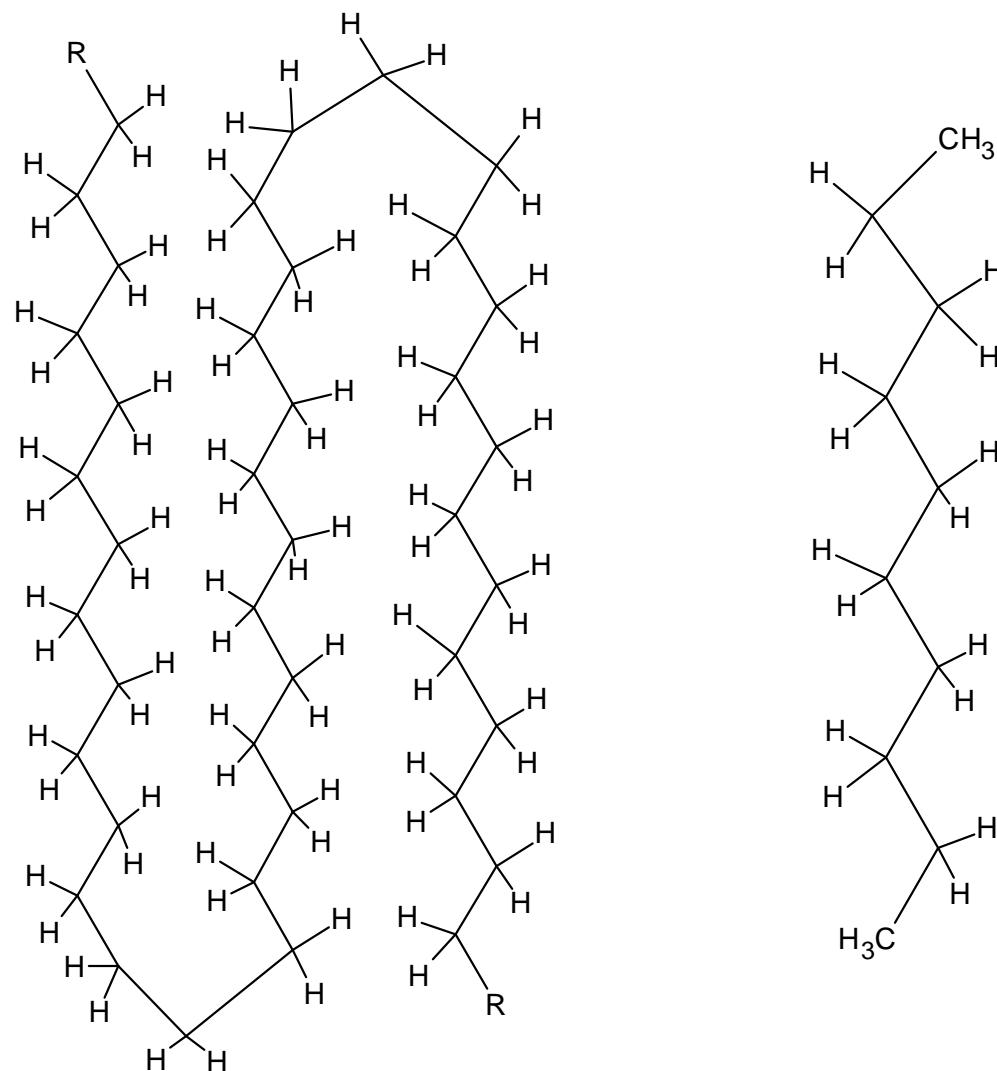


4<sup>th</sup> Ed Cpt 2 Polymer Structure

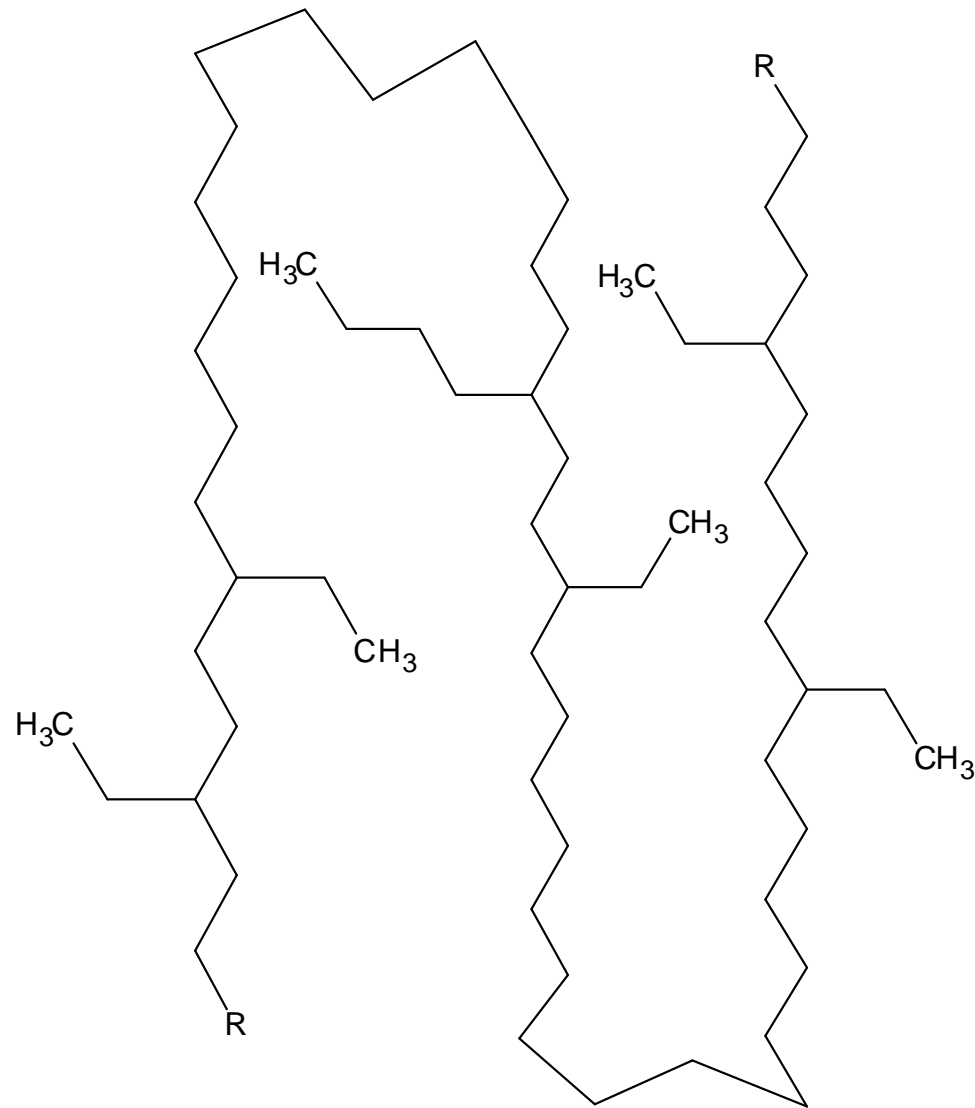
## Table 2.1 Typical properties of straight chain hydrocarbons.

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.



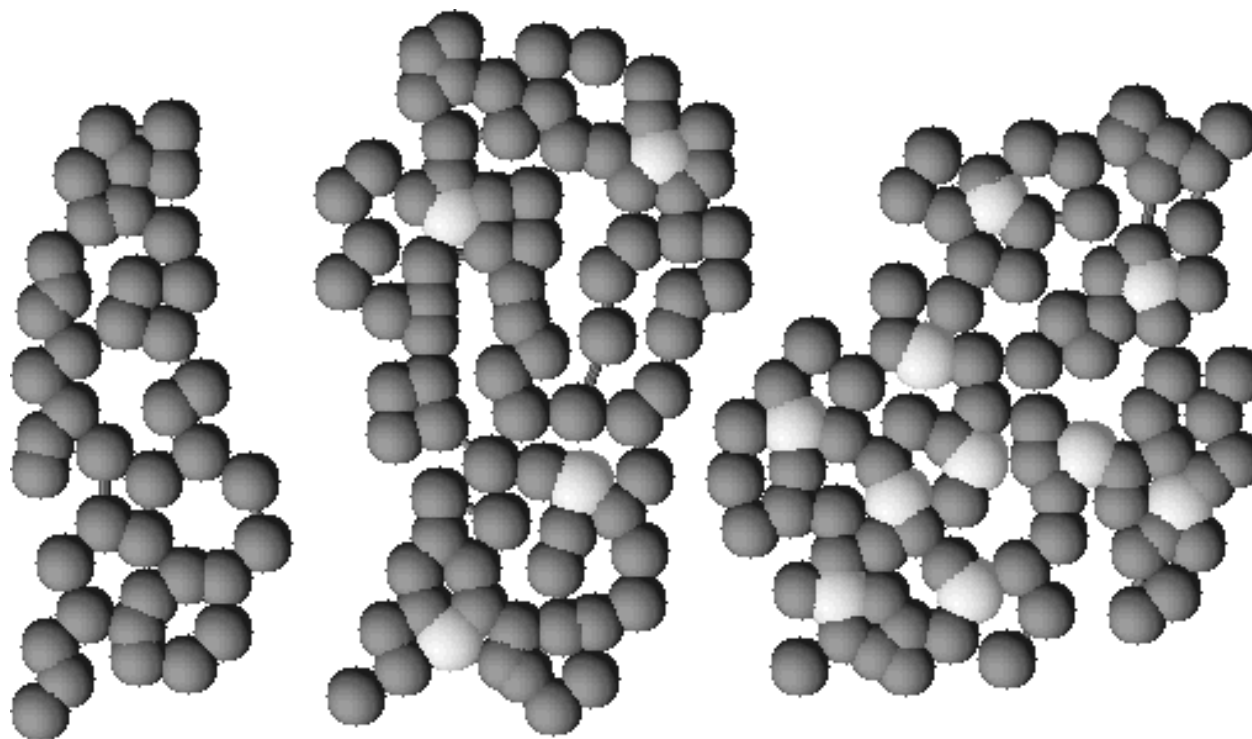
**Figure 2.2** Simulated structural formula for branched low-density polyethylene (LDPE); compare with Figure 2.1 for HDPE.



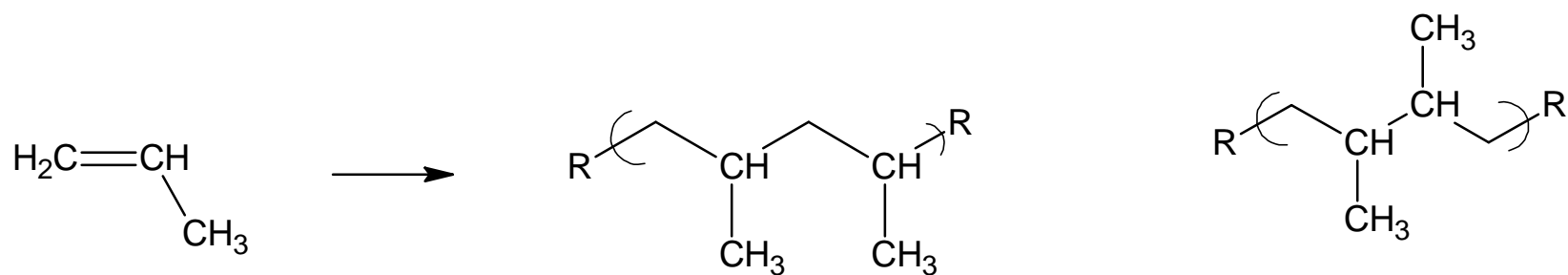
**Table 2.2** Types of Commercial Polyethylene

• 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

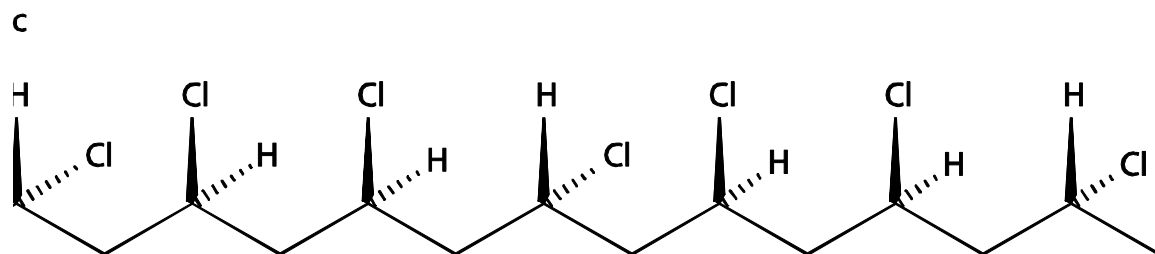
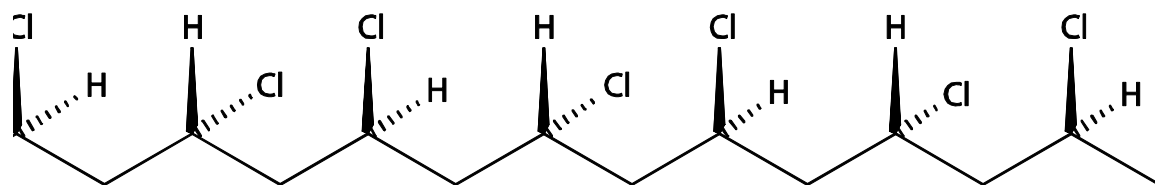
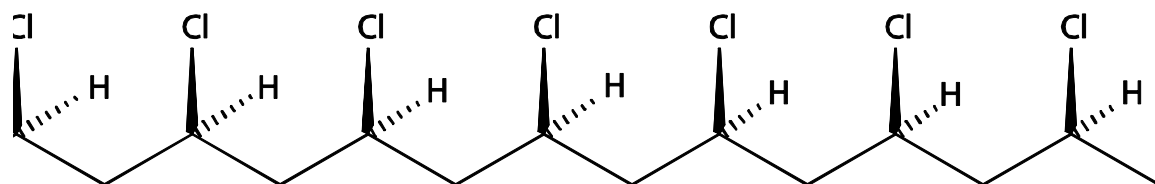
**Figure 2.3** Skeletal structural formulas of a linear polymer (left), and a network (crosslinked) polymer with low crosslinking density (middle) and high density crosslinking (right). Cross-link sites are noted by the non-darkened spheres.



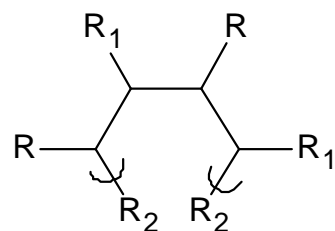
**Figure 2.4** Simulated structural formulas showing the usual head-to-tail, middle, and unusual head-to-head, right, configurations of polypropylene.



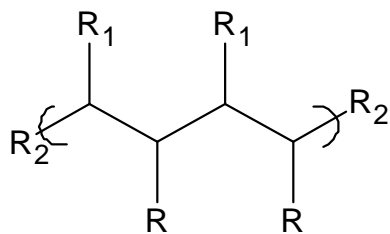
**Figure 2.5** Skeletal formulas of isotactic (top), syndiotactic (middle), and atactic (bottom) of poly(vinyl chloride), PVC.



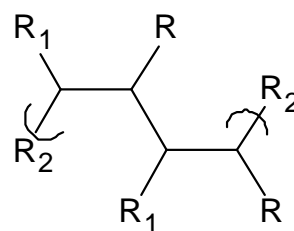




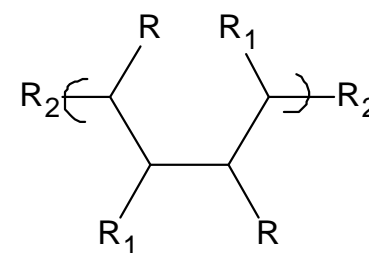
**Erythrodiisotactic**



**Threodiisotactic**



**Erythrodisyndiotactic**



**Threodisyndiotactic**

**Figure 2.6** Simulated formulas of ditactic isomers where R<sub>2</sub> are chain extensions and R and R<sub>1</sub> are not hydrogen.

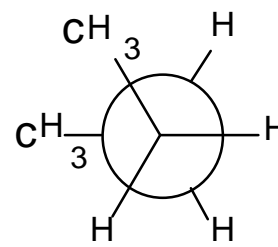
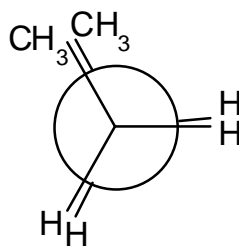
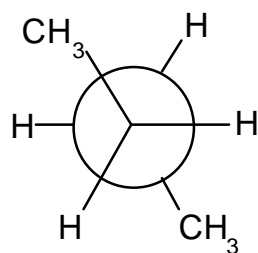


Figure 2.7 Newman projections of designated conformers of n-butane- Anti (left), Eclipsed (middle) and Gauche (right).

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

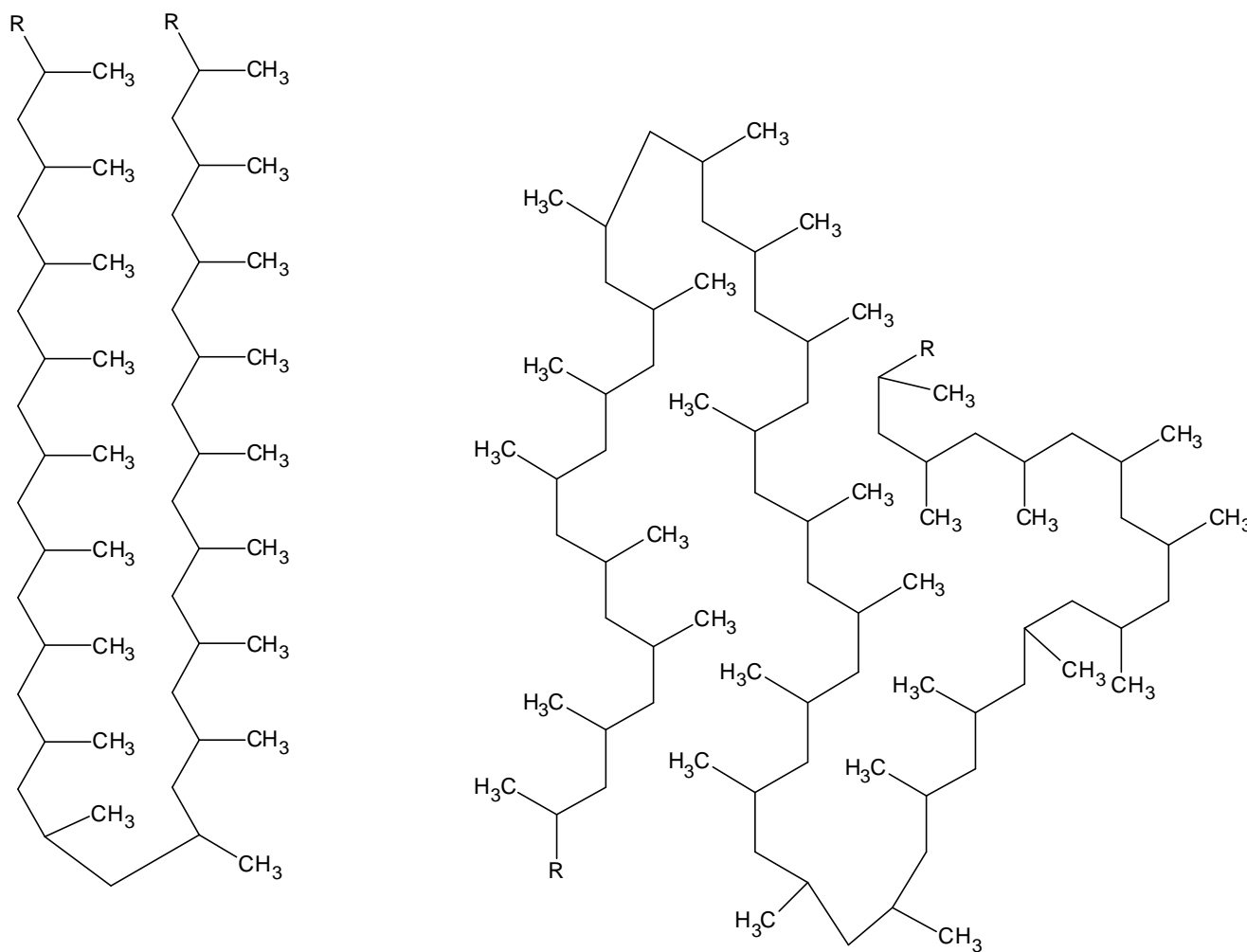
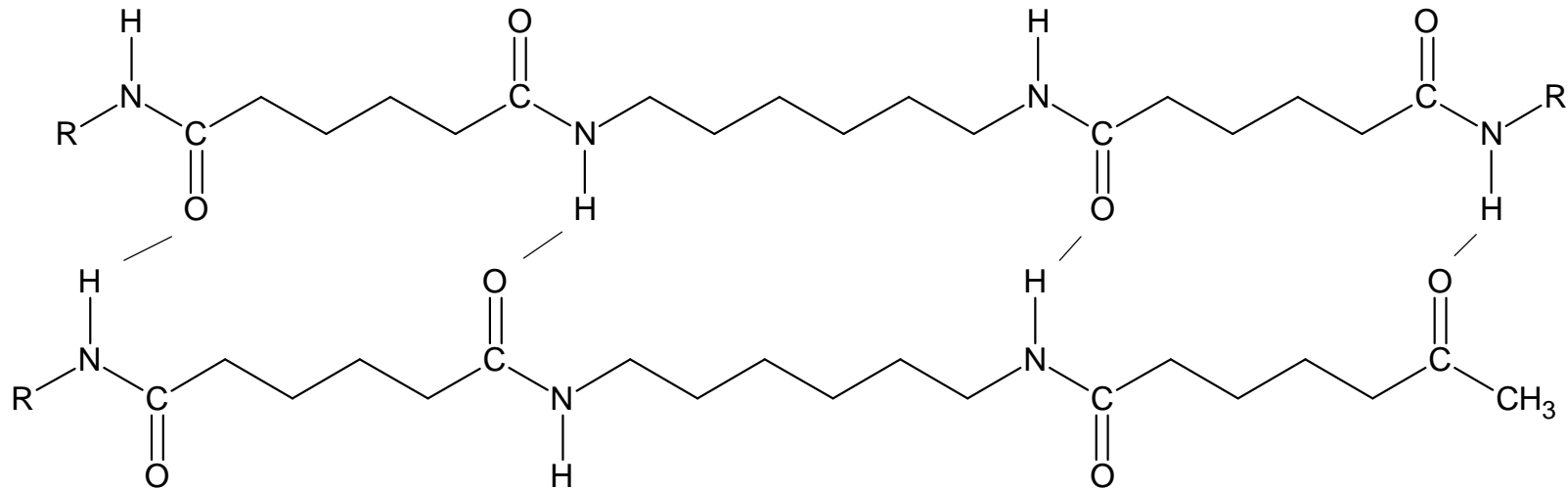


Table 2.2b. General classes of secondary forces.

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

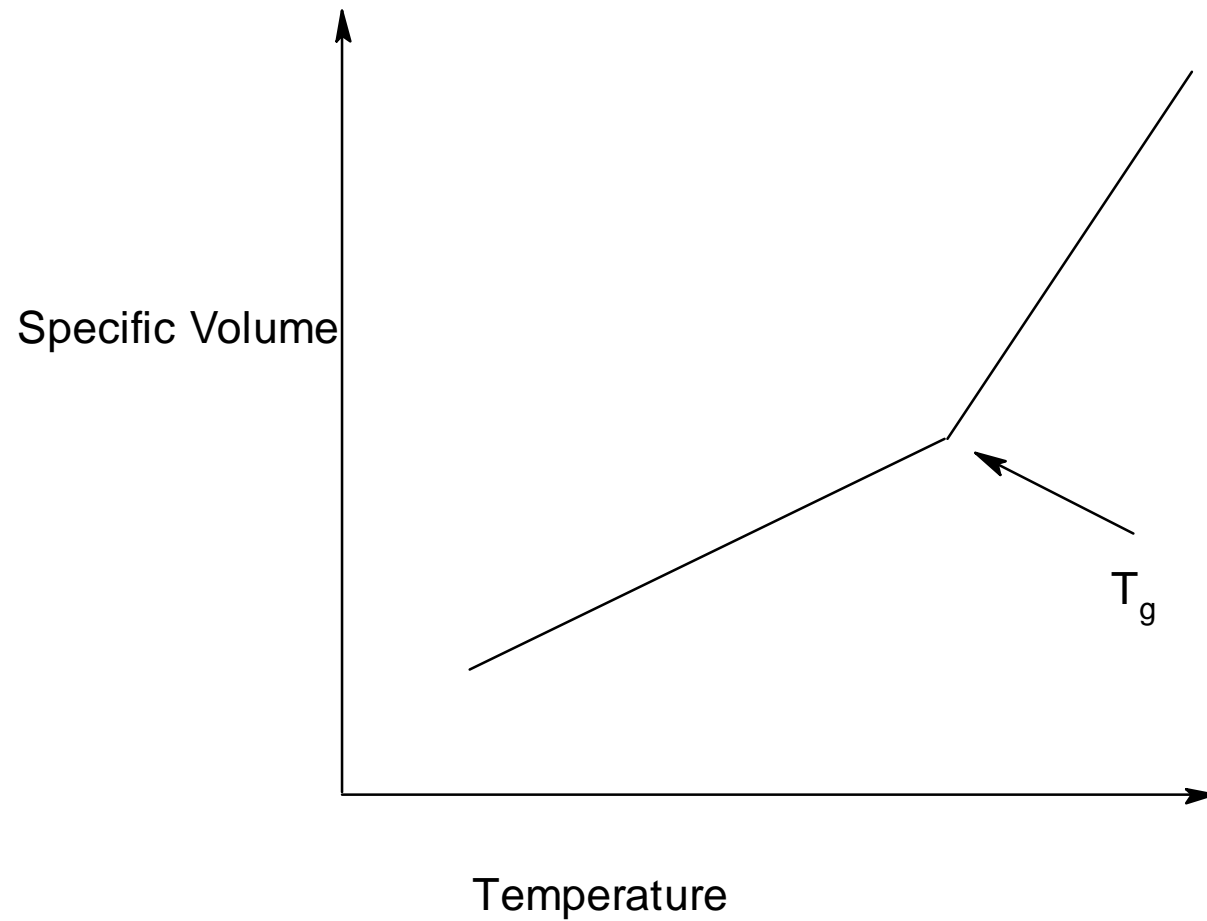
**Figure 2.9** Typical hydrogen-bonding (shown as “-” between hydrogen on nitrogen and oxygen for nylon 66.



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

<b>Polymer</b>	<b>Critical Chain Length</b> (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 <sup>a</sup>
• 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.

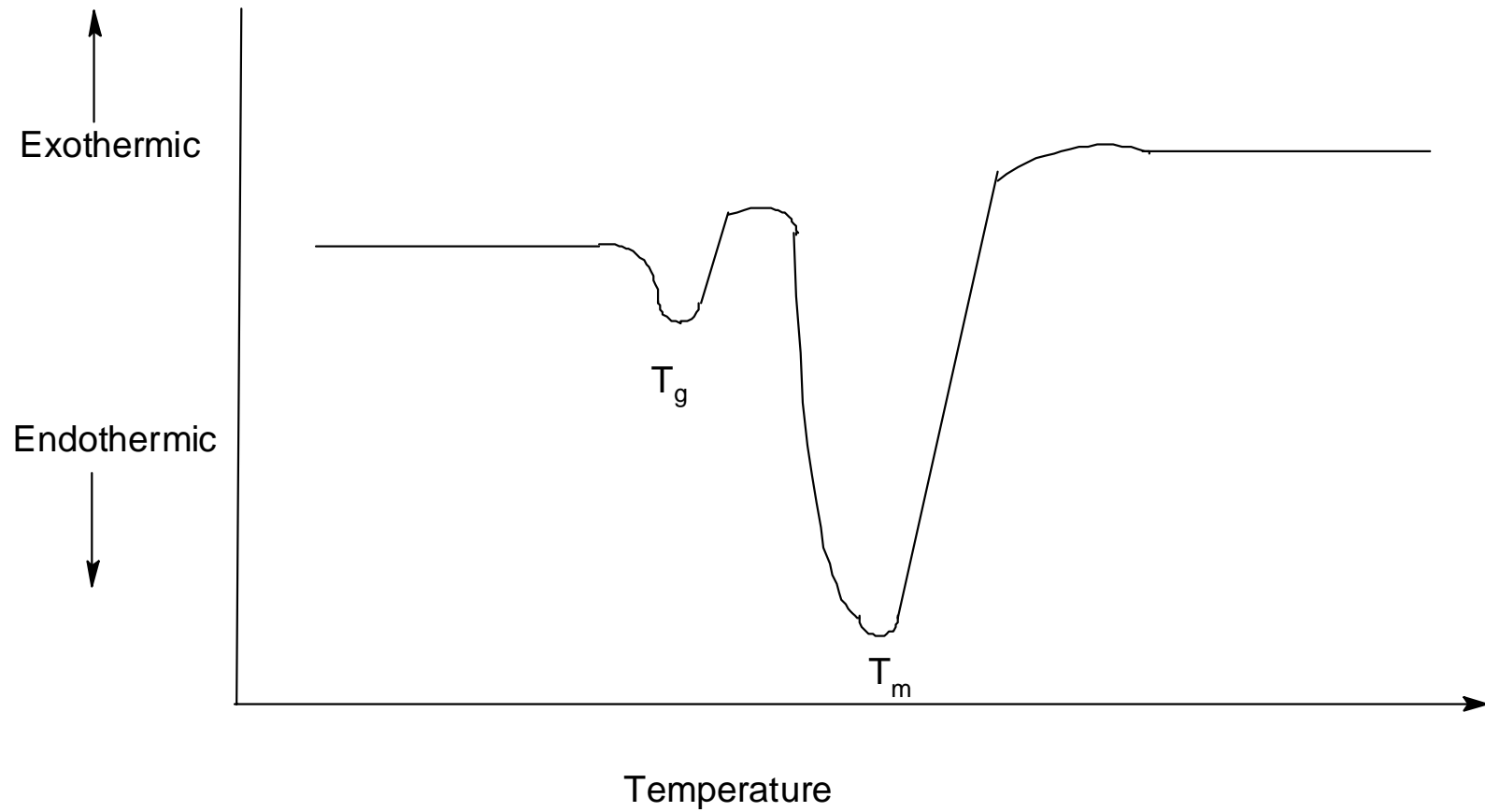
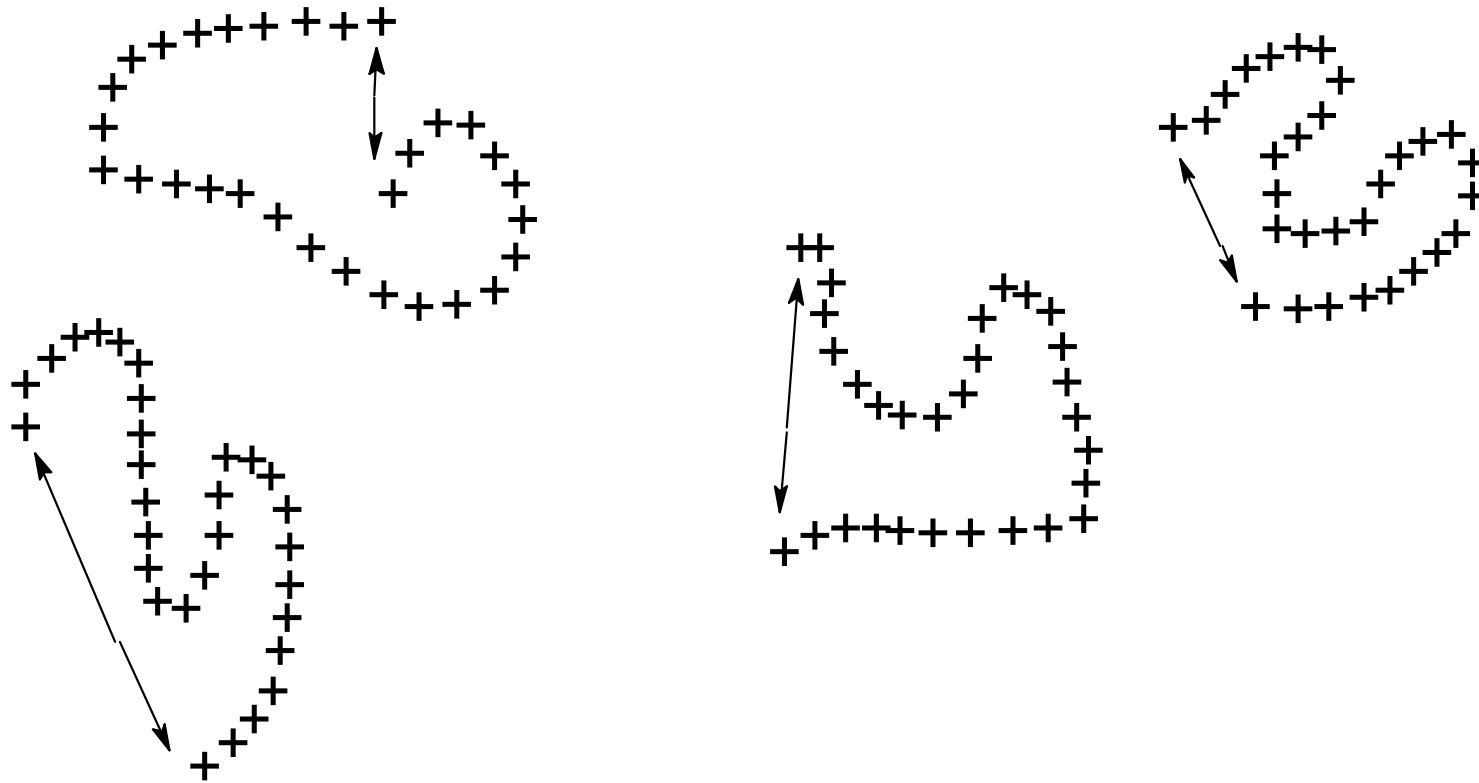
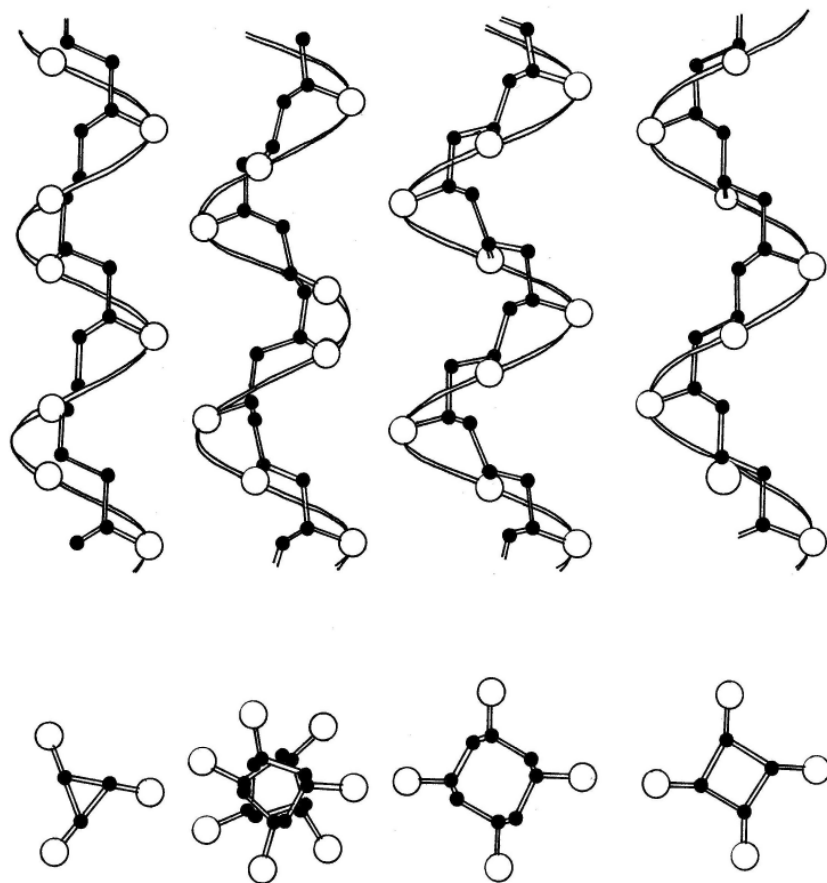


Figure 2.12 End-to-end distances for four 30-unit chains.



**Figure 2.13** Helical conformation of isotactic vinyl polymers. (From N. Gaylord, in *Linear and Stereoregular 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.

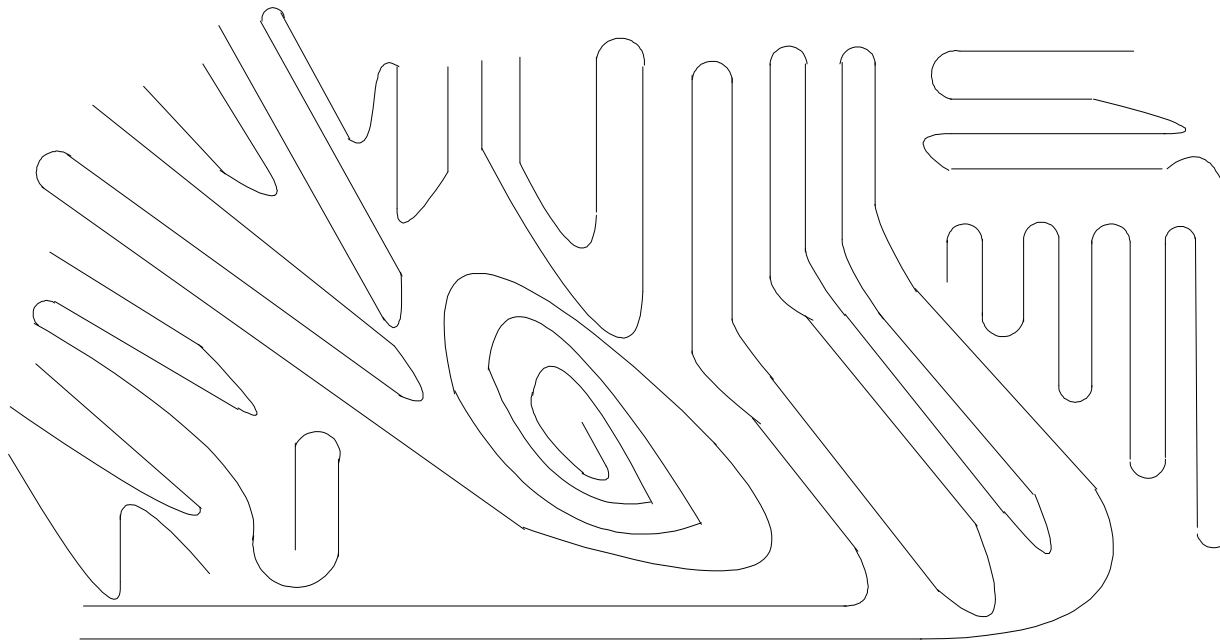
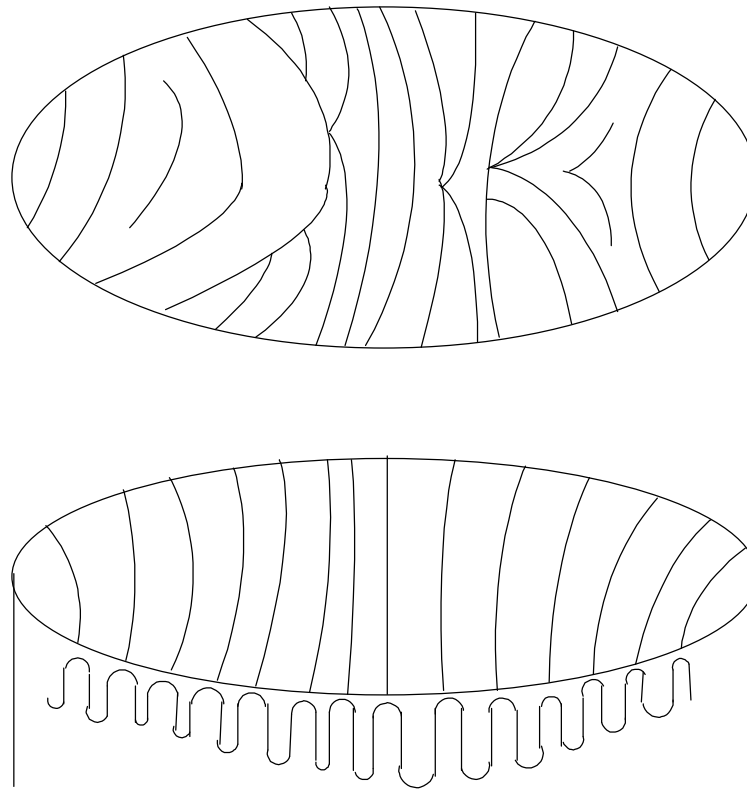
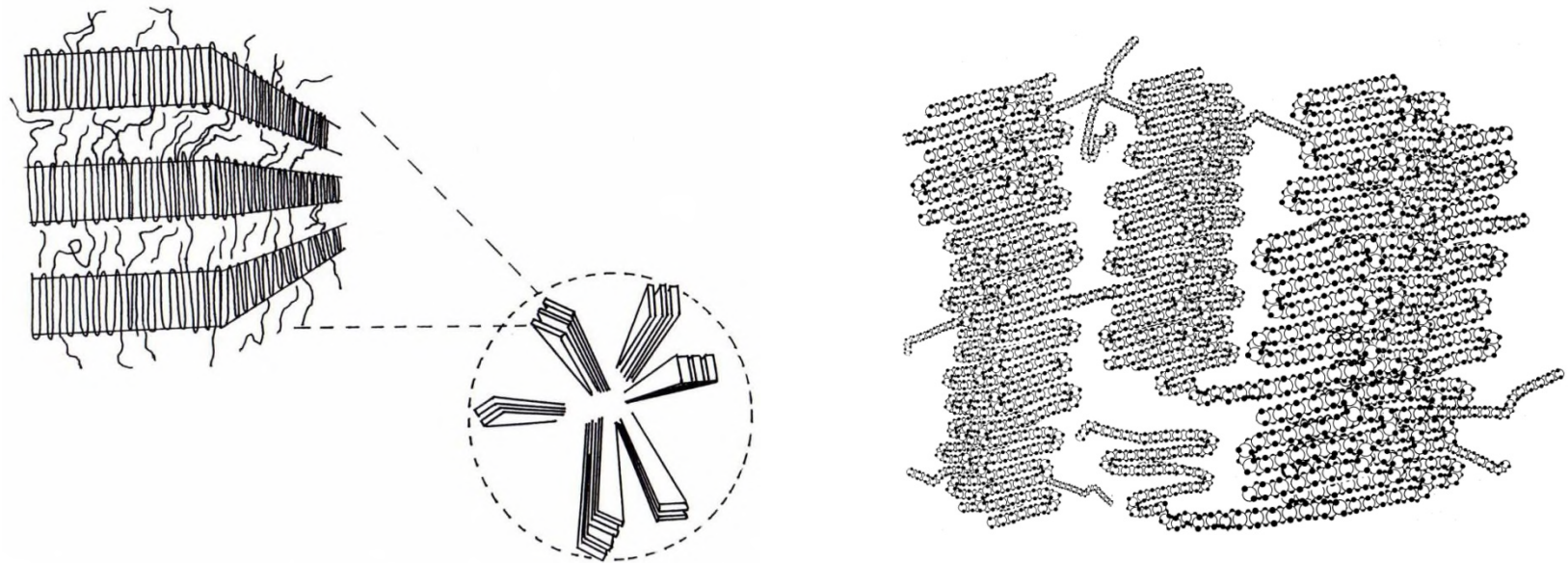


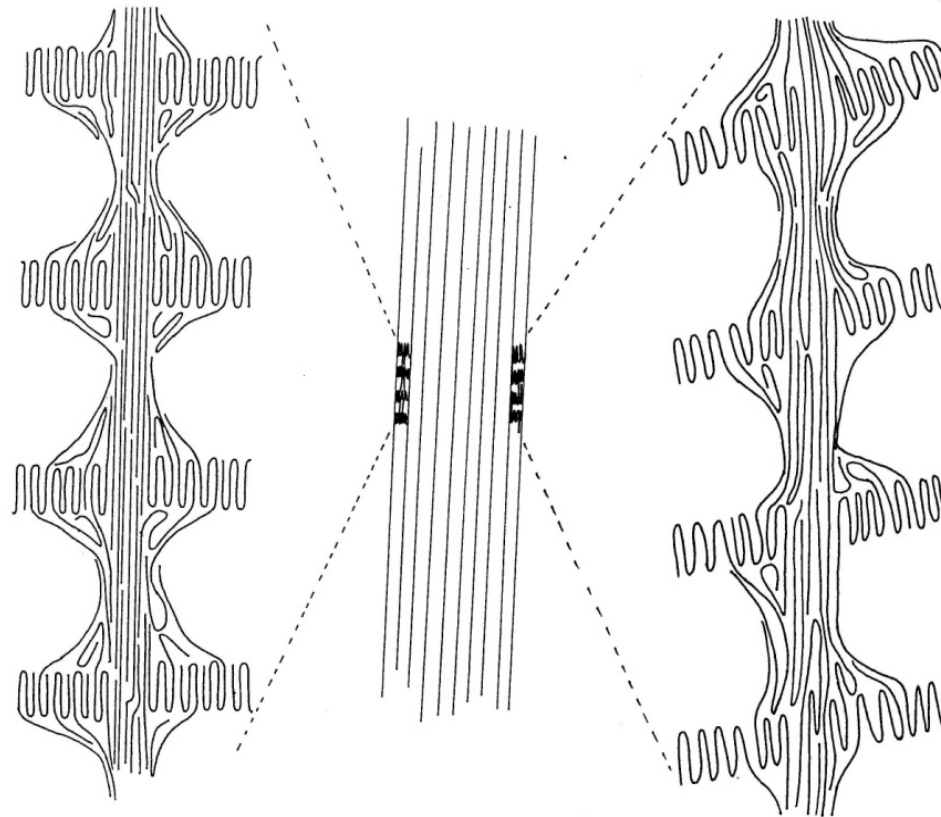
Figure 2.15 Structure of a spherulite from the bulk. Bottom shows a slice of a simple spherulite. As further growth occurs, filling in, branch points, etc. occur as shown above (top). The contour lines are simply the hairpin turning points for the folded chains.



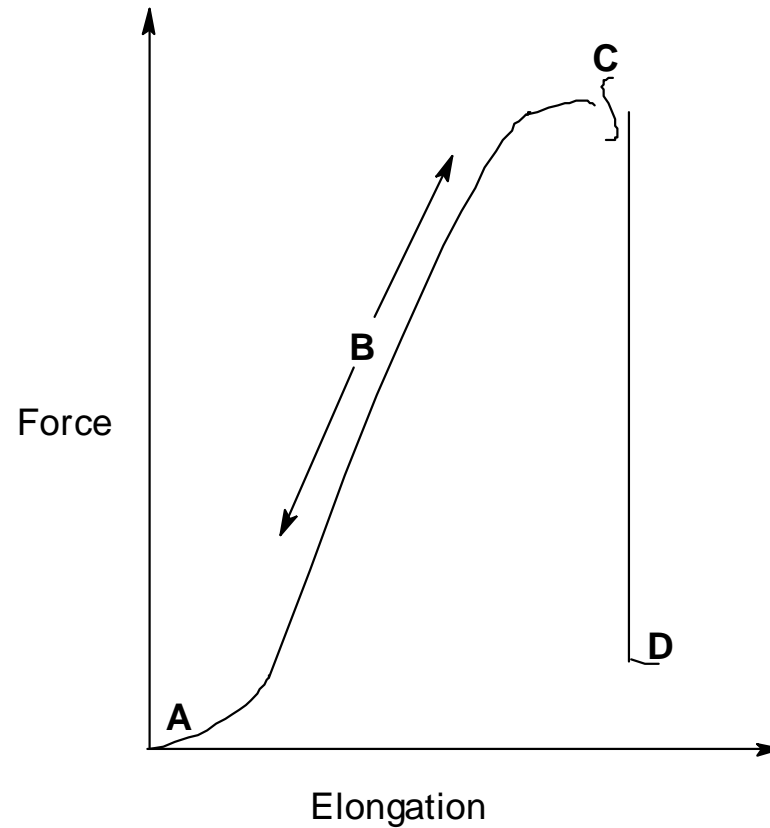
**Figure 2.16** Spherulite structure showing the molecular-level lamellar chain-folded platelets and tie and frayed chain arrangements, left, and a more complete model of two sets of three lamellar chain-folded platelets formed from polyethylene, right. Each platelet contains about 850 ethylene units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



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

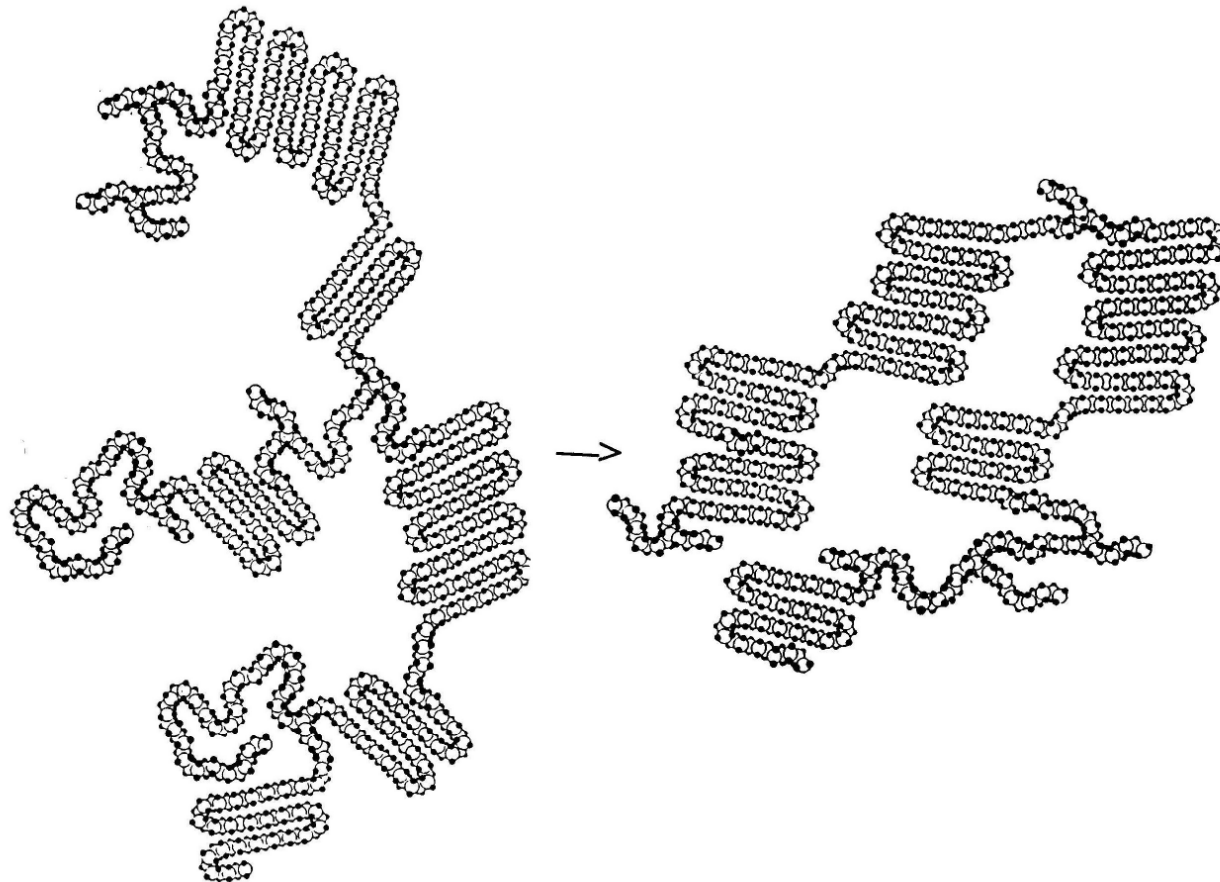


**Figure 2.18** Elongation of an elastomer as a function of applied force, stress, where A is the original “relaxed” state, B represents movement to full extension, C is the point at which the elastomer “breaks”, and D represents force necessary to pull two separate pieces of elastomer apart.

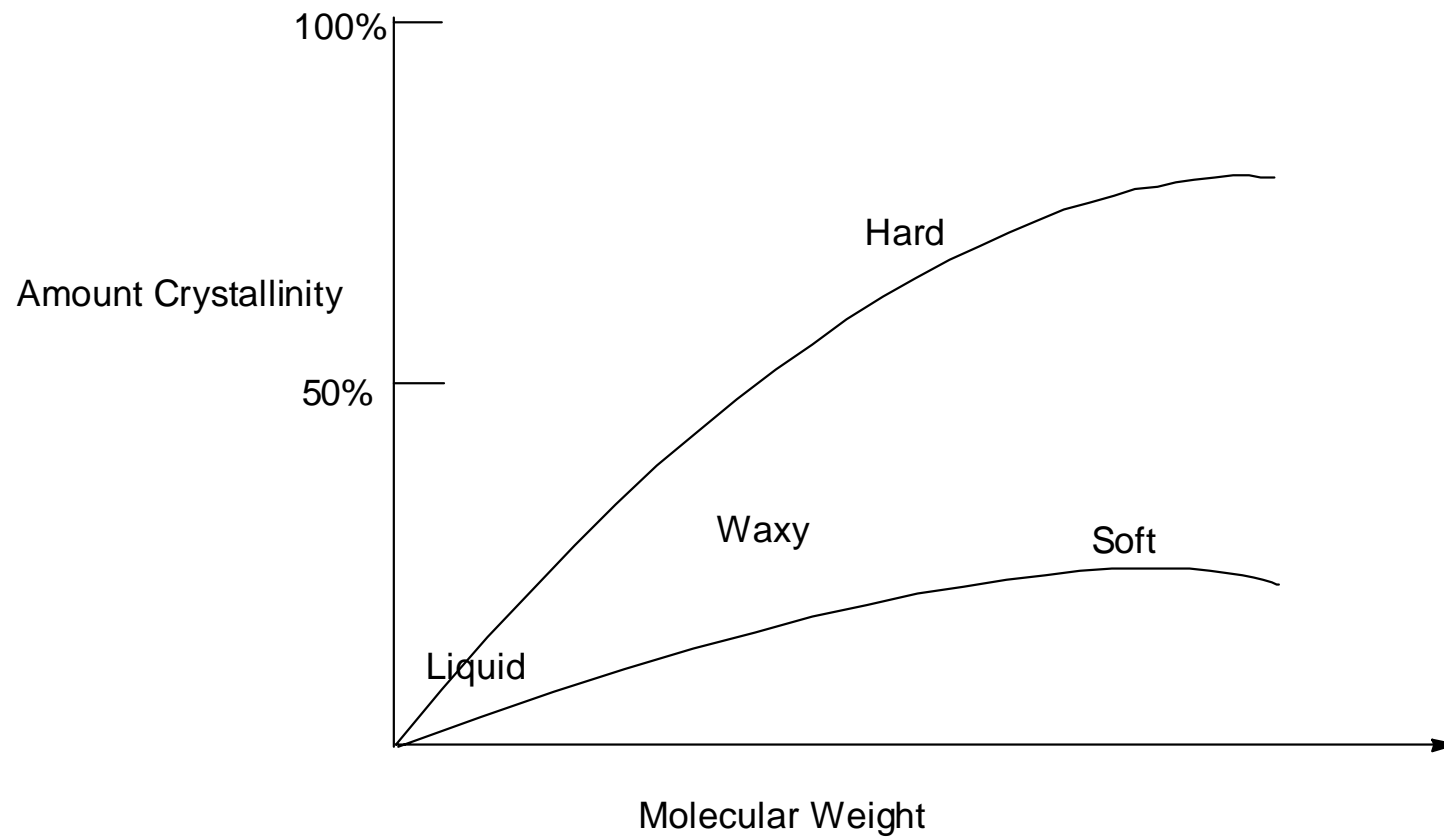




**Figure 2.19** Idealized structure illustrating crystalline (ordered) and amorphous (nonordered) regions of lightly branched polyethylene chains for a prestressed and stressed orientation.



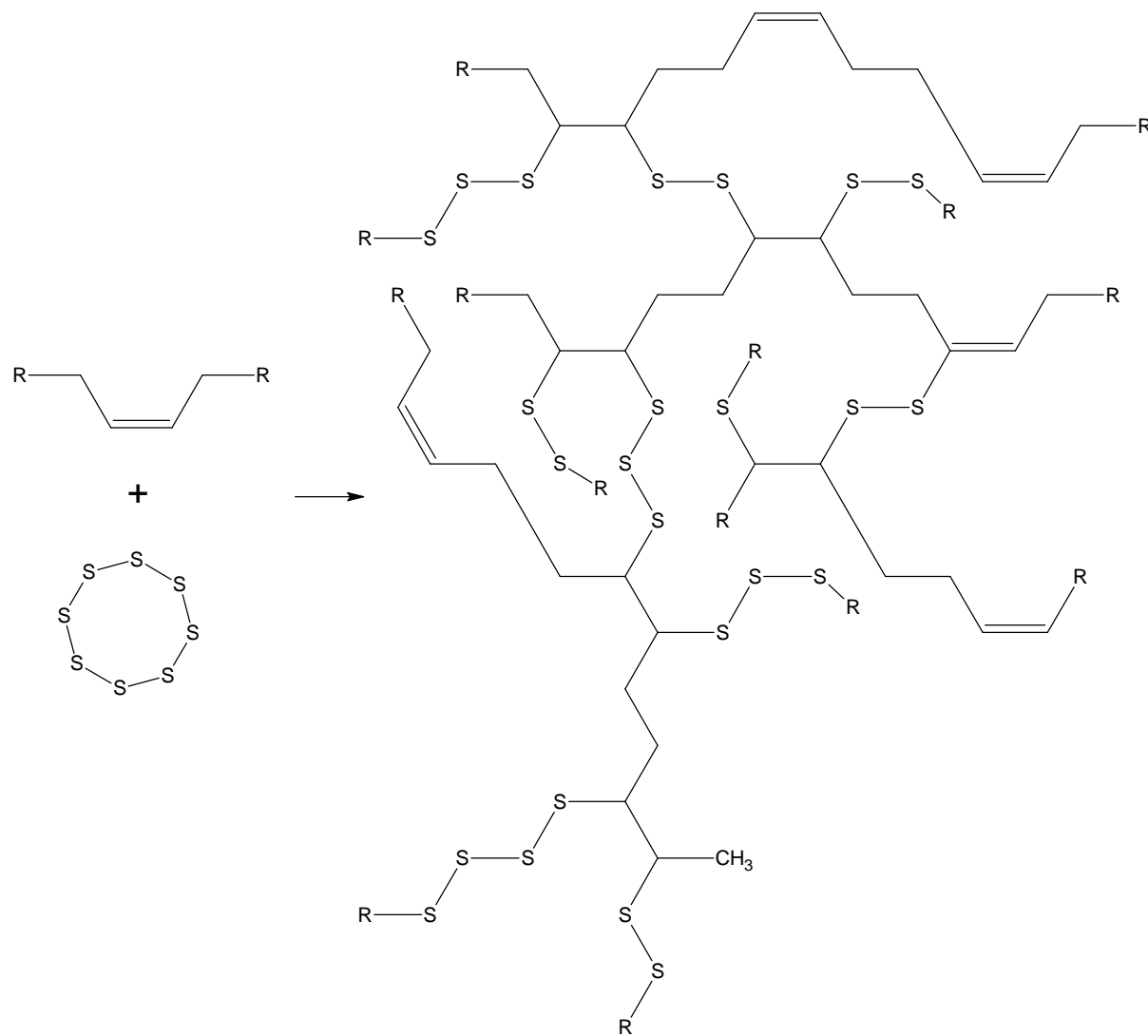
**Figure 2.20** General physical states of materials as a function of crystallinity and molecular weight.



**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.

