

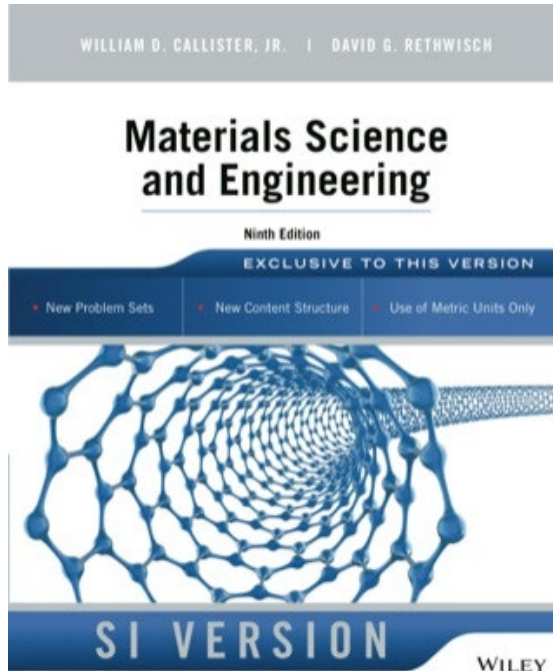
# Materials Science A244

## Week 2 - Lecture 2: Structure of Polymers



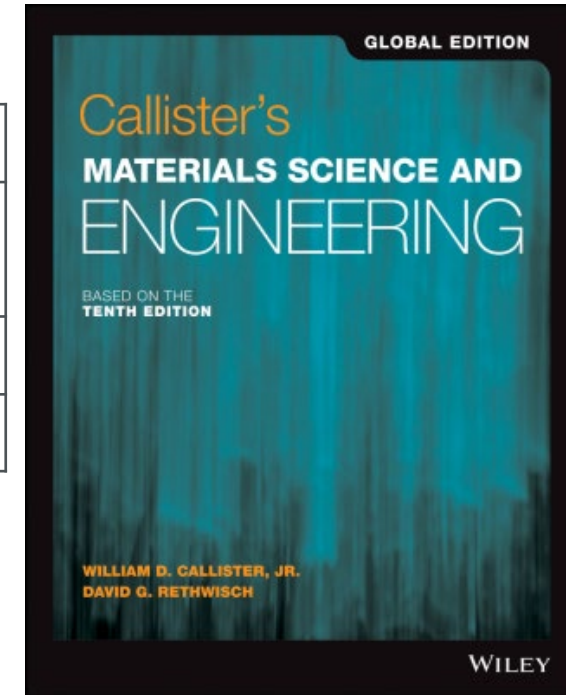
Stellenbosch  
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forward together  
sonke siya phambili  
saam vorentoe



← Callister 9th ed	Topics	Callister 10th ed →
5.1 – 5.8	Molecular considerations	14.1 – 14.8
5.9 – 5.10	Types of polymers	14.9 – 14.10
5.11	Polymer crystals	14.12

*Note: 4.13 9<sup>th</sup> / 14.13 10<sup>th</sup> Polymer crystallinity is covered in Week 2, Lecture 1*

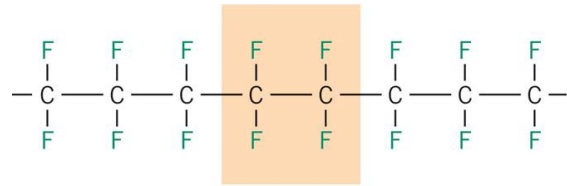


Prof Deborah Blaine  
Mechanical & Mechatronics Engineering

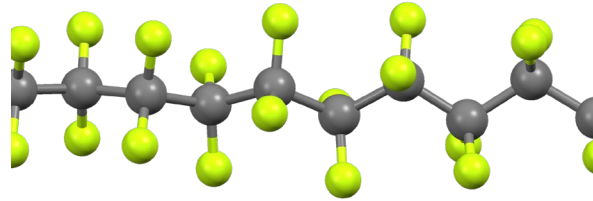


# What is a polymer?

Greek *poly-* many, *-mer* parts: molecular chains of repeating units

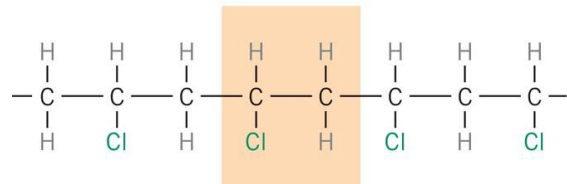


Repeat unit  
(a)

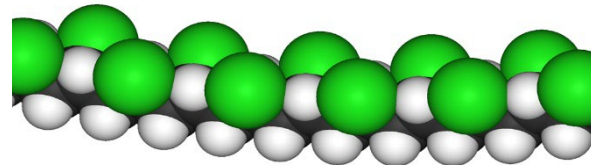


Source: Wikipedia

Ball-and-stick model of a  
perfluorodecyl chain,  $-\text{C}_{10}\text{F}_{21}$

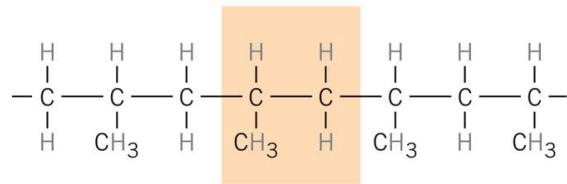


Repeat unit  
(b)

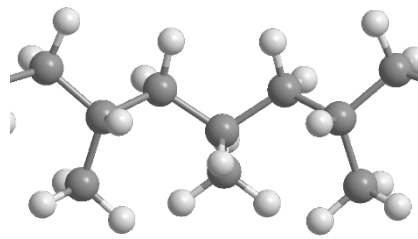


Source: Wikipedia

Space-filling model of a part of a PVC chain



Repeat unit  
(c)



Source: Wikipedia

Ball-and-stick model of polypropylene

Poly(tetrafluoroethene) – PTFE - Teflon®



Source: PTFE machinery



shutterstock.com · 1529425790

Polyvinyl chloride - PVC



Source: Indiamart

Polypropylene - PP



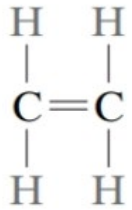
Source: Adreco plastics

# Hydrocarbons (Koolwaterstowwe)

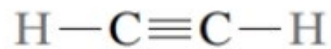
Most polymers are organic, many organic materials are hydrocarbons (C + H)

## Saturated (all single bonds)

### Unsaturated



Ethylene – carbon double bond



Acetylene – carbon triple bond



**Table 5.1**

Compositions and  
Molecular Structures  
for Some Paraffin  
Compounds:  $\text{C}_n\text{H}_{2n+2}$

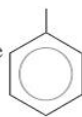
Name	Composition	Structure	Boiling Point (°C)
Methane	$\text{CH}_4$	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$	-164
Ethane	$\text{C}_2\text{H}_6$	$\begin{array}{cc} \text{H} & \text{H} \\   &   \\ \text{H}-\text{C} & -\text{C}-\text{H} \\   &   \\ \text{H} & \text{H} \end{array}$	-88.6
Propane	$\text{C}_3\text{H}_8$	$\begin{array}{ccc} \text{H} & \text{H} & \text{H} \\   &   &   \\ \text{H}-\text{C} & -\text{C} & -\text{C}-\text{H} \\   &   &   \\ \text{H} & \text{H} & \text{H} \end{array}$	-42.1
Butane	$\text{C}_4\text{H}_{10}$		-0.5
Pentane	$\text{C}_5\text{H}_{12}$		36.1
Hexane	$\text{C}_6\text{H}_{14}$		69.0

# Hydrocarbons (Koolwaterstowwe)

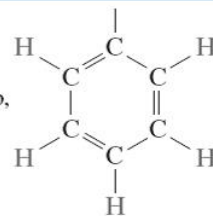
**Table 5.2**  
Some Common  
Hydrocarbon Groups

Family	Characteristic Unit		Representative Compound
Alcohols	$R-OH$	$\begin{array}{c} H \\   \\ H-C-OH \\   \\ H \end{array}$	Methyl alcohol
Ethers	$R-O-R'$	$\begin{array}{cc} H & H \\   &   \\ H-C-O-C-H \\   &   \\ H & H \end{array}$	Dimethyl ether
Acids	$\begin{array}{c} OH \\   \\ R-C \\    \\ O \end{array}$	$\begin{array}{cc} H & OH \\   &   \\ H-C-C \\   &    \\ H & O \end{array}$	Acetic acid
Aldehydes	$\begin{array}{c} R \\   \\ C=O \\   \\ H \end{array}$	$\begin{array}{c} H \\   \\ C=O \\   \\ H \end{array}$	Formaldehyde
Aromatic hydrocarbons <sup>a</sup>			Phenol

<sup>a</sup>The simplified structure

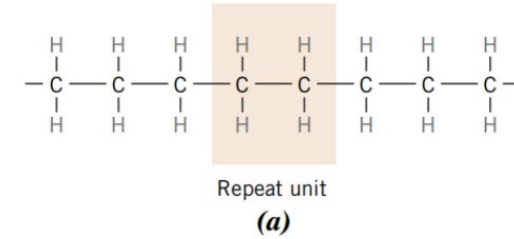


denotes a phenyl group,

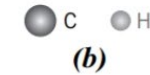
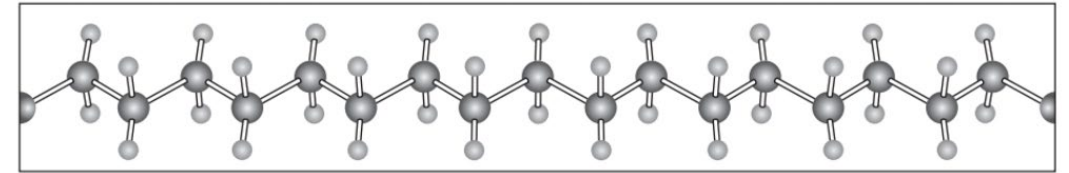


# Polymers and their chemistry

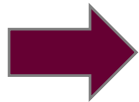
- Polymers are huge molecules, *macromolecules*, compared to hydrocarbon molecule.
- They are synthesized from a small molecule, the *monomer*, and made up of repeating units, *mers*, of this monomer.



## By example: Polyethylene (PE)



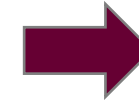
Monomer  
Ethylene  $C_2H_4$   
Gas at RT



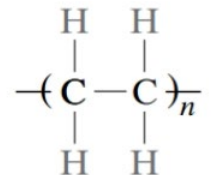
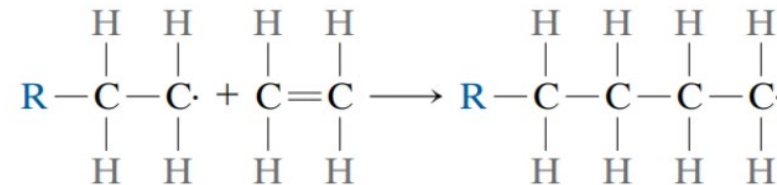
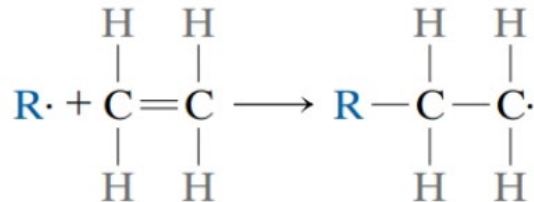
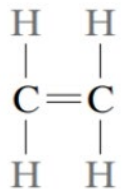
Initiation reaction  
Initiator (R) reacts with ethylene



Addition reaction  
Additional ethylene groups  
added to chain



Polymer chain  
Polyethylene

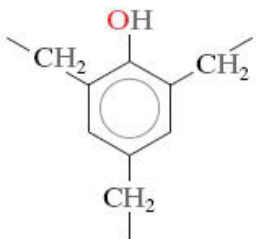



# Common polymers

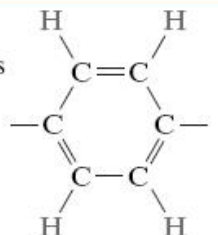
**Table 5.3** Repeat Units for Ten of the More Common Polymeric Materials

Polymer	Repeat Unit
Polyethylene (PE)	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{H} \end{array}$
Poly(vinyl chloride) (PVC)	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{Cl} \end{array}$
Polytetrafluoroethylene (PTFE)	$\begin{array}{c} \text{F} \quad \text{F} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{F} \quad \text{F} \end{array}$
Polypropylene (PP)	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{CH}_3 \end{array}$
Polystyrene (PS)	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{C}_6\text{H}_5 \end{array}$

**Table 5.3** (Continued)

Polymer	Repeat Unit
Poly(methyl methacrylate) (PMMA)	$\begin{array}{c} \text{H} \quad \text{CH}_3 \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{C}=\text{O} \\   \\ \text{O} \\   \\ \text{CH}_3 \end{array}$
Phenol-formaldehyde (Bakelite)	
Poly(hexamethylene adipamide) (nylon 6,6)	$\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \quad \text{O} \\   \quad    \quad   \quad    \\ -\text{N}-\left[ \begin{array}{c} \text{H} \\   \\ -\text{C}- \\   \\ \text{H} \end{array} \right]_6 -\text{N}-\text{C}-\left[ \begin{array}{c} \text{H} \\   \\ -\text{C}- \\   \\ \text{H} \end{array} \right]_4 -\text{C}- \\   \quad \quad \quad   \\ \text{H} \quad \quad \quad \text{H} \end{array}$
Poly(ethylene terephthalate) (PET, a polyester)	$\begin{array}{c} \text{O} \quad \text{O} \quad \text{H} \quad \text{H} \\    \quad    \quad   \quad   \\ -\text{C}-\text{C}_6\text{H}_4-\text{C}-\text{O}-\text{C}-\text{C}-\text{O}- \\    \quad   \quad   \\ \text{O} \quad \text{H} \quad \text{H} \end{array}$
Polycarbonate (PC)	$\begin{array}{c} \text{O} \quad \text{CH}_3 \quad \text{O} \quad \text{O} \\   \quad   \quad   \quad    \\ -\text{O}-\text{C}_6\text{H}_4-\text{C}-\text{C}_6\text{H}_4-\text{O}-\text{C}- \\   \quad \quad \quad   \\ \text{CH}_3 \quad \quad \quad \text{CH}_3 \end{array}$

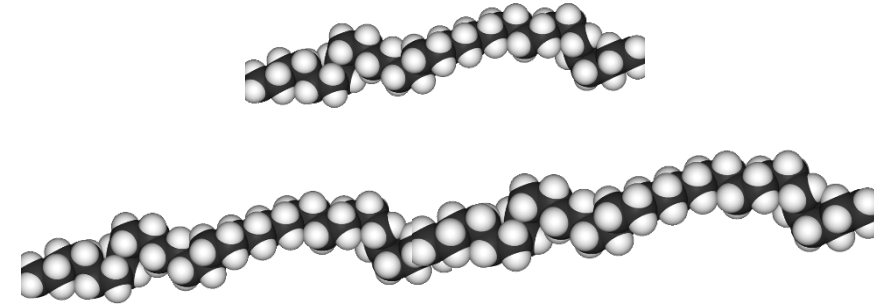
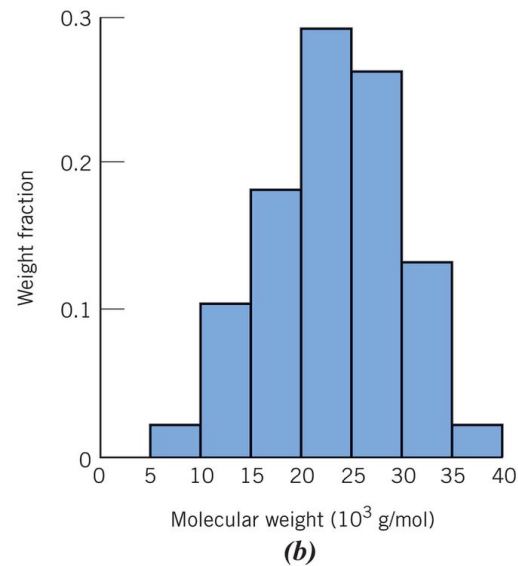
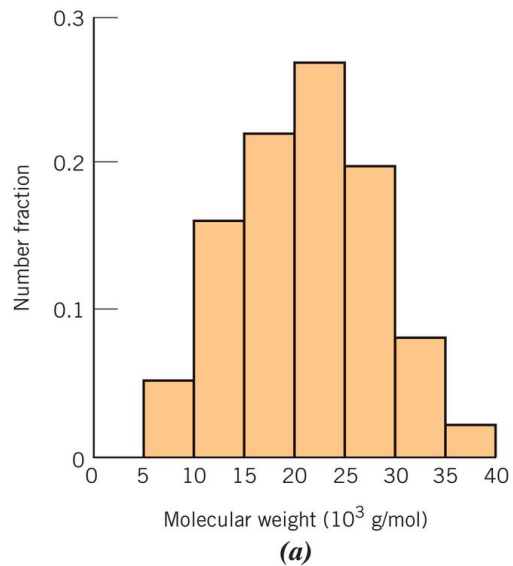
<sup>a</sup> The  symbol in the backbone chain denotes an aromatic ring as





# Molecular weight & Degree of polymerization

- Polymers are made up of many molecular chains; each chain has a different length and therefore different mass



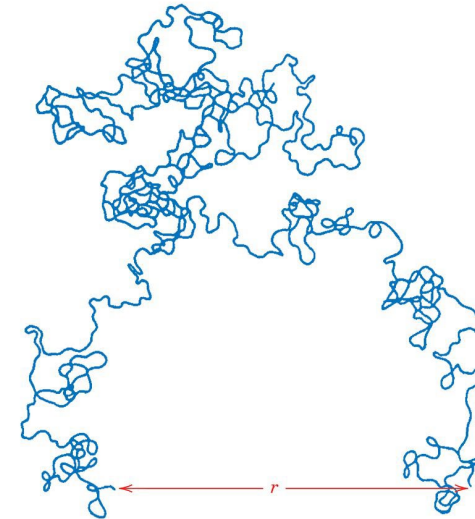
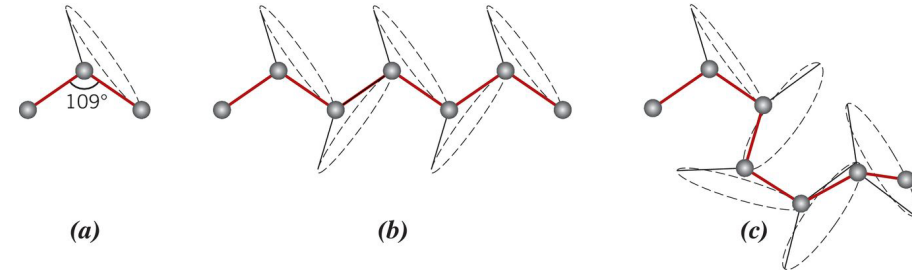
**Degree of polymerization** is the average number of repeating units in a molecular or polymer chain

**Molecular weight** is the average mass of all the chains in a polymer, weighted by count (number) or by mass (weight)

Both these parameters give an indication of the **average size** of the polymer or molecular chains in a polymer.

# Molecular shape

- Molecular chains are not straight; they can bend, twist and rotate around their backbone chain atoms.
- Polymers consist of large numbers of molecular chains, each of which may bend, coil, and kink
- The end-to-end distance,  $r$ , of the polymer is much shorter than the actual molecular chain length (along the twists and turns)
- Bulky side groups inhibit the twists and turns of a polymer chain.



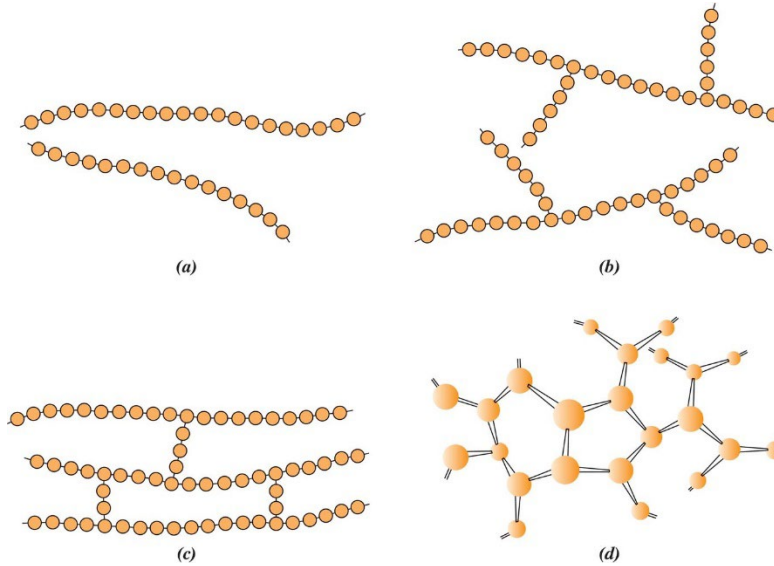
From Physics of Rubber Elasticity, 2nd edition, by Treloar (1958), Fig. 3.3, p. 47. By permission of Oxford University Press.



# Molecular structure and configuration

## Linear polymers

- repeat units are joined together end to end in single chains.
- Flexible
- Examples: HDPE, PVC, PMMA, Nylon (PA)



## Branched polymers

- side-branch chains are connected to the main chain
- Side-branches influence packing
- Examples: LDPE

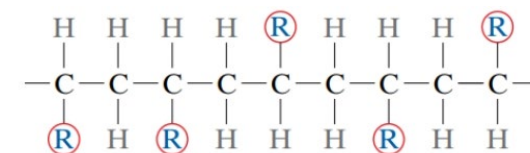
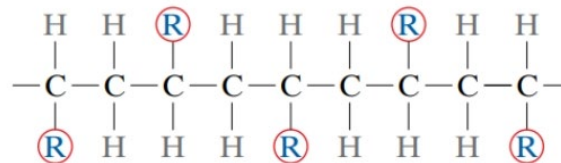
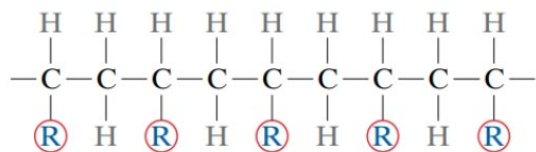
## Crosslinked polymers

- adjacent linear chains are joined one to another at various positions by covalent bonds
- Many rubbers are cross-linked, called vulcanisation

## Network polymers

- Three-dimensional networks of covalent bonds
- Examples: epoxies, poly- urethanes, and phenol-formaldehyde

Different atomic configurations are possible for the same composition: this is called **isomerism**.



# Thermoplastic and Thermosetting polymers

Thermoplastic	Thermoset
Soften when heated, harden when cooled	Burn or decompose when heated
Repeatable and reversible process	Become permanently hard when they form (cure)
Mostly linear polymers, may have some branching	Mostly network polymers, some cross-linked
Ductile, easy to form	Hard and strong, dimensional stability
Examples: PE, polystyrene, PVC	Examples: vulcanised rubber, epoxies, polyester resin



Lego blocks are made from the thermoplastic polymer acrylonitrile butadiene styrene (ABS) by injection moulding

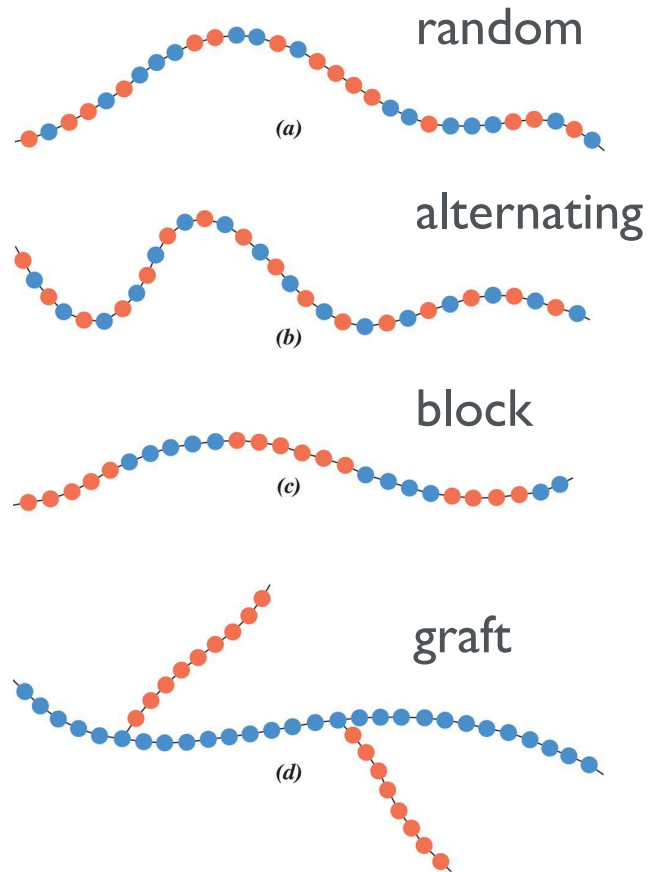
Photos: Murrayplastics.com, Ampa Plastics Group










Polyester resin, a thermosetting polymer, is painted on to fibre glass, where it sets to create a polymer matrix composite.

Source: acrylgiessen.com

# Copolymers: two or more monomers polymerised together

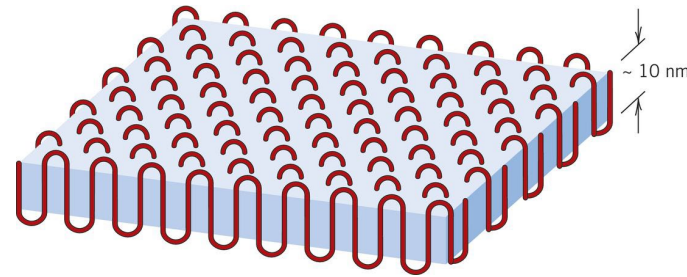
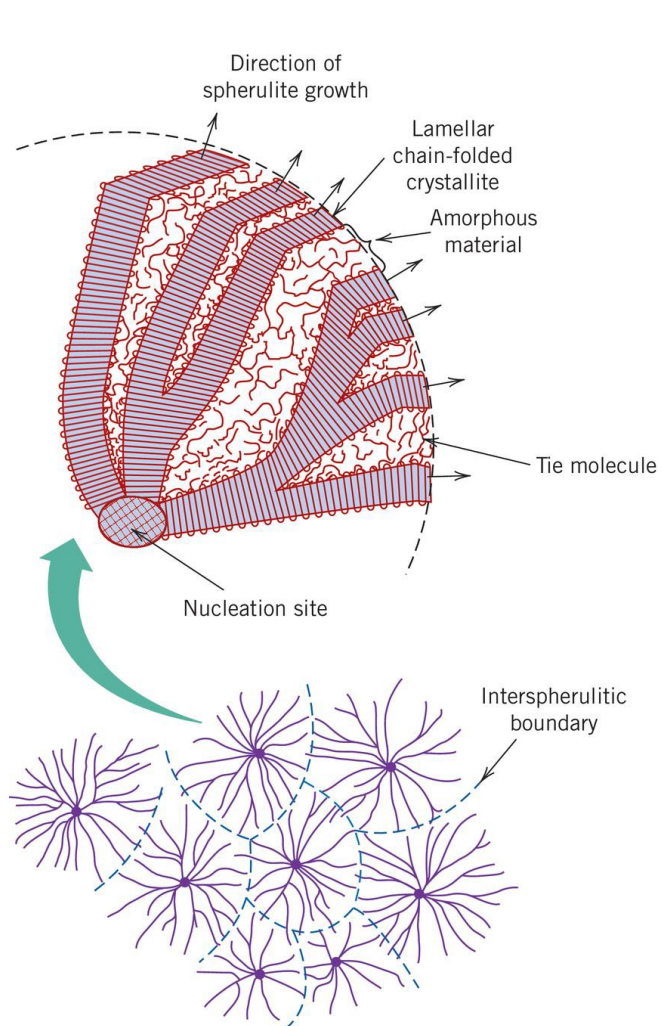


**Table 5.5** Chemical Repeat Units That Are Employed in Copolymer Rubbers

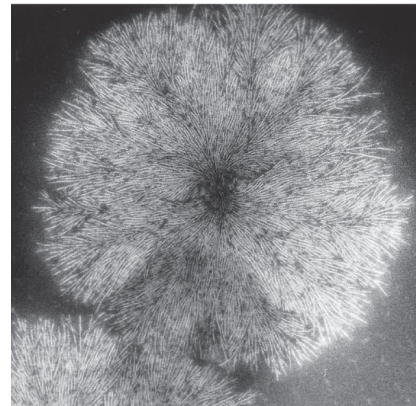
Repeat Unit Name	Repeat Unit Structure	Repeat Unit Name	Repeat Unit Structure
 Acrylonitrile Repeat Units for Rubbers	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{C}\equiv\text{N} \end{array}$	 Isoprene	$\begin{array}{c} \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ -\text{C}-\text{C}=\text{C}-\text{C}- \\   \quad \quad \quad   \\ \text{H} \quad \quad \quad \text{H} \end{array}$
 Styrene	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{C}_6\text{H}_5 \end{array}$	 Isobutylene	$\begin{array}{c} \text{H} \quad \text{CH}_3 \\   \quad   \\ -\text{C}-\text{C}- \\   \quad   \\ \text{H} \quad \text{CH}_3 \end{array}$
 Butadiene	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ -\text{C}-\text{C}=\text{C}-\text{C}- \\   \quad \quad \quad   \\ \text{H} \quad \quad \quad \text{H} \end{array}$	 Dimethylsiloxane	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ \text{CH}_3 \end{array}$
 Chloroprene	$\begin{array}{c} \text{H} \quad \text{Cl} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ -\text{C}-\text{C}=\text{C}-\text{C}- \\   \quad \quad \quad   \\ \text{H} \quad \quad \quad \text{H} \end{array}$		



# Polymer Crystals



Rubber spherulite

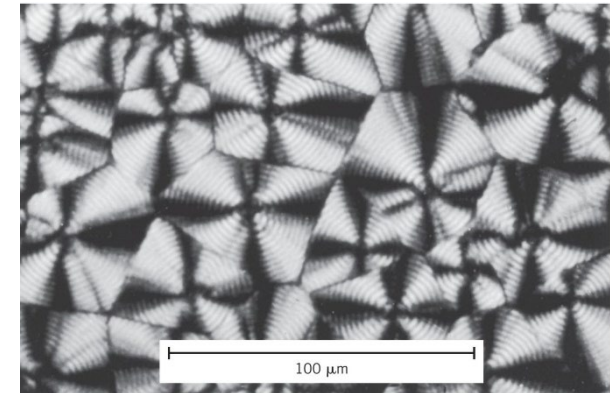


(d)

Photograph of Figure (d) supplied by P. J. Phillips. First published in R. Bartnikas and R. M. Eichhorn, Engineering Dielectrics, Vol. IIA, Electrical Properties of Solid Insulating Materials: Molecular Structure and Electrical Behavior, 1983. Copyright ASTM, 1916 Race Street, Philadelphia, PA 19103. Reprinted with permission.

**Crystalites:** small crystalline regions of chain-folded lamellae

**Spherulite:** Spherical structure of crystallites emanating from a nucleation site at the core with amorphous regions in between crystalites



Courtesy F. P. Price, General Electric Company

Polyethylene spherulites

Thank you | Dankie | Enkosi



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