

Polymerisation

Polymerization is a process of reacting monomer molecules together in a chemical reaction to form linear chains or a three-dimensional network of polymer chains. There are many forms of polymerization and different systems exist to categorize them.

The main categories are

- Addition polymerisation
- Condensation polymerisation

Terminology in the literature to represent these types of polymerizations is not standard: there are multiple terms for the same type. For example, "step polymerization" and "step-growth polymerization" refer to the same type of polymerization.

Overview

Addition polymerization involves the linking together of molecules incorporating double or triple chemical bonds. These unsaturated *monomers* (the identical molecules which make up the polymers) have extra, internal, bonds which are able to break and link up with other monomers to form the repeating chain. Addition polymerization is involved in the manufacture of polymers such as polyethene, polypropylene and polyvinyl chloride (PVC). A special case of addition polymerization leads to living polymerization.

Condensation polymerization occurs when monomers bond together through condensation reaction. Typically these reactions can be achieved through reacting molecules incorporating alcohol, amine, or carboxylic acid (or other carboxyl derivative) functional groups. When an amine reacts with a carboxylic acid an amide or peptide bond is formed, with the release of water (hence *condensation* polymerization.) This is the process through which amino acids link up to form proteins.

The chain growth-step growth system categorizes polymers based on their mechanism. While most polymers will fall into their similar category from the addition-condensation method of categorization, there are a few exceptions.

Chain growth polymers are defined as polymers formed by the reaction of monomer with a reactive center. These polymers grow to high molecular weight at a very fast rate. It is important to note that the overall conversion rates between chain and step growth polymers are similar, but that high molecular weight polymers are formed in addition reactions much more quickly than with step polymerizations.

Step growth polymers are defined as polymers formed by the **stepwise reaction between functional groups of monomer**. Most step growth polymers are also classified as condensation polymers, but not all step growth polymers (like polyurethanes formed from isocyanate and alcohol bifunctional monomers) release condensates. Step growth polymers increase in molecular weight at a very slow rate at lower conversions and only reach moderately high molecular weights at very high conversion (i.e. >95%).

To alleviate inconsistencies in these naming methods, adjusted definitions for condensation and addition polymers have been developed. **A condensation polymer is defined as a polymer that involves elimination of small molecules during its synthesis, or contains functional groups as part of its backbone chain, or its repeat unit does not contain all the atoms present in the hypothetical monomer to which it can be degraded.**

Addition polymerization involves the breaking of double or triple bonds, which are used to link monomers into chains. It is useful to distinguish four polymerization procedures fitting this general description.

- **Radical Polymerization** The initiator is a radical, and the propagating site of reactivity (*) is a carbon radical.
- **Cationic Polymerization** The initiator is an acid, and the propagating site of reactivity (*) is a carbocation.
- **Anionic Polymerization** The initiator is a nucleophile, and the propagating site of reactivity (*) is

a carbanion.

- **Coordination Catalytic Polymerization** The initiator is a transition metal complex, and the propagating site of reactivity (*) is a terminal catalytic complex.

In the polymerization of ethene (fig. 1), its pi bond is broken and these two electrons rearrange to create a new propagating center like the one that attacked it. The form this propagating center takes depends on the specific type of addition mechanism. There are several mechanisms through which this can be initiated. The free radical mechanism was one of the first methods to be used. Free radicals are very reactive atoms or molecules which have unpaired electrons. Taking the polymerization of ethene as an example, the free radical mechanism can be divided into three stages: **initiation, propagation and termination**.

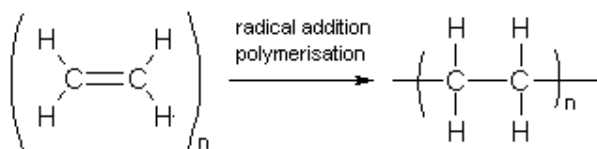


Fig 1: The polymerisation of ethene into poly(ethene)

Initiation is the creation of free radicals necessary for propagation. The radicals can be created from radical initiators, such as organic peroxide molecules, molecules containing an O-O single bond, by reacting oxygen with ethene. The products formed are unstable and easily break down into two radicals. In an ethene monomer, one electron pair is held securely between the two carbons in a sigma bond. The other is more loosely held in a pi bond. The free radical uses one electron from the pi bond to form a more stable bond with the carbon atom. The other electron returns to the second carbon atom, turning the whole molecule into another radical.

Propagation is the rapid reaction of this radicalised ethene molecule with another ethene monomer, and the subsequent repetition to create the repeating chain.

Termination occurs when a radical reacts in a way that prevents further propagation. The most common method of termination is by coupling where two radical species react with each other forming a single molecule. Another, less common method of termination is disproportionation where two radicals meet, but instead of coupling, they exchange a proton, which gives two terminated chains, one saturated and the other with a terminal double bond.

Free radical addition polymerization of ethylene must take place at high temperatures and pressures, approximately 300°C and 2000 At. While most other free radical polymerizations do not require such extreme temperatures and pressures, they do tend to lack control. One effect of this lack of control is a high degree of branching. Also, as termination occurs randomly, when two chains collide, it is impossible to control the length of individual chains. A newer method of polymerization similar to free radical, but allowing more control involves the Ziegler-Natta catalyst.

The problem of branching occurs during propagation, when a chain curls back on itself and breaks - leaving irregular chains sprouting from the main carbon backbone. Branching makes the polymers less dense and results in low tensile strength and melting points. **Developed by Karl Ziegler and Giulio Natta in the 1950s, Ziegler-Natta catalysts (triethylaluminium in the presence of a metal(IV) chloride) largely solved this problem.** Instead of a free radical reaction, the initial ethene monomer inserts between the aluminium atom and one of the ethyl groups in the catalyst. The polymer is then able to grow out from the aluminium atom and results in almost totally unbranched chains. With the new catalysts, **the tacticity** of the polypropene chain, the alignment of alkyl groups, was also able to be controlled. Different metal chlorides allowed the selective production of each form i.e., **syndiotactic, isotactic and atactic** polymer chains could be selectively created.

However there were further complications to be solved. If the Ziegler-Natta catalyst was poisoned or damaged then the chain stopped growing. Also, Ziegler-Natta monomers have to be small, and it was still impossible to control the molecular mass of the polymer chains. Again new catalysts, the [metallocenes](#), were developed to tackle these problems. Due to their structure they have less premature chain termination and branching.

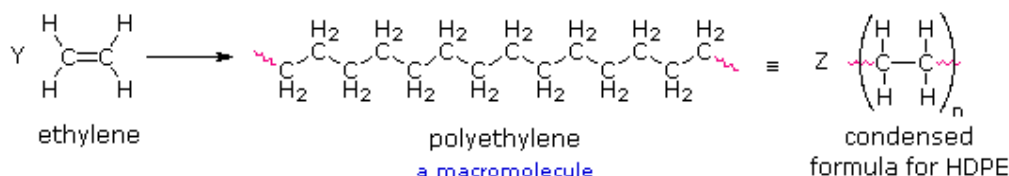
Other forms of addition polymerization include cationic and anionic polymerization. While not used to a large extent in industry yet due to stringent reaction conditions such as lack of water and oxygen, these methods provide ways to polymerize some monomers that cannot be polymerized by free radical methods such as polypropylene. Cationic and anionic mechanisms are also more ideally suited for living polymerizations, although free radical living polymerizations have also been developed.

History

Polymerization dates back to the beginning of [DNA](#) based life, as both DNA and [proteins](#) can be considered polymers. The first 'synthetic' polymers of the 19th century were actually formed by modifying natural polymers. For example [nitrocellulose](#) was manufactured by reacting [cellulose](#) with [nitric acid](#). The first genuinely man-made polymer, the phenol-formaldehyde resin [bakelite](#), was synthesized in 1872. However, research into polymers and polymerization only really accelerated in the 1930s after the serendipitous discovery of [polyethene](#) by the chemical company [ICI](#).

2. Writing Formulas for Polymeric Macromolecules

The repeating structural unit of most simple polymers not only reflects the monomer(s) from which the polymers are constructed, but also provides a concise means for drawing structures to represent these macromolecules. For polyethylene, arguably the simplest polymer, this is demonstrated by the following equation. Here ethylene (ethene) is the monomer, and the corresponding linear polymer is called **high-density polyethylene (HDPE)**. **HDPE** is composed of macromolecules in which n ranges from 10,000 to 100,000 (molecular weight 2×10^5 to 3×10^6).



The HDPE molecules, are all long carbon chains, but the lengths may vary by thousands of monomer units. Because of this, polymer molecular weights are usually given as averages.

Many polymeric materials having chain-like structures similar to polyethylene are known. Polymers formed by a straightforward linking together of monomer units, with no loss or gain of material, are called **addition polymers** or **chain-growth polymers**. A listing of some important addition polymers and their monomer precursors is presented in the following table.

Some Common Addition Polymers				
Name(s)	Formula	Monomer	Properties	Uses
Polyethylene low density (LDPE)	$-(\text{CH}_2-\text{CH}_2)_n-$	ethylene $\text{CH}_2=\text{CH}_2$	soft, waxy solid	film wrap, plastic bags
Polyethylene high density (HDPE)	$-(\text{CH}_2-\text{CH}_2)_n-$	ethylene $\text{CH}_2=\text{CH}_2$	rigid, translucent solid	electrical insulation bottles, toys
Polypropylene (PP) different grades	$-\text{[CH}_2-\text{CH}(\text{CH}_3)]_n-$	propylene $\text{CH}_2=\text{CHCH}_3$	<u>atactic</u> : soft, elastic solid <u>isotactic</u> : hard, strong solid	similar to LDPE carpet, upholstery
Poly(vinyl chloride) (PVC)	$-(\text{CH}_2-\text{CHCl})_n-$	vinyl chloride $\text{CH}_2=\text{CHCl}$	strong rigid solid	pipes, siding, flooring
Poly(vinylidene chloride) (Saran A)	$-(\text{CH}_2-\text{CCl}_2)_n-$	vinylidene chloride $\text{CH}_2=\text{CCl}_2$	dense, high-melting solid	seat covers, films
Polystyrene (PS)	$-\text{[CH}_2-\text{CH}(\text{C}_6\text{H}_5)]_n-$	styrene $\text{CH}_2=\text{CHC}_6\text{H}_5$	hard, rigid, clear solid soluble in organic solvents	toys, cabinets packaging (foamed)
Polyacrylonitrile	$-(\text{CH}_2-\text{CHCN})_n-$	acrylonitrile	high-melting solid	rugs, blankets

PAN, Orlon, Acrilan)		$\text{CH}_2=\text{CHCN}$	soluble in organic solvents	clothing
Polytetrafluoroethylene PTFE	$-(\text{CF}_2-\text{CF}_2)_n-$	tetrafluoroethylene $\text{CF}_2=\text{CF}_2$	resistant, smooth solid	non-stick surfaces electrical insulation
Poly(methyl methacrylate) PMMA, Lucite, Plexiglas)	$-\text{[CH}_2-\text{C(CH}_3\text{)CO}_2\text{CH}_3\text{]}_n-$	methyl methacrylate $\text{CH}_2=\text{C(CH}_3\text{)CO}_2\text{CH}_3$	hard, transparent solid	lighting covers, signs skylights
Poly(vinyl acetate) PVAc)	$-(\text{CH}_2-\text{CHOCOCH}_3)_n-$	vinyl acetate $\text{CH}_2=\text{CHOCOCH}_3$	soft, sticky solid	latex paints, adhesives



To account for the differences noted here we need to consider the nature of the aggregate macromolecular structure, or **morphology**, of each substance. Because polymer molecules are so large, they generally pack together in a non-uniform fashion, with ordered or crystalline-like regions mixed together with **disordered or amorphous domains**. In some cases the entire solid may be amorphous, composed entirely of coiled and tangled macromolecular chains. **Crystallinity occurs when linear polymer chains are structurally oriented in a uniform three-dimensional matrix**. In the diagram on the right, crystalline domains are

colored blue.

Increased crystallinity is associated with an increase in rigidity, tensile strength and opacity (due to light scattering). **Amorphous polymers are usually less rigid, weaker and more easily deformed. They are often transparent.**

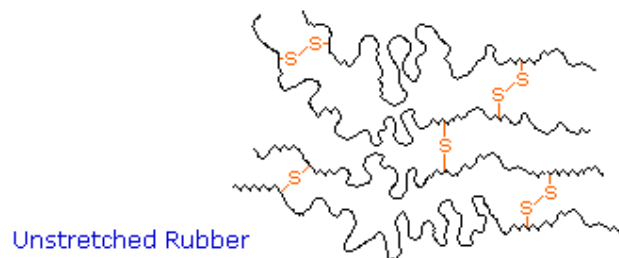
Three factors that influence the degree of crystallinity are:

- i) Chain length**
- ii) Chain branching**
- iii) Interchain bonding**

The importance of the first two factors is nicely illustrated by the differences between LDPE and HDPE. As noted earlier, **HDPE is composed of very long unbranched hydrocarbon chains**. These pack together easily in crystalline domains that alternate with amorphous segments, and the resulting material, while relatively strong and stiff, retains a degree of flexibility. **In contrast, LDPE is composed of smaller and more highly branched chains which do not easily adopt crystalline structures**. This material is therefore softer, weaker, less dense and more easily deformed than HDPE. As a rule, mechanical properties such as ductility, tensile strength, and hardness rise and eventually level off with increasing chain length.

The nature of cellulose supports the above analysis and demonstrates the importance of the third factor (iii). To begin with, cellulose chains easily adopt a stable rod-like conformation. These molecules align themselves side by side into fibres that are stabilized by inter-chain hydrogen bonding between the three hydroxyl groups on each monomer unit. Consequently, crystallinity is high and the cellulose molecules do not move or slip relative to each other. The high concentration of hydroxyl groups also accounts for the facile absorption of water that is characteristic of cotton.

Natural rubber is a completely amorphous polymer. Unfortunately, the potentially useful properties of raw latex rubber are limited by temperature dependence; however, these properties can be modified by chemical change. **The cis-double bonds in the hydrocarbon chain provide planar segments that stiffen, but do not straighten the chain**. If these rigid segments are completely removed by hydrogenation (H_2 & Pt catalyst), the chains lose all constraint, and the product is a low melting paraffin-like semisolid of little value. If instead, the chains of rubber molecules are slightly cross-linked by sulfur atoms, a process called **vulcanization** which was discovered by Charles Goodyear in 1839, **the desirable elastomeric properties of rubber are substantially improved**. At 2 to 3% crosslinking a useful soft rubber, that no longer suffers stickyness and brittleness problems on heating and cooling, is obtained. At 25 to 35% crosslinking a rigid hard rubber product is formed. The following illustration shows a cross-linked section of amorphous rubber.

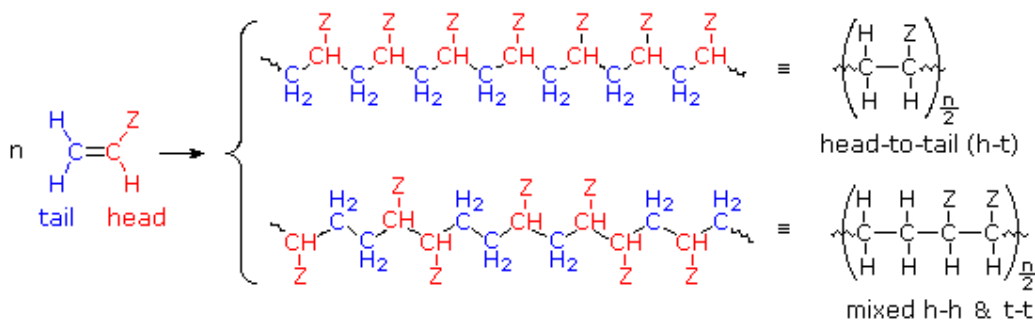


On heating or cooling most polymers undergo thermal transitions that provide insight into their morphology. These are defined as the **melt transition, T_m** , and the **glass transition, T_g** .

Rubber is a member of an important group of polymers called elastomers. Elastomers are amorphous polymers that have the ability to stretch and then return to their original shape at temperatures above T_g . This property is important in applications such as gaskets and O-rings, so the development of synthetic elastomers that can function under harsh or demanding conditions remains a practical goal. At temperatures below T_g elastomers become rigid glassy solids and lose all elasticity. A tragic example of this caused the space shuttle Challenger disaster. The heat and chemical resistant O-rings used to seal sections of the solid booster rockets had an unfortunately high T_g near 0 °C. The unexpectedly low temperatures on the morning of the launch were below this T_g , allowing hot rocket gases to escape the seals.

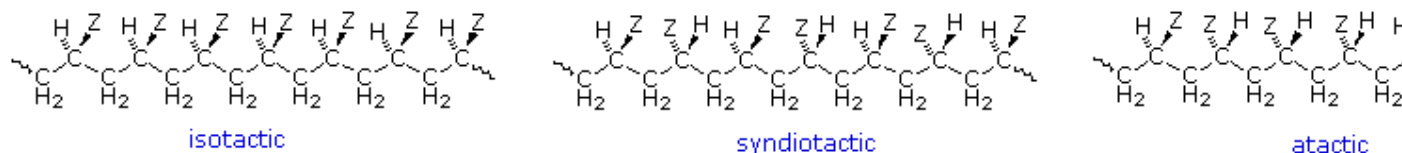
4. Regio and Stereoisomerization in Macromolecules

Symmetrical monomers such as ethylene and tetrafluoroethylene can join together in only one way. Monosubstituted monomers, on the other hand, may join together in two organized ways, described in the following diagram, or in a third random manner. Most monomers of this kind, including propylene, vinyl chloride, styrene, acrylonitrile and acrylic esters, prefer to join in a head-to-tail fashion, with some randomness occurring from time to time. The reasons for this regioselectivity will be discussed in the synthetic methods section.



Regioisomeric Polymers from Substituted Monomers

If the polymer chain is drawn in a zig-zag fashion, as shown above, each of the substituent groups (Z) will necessarily be located above or below the plane defined by the carbon chain. Consequently we can identify three configurational isomers of such polymers. **If all the substituents lie on one side of the chain** the configuration is called **isotactic**. **If the substituents alternate from one side to another in a regular manner** the configuration is termed **syndiotactic**. Finally, **a random arrangement of substituent groups** is referred to as **atactic**. Examples of these configurations are shown here.



Many common and useful polymers, such as polystyrene, polyacrylonitrile and poly(vinyl chloride) are atactic as normally prepared. Customized catalysts that effect stereoregular polymerization of polypropylene and some other monomers have been developed, and the improved properties associated with the increased crystallinity of these products has made this an important field of investigation.

Copolymers

The synthesis of macromolecules composed of more than one monomeric repeating unit has been explored as a means of controlling the properties of the resulting material. In this respect, it is useful to distinguish several ways in which different monomeric units might be incorporated in a polymeric molecule. The following examples refer to a two component system, in which one monomer is designated **A** and the other **B**.

Statistical Copolymers Also called random copolymers. Here the monomeric units are distributed randomly, and sometimes unevenly, in the polymer chain:
~ABBAABAABBBABAABA~.

Alternating Copolymers Here the monomeric units are distributed in a regular alternating fashion, with nearly equimolar amounts of each in the chain:
~ABABABABABABABAB~.

Block Copolymers Instead of a mixed distribution of monomeric units, a long sequence or block of one monomer is joined to a block of the second monomer:
~AAAAA-BBBBBBB~AAAAAA~BBB~.

Graft Copolymers As the name suggests, side chains of a given monomer are attached to the main chain of the second monomer:
~AAAAAA(BBBBBBB~)AAAAAA(BBBB~)AAA~.

1. Addition Copolymerization

Some Useful Copolymers			
Monomer A	Monomer B	Copolymer	Uses
$\text{H}_2\text{C}=\text{CHCl}$	$\text{H}_2\text{C}=\text{CCl}_2$	Saran	films & fibers
$\text{H}_2\text{C}=\text{CHC}_6\text{H}_5$	$\text{H}_2\text{C}=\text{C}-\text{CH}=\text{CH}_2$	SBR styrene butadiene rubber	tires
$\text{H}_2\text{C}=\text{CHCN}$	$\text{H}_2\text{C}=\text{C}-\text{CH}=\text{CH}_2$	Nitrile Rubber	adhesives hoses
$\text{H}_2\text{C}=\text{C}(\text{CH}_3)_2$	$\text{H}_2\text{C}=\text{C}-\text{CH}=\text{CH}_2$	Butyl Rubber	inner tubes
$\text{F}_2\text{C}=\text{CF}(\text{CF}_3)$	$\text{H}_2\text{C}=\text{CHF}$	Viton	gaskets

A terpolymer of acrylonitrile, butadiene and styrene, called ABS rubber, is used for high-impact containers, pipes and gaskets.

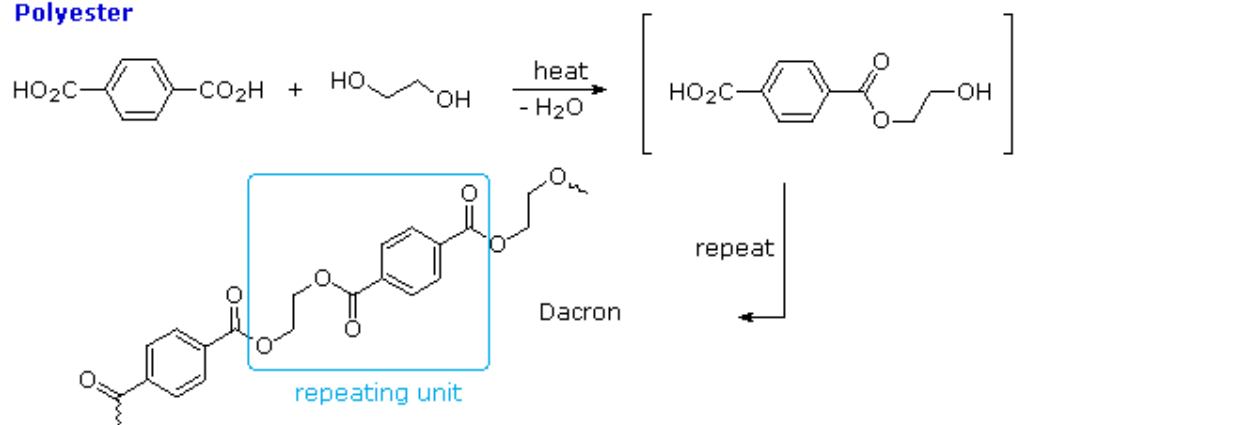
Condensation Polymers

A large number of important and useful polymeric materials are not formed by chain-growth processes involving reactive species such as radicals, but proceed instead by conventional functional group transformations of polyfunctional reactants. These polymerizations often (but not always) occur with loss of a small byproduct, such as water, and generally (but not always) combine two different components in an alternating structure. The polyester Dacron and the polyamide Nylon 66, shown here, are two examples of synthetic condensation polymers, also known as **step-growth** polymers. In contrast to chain-growth polymers, most of which grow by carbon-carbon bond formation, step-growth polymers generally grow by carbon-heteroatom bond formation (C-O & C-N in Dacron & Nylon respectively). Although polymers of this kind might be considered to be alternating copolymers, the repeating monomeric unit is usually defined as a combined moiety.

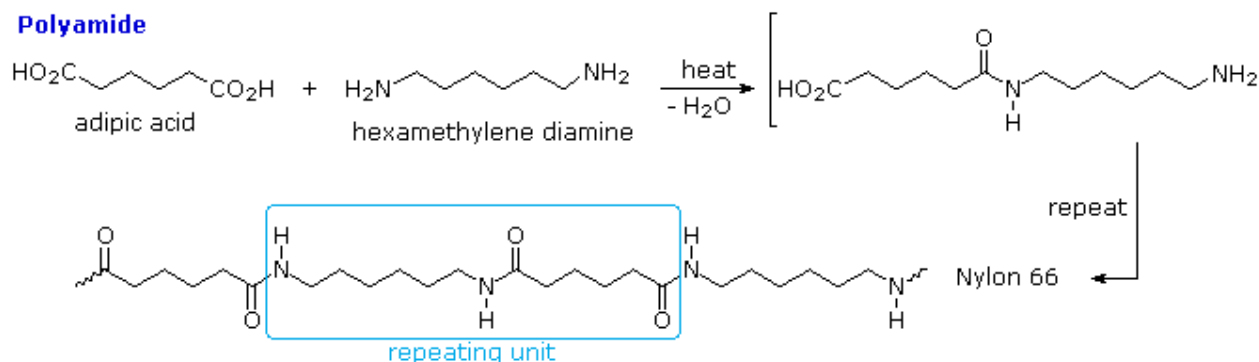
Examples of naturally occurring condensation polymers are cellulose, the polypeptide chains of proteins, and poly(β -hydroxybutyric acid), a polyester synthesized in large quantity by certain soil and water bacteria. Formulas for these will be displayed below by clicking on the diagram.

Examples of Condensation Polymers

Polyester



Polyamide

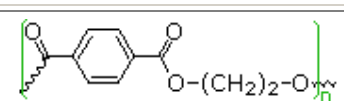
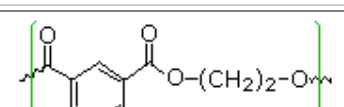


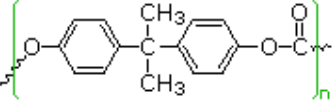
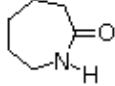
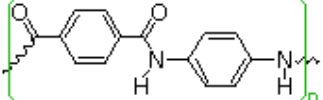
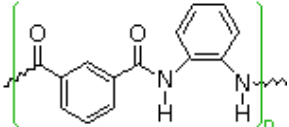
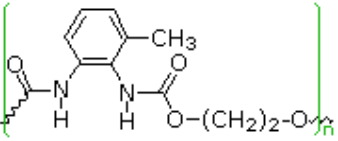
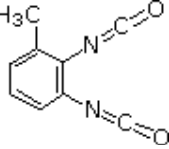
1. Characteristics of Condensation Polymers

Condensation polymers form more slowly than addition polymers, often requiring heat, and they are generally lower in molecular weight. The terminal functional groups on a chain remain active, so that groups of shorter chains combine into longer chains in the late stages of polymerization. The presence of polar functional groups on the chains often enhances chain-chain attractions, particularly if these involve hydrogen bonding, and thereby crystallinity and tensile strength. The following examples of condensation polymers are illustrative.

Note that for commercial synthesis the carboxylic acid components may actually be employed in the form of derivatives such as simple esters. Also, the polymerization reactions for Nylon 6 and Spandex do not proceed by elimination of water or other small molecules. Nevertheless, the polymer clearly forms by a step-growth process.

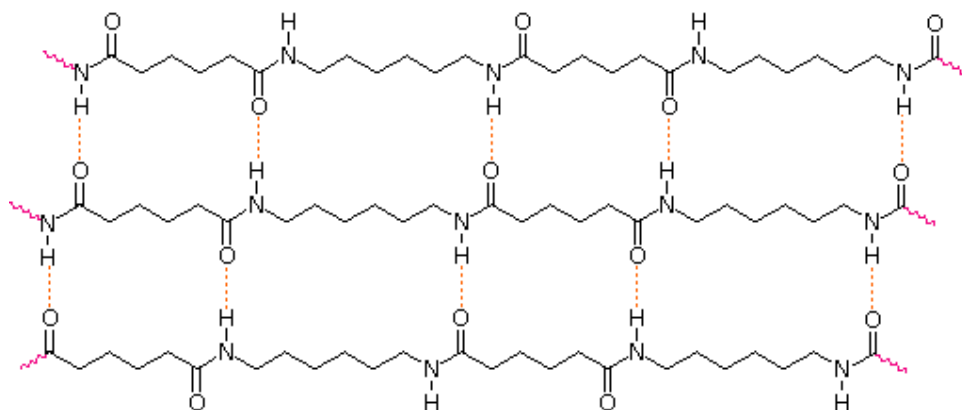
Some Condensation Polymers

Formula	Type	Components	T _g °C	T _m °C
$\sim[\text{CO}(\text{CH}_2)_4\text{CO}-\text{OCH}_2\text{CH}_2\text{O}]_n\sim$	polyester	HO ₂ C-(CH ₂) ₄ -CO ₂ H HO-CH ₂ CH ₂ -OH	< 0	50
	polyester Dacron Mylar	para HO ₂ C-C ₆ H ₄ -CO ₂ H HO-CH ₂ CH ₂ -OH	70	265
	polyester	meta HO ₂ C-C ₆ H ₄ -CO ₂ H HO-CH ₂ CH ₂ -OH	50	240

	polycarbonate Lexan	$(\text{HO}-\text{C}_6\text{H}_4)_2\text{C}(\text{CH}_3)_2$ (Bisphenol A) $\text{X}_2\text{C}=\text{O}$ (X = OCH₃ or Cl)	150	267
$\sim[\text{CO}(\text{CH}_2)_4\text{CO}-\text{NH}(\text{CH}_2)_6\text{NH}]_n\sim$	polyamide Nylon 66	$\text{HO}_2\text{C}-(\text{CH}_2)_4-\text{CO}_2\text{H}$ $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$	45	265
$\sim[\text{CO}(\text{CH}_2)_5\text{NH}]_n\sim$	polyamide Nylon 6 Perlon		53	223
	polyamide Kevlar	para $\text{HO}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{H}$ para $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$	---	500
	polyamide Nomex	meta $\text{HO}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{H}$ meta $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$	273	390
	polyurethane Spandex	$\text{HOCH}_2\text{CH}_2\text{OH}$ 	52	---

The difference in T_g and T_m between the first polyester (completely aliphatic) and the two nylon polyamides (5th & 6th entries) shows the effect of intra-chain hydrogen bonding on crystallinity. The replacement of flexible alkylidene links with rigid benzene rings also stiffens the polymer chain, leading to increased crystalline character, as demonstrated for polyesters (entries 1, 2 & 3) and polyamides (entries 5, 6, 7 & 8). The high T_g and T_m values for the amorphous polymer Lexan are consistent with its brilliant transparency and glass-like rigidity. Kevlar and Nomex are extremely tough and resistant materials, which find use in bullet-proof vests and fire resistant clothing.

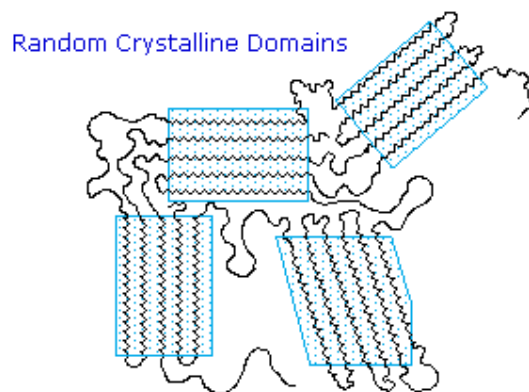
Interchain Hydrogen Bonding Enhances Crystallinity



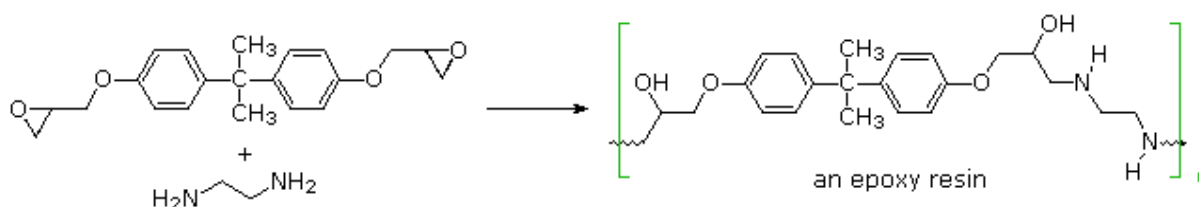
Many polymers, both addition and condensation, are used as fibers. The chief methods of spinning synthetic polymers into fibers are from melts or viscous solutions. Polyesters, polyamides and polyolefins are usually spun from melts, provided the T_m is not too high. Polyacrylates suffer thermal degradation and are therefore spun from solution in a volatile solvent. **Cold-drawing** is an important physical treatment that improves the strength and appearance of these polymer fibers. At temperatures above T_g , a thicker than desired fiber can be forcibly stretched to many times its length; and in so doing the polymer chains become untangled, and tend to align in a parallel fashion. This cold-drawing procedure organizes randomly oriented crystalline domains, and also aligns amorphous domains so they become more crystalline. In these cases, the physically oriented morphology is stabilized and retained in the final product. This contrasts with elastomeric polymers, for which the stretched or aligned morphology is unstable relative to the amorphous random coil

morphology.

By clicking on the following diagram, a cartoon of these changes will toggle from one extreme to the other. This cold-drawing treatment may also be used to treat polymer films (e.g. Mylar & Saran) as well as fibers.



Step-growth polymerization is also used for preparing a class of adhesives and amorphous solids called epoxy resins. Here the covalent bonding occurs by an S_N2 reaction between a nucleophile, usually an amine, and a terminal epoxide. In the following example, the same bisphenol A intermediate used as a monomer for Lexan serves as a difunctional scaffold to which the epoxide rings are attached. Bisphenol A is prepared by the acid-catalyzed condensation of acetone with phenol.



Thermosetting vs. Thermoplastic Polymers

Most of the polymers described above are classified as **thermoplastic**. This reflects the fact that above T_g they may be shaped or pressed into molds, spun or cast from melts or dissolved in suitable solvents for later fashioning. Because of their high melting point and poor solubility in most solvents, Kevlar and Nomex proved to be a challenge, but this was eventually solved.

Another group of polymers, characterized by a high degree of cross-linking, resist deformation and solution once their final morphology is achieved. Such polymers are usually prepared in molds that yield the desired object. Because these polymers, once formed, cannot be reshaped by heating, they are called **thermosets**. Partial formulas for four of these will be shown below by clicking the appropriate button. The initial display is of Bakelite, one of the first completely synthetic plastics to see commercial use.

