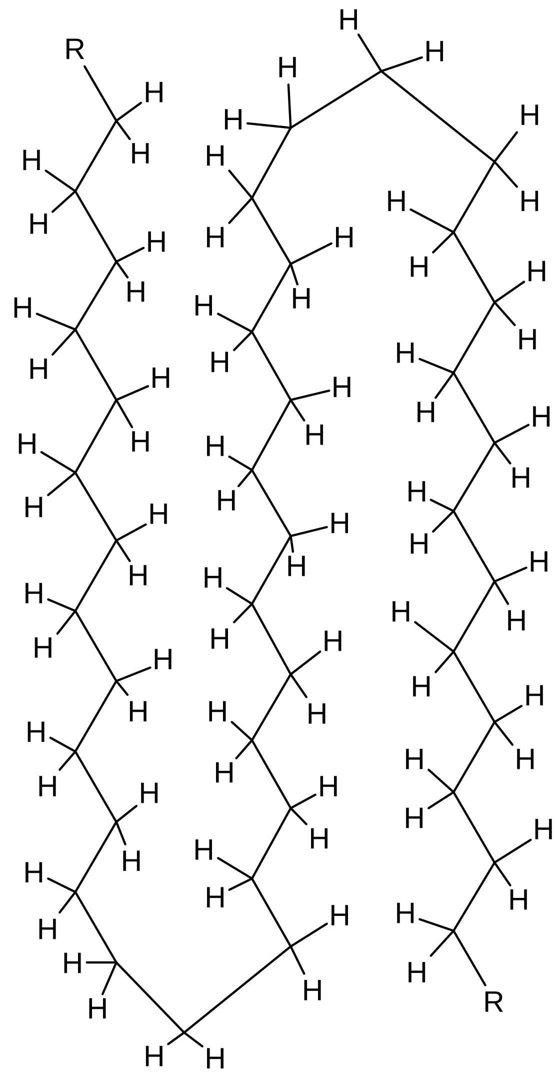
33. b.

# $4^{th}$ Ed Cpt 2 Polymer Structure

# **Table 2.1** Typical properties of straight chain hydrocarbons.

| **Average number of carbon atoms** | **Boiling range,°C** | **Name** | **Physical state at room temp.** | **Typical uses** |
|---|---|---|---|---|
| 1-4 | <30 | Gas | Gas | Heating |
| 5-10 | 30-180 | Gasoline | Liquid | Automotive fuel |
| 11-12 | 180-230 | Kerosene | Liquid | Jet fuel, heating |
| 13-17 | 230-300 | Light gas oil | Liquid | Diesel fuel, heating |
| 18-25 | 305-400 | Heavy gas oil | Viscous liquid | Heating |
| 26-50 | Decomposes | Wax | Waxy | Wax candles |
| 50-1000 | Decomposes | | Tough waxy to solid | Wax coatings food containers |
| 1000-5000 | Decomposes | Polyethylene | Solid | Bottles, containers, films |
| >5000 | Decomposes | Polyethylene | Solid | Waste bags, ballistic wear, fibers, automotive parts, truck liners |

**Figure 2.1** Simulated structure of high-density polyethylene (HDPE), left, contrasted with the structural formula of linear or normal decane, right.



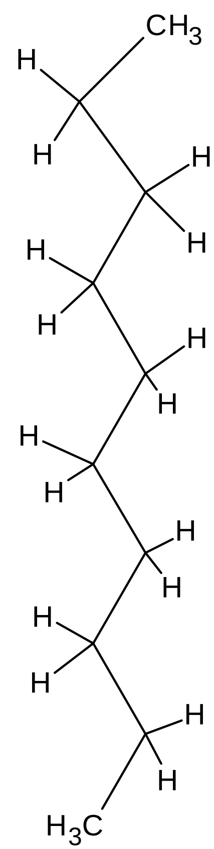
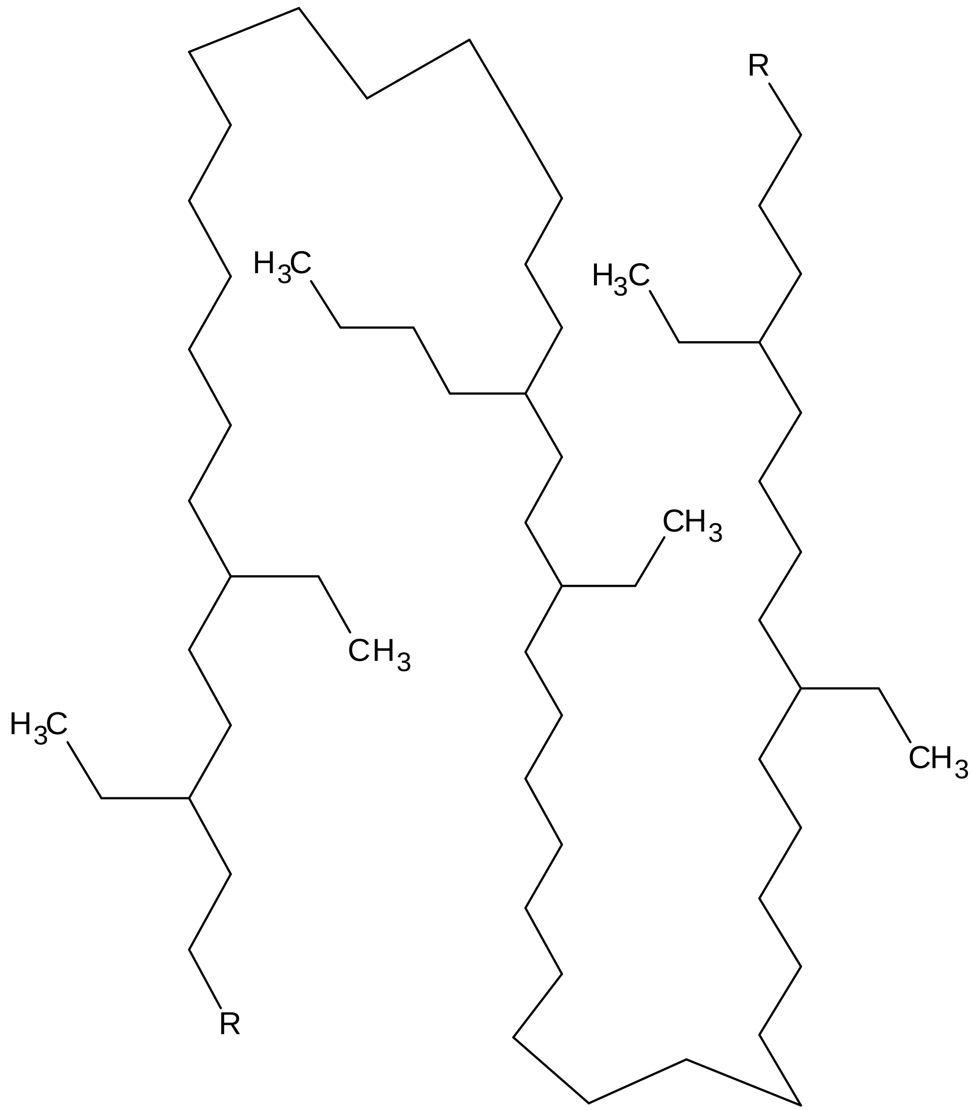


**Figure 2.2** Simulated structural formula for branched low-density polyethylene (LDPE); compare with Figure 2.1 for HDPE.



# **Table 2.2** Types of Commercial Polyethylene

| General structure | %-Crystallinity | Density (g/cc) |
|---|---|---|
| LDPE-Linear with branching | 50 | 0.92-0.94 |
| LLDPE-Linear with less branching | 50 | 0.92-0.94 |
| HDPE-Linear with little branching | 90 | 0.95 |

**Figure 2.3** Skeletal structural formulas of a linear polymer (left), and a network (crosslinked) polymer with low crosslinking density (middle) and high density crosslinking (right). Cross-link sites are noted by the non-darkened spheres.

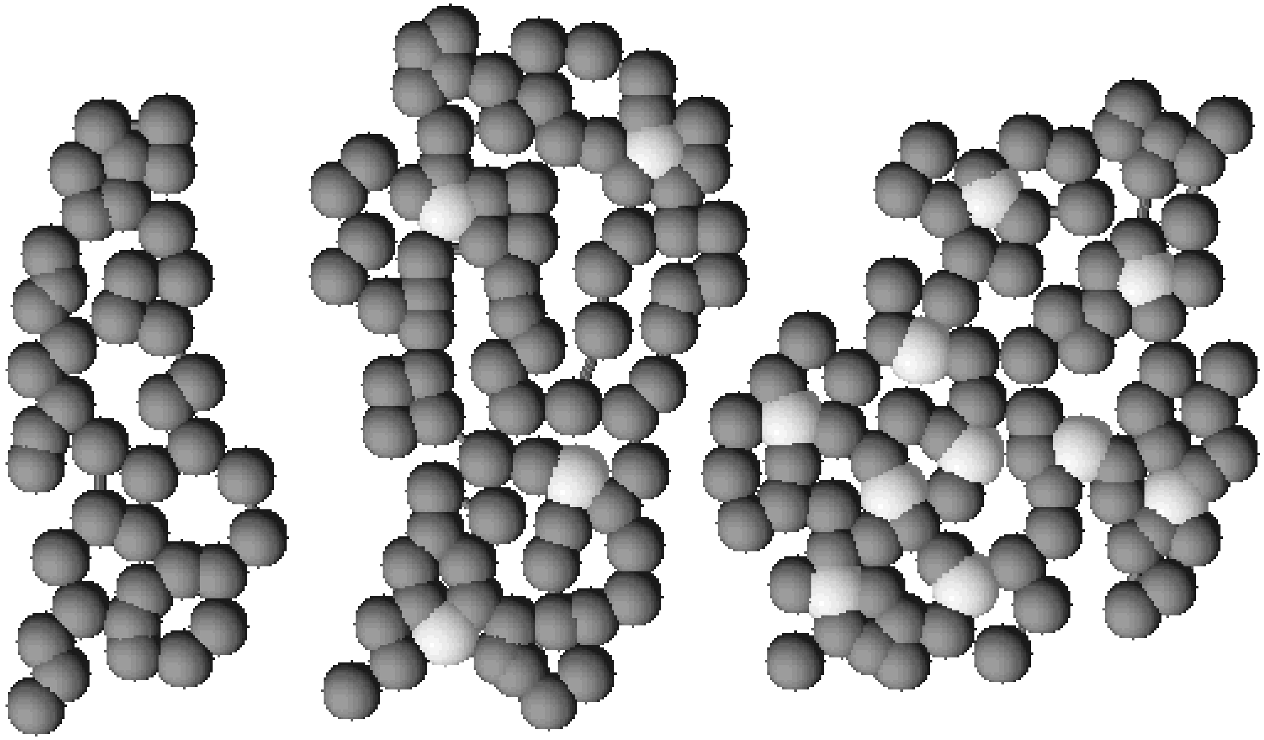


**Figure 2.4** Simulated structural formulas showing the usual head-to-tail, middle, and unusual head-to-head, right, configurations of polypropylene.

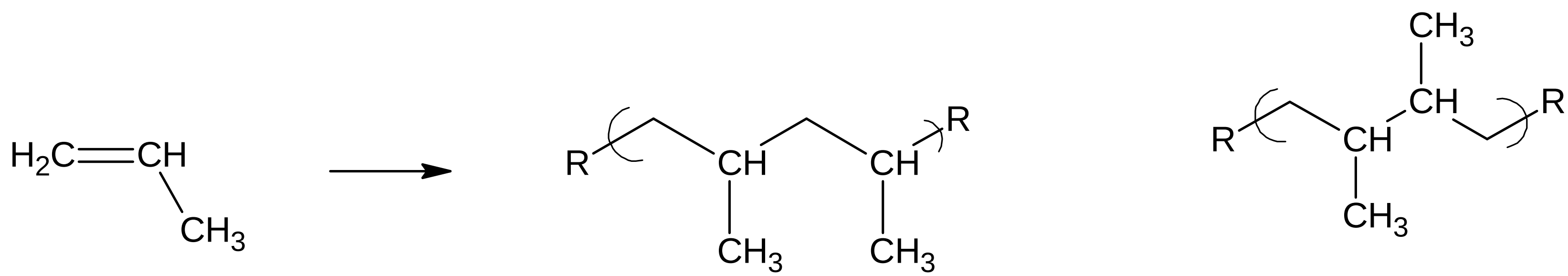
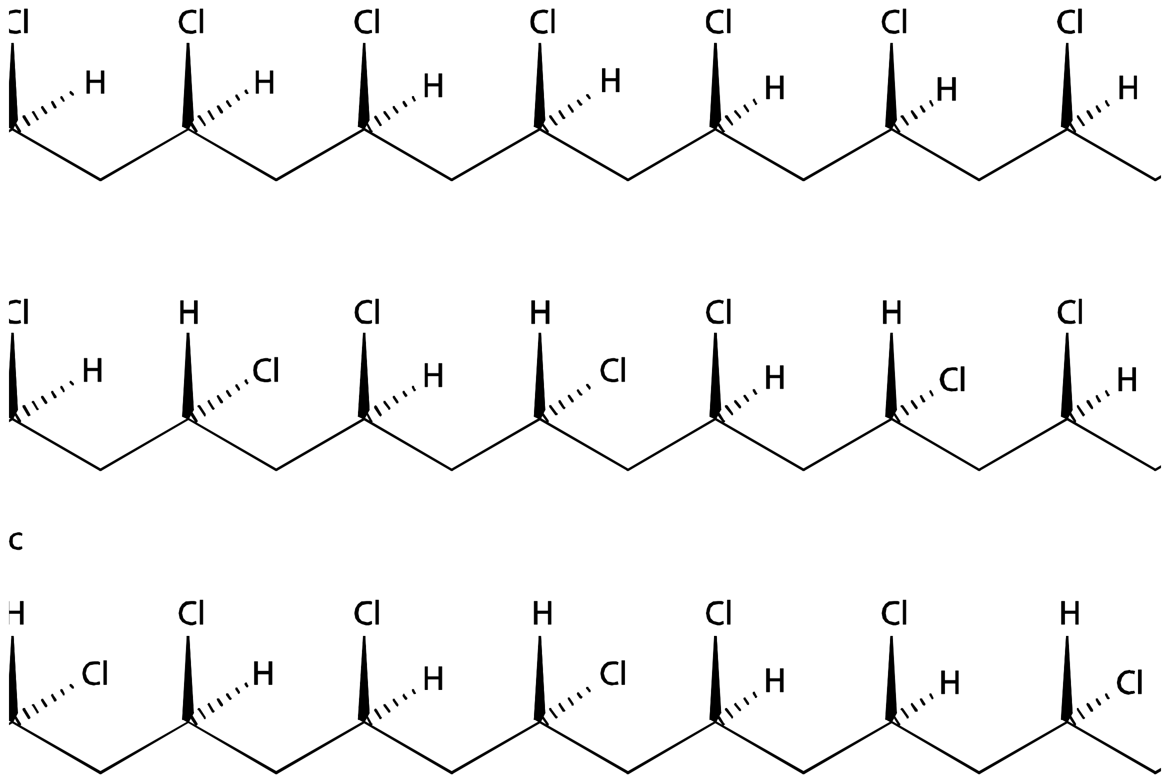
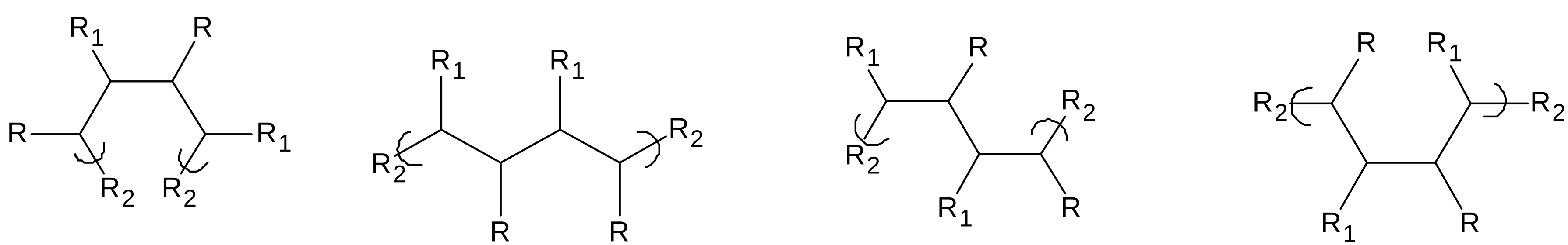


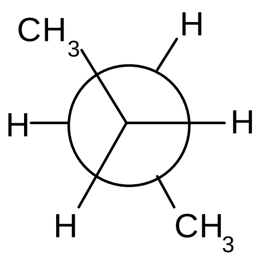
**Figure 2.5** Skeletal formulas of isotactic (top), syndiotactic (middle), and atactic (bottom) of poly(vinyl chloride), PVC.

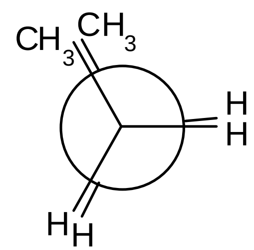





**Erythrodiisotactic** **Threodiisotactic** **Erythrodisyndiotactic** **Threodisyndiotactic**

**Figure 2.6** Simulated formulas of ditactic isomers where $R_2$ are chain extensions and R and $R_1$ are not hydrogen.



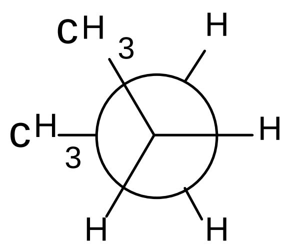




Figure 2.7 Newman projections of designated conformers of n-butane- Anti (left), Eclipsed (middle) and Gauche (right).

**Figure 2.8** Representation of a crystalline portion from isotactic polypropylene, left, and an amorphous portion from atactic polypropylene, right.

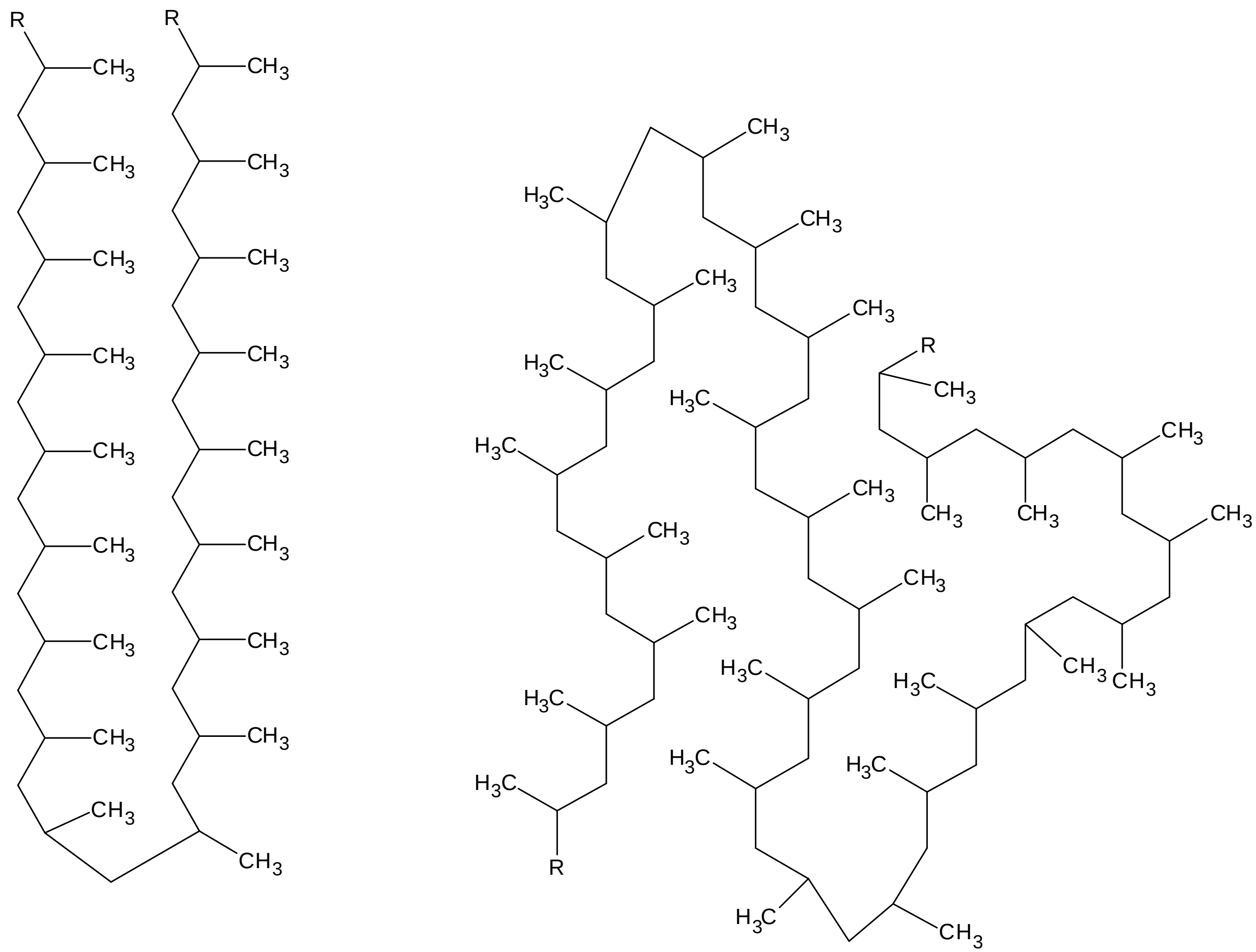
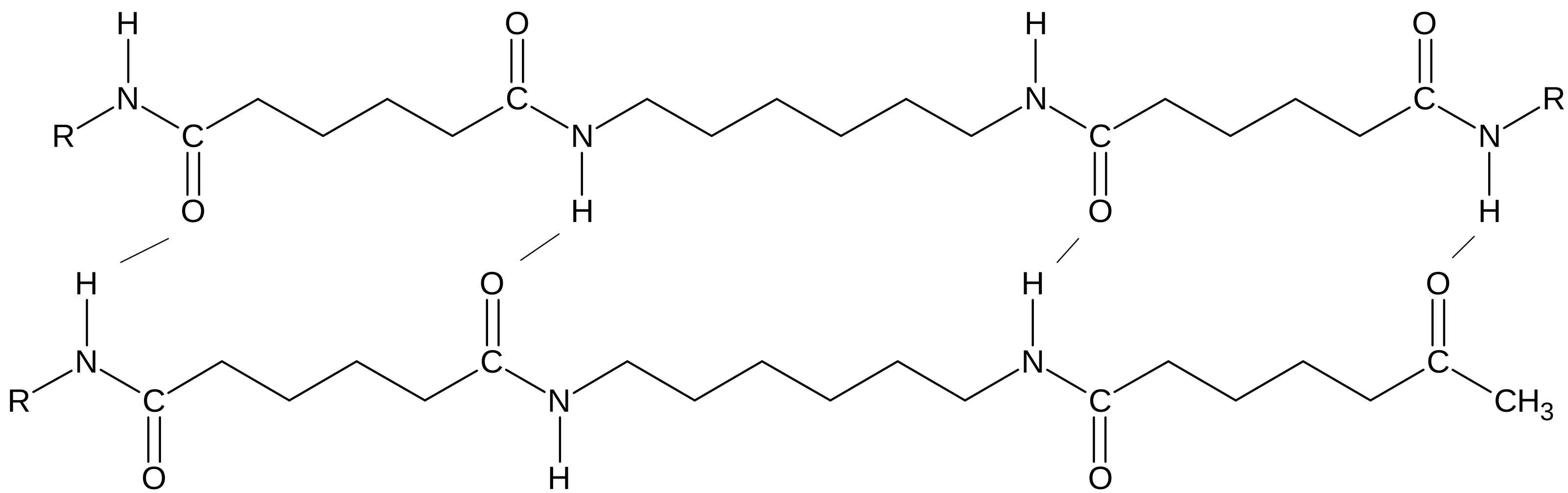


Table 2.2b. General classes of secondary forces.

| Type | Relative Strength |
| --- | --- |
| • Ion-dipole | Strongest |
| • Dipole-dipole | |
| • Dipole-induced dipole | |
| • Induces dipole-induced dipole | Weakest |

**Figure 2.9** Typical hydrogen-bonding (shown as “-“ between hydrogen on nitrogen and oxygen for nylon 66.

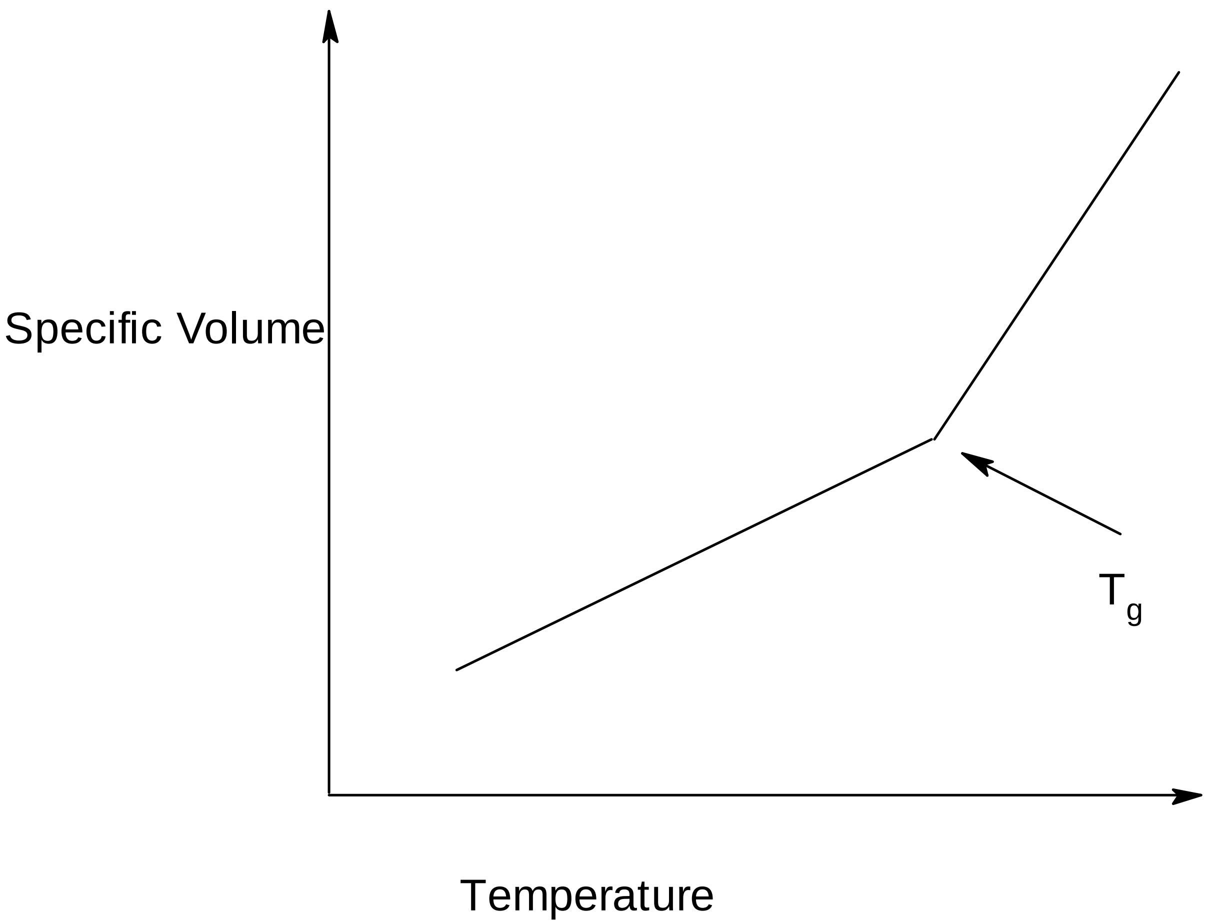


## Table 2.3 Critical chain lengths for some common polymers.

| Polymer | Critical Chain Length (Number of repeat units) |
|---|---|
| Polycarbonate | 20 |
| 1,4-Polybutadiene | 110 |
| Poly(decamethylene adipate) | 11 |
| Polydimethylsiloxane | 450 |
| Polyethylene | 150 |
| Poly(ethylene oxide) | 100 |
| Poly(methyl methacrylate) | 160 |
| Polypropylene | 170 |
| Poly(propylene oxide) | 100 |
| Polystyrene | 300 |
| Poly(vinyl acetate) | 250 |
| Poly(vinyl alcohol) | 170 |
| Poly(vinyl chloride) | 175 |

- modified from L. H. Sperling, Introduction to Physical Polymer Science, 4th Edition, Wiley, Hoboken, NJ,

Figure 2.10 Determination of $T_g$ by noting the abrupt change in specific volume.



# **Table 2.4** Approximate Glass Transition Temperatures ($T_g$) for Selected Polymers

| Polymer | $T_g$ (K) | Polymer | $T_g$ (K) |
|---|---|---|---|
| Cellulose acetate butyrate | 323 | Cellulose triacetate | 430 |
| Polyethylene (LDPE) | 148 | Polytetrafluoroethylene | 160,400[a] |
| a-Polypropylene | 253 | Poly(ethyl acrylate) | 249 |
| i-Polypropylene | 373 | Poly(methyl acrylate) | 279 |
| Polyacrylonitrile | 378 | alpha-Poly(butyl methacrylate) | 339 |
| Poly(vinyl acetate) | 301 | alpha-Poly(methyl acrylate) | 378 |
| Poly(vinyl alcohol) | 358 | Poly(vinyl chloride) | 354 |
| cis-Poly-1,3-butadiene | 165 | Nylon-66 | 330 |
| trans-Poly-1,3-butadiene | 255 | Poly(ethylene adipate) | 223 |
| Polydimethylsiloxane | 150 | Poly(ethylene terephthalate) | 342 |
| Polystyrene | 373 | | |

a. Two major transitions observed.

Figure 2.11 Typical DSC thermogram of a polymer.

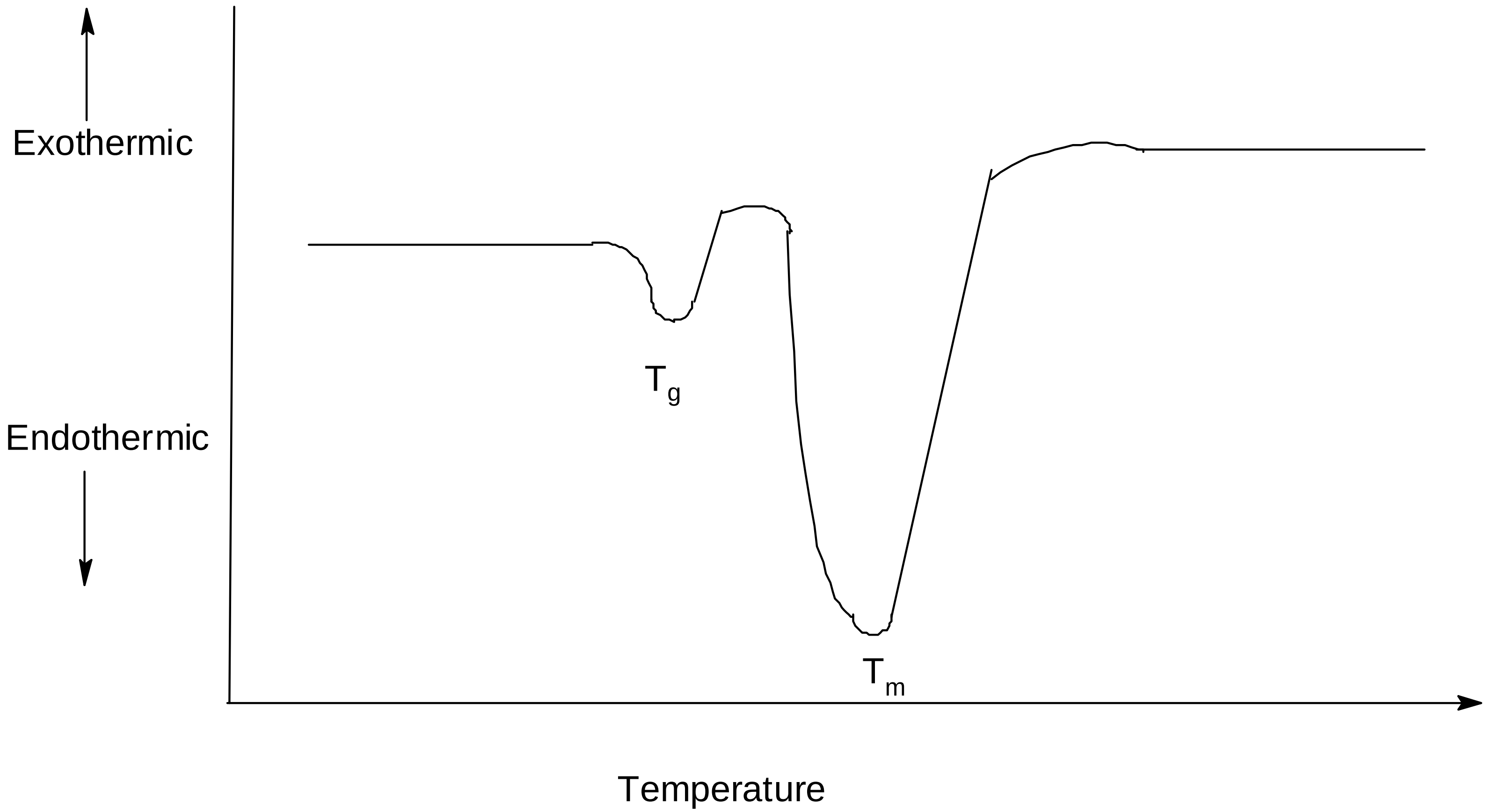


Figure 2.12 End-to-end distances for four 30-unit chains.

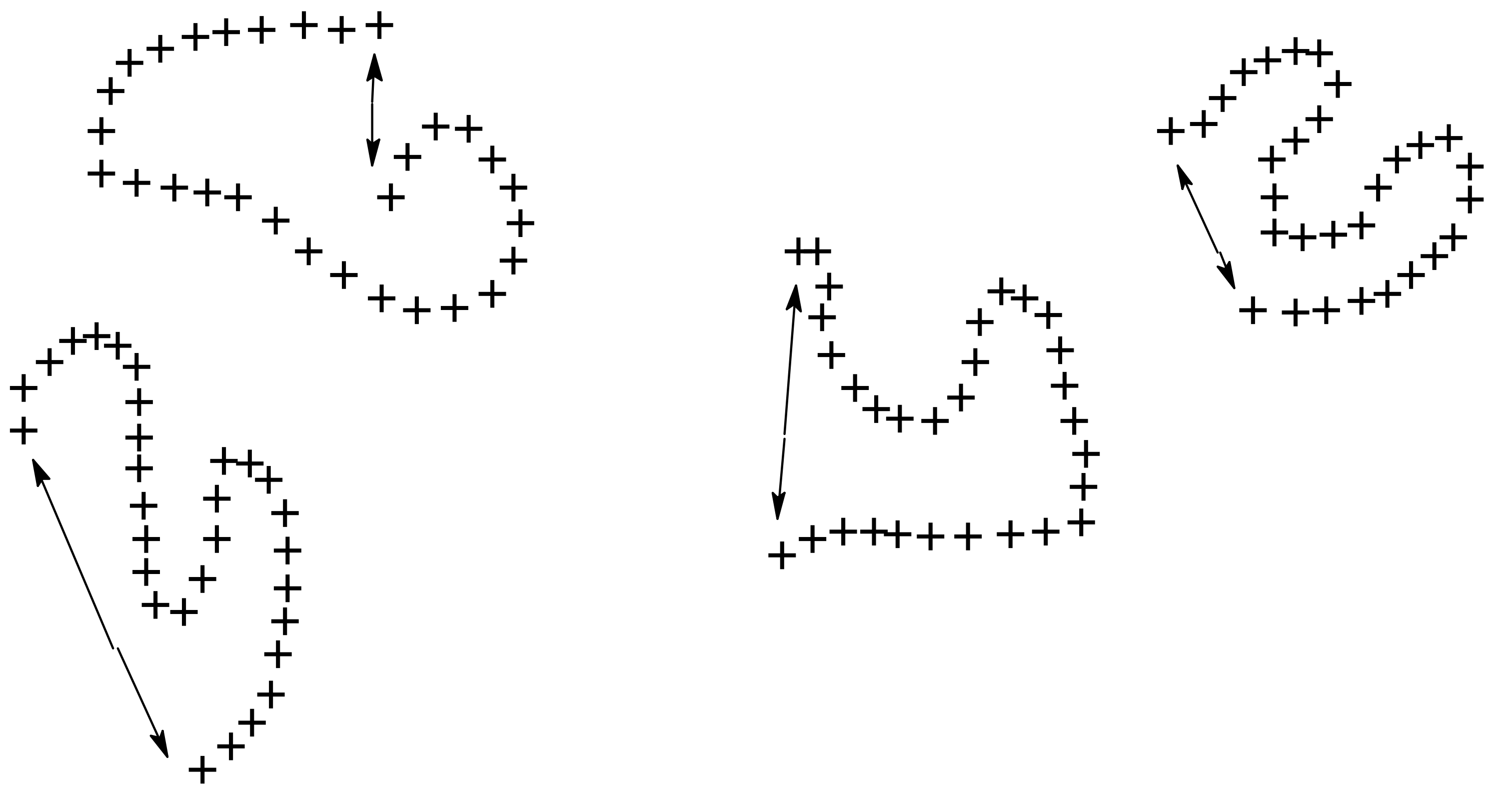


**Figure 2.13** Helical conformation of isotactic vinyl polymers. (From N. Gaylord, in Linear and Steroregular Addition Polymers (N. Gaylord and H. Mark, eds.), Wiley, NY, 1959.

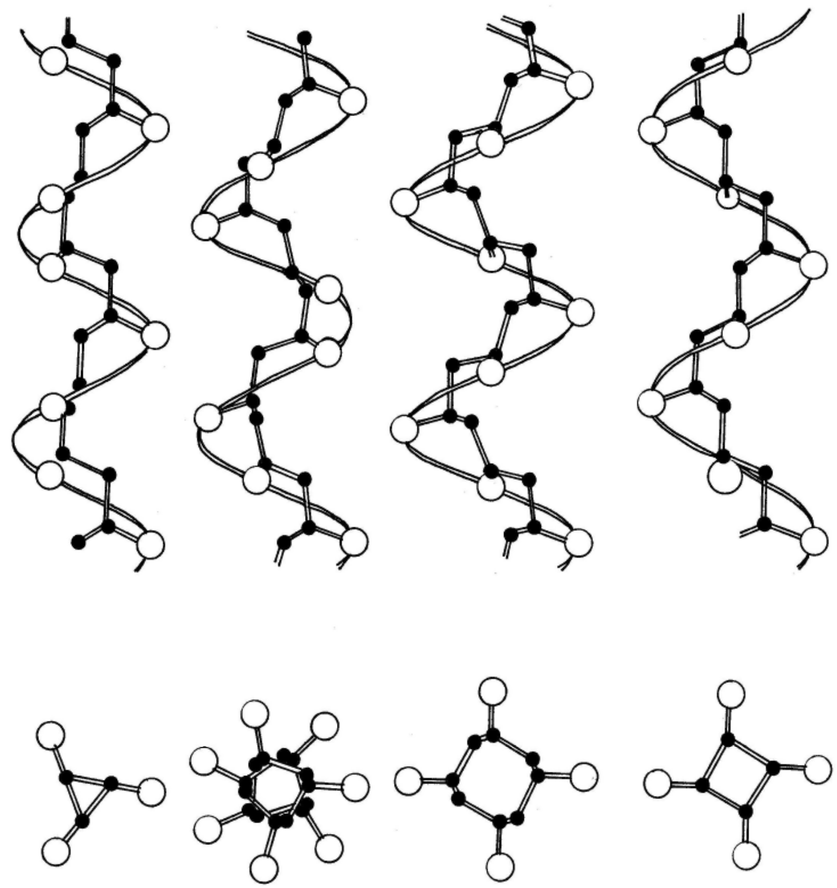


**Figure 2.14** Schematic two-dimensional representation of a modified micelle model of the crystalline-amorphous structure of polymers.

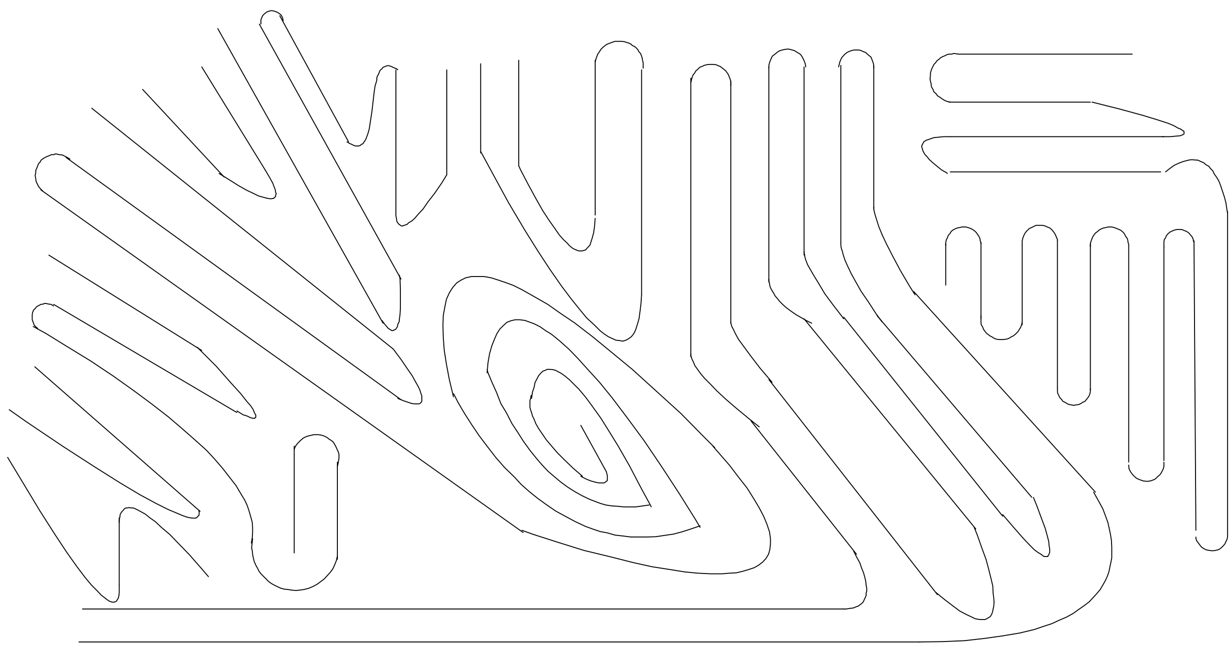


Figure 2.15 Structure of a spherulite from the bulk. Bottom shows a slice of a simple spherulite. As further growth occurs, filling in, branch points, etc. occur as shown above (top). The contour lines are simply the hairpin turning points for the folded chains.

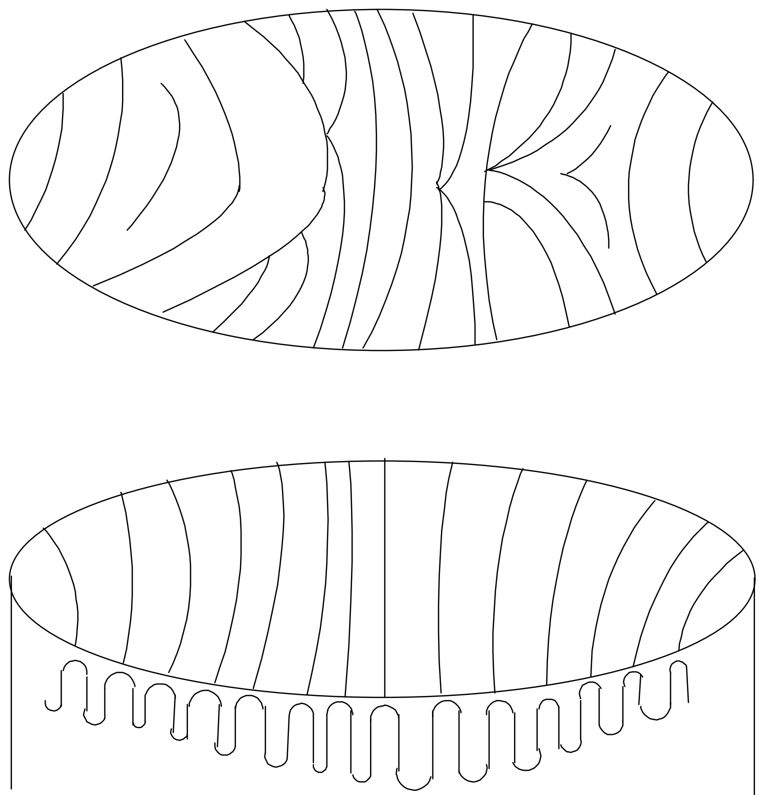


**Figure 2.16** Spherulite structure showing the molecular-level lamellar chain-folded platelets and tie and frayed chain arrangements, left, and a more complete model of two sets of three lamellar chain-folded platelets formed from polyethylene, right. Each platelet contains about 850 ethylene units as shown here.

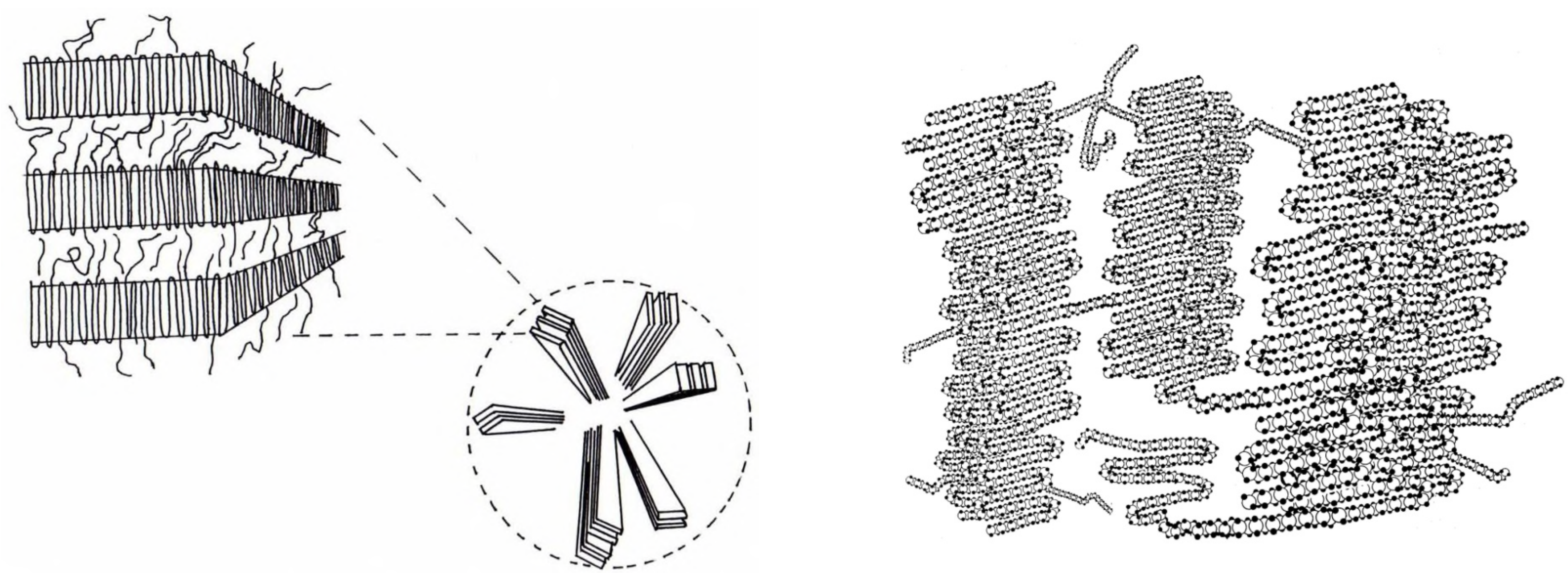


**Figure 2.17** Crystalline polymer structures formed under applied tension including flow conditions. Middle shows the tertiary mono-fibrilar structure including platelets and at the left shows these mono-fibrilar structures bundled together forming a quaternary structure fibril. Right shows the distorted shish kebab formed with more rapid flow.

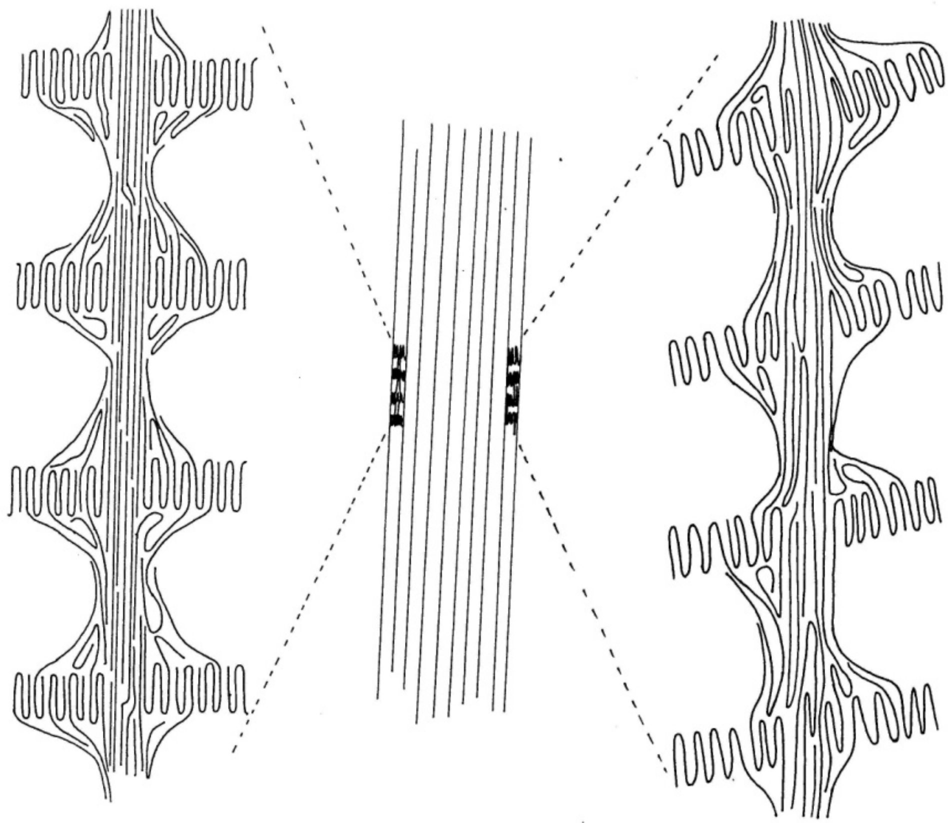


**Figure 2.18** Elongation of an elastomer as a function of applied force, stress, where A is the original "relaxed" state, B represents movement to full extension, C is the point at which the elastomer "breaks", and D represents force necessary to pull two separate pieces of elastomer apart.

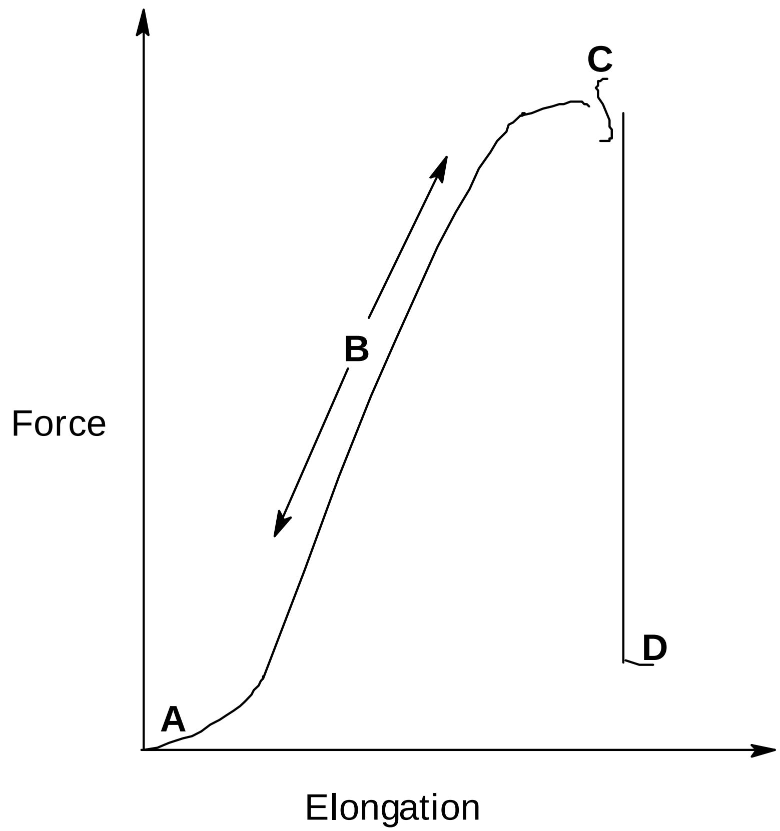


**Figure 2.19** Idealized structure illustrating crystalline (ordered) and amorphous (nonordered) regions of lightly branched polyethylene chains for a prestressed and stressed orientation.

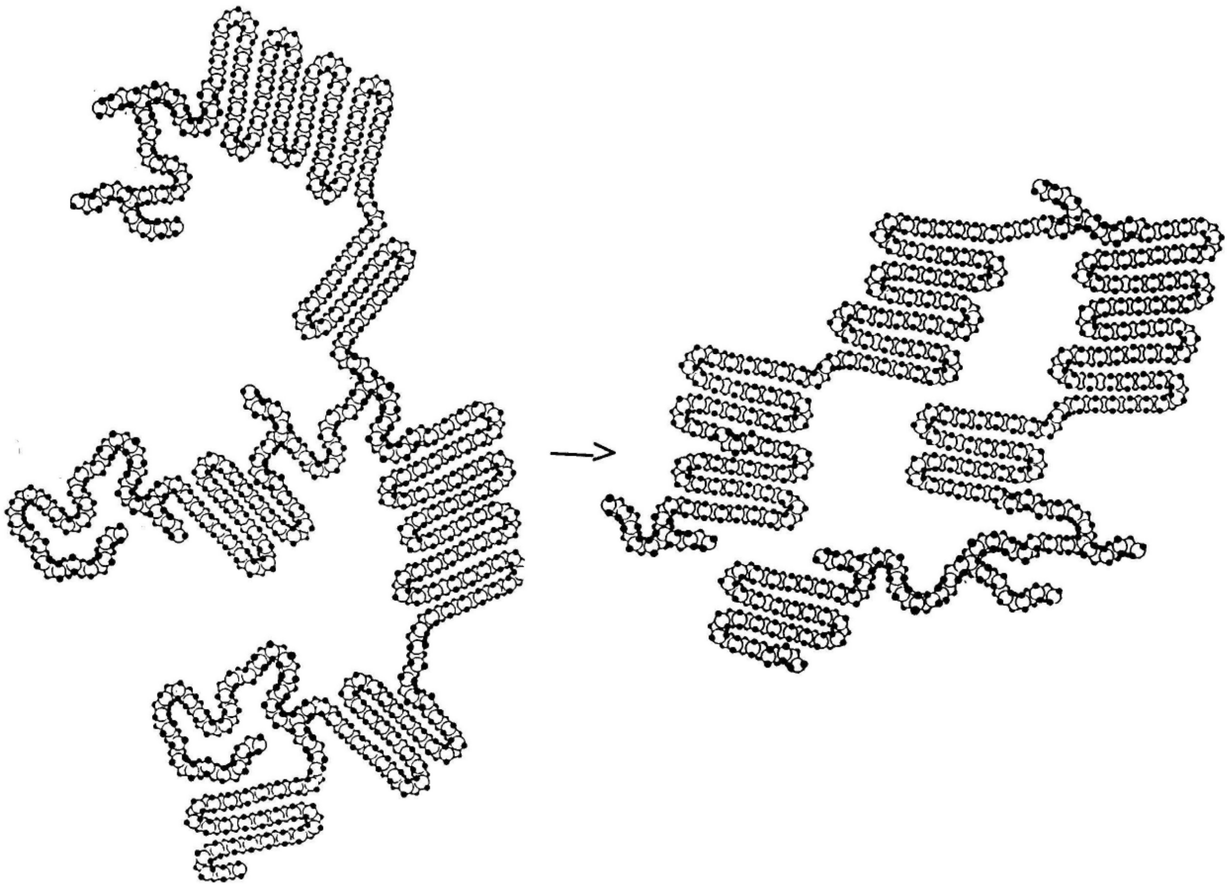


**Figure 2.20** General physical states of materials as a function of crystallinity and molecular weight.

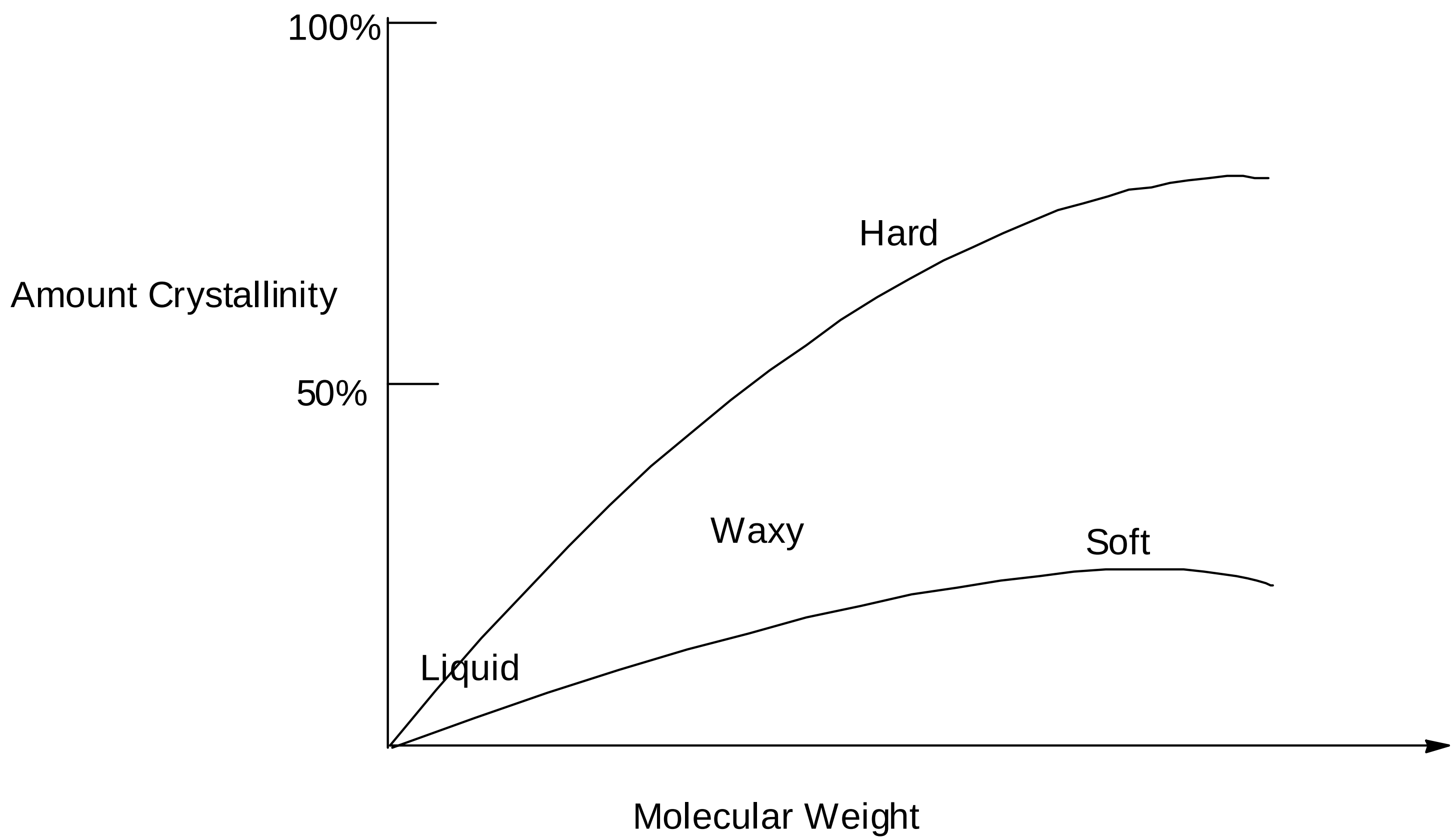


**Table 2.6.** General property correlations with $T_g$.

| | |
|---|---|
| • Cross-linked elastomers | Above $T_g$ |
| • Linear (or branched) amorphous adhesives | Above $T_g$ |
| • Amorphous plastics | Generally above $T_g$ |
| • Largely crystalline plastics | Generally above $T_{g,}$ Below $T_m$ |
| • Crystalline fibers | Below $T_m$ |
| • Coatings | At or near $T_g$ |

**Figure 2.21** Chemical cross-linking of cis-1,4-butadiene through reaction with sulfur.

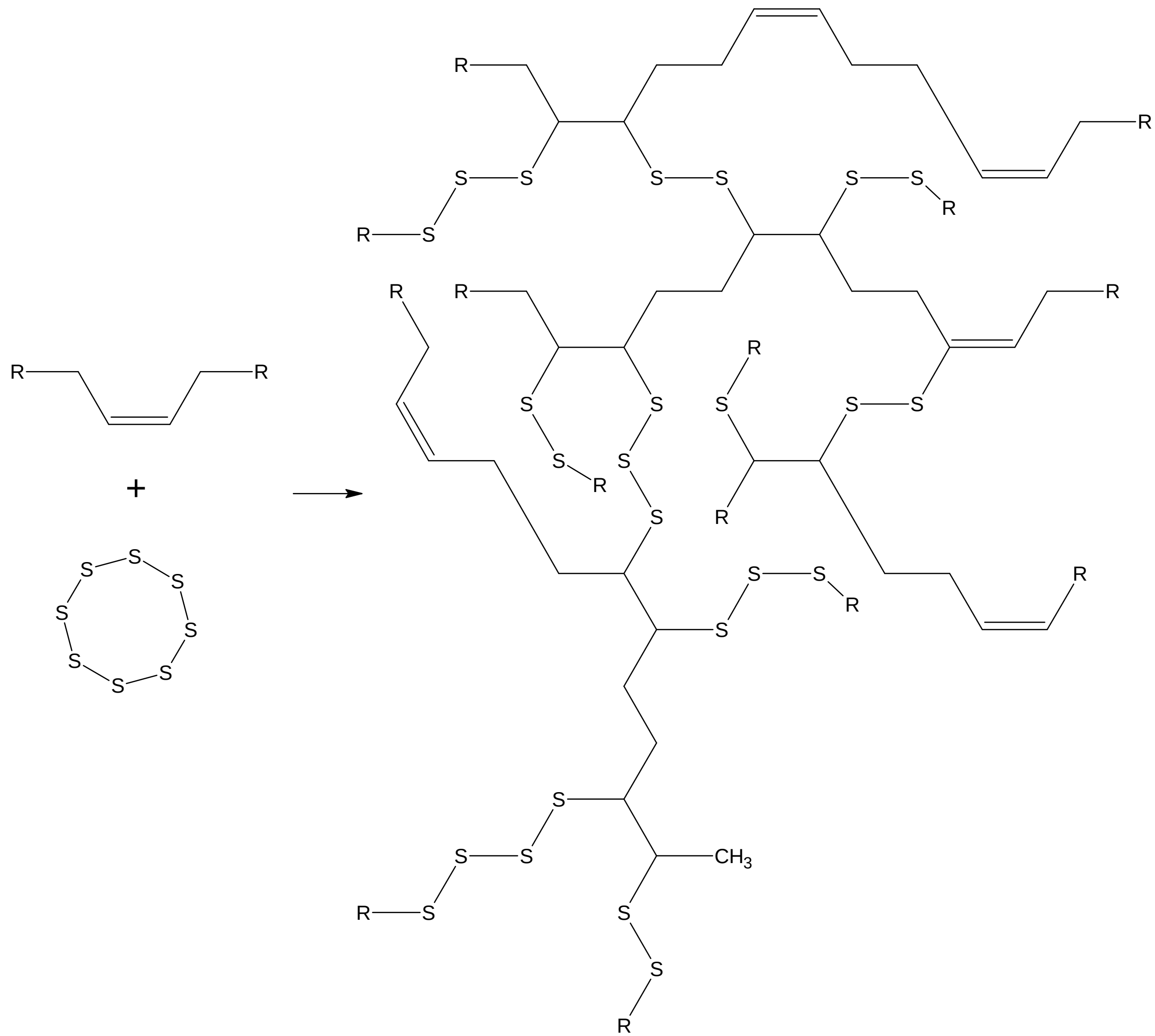


**Figure 2.22** Illustration of two types of physical cross-linking-chain entanglement and crystalline regions.