

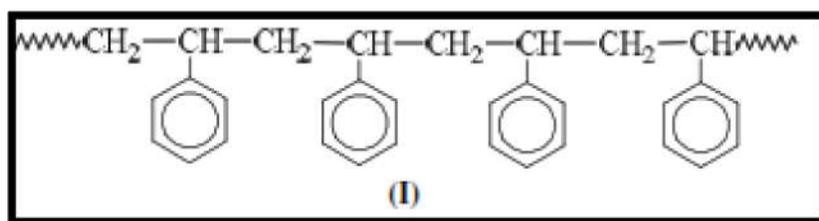
**5<sup>th</sup> SEMESTER**  
**DISCIPLINE SPECIFIC ELECTIVES (DSEs)**  
**OPTION – II**  
**CH516DB CHEMISTRY – POLYMER CHEMISTRY**

## UNIT I: INTRODUCTION

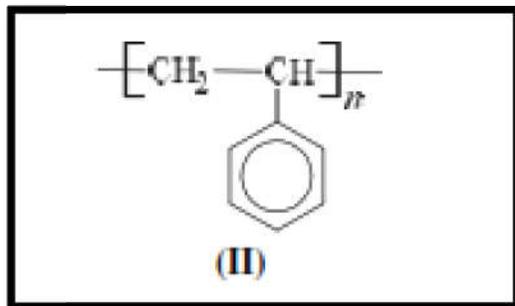
### Polymers

The term polymer stems from the Greek roots poly (many) and meros (part). The word thus means “many parts” and designates a molecule made up by the repetition of some simpler unit called a mer. Polymers contain thousands to millions of atoms in a molecule that is large; they are also called macromolecules. Polymers are prepared by joining a large number of small molecules called monomers.

The structure of polystyrene, for example, can be written as



or, more conveniently, as (II), which depicts the mer or repeating unit of the molecule within parentheses with a subscript, such as  $n$ , to represent the number of repeating units in the polymer molecule.



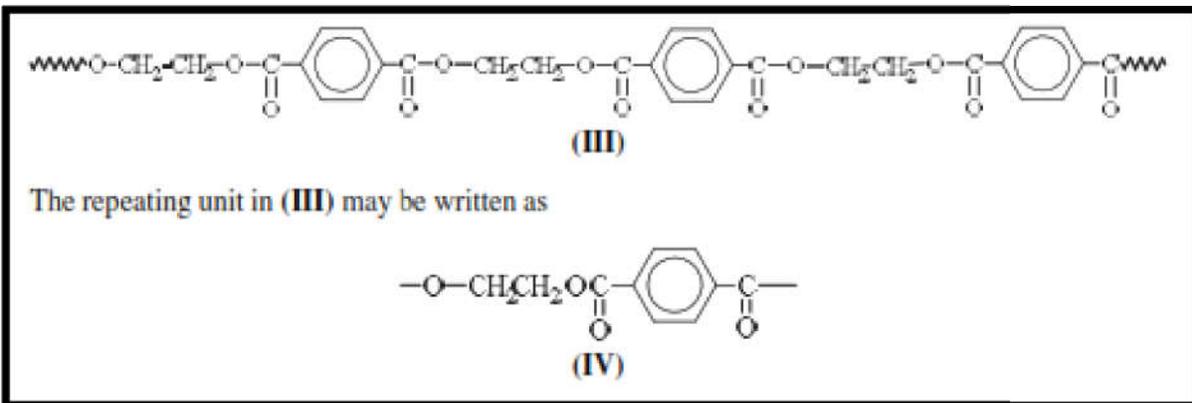
or, more conveniently, as (II), which depicts the mer or repeating unit of the molecule within parentheses with a subscript, such as  $n$ , to represent the number of repeating units in the polymer molecule.

The value of  $n$  usually ranges from a few hundred to several thousand, depending on the molecular weight of the polymer. The polymer molecular weight may extend, on the higher side, to several millions. Often the term high polymer is also used to emphasize that the polymer under consideration is of very high molecular weight.

## Monomers

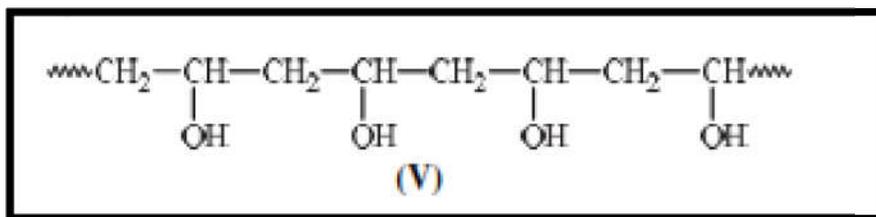
Monomers are generally simple organic molecules from which the polymer molecule is made. The structure of the repeating unit of a polymer is essentially that or closely related to that of the monomer molecule(s). The formula of the polystyrene repeating unit (II) is thus seen to be essentially the same as that of the monomer styrene CH

.The repeating unit of a linear polymer is a small portion of the macromolecule such that linking together these units one after another gives rise to the formula of the whole molecule. A repeating unit may be a single component such as (II) for the polymer (I), or it may consist of the residues of several components, as in poly(ethylene terephthalate), which has the structure :

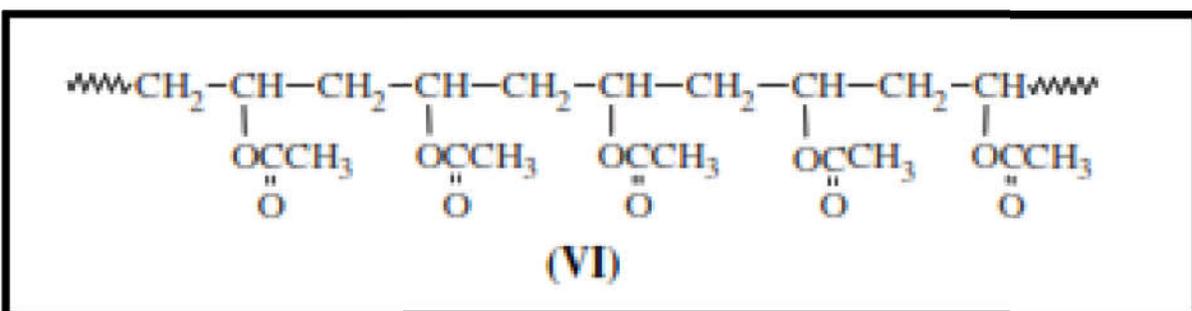


Thus, the whole molecule of (III) can be built by linking the left-hand atom shown in (IV) to the right-hand atom, and so on.

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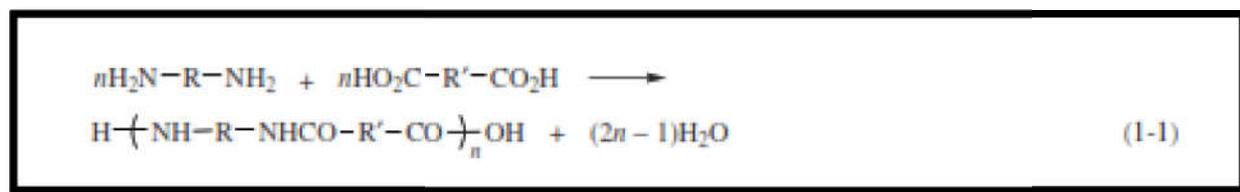
The obvious precursor monomer for this polymer is vinyl alcohol,  $\text{CH}=\text{CH}-\text{OH}$ , which is an unstable tautomer of acetaldehyde and does not exist. Poly(vinyl alcohol) is instead made by alcoholysis of poly(vinyl acetate),



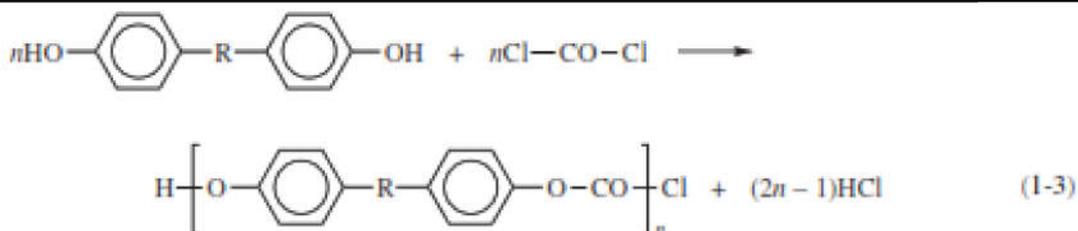
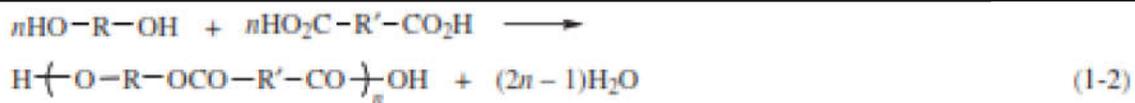
(VI) which, in turn, is synthesized by polymerization of the monomer vinyl acetate,  
CH=CHOOCCH

## Polymer Composition and Structure

Polymers were originally classified by Carothers [1929] into condensation and addition polymers on the basis of the compositional difference between the polymer and the monomer(s) from which it was synthesized. Condensation polymers were those polymers that were formed from polyfunctional monomers by the various condensation reactions of organic chemistry with the elimination of some small molecule such as water. An example of such a condensation polymer is the polyamides formed from diamines and diacids with the elimination of water according to



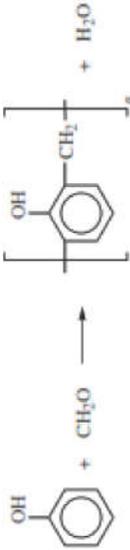
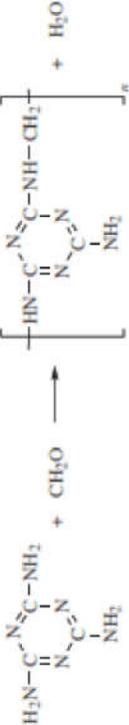
where R and R' are aliphatic or aromatic groupings. The unit in parentheses in the polyamide formula repeats itself many times in the polymer chain and is termed the repeating unit. The elemental composition of the repeating unit differs from that of the two monomers by the elements of water. The polyamide synthesized from hexamethylene diamine, and adipic acid is the extensively used fiber and plastic known commonly as nylon 6/6 or poly(hexamethylene adipamide). Other examples of condensation polymers are the polyesters formed from diacids and diols with the elimination of water and the polycarbonates from the reaction of an aromatic dihydroxy reactant and phosgene with the elimination of hydrogen chloride:



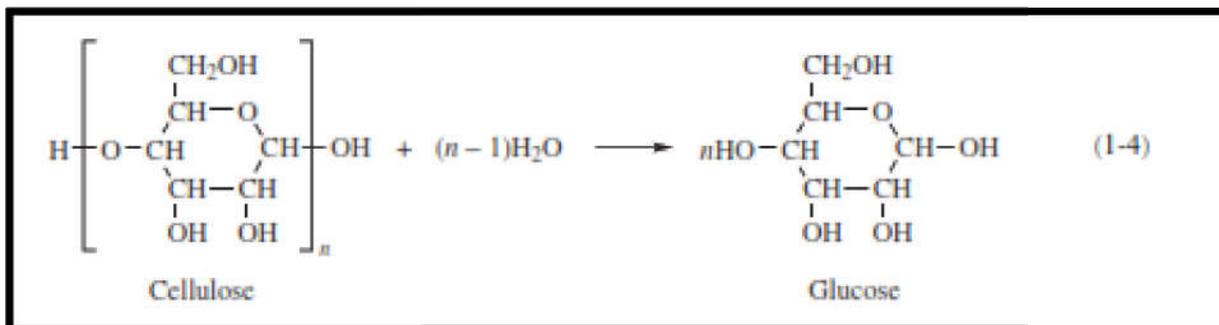
The common condensation polymers and the reactions by which they are formed are shown in Table 1-1. It should be noted from Table 1-1 that for many of the condensation polymers there are different combinations of reactants that can be employed for their synthesis. Thus polyamides can be synthesized by the reactions of diamines with diacids or diacyl chlorides and by the self-condensation of amino acids. Similarly, polyesters can be synthesized from diols by esterification with diacids or ester interchange with diesters.

Some naturally occurring polymers such as cellulose, starch, wool, and silk are classified as condensation polymers, since one can postulate their synthesis from certain hypothetical reactants by the elimination of water. Thus cellulose can be thought of as the polyether formed by the dehydration of glucose. Carothers included such polymers by defining condensation polymers as those in which the formula of the repeating unit lacks certain atoms that are present in the monomer(s) from which it is formed or to which it may be degraded.

TABLE 1-1 Typical Condensation Polymers

Type	Characteristic Linkage	Polymerization Reaction
Polyamide	-NH-CO-	$\text{H}_2\text{N}-\text{R}-\text{NH}_2 + \text{HO}_2\text{C}-\text{R}'-\text{CO}_2\text{H} \longrightarrow \text{H} \left[ \text{NH}-\text{R}-\text{NHCO}-\text{R}'-\text{CO} \right]_n \text{OH} + \text{H}_2\text{O}$ $\text{H}_2\text{N}-\text{R}-\text{NH}_2 + \text{ClCO}-\text{R}'-\text{COCl} \longrightarrow \text{H} \left[ \text{NH}-\text{R}-\text{NHCO}-\text{R}'-\text{CO} \right]_n \text{Cl} + \text{HCl}$ $\text{H}_2\text{N}-\text{R}-\text{CO}_2\text{H} \longrightarrow \text{H} \left[ \text{NH}-\text{R}-\text{CO} \right]_n \text{OH} + \text{H}_2\text{O}$
Protein, wool, silk	-NH-CO-	<p>Naturally occurring polypeptide polymers; degradable to mixtures of different amino acids.</p> $\text{H} \left[ \text{NH}-\text{R}-\text{CONH}-\text{R}'-\text{CO} \right]_n \text{OH} + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{N}-\text{R}-\text{CO}_2\text{H} + \text{H}_2\text{N}-\text{R}'-\text{CO}_2\text{H}$
Polyester	-CO-O-	$\text{HO}-\text{R}-\text{OH} + \text{HO}_2\text{C}-\text{R}'-\text{CO}_2\text{H} \longrightarrow \text{H} \left[ \text{O}-\text{R}-\text{OCO}-\text{R}'-\text{CO} \right]_n \text{OH} + \text{H}_2\text{O}$ $\text{HO}-\text{R}-\text{OH} + \text{R}''\text{O}_2\text{C}-\text{R}'-\text{CO}_2\text{R}'' \longrightarrow \text{H} \left[ \text{O}-\text{R}-\text{OCO}-\text{R}'-\text{CO} \right]_n \text{OH} + \text{R}''\text{OH}$ $\text{HO}-\text{R}-\text{CO}_2\text{H} \longrightarrow \text{H} \left[ \text{O}-\text{R}-\text{CO} \right]_n \text{OH} + \text{H}_2\text{O}$
Polyurethane	-O-CO-NH-	$\text{HO}-\text{R}-\text{OH} + \text{OCN}-\text{R}'-\text{NCO} \longrightarrow \text{H} \left[ \text{O}-\text{R}-\text{OCO}-\text{NH}-\text{R}'-\text{NH}-\text{CO} \right]_n$
Polysiloxane	-Si-O-	$\text{Cl}-\text{SiR}_2-\text{Cl} \xrightarrow[\text{-HCl}]{\text{H}_2\text{O}} \text{HO}-\text{SiR}_2-\text{OH} \longrightarrow \text{H} \left[ \text{O}-\text{SiR}_2 \right]_n \text{OH} + \text{H}_2\text{O}$
Phenol-formaldehyde	-Ar-CH <sub>2</sub> -	
Urea-formaldehyde	-NH-CH <sub>2</sub> -	$\text{H}_2\text{N}-\text{CO}-\text{NH}_2 + \text{CH}_2\text{O} \longrightarrow \left[ \text{HN}-\text{CO}-\text{NH}-\text{CH}_2 \right]_n + \text{H}_2\text{O}$
Melamine-formaldehyde	-NH-CH <sub>2</sub> -	
Polysulfide	-S <sub>n</sub> -	$\text{Cl}-\text{R}-\text{Cl} + \text{Na}_2\text{S}_n \longrightarrow \left[ \text{S}_n-\text{R} \right]_n + \text{NaCl}$
Polyacetal	-O-CH-O-   R	$\text{R}-\text{CHO} + \text{HO}-\text{R}'-\text{OH} \longrightarrow \left[ \text{O}-\text{R}'-\text{OCHR} \right]_n + \text{H}_2\text{O}$

In this sense cellulose is considered a condensation polymer, since its hydrolysis yields glucose, which contains the repeating unit of cellulose plus the elements of water



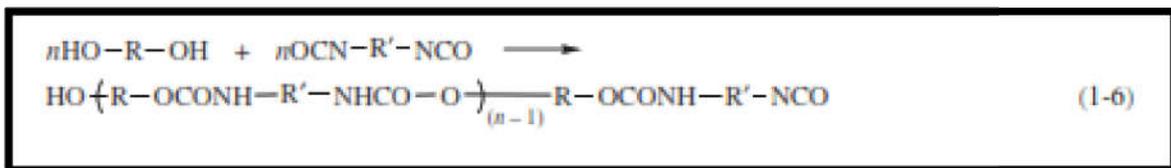
Addition polymers were classified by Carothers as those formed from monomers without the loss of a small molecule. Unlike condensation polymers, the repeating unit of an addition polymer has the same composition as the monomer. The major addition polymers are those formed by polymerization of monomers containing the carbon-carbon double bond. Such monomers will be referred to as vinyl monomers. (The term vinyl, strictly speaking, refers to a CH=CH-group attached to some substituent. Our use of the term vinyl monomer is broader—it applies to all monomers containing a carbon-carbon double bond, including monomers such as methyl methacrylate, vinylidene chloride, and 2-butene as well as vinyl chloride and styrene. The term substituted ethylenes will also be used interchangeably with the term vinyl monomers.) Vinyl monomers can be made to react with themselves to form polymers by conversion of their double bonds into saturated linkages, for example



where Y can be any substituent group such as hydrogen, alkyl, aryl, nitrile, ester, acid, ketone, ether, and halogen.

The development of polymer science with the study of new polymerization processes and polymers showed that the original classification by Carothers was not entirely adequate and left

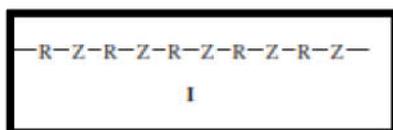
much to be desired. Thus, for example, consider the polyurethanes, which are formed by the reaction of diols with diisocyanates without the elimination of any small molecule:



Using Carothers' original classification, one would classify the polyurethanes as addition polymers, since the polymer has the same elemental composition as the sum of the monomers. However, the polyurethanes are structurally much more similar to the condensation polymers than to the addition polymers. The urethane linkage (-NH-CO-O-) has much in common with the ester (-CO-O-) and amide (-NH-CO-)

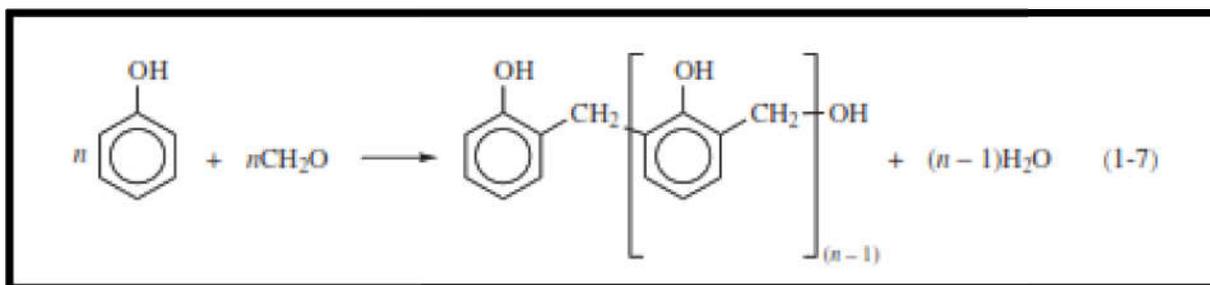
To avoid the obviously incorrect classification of polyurethanes as well as of some other polymers as addition polymers, polymers have also been classified from a consideration of the chemical structure of the groups present in the polymer chains.

Condensation polymers have been defined as those polymers whose repeating units are joined together by functional units of one kind or another such as the ester, amide, urethane, sulfide, and ether linkages. Thus the structure of condensation polymers has been defined by

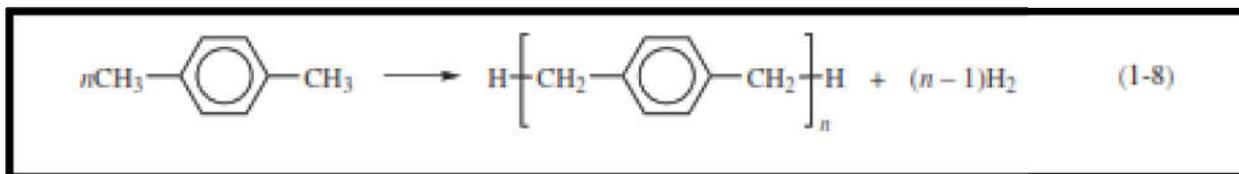


where R is an aliphatic or aromatic grouping and Z is a functional unit such as -OCO-, -NHCO-, -S-, -OCONH-, -O-, -OCOO- and -SO<sub>2</sub>-. Addition polymers, on the other hand, do not contain such functional groups as part of the polymer chain. Such groups may, however, be present in addition polymers as pendant substituents hanging off the polymer chain. According to this classification, the polyurethanes are readily and more correctly classified as condensation polymers.

It should not be taken for granted that all polymers that are defined as condensation polymers by Carothers' classification will also be so defined by a consideration of the polymer chain structure. Some condensation polymers do not contain functional groups such as ester or amide in the polymer chain. An example is the phenol-formaldehyde polymers produced by the reaction of phenol (or substituted phenols) with formaldehyde



These polymers do not contain a functional group within the polymer chain but are classified as condensation polymers, since water is split out during the polymerization process. Another example is poly(p-xylene), which is produced by the oxidative coupling (dehydrogenation) of p-xylene:

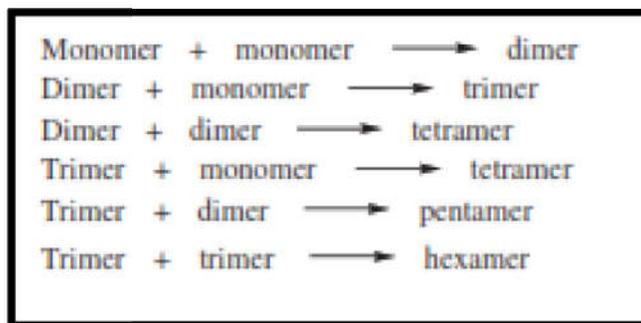


In short a polymer is classified as a condensation polymer if its synthesis involves the elimination of small molecules, or it contains functional groups as part of the polymer chain, or its repeating unit lacks certain atoms that are present in the (hypothetical) monomer to which it can be degraded. If a polymer does not fulfill any of these requirements, it is classified as an addition polymer.

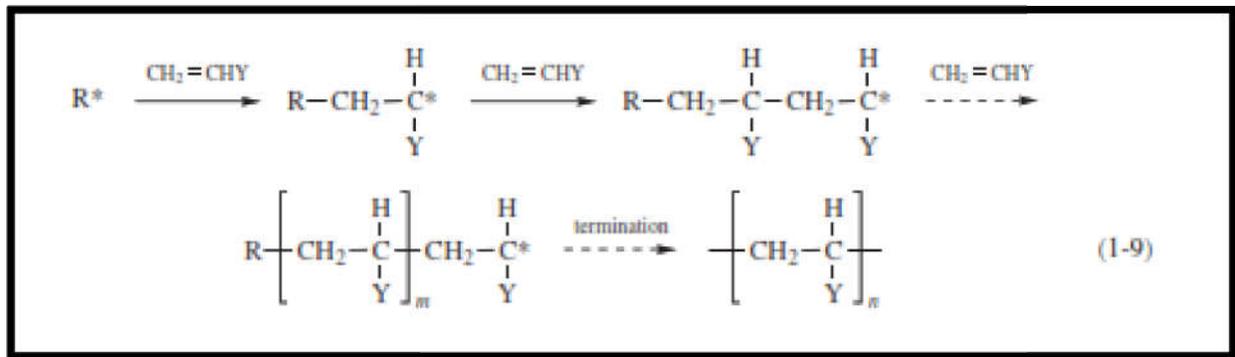
## Polymerization Mechanism

Chain and step polymerizations differ in several features, but the most important difference is in the identities of the species that can react with each other. Another difference is the manner in which polymer molecular size depends on the extent of conversion.

Step polymerizations proceed by the stepwise reaction between the functional groups of reactants and the size of the polymer molecules increases at a relatively slow pace in such polymerizations. One proceeds from monomer to dimer, trimer, tetramer, pentamer, and so on until eventually large-sized polymer molecules have been formed. The characteristic of step polymerization that distinguishes it from chain polymerization is that reaction occurs between any of the different-sized species present in the reaction system.



The situation is quite different in chain polymerization where an initiator is used to produce an initiator species  $R^*$  with a reactive center. The reactive center may be either a free radical, cation, or anion. Polymerization occurs by the propagation of the reactive center by the successive additions of large numbers of monomer molecules in a chain reaction. The distinguishing characteristic of chain polymerization is that polymer growth takes place by monomer reacting only with the reactive center. Monomer does not react with monomer and the different-sized species such as dimer, trimer, tetramer, and n-mer do not react with each other. By far the most common example of chain polymerization is that of vinyl monomers. The process can be depicted as



Each monomer molecule that adds to a reactive center regenerates the reactive center. Polymer growth proceeds by the successive additions of hundreds or thousands or more monomer molecules. The growth of the polymer chain ceases when the reactive center is destroyed by one or more of a number of possible termination reactions.

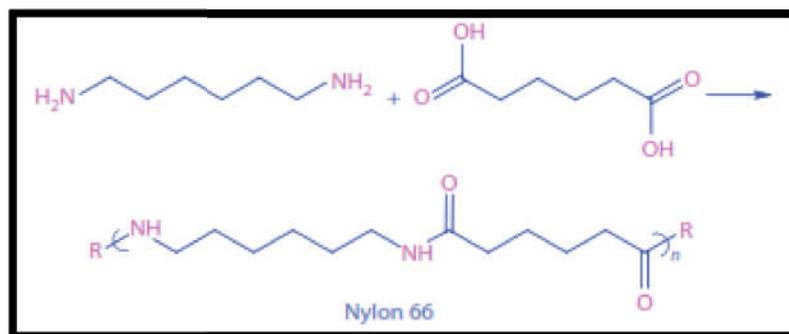
The typical step and chain polymerizations differ significantly in the relationship between polymer molecular weight and the percent conversion of monomer. Thus if we start out step and chain polymerizations side by side, we may observe a variety of situations with regard to their relative rates of polymerization. However, the molecular weights of the polymers produced at any time after the start of the reactions will always be very characteristically different for the two polymerizations. If the two polymerizations are stopped at 0.1% conversion, 1% conversion, 10% conversion, 40% conversion, 90% conversion, and so on, one will always observe the same behavior. The chain polymerization will show the presence of high-molecular-weight polymer molecules at all percents of conversion. There are no intermediate-sized molecules in the reaction mixture—only monomer, high-polymer, and initiator species. The only change that occurs with conversion (i.e., reaction time) is the continuous increase in the number of polymer molecules. On the other hand, high-molecular-weight polymer is obtained in step polymerizations only near the very end of the reaction (>98% conversion). Thus both polymer size and the amount of polymer are dependent on conversion in step polymerization.

## Nomenclature Of Polymers

### Common Names

Some names are derived from the place of origin of the material, such as Hevea brasiliensis—literally “rubber from Brazil”—for natural rubber. Other polymers were named after their discoverer, as is Bakelite, the three-dimensional polymer produced by condensation of phenol and formaldehyde, which was commercialized by Leo Baekeland in 1905.

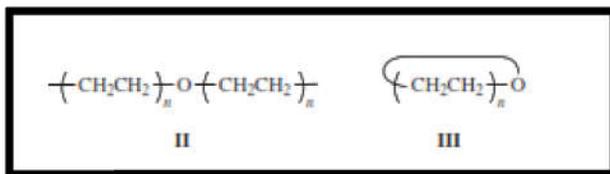
For some important groups of polymers, special names and systems of nomenclature were developed. For instance, the nylons were named according to the number of carbons in the diamine and dicarboxylic acid reactants used in their synthesis. The nylon produced by the condensation of 1,6-hexamethylenediamine (6 carbons) and adipic acid (6 carbons) is called nylon 66. Even here, there is no set standard as to how nylon 66 is to be written with alternatives including nylon 66 and nylon 66.



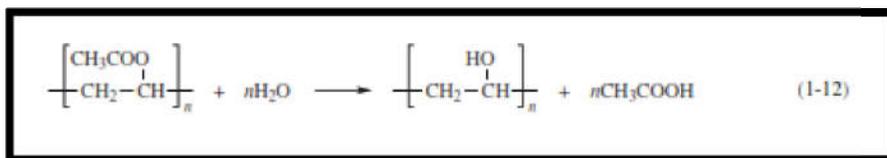
### Source-Based Names

The most simple and commonly used nomenclature system is probably that based on the source of the polymer. This system is applicable primarily to polymers synthesized from a single monomer as in addition and ring-opening polymerizations. Such polymers are named by adding the name of the monomer onto the prefix “poly” without a space or hyphen. Thus the polymers from ethylene and acetaldehyde are named polyethylene and polyacetaldehyde, respectively. When the monomer has a substituted parent name or a multiworded name or an abnormally long name, parentheses are placed around its name following the prefix “poly.” The polymers from

3-methyl-1-pentene, vinyl chloride, propylene oxide, chlorotrifluoroethylene, and E-caprolactam are named poly(3-methyl-1-pentene), poly(vinyl chloride), poly(propylene oxide), poly(chlorotrifluoroethylene), and poly(E-caprolactam), respectively. Other examples are listed in Table 1-2. The parentheses are frequently omitted in common usage when naming polymers. Although this will often not present a problem, it is incorrect and in some cases the omission can lead to uncertainty as to the structure of the polymer named. Thus the use of polyethylene oxide instead of poly(ethylene oxide) can be ambiguous in denoting one of the following possible structures:

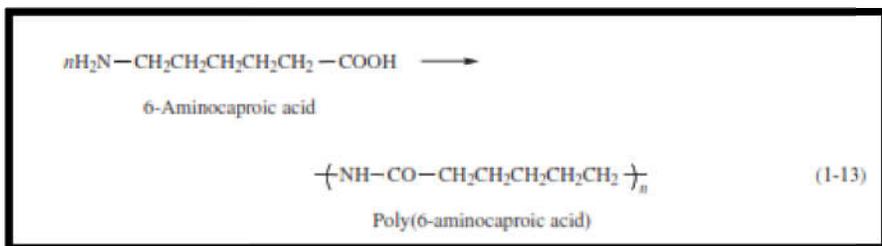


Some polymers are named as being derived from hypothetical monomers. Thus poly(vinyl alcohol) is actually produced by the hydrolysis of poly(vinyl acetate)



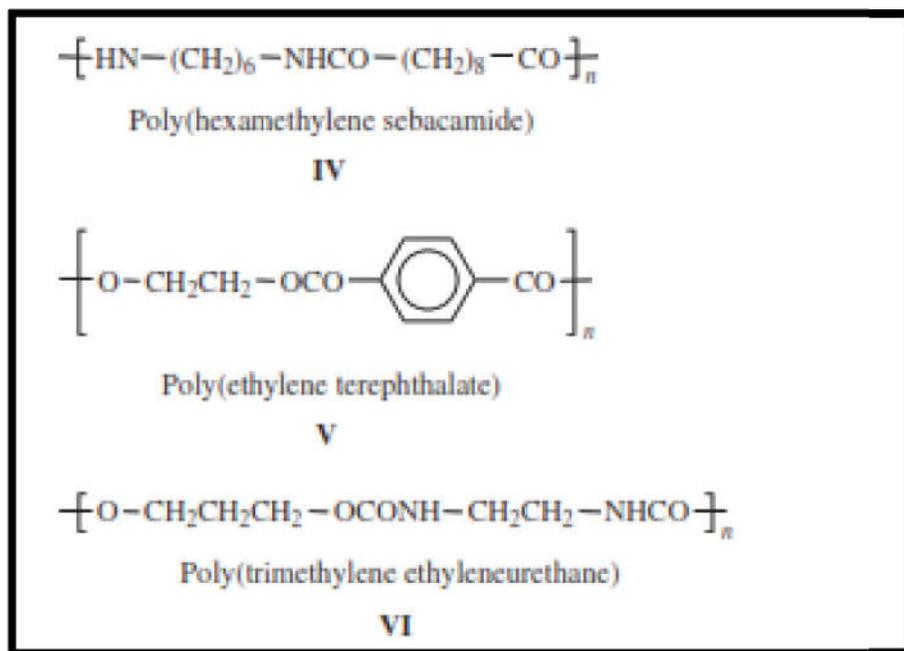
It is, however, named as a product of the hypothetical monomer vinyl alcohol (which in reality exists exclusively as the tautomer-acetaldehyde).

Condensation polymers synthesized from single reactants are named in a similar manner. Examples are the polyamides and polyesters produced from amino acids and hydroxy acids, respectively. Thus, the polymer from 6-aminocaproic acid is named poly(6-aminocaproic acid)



## Nomenclature Based on Structure (Non-IUPAC)

A number of the more common condensation polymers synthesized from two different monomers have been named by a semisystematic, structure-based nomenclature system other than the more recent IUPAC system. The name of the polymer is obtained by following the prefix poly without a space or hyphen with parentheses enclosing the name of the structural grouping attached to the parent compound. The parent compound is the particular member of the class of the polymer—the particular ester, amide, urethane, and so on. Thus the polymer from hexamethylene diamine and sebacic acid is considered as the substituted amide derivative of the compound sebacic acid,  $\text{HO}_2\text{C}(\text{CH}_2)_8\text{CO}_2\text{H}$  and is named poly(hexamethylene sebacamide). Poly(ethylene terephthalate) is the polymer from ethylene glycol and terephthalic acid, The polymer from trimethylene glycol and ethylene diisocyanate is poly(trimethylene ethyleneurethane)



## Trade Names and Brand Names

Trade (and/or brand) names and abbreviations are often used to describe material. They may be used to identify the product of a manufacturer, processor, or fabricator, and may be associated with a particular product or with a material or modified material, or a material grouping. Tradenames (or trade names) are used to describe specific groups of materials that are produced by a specific company or under license of that company. Bakelite is the tradename given for the phenol-formaldehyde condensation product developed by Baekeland. A sweater whose contents are described as containing Orlon contains polyacrylonitrile fibers that are “protected” under the Orlon trademark and produced or licensed to be produced by the holder of the Orlon trademark. Carina, Cobex, Dacovin, Darvic, Elvic, Geon, Koroseal, Marvinol, Mipolam, Opalon, Pliofex, Rucon, Solvic, Trulon, Velon, Vinoflex, Vygen, and Vyram are all tradenames for poly(vinyl chloride) manufactured by different companies. Some polymers are better known by their tradename than their generic name. For instance, polytetrafluoroethylene is better known as Teflon, the tradename held by Dupont.

Abbreviations, generally initials in capital letters, are also employed to describe polymers. Table P.3 contains a listing of some of the more widely used abbreviations and the polymer associated with the abbreviation.

<b>Abbreviation</b>	<b>Polymer</b>	<b>Abbreviation</b>	<b>Polymer</b>
ABS	Acrylonitrile-butadiene-styrene terpolymer	CA	Cellulose acetate
EP	Epoxy	HIPS	High-impact polystyrene
MF	Melamine-formaldehyde	PAA	Poly(acrylic acid)
PAN	Polyacrylonitrile	SBR	Butadiene-styrene copolymer
PBT	Poly(butylene terephthalate)	PC	Polycarbonate
PE	Polyethylene	PET, PETE	Poly(ethylene terephthalate)
PF	Phenyl-formaldehyde	PMMA	Poly(methyl methacrylate)
PP	Polypropylene	PPO	Poly(phenylene oxide)
PS	Polystyrene	PTFE	Polytetrafluoroethylene
PU	Polyurethane	PVA, PVAc	Poly(vinyl acetate)
PVA, PVAI	Poly(vinyl alcohol)	PVB	Poly(vinyl butyral)
PVC	Poly(vinyl chloride)	SAN	Styrene-acrylonitrile
UF	Urea-formaldehyde		

## Molecular Weight Averages

### 4.2.1 Arithmetic Mean

The distribution of molecular weights in a polymer sample is commonly expressed as the proportions of the sample with particular molecular weights. The various molecular weight averages

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used for polymers can be shown to be simply arithmetic means of molecular weight distributions.

Let us assume that unit volume of a polymer sample contains a total of  $A$  molecules consisting of  $a_1$  molecules with molecular weight  $M_1$ ,  $a_2$  molecules with molecular weight  $M_2$ , .....  $a_j$  molecules with molecular weight  $M_j$ . The arithmetic mean molecular weight  $\bar{M}$  is then the total measured quantity divided by the total number of molecules :

$$\begin{aligned}\bar{M} &= \frac{a_1M_1 + a_2M_2 + \cdots + a_jM_j}{a_1 + a_2 + \cdots + a_j} \\ &= \frac{a_1M_1 + a_2M_2 + \cdots + a_jM_j}{A} \\ &= \frac{a_1}{A}M_1 + \frac{a_2}{A}M_2 + \cdots + \frac{a_j}{A}M_j\end{aligned}\quad (4.1)$$

The ratio  $a_i/A$  represents the proportion of molecules with molecular weight  $M_i$ . Denoting this proportion by  $f_i$ , the arithmetic mean molecular weight will be given by

$$\bar{M} = f_1M_1 + f_2M_2 + \cdots + f_jM_j = \sum_i f_iM_i \quad (4.2)$$

Equation (4.2) gives the arithmetic mean of the distribution of molecular weights. Almost all molecular weight averages can be related to this equation.

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If we substitute the proportion of species  $f_i$ , which have molecular weight  $M_i$ , by the corresponding mole fraction  $n_i$  in Eq. (4.2), we obtain the definition of number-average molecular weight,  $\bar{M}_n$ , representing the number distribution :

$$\bar{M} = \sum_i n_iM_i = \bar{M}_n \quad (4.3)$$

The mole fraction  $n_i$  is also the differential number function, and a plot of  $n_i$  versus  $M_i$  represents a differential number distribution curve, as shown in Fig. 4.1(a). The distribution being normalized, the scale of the ordinate in this figure goes from 0 to 1, and the area under the curve is unity.

The cumulative number (or mole) fraction is defined as

$$\hat{n}(M_i) = \sum_i n_i \quad (4.4)$$

where  $n_i$  is the mole fraction of molecules with molecular weight  $M_i$  and  $\hat{n}(M_i)$  is the cumulative mole fraction with molecular weight  $\leq M_i$ . A plot of  $\hat{n}(M_i)$  against the corresponding  $M_i$  yields an integral number distribution curve, as in Fig. 4.1(b). The units of ordinate are mole fractions and extend from 0 to 1; the distribution is therefore said to be *normalized*.

While Eq. (4.3) gives a simple definition of the number average molecular weight  $\bar{M}_n$ , we can derive other equivalent definitions following a simple arithmetic. For this let us define the following terms, some of which have already been used above.

$n_i$  : mole fraction of species  $i$  (that is, molecules of same size with molecular weight  $M_i$ ) in a sample  
 $N_i$  : moles of species  $i$   
 $N$  : total of all  $N_i$ 's  
 $w_i$  : weight fraction of species  $i$   
 $W_i$  : weight of species  $i$   
 $W$  : sum of all  $W_i$ 's

It now follows that  $n_i = N_i / \sum N_i = N_i / N$  (4.4a)

$$W_i = N_i M_i \quad (4.4b)$$

$$w_i = W_i / \sum W_i = N_i M_i / \sum N_i M_i \quad (4.4c)$$

and

$$\bar{M}_n = \sum n_i M_i = \frac{\sum N_i M_i}{\sum N_i} \quad (4.5)$$

$$= \frac{\sum W_i}{\sum N_i} = \frac{W}{\sum (W_i / M_i)} = \frac{1}{\sum (w_i / M_i)} \quad (4.6)$$

The number-average degree of polymerization,  $\overline{DP}_n$ , is defined as

$$\begin{aligned} \overline{DP}_n &= \frac{\text{Number-average molecular weight}}{\text{Mer weight}} \\ &= \frac{\bar{M}_n}{M_0} = \frac{\sum n_i M_i}{M_0} = \sum n_i x_i \end{aligned} \quad (4.7)$$

which may also be written as  $\overline{DP}_n = \sum n_x x$  (4.7a)

where  $n_x$  is the number fraction of molecules containing  $x$  number of repeating units.

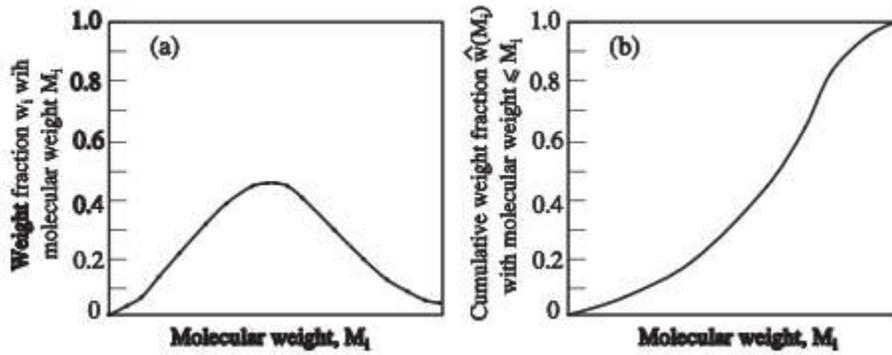
Alternatively, from Eq. (4.6)

$$\overline{DP}_n = \frac{\bar{M}_n}{M_0} = \frac{1}{M_0 \sum (w_i / M_i)} = \frac{1}{\sum (w_x / x)} \quad (4.8)$$

which may also be written as

$$\overline{DP}_n = 1 / \sum (w_x / x) \quad (4.8a)$$

where  $w_x$  is the weight fraction of molecules containing  $x$  number of repeating units.



### Weight-Average Molecular Weight

The situation for weight distribution corresponds to that for a number distribution described in the previous section. Thus recording the weight of each species in the sample, instead of the number of molecules of each size, would give a weight distribution. The differential weight fraction is simply the weight fraction  $w_i$ , while the integral (cumulative) weight fraction  $\hat{w}(M_i)$  is given by

$$\hat{w}(M_i) = \sum_i w_i \quad (4.9)$$

and is equal to the weight fraction of all species with molecular weight not greater than  $M_i$ .

A plot of  $w_i$  against  $M_i$  yields a normalized differential weight distribution curve, as in Fig. 4.2(a) and that of  $\hat{w}(M_i)$  against  $M_i$  yields a normalized integral distribution curve, as in Fig. 4.2(b). The scale of the ordinate in both these figures goes from 0 to 1. Substituting  $w_i$  for  $f_i$  in Eq. (4.2) produces the following expression for the arithmetic mean of the weight distribution:

$$\bar{M} = \sum_i w_i M_i = \bar{M}_w \quad (4.10)$$

$\bar{M}_w$  is the weight-average molecular weight. Combining Eqs. (4.10) and (4.4c) it can also be expressed as

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad (4.11)$$

The weight-average degree of polymerization,  $\overline{DP}_w$ , is defined as

$$\begin{aligned} \overline{DP}_w &= \frac{\text{Weight-average molecular weight}}{\text{Mer weight}} \\ &= \frac{\bar{M}_w}{M_0} = \frac{\sum w_i M_i}{M_0} = \sum w_i x_i \end{aligned} \quad (4.12)$$

which may also be written as

$$\overline{DP}_w = \sum w_x x \quad (4.12a)$$

where  $w_x$  is the weight fraction of molecules containing  $x$  number of repeating units.

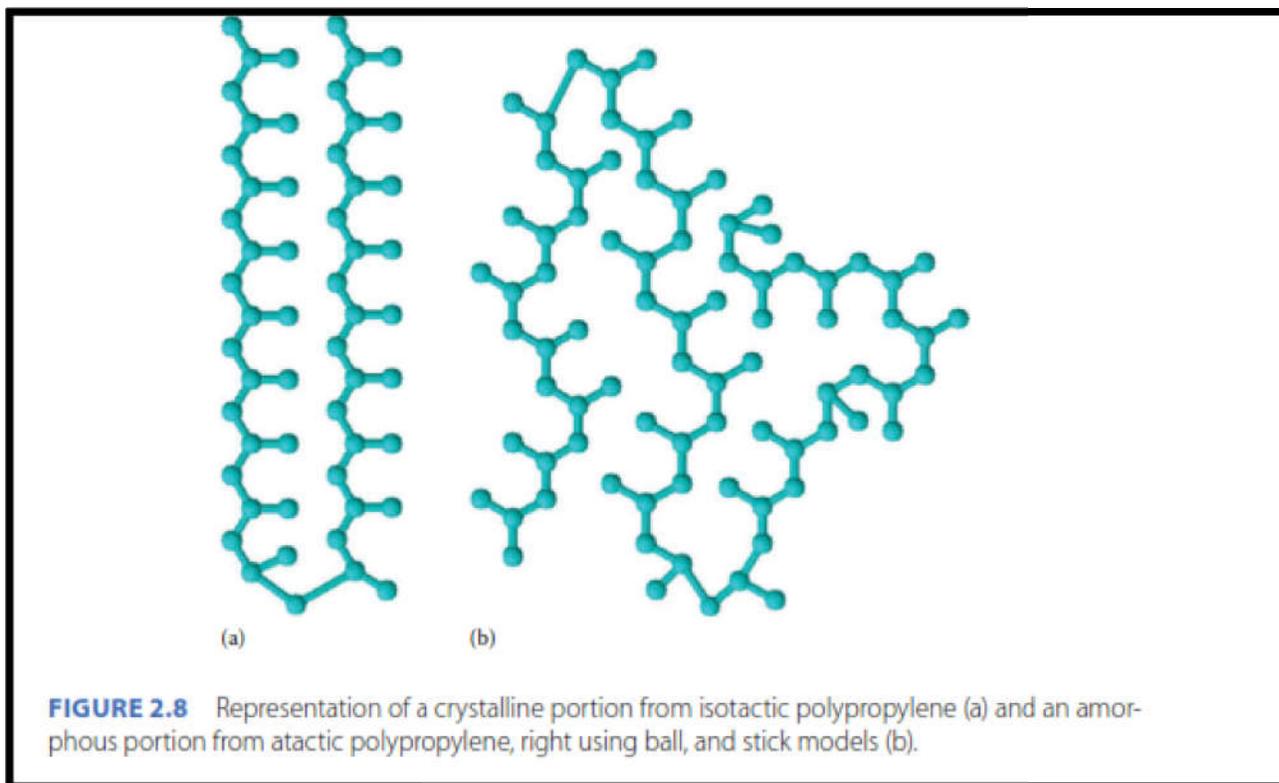
If all species in a polymer sample have the same molecular weight (that is, the polymer is *monodisperse*) then  $\overline{M}_n = \overline{M}_w = \overline{M}_z$  ( $\overline{M}_z$  denotes the  $z$ -average molecular weight). Such monodispersity is, however, not found in synthetic polymers and it is always true that  $\overline{M}_z > \overline{M}_w > \overline{M}_n$ . The ratio  $\overline{M}_w/\overline{M}_n$ , called the *polydispersity index* (PDI), is commonly used as a simple measure of the *polydispersity* of the polymer sample, though it is not a sound statistical measure of the distribution breadth. The breadth and shape of the distribution curve are characterized more appropriately with parameters derived from the moments of distribution.

## Molecular Interactions

Forces in nature are often divided into primary forces (typically greater than 200 kJ/mol) and secondary forces (typically less than 40 kJ/mol). “Primary bonding” forces can further be subdivided into ionic (characterized by a lack of directional bonding, occurs between atoms of large differences in electronegativity, normally not found in polymer backbones), metallic (the number of outer, valence electrons is too small to provide complete outer shells; often considered as charged atoms surrounded by a potentially fluid sea of electrons; lack of bonding direction), and covalent (including dative and coordinate) bonding (the major bonding in organic compounds and polymers, directional). The bonding length of primary bonds is generally about 0.1–0.22 nm. The carbon–carbon bond length is about 0.15–0.16 nm. Atoms in individual polymer chains are joined to one another by covalent bonds with bonding energies about 320–370 kJ/mol.

Polymer molecules are also attracted to one another through secondary forces. Secondary forces, often called “van der Waals forces” because they are the forces responsible for the van der Waals corrections to the ideal gas relationships, are of longer distance in interaction, in comparison to primary forces and of less energy. Secondary bonding distances are generally on the order of 0.25–0.5 nm. The force of these interactions is inversely proportional to some power of the distance, generally 2 or greater (i.e., force is proportional to  $1/(\text{distance})^r$ ). Thus, many physical properties are sensitive to the polymer conformation (arrangements related to rotation about single bonds) and configuration (arrangements related to the actual chemical bonding about a

given atom), since both affect the proximity one chain can have relative to another. Thus, amorphous PP is more flexible than crystalline (generally isotactic or syndiotactic) PP because the crystalline PP has the units closer to one another allowing the secondary bonding to be stronger (Figure 2.8).



These intermolecular forces are also responsible for the increase in boiling points within a homologous series such as the alkanes, for the higher-than-expected boiling points of polar molecules such as alkyl chlorides, and for the abnormally high boiling points of water, alcohols, amines, and amides. While the forces responsible for these increases in boiling points are all van der Waals forces, the forces can be further subdivided in accordance to their source and intensity.

Secondary forces are often divided into four groups. These are shown in Table 2.3. The strongest of these are the ion-dipole forces illustrated by the dissolving of common table salt, NaCl, in water. Water possesses a strong dipole and NaCl (actually when dissolved existing as Na<sup>+</sup> and Cl<sup>-</sup>) represents ionic compounds. It is often said that salt dissolves in water because the dipole

nature of water is sufficient to overcome the ionic forces holding the salt atoms together. In truth, when considering dissolving and mixing, the major driving factor is that mixing and dissolving allow an increase in disorder or increase in entropy. The next chapter deals in greater depth with the phenomenon of dissolving of polymers.

The next strongest group of secondary forces is the dipole–dipole force. Polar molecules such as ethyl chloride and PVC are attracted to each other by both the London forces (described in the following text), but also dipole–dipole interactions resulting from the electrostatic attraction of a chlorine atom in one molecule to a hydrogen atom in another molecule. These dipole–dipole forces are of the order of 8–25 kJ/mol, generally greater than the London forces and they are temperature dependent. Hard plastics, such as PVC, have dipole–dipole attractive forces present between the chains.

Probably, the most important of the dipole–dipole interactions is referred to as “hydrogen bonding.” Strongly polar molecules such as ethanol, poly(vinyl alcohol), cellulose, and proteins are attracted to each other by this special type of dipole–dipole force. Hydrogen bonding occurs when a hydrogen atom that is bonded to a highly electronegative element, such as nitrogen or oxygen, comes close to another highly electronegative element. These forces are on the order of 40 kJ/mol, and for something like hydrogen fluoride, they are almost as strong as primary bonding. Intermolecular hydrogen bonding is usually present in classical fibers such as cotton, wool, and silk and synthetic polymers such as nylon (Figure 2.9), polyacrylonitrile, polyesters, and polyurethanes. Intramolecular hydrogen bonds are responsible for the helices observed in starch and globular proteins.

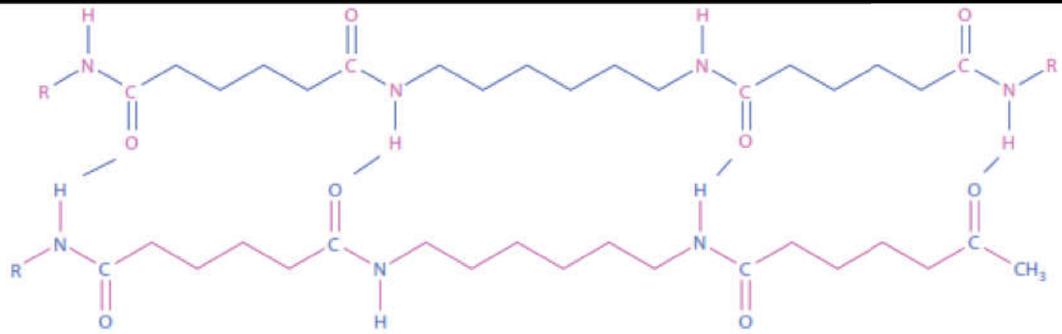
<b>Type</b>	<b>Relative Strength</b>
Ion-dipole	Strongest
Dipole–dipole	
Dipole-induced dipole	
Induced dipole-induced dipole	Weakest

The next strongest secondary force group is the “dipole-induced dipole.” This group is illustrated by the distortion of nonpolar oxygen molecules by polar water molecules allowing for the presence of sufficient oxygen to allow fish and plants to survive under water. But it is not sufficient to provide enough oxygen to support humans and mammals in water without them rising to the surface periodically to obtain enough oxygen to survive.

The weakest of the secondary forces is the “induced dipole-induced dipole” force. All molecules including nonpolar molecules, such as heptane and PE, are attracted to each other by these induced-dipole induced-dipole forces also called “London” or “dispersion forces.” The temporary or transient dipoles are due to instantaneous fluctuations in the electron cloud density. The energy range of these forces is fairly constant and about 8 kJ/mol. This force is independent of temperature and is the major force between chains in largely nonpolar polymers such as those in classical elastomers and soft plastics such as PE.

It is of interest to note that methane, ethane, and ethylene are all gases; hexane, octane, and nonane are all liquids (at room conditions), while low-molecular-weight PE is a waxy solid. This trend is primarily due to an increase in the mass per molecule and to an increase in the London forces per polymer chain. The London force interaction between methylene units is about 8 kJ/mol. Thus, for methane molecules the attractive force is about 8 kJ/mol, for octane it is about 64 kJ/mol, and for PE with 1000 ethylene (or 2000 methylenes), it is about 2,000 methylene units  $\times$  8 kJ/mol per methylene unit = 16,000 kJ/mol well sufficient to make PE a solid and to break backbone bonds before it boils. (Polymers do not boil because the energy necessary to make a chain volatile is greater than the primary backbone bond energy.)

In addition to the contribution of intermolecular forces, chain entanglement is also an important contributory factor to the physical properties of polymers. While paraffin wax and HDPE are homologs, the chain length of paraffin is too short to permit chain entanglement and hence it lacks the strength and many other physical characteristic properties of HDPE.



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

## Colligative Property Measurement

### Osmotic Pressure

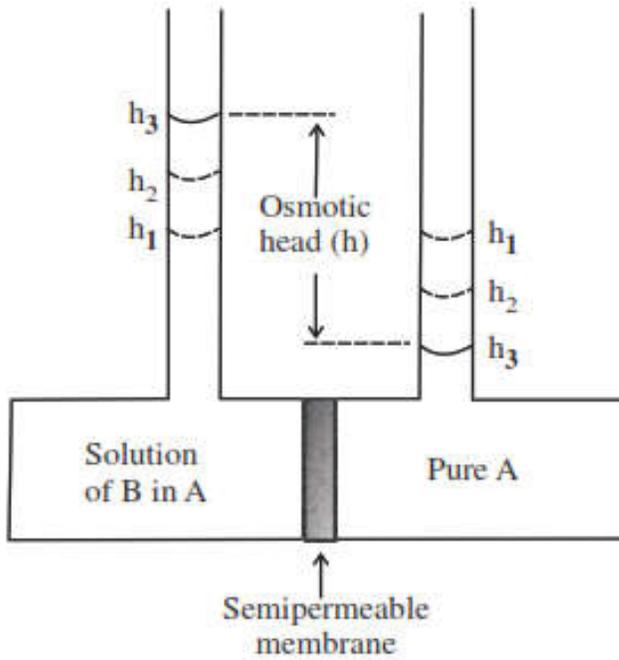
Osmotic pressure is the most important among all colligative properties for the determination of molecular weights of synthetic polymers (see Table 4.1 for comparison). To explain osmotic pressure, let us imagine a box (Fig. 4.3) divided into two chambers by a semipermeable membrane that allows the solvent to pass through it but not the solute. Suppose that the right chamber is filled with pure solvent A and the left chamber with a solution of B in A such that initially the heights of the liquids in the two capillary tubes are equal. The chambers are thus initially at equal pressures, that is,  $P_R = P_L$ , where the subscripts stand for right and left. Let us assume that thermal equilibrium is always maintained, that is,  $T_R = T_L = T$ .

The chemical potential of the solvent A on the right  $\mu_{A,R}$  is  $\mu_A^\circ$ , representing chemical potential of pure solvent A. If the solution on the left is dilute enough to be considered ideally dilute, then  $\mu_{A,L} = \mu_A^\circ + RT \ln x_A$ , which is less than  $\mu_{A,R} = \mu_A^\circ$ , since  $x_A$  being mole fraction of A in solution is less than 1. Since  $\mu_{A,R} > \mu_{A,L}$ , solvent A will flow through the membrane from right to left and the liquid height in the left tube will rise, thereby increasing the pressure in the left chamber. For an ideally dilute solution, the partial molar volume  $\bar{V}_A$  for the solvent is the same as for the pure

**Table 4.1** A Comparison of Colligative Properties of a 1% (w/v) Solution of Polystyrene of Molecular Weight 20,000 in Benzene

Property	Value
Vapor pressure lowering	0.004 mm Hg
Boiling point elevation	0.0013°C
Freezing point depression	0.0025°C
Osmotic pressure	15 cm solvent

Source: Billmeyer, Jr., 1984



**Figure 4.3** Schematic diagram showing the development of osmotic head as a function of time, where  $h_1$  represents the initial liquid levels,  $h_2$  the levels after some time, and  $h_3$  the levels when equilibrium is attained.

solvent, i.e.,  $\bar{V}_A^o = V_A^o$ , and since, in general,  $(\partial\mu_i/\partial P) = \bar{V}_i$ , one can write  $(\partial\mu_A/\partial P)_T = \bar{V}_A = V_A^o$ . Since  $V_A^o$  is positive, the increase in pressure will increase  $\mu_{A,L}$  until finally equilibrium is reached, that is,  $\mu_{A,L} = \mu_{A,R} = \mu_A^o$ . (Note that the membrane being impermeable to solute B, there is no equilibrium relation for  $\mu_B$ .)

Let the equilibrium pressures in the right and left chambers be  $P$  and  $P + \Pi$ , respectively. The difference in pressures, viz.,  $\Pi$ , is the *osmotic pressure*. This extra pressure makes the chemical potential of the solvent ( $\mu_A$ ) in solution equal to that ( $\mu_A^o$ ) in pure solvent. If the solution in the left chamber is dilute enough to be considered as ideally dilute, then at equilibrium  $\mu_{A,R} = \mu_{A,L}$ , or

$$\mu_A^o(P, T) = \mu_A^o(P + \Pi, T) + RT \ln x_A \quad (4.32)$$

where the right side of the equation follows from the general relation:  $\mu_i = \mu_i^o + RT \ln x_i$ . Since  $(\partial\mu_i/\partial T)_P = -\bar{S}_i$  and  $(\partial\mu_i/\partial P)_T = \bar{V}_i$ , it follows that  $d\mu_A^o = -S_A^o dT + V_A^o dP$ . Thus, at constant  $T$ ,  $d\mu_A^o = V_A^o dP$ . Integration from  $P$  to  $P + \Pi$  then gives

$$\mu_A^o(P + \Pi, T) - \mu_A^o(P, T) = \int_P^{P+\Pi} V_A^o dP \quad (4.33)$$

Substitution of Eq. (4.33) into Eq. (4.32) gives

$$RT \ln x_A = - \int_P^{P+\Pi} V_A^o dP \quad (4.34)$$

Considering that liquids are rather incompressible,  $V_A^o$  would hardly vary with pressure and we can take  $V_A^o$  as practically constant. The integral in Eq. (4.34) then becomes  $V_A^o \Pi$  and Eq. (4.34) thus

gives  $\Pi = -(RT/V_A^0) \ln x_A$ . With  $x_A = 1 - x_B$ , we have  $\ln x_A = -x_B - x_B^2/2 - \dots \approx -x_B$ , where, since  $x_B \ll 1$ , we can neglect  $x_B^2$  and higher powers. Therefore,

$$\Pi = (RT/V_A^0)x_B \quad (4.35)$$

Since the solution is quite dilute, we have  $x_B = (n_B)/(n_A + n_B) \approx n_B/n_A$  and therefore,

$$\Pi = \frac{RT}{V_A^0} \frac{n_B}{n_A} \quad (4.36)$$

where  $n_A$  and  $n_B$  are the number of moles of solvent and solute in the solution that is in equilibrium with pure solvent A across the membrane.

Since the solution is quite dilute, the solution volume  $V$  is approximately equal to that of the solvent  $n_A V_A^0$  and Eq. (4.36) becomes

$$\Pi V = n_B RT \quad (4.37)$$

$$\text{or } \Pi = C_B RT \quad (4.38)$$

where the concentration  $C_B$  in moles/volume equals  $n_B/V$ . Both Eq. (4.37), which has formal resemblance to the equation of state for an ideal gas,  $PV = nRT$ , where  $n$  is the number of moles of gas in volume  $V$ , and the equivalent Eq. (4.38) are called the *van't Hoff law*. It is valid in the limit of infinite dilution, where the solution behaves ideally. The osmotic pressure in a nonideally dilute two-component solution is, however, given by

$$\Pi = RT (M_B^{-1} c_B + A_2 c_B^2 + A_3 c_B^3 + \dots) \quad (4.39)$$

which has formal resemblance to the virial equation for gases. In Eq. (4.39),  $M_B$  is the solute molecular weight and  $c_B$  is the solute mass concentration defined as  $c_B = m_B/V$ , where  $m_B$  is the

mass of solute B in the solution of volume  $V$ . The quantities  $A_2, A_3, \dots$  are related to the solute-solvent interaction and are functions of temperature. In the limit of infinite dilution,  $c_B$  approaches zero, and Eq. (4.39) approximates to

$$\Pi = RT c_B / M_B = RT m_B / M_B V = RT n_B / V = C_B RT \quad (4.40)$$

which is the van't Hoff law [Eq. (4.38)].

Though the osmotic pressure, according to Eq. (4.40), is inversely proportional to solute molecular weight, the relatively large, measurable values of  $\Pi$  obtained even for dilute solutions (see Table 4.1) make osmotic pressure measurements valuable in determining molecular weights of substances with high molecular weights like polymers.

**Virial Equations** The osmotic data of a real solution are expressed, according to Eq. (4.39) and omitting the subscript for solute, as

$$\frac{\Pi}{c} = RT \left[ \frac{1}{M} + A_2 c + A_3 c^2 + \dots \right] \quad (4.41)$$

where  $A_2$  and  $A_3$  are called the second and third virial coefficients. Two alternative forms of Eq. (4.41) are

$$\frac{\Pi}{c} = \frac{RT}{M} \left[ 1 + \Gamma_2 c + \Gamma_3 c^2 + \dots \right] \quad (4.42)$$

and

$$\frac{\Pi}{c} = \frac{RT}{M} + Bc + Cc^2 + \dots \quad (4.43)$$

Obviously, the three forms of the virial equation are equivalent (Rudin, 1982), if

$$B = RTA_2 = (RT/M)\Gamma_2 \quad (4.44)$$

The virial coefficients are often reported in the literature without specifying the equation to which they apply, and this can usually be deduced by inspecting their units.

At low solution concentrations, the  $c^2$  terms in any of the above virial equations, Eqs. (4.41) to (4.43), will be very small, and the data of  $\Pi/c$  versus  $c$  will be expected to be linear with intercepts at  $c = 0$  yielding values of  $M^{-1}$  and slopes giving the second virial coefficient of the polymer solution.

The value of the third virial coefficient  $\Gamma_3$  in Eq. (4.42) is often assumed to be equal to  $(\Gamma_2/2)^2$ , so that Eq. (4.42) can be rewritten as

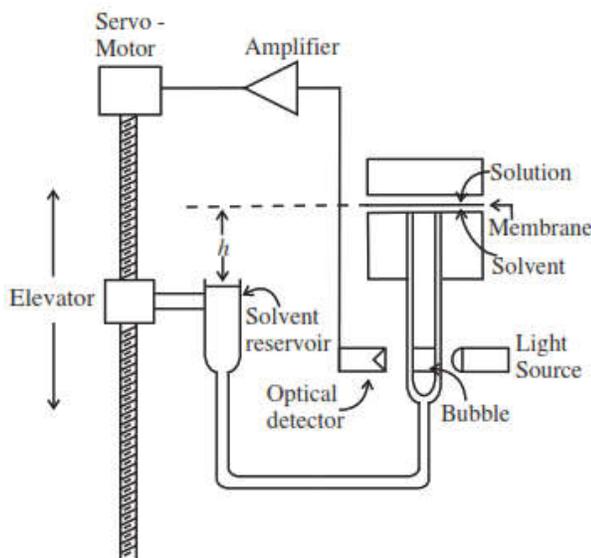
$$\left( \frac{\Pi}{c} \right)^{1/2} = \left( \frac{RT}{M} \right)^{1/2} \left( 1 + \frac{1}{2} \Gamma_2 c \right) \quad (4.45)$$

This form is sometimes convenient to use for extrapolation of  $\Pi/c$  data to zero concentration because, for solutions in good solvents, plots given by Eqs. (4.41)-(4.43) are not linear.

The nonideality of polymer solutions is incorporated in the virial coefficients. Predicting non-ideality of polymer solutions means, in reality, predictions of the second virial coefficient. Better solvents generally produce greater swelling of macromolecules and result in higher virial coefficients. Most polymers become more soluble in their solvents as the temperature is increased which is reflected in an increase of the virial coefficient. Conversely, the second virial coefficient reduces as the temperature is reduced and at a sufficiently low temperature it may actually be zero. This is the *Flory theta temperature*, which has been defined in Chapter 3 as that temperature at which a given polymer of infinitely high molecular weight would be insoluble at great dilution in a given solvent.

**Practical Aspects of Osmometry** In static osmometers, the heights of liquid in capillary tubes attached to the solvent and solution compartments (Fig. 4.3) are measured. At equilibrium, the hydrostatic pressure corresponding to the difference in liquid heights is the osmotic pressure. The main disadvantage of this static procedure is the length of time required for attainment of equilibrium.

It may be noted that the osmotic pressure is essentially the extra pressure that must be applied to the solution to maintain equilibrium when solution and pure solvent are separated by a semipermeable membrane. This extra pressure can be measured by attaching a counter pressure device to the solution tube (Fig. 4.3).



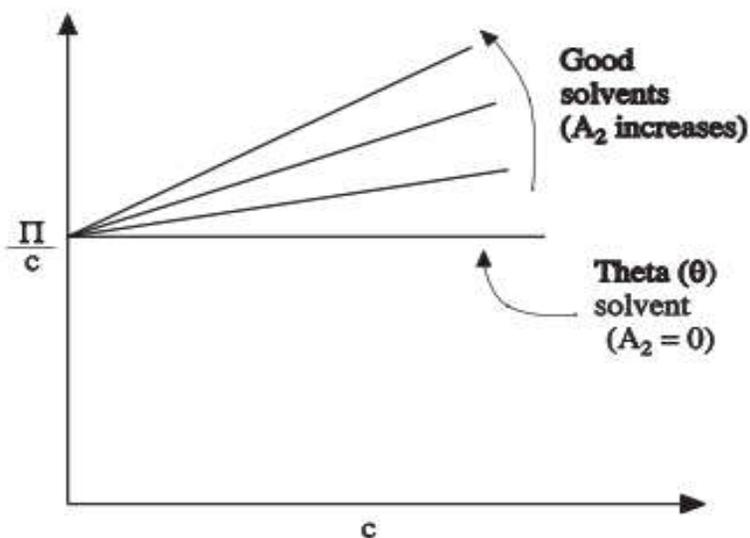
**Figure 4.4** Schematic diagram of essential components of a high-speed membrane osmometer. (Hewlett-Packard Corp., Avondale, Pa.)

This method of determining the osmotic pressure is conveniently referred to as the 'dynamic equilibrium' technique. It is especially useful when rapid determinations of osmotic pressure are required. Dynamic osmometers reach equilibrium pressures in 10 to 30 minutes, as compared to hours in the static method, and indicate osmotic pressure automatically. There are several types. Some models employ sensors to measure solvent flow through the membrane and adjust a counteracting pressure to maintain a zero net flow. In a commercially available high-speed membrane osmometer, schematically shown in Fig. 4.4, the movement of an air bubble inside the capillary immediately below the solvent cell is used to indicate this solvent flow. Such movement is immediately detected by a photocell, which in turn is coupled to a servomechanism that controls the flow.

The data obtained by osmotic pressure measurements are pressures (*osmotic heads*) in terms of heights ( $h$ ) of solvent columns at different concentrations ( $c$ ) of the polymer solution. In applying the data,  $h/c$  is plotted against  $c$  and extrapolated to  $c = 0$ , yielding the value of  $(h/c)_c$ . The column height  $h$  is then converted to osmotic pressure  $\Pi$  by  $\Pi = h\rho g$ , where  $\rho$  is the density of the solvent and  $g$  is the gravitational acceleration constant, and  $\bar{M}_n$  is calculated from Eqs. (4.41)-(4.43), which in the limit of  $c \rightarrow 0$  reduce to

$$\left(\frac{\Pi}{c}\right)_c = \frac{RT}{\bar{M}_n} \quad (4.46)$$

The second virial coefficient can be obtained from the slope of the straight line portion of the  $(\Pi/c)$  versus  $c$  plot by removing the  $c^2$  terms in Eqs. (4.41)-(4.43). When plotted according to



**Figure 4.5** Schematic illustration of the effect of solvating power of solvent on reduced osmotic pressure ( $\Pi/c$ ) versus concentration ( $c$ ) plots for the same polymer. (After Rudin, 1982.)

Eq. (4.41), the osmotic pressures of solutions of the same polymer in different solvents should yield plots with the same intercept (at  $c = 0$ ) but with different slopes (see Fig. 4.5), since the second virial coefficient, which reflects polymer-solvent interactions, will be different in solvents of differing solvent power. For example, the second virial coefficient can be related to the Flory-Huggins interaction parameter  $\chi$  (see p. 110) by

$$A_2 = \left(\frac{1}{2} - \chi\right)v_2^2/V_1^0 \quad (4.47)$$

where  $v_2$  is the specific volume of the polymer,  $V_1^0$  is the molar volume of the solvent, and  $\chi$  is an interaction energy per mol of the solvent divided by  $RT$ . For a theta solvent,  $\chi = 0.5$  and  $A_2 = 0$ . Better solvents have lower  $\chi$  values and higher second virial coefficients. Equation (4.47) can be used to determine  $\chi$  from osmotic measurements.

## Light-Scattering Photometry

Ever watch a dog or young child chase moonbeams? The illumination of dust particles is an illustration of light scattering, not of reflection. Reflection is the deviation of incident light through one particular angle such that the angle of incidence is equal to the angle of reflection. Scattering is the radiation of light in all direction. Thus, in observing the moonbeam, the dust particle directs a beam toward you regardless of your angle in relation to the scattering particle.

The energy scattered per second (scattered flux) is related to the size and shape of the scattering particle and to the scattering angle.

Scattering of light is all about us—the fact that the sky above us appears blue, the clouds white, and the sunset is shades of reds and oranges is a consequence of preferential scattering of light from air molecules, water droplets, and dust particles. This scattered light carries messages about the scattering objects.

The measurement of light scattering is the most widely used technique for the determination of  $M_w$ . This technique is based on the optical heterogeneity of polymer solutions and was developed by Nobel Laureate Peter Debye in 1944.

Today, modern instruments utilize lasers as the radiation source because they provide a monochromatic, intense, and well-defined light source. Depending upon the size of the scattering object, the intensity of light can be essentially the same or vary greatly with respect to the direction of the oncoming radiation. For small particles the light is scattered equally independent of the angle the observer is to the incoming light. For larger particles, the intensity of scattered light varies with respect to the angle of the observer to the incoming light. For small molecules at low concentrations, this scattering is described in terms of the Rayleigh ratio.

In 1871, Rayleigh showed that induced oscillatory dipoles were developed when light passed through gases and that the amount (intensity) of scattered light was inversely proportional to the fourth power of the wavelength of light. This investigation was extended to liquids by Einstein and Smoluchowski in 1908. These oscillations reradiate the light energy—producing turbidity, that is, the Tyndall effect. Other sources of energy, such as x-rays or laser beams, may be used in place of visible light sources.

For light-scattering measurements, the total amount of the scattered light is deduced from the decrease in intensity of the incident beam,  $I_0$ , as it passes through a polymer sample. This can be described in terms of Beer's law for the absorption of light as follows:

(3.11)

$$\frac{I}{I_0} = e^{-\tau}$$

where  $\tau$  is the measure of the decrease of the incident beam intensity per unit length ( $l$ ) of a given solution and is called the turbidity of the solution.

The intensity of scattered light or turbidity ( $\tau$ ) is proportional to the square of the difference between the index of refraction ( $n$ ) of the polymer solution and of the solvent ( $n_0$ ), to the molecular weight of the polymer ( $M_w$ ), and to the inverse fourth power of the wavelength of light used ( $\lambda$ ). Thus,

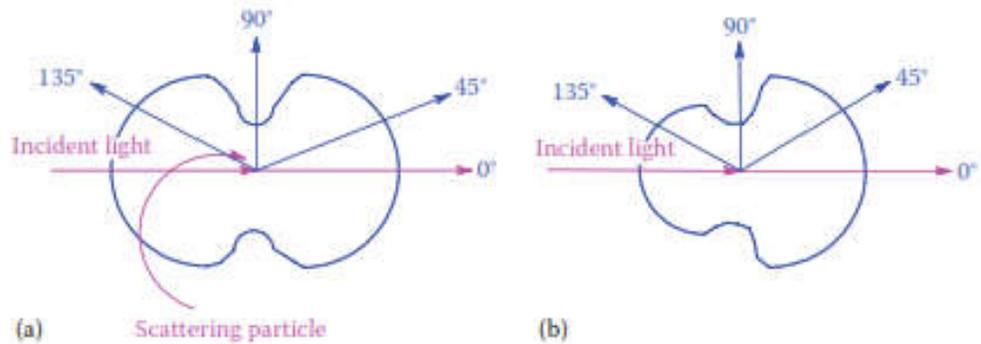
(3.12)

$$\frac{Hc}{\tau} = \frac{1}{M_w P_0} (1 + 2Bc + Cc^2 + \dots)$$

where the expression for the constant  $H$  is as follows:

(3.13)

$$H = \left[ \frac{32\pi^2}{3} \right] \left[ \frac{n_0^2 (dn/dc)^2}{\lambda^4 N} \right] \quad \text{and} \quad \tau = K' n^2 \left( \frac{i_{90}}{i_0} \right)$$



**FIGURE 3.10** Light-scattering envelopes. Distance for the scattering particle to the boundaries of the envelope represents an equal magnitude of scattered light as a function of angle for a small scattering particle (a) and a large scattering particle (b).

where

$n_0$  is the index of refraction of the solvent

$n$  is the index of refraction of the solution

$c$  is the polymer concentration; the virial constants  $B$ ,  $C$ , etc., are related to the interaction of the solvent

$P_0$  is the particle scattering factor

$K'$  is a constant

$N$  is Avogadro's number

The expression  $dn/dc$  is the specific refractive increment and is determined by taking the slope of the refractive index readings as a function of polymer concentration

In the determination of  $\overline{M}_w$ , one measures the intensity of scattered light at different concentrations and at different angles ( $\theta$ ). The incident light sends out a scattering envelope that has four equal quadrants (Figure 3.10a) for small particles. The ratio of scattering at  $45^\circ$  compared with that for  $135^\circ$  is called the *dissymmetry factor* or *dissymmetry ratio*  $Z$ . The reduced dissymmetry factor  $Z_0$  is the intercept of the plot of  $Z$  as a function of concentration extrapolated to zero concentration.

For polymer solutions containing polymers of moderate to low molecular weight,  $P_0$  is 1, and Equation 3.14 reduces to 3.18, an equation for a straight line ( $y = b + mx$ ):

$$(3.14) \quad \frac{Hc}{\tau} = \frac{1}{M_w} (1 + 2Bc + Cc^2 + \dots)$$

Several expressions are generally used in describing the relationship between values measured by light-scattering photometry and molecular weight. One is given in Equation 3.12 and others, such as Equation 3.15, are analogous except that constants have been rearranged:

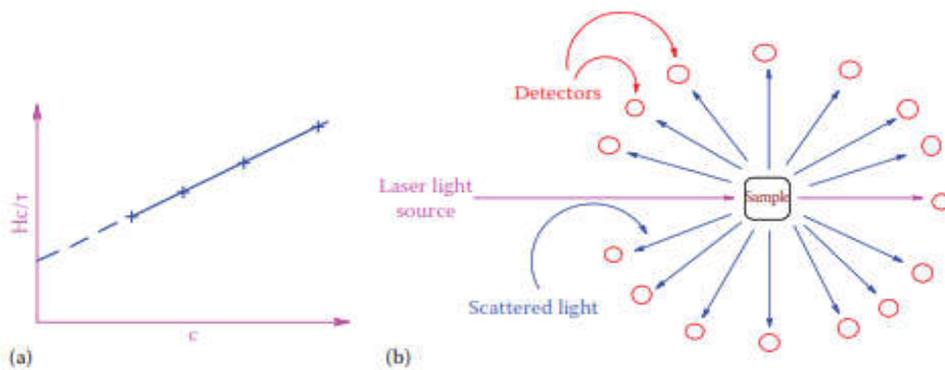
$$(3.15) \quad \frac{Kc}{R} = \frac{1}{\bar{M}_w} (1 + 2Bc + Cc^2 + \dots)$$

where  $K = [2\pi^2 n^2 / N\lambda^4] [dn/dc]^2$ .

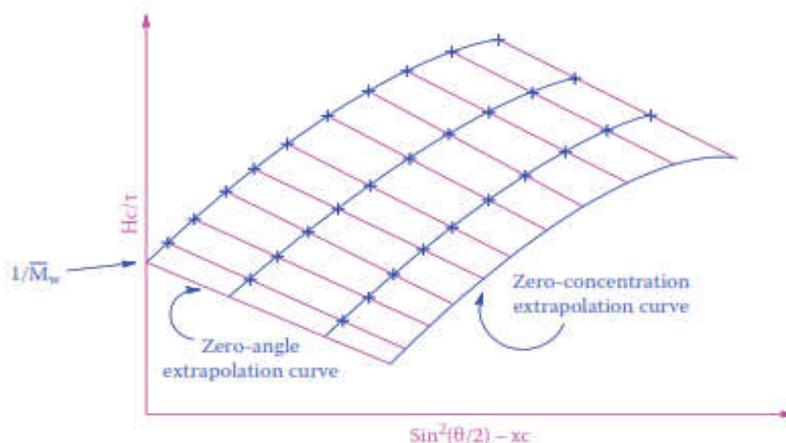
At low polymer concentrations, Equation 3.12 reduces to Equation 3.16, which is an equation of a straight line ( $y = b + mx$ ):

$$(3.16) \quad \frac{Hc}{\tau} = \frac{1}{\bar{M}_w} + \frac{2Bc}{\bar{M}_w}$$

When the ratio of the concentration  $c$  to the turbidity  $\tau$  (tau; related to the intensity of scattering at  $0^\circ$  and  $90^\circ$ ) multiplied by the constant  $H$  is plotted against concentration (Figure 3.11), the intercept of the extrapolated line is the reciprocal of  $\bar{M}_w$  and the slope contains the viral constant  $B$ .  $Z_0$  is directly related to the particle scattering factor, and both are related to both the size and shape of the scattering particle. As the size of the scattering particle, the individual polymer chain, approaches about one-twentieth the wavelength of the incident light, scattering interference



**FIGURE 3.11** (a) Typical simple plot used to determine  $1/\overline{M}_w$  from scattering data. (b) Multiple detector arrangement showing a sample surrounded by an array of detectors.



**FIGURE 3.12** Zimm plot for a polymer scaled with a negative concentration coefficient ( $x$ ) to improve data aesthetics and accessibility.

occurs giving a scattering envelope that is no longer symmetrical (Figure 3.10b). Here, the scattering dependency on molecular weight reverts back to the relationship given in Equation 3.12.

The molecular weight for dilute polymer solutions is typically found using one of two techniques. The first technique is called the dissymmetrical method or approach because it utilizes the determination of  $Z_0$  as a function of the particle scattering factor as a function of polymer shape.  $\overline{M}_w$  is determined from the intercept through substitution of the determined particle scattering factor. The weakness in this approach is the necessity of having to assume a shape for the polymer in a particular solution. For small  $Z_0$  values, choosing an incorrect polymer shape results in a small error, but for larger  $Z_0$  values, the error becomes significant.

The second approach uses multiple detectors (Figure 3.11) allowing a double extrapolation to zero concentration and zero angle with the data forming what is called a *Zimm plot* (Figure 3.12). The extrapolation to zero angle corrects for finite particle size effects. The radius of gyration, related to polymer shape and size, can also be determined from this plot. The second extrapolation to zero concentration corrects for concentration factors. The intercepts of both plots are equal to  $1/\overline{M}_w$ .

The Zimm plot approach does not require knowing or having to assume a particular shape for the polymer in solution.

Related to the Zimm plot is the Debye plot. In the Zimm approach, different concentrations of the polymer solution are used. In the Debye approach, one low concentration sample is used with  $1/\overline{M}_w$  plotted against  $\sin^2(\theta/2)$ , essentially one-half of the Zimm plot.

## **GEL PERMEATION CHROMATOGRAPHY**

Gel permeation chromatography (GPC) is a form of chromatography that is based on separation by molecular size rather than chemical properties. GPC or size exclusion chromatography (SEC) is widely used for molecular weight and MWD determination. In itself, SEC does not give an absolute molecular weight and must be calibrated against polymer samples whose molecular weight has been determined by a technique that does give an absolute molecular weight.

Gel permeation chromatography (GPC) also known as SEC is an HPLC technique whereby the polymer chains are separated according to differences in hydrodynamic volume. This separation is made possible by the use of special packing material in the column. The packing material is usually polymeric porous spheres often composed of polystyrene cross-linked by addition of varying amounts of divinylbenzene. Retention in the column is mainly governed by the partitioning (or exchanging) of polymer chains between the mobile (or eluent) phase flowing through the column and the stagnate liquid phase that is present in the interior of the packing material.

Through control of the amount of cross-linking, nature of the packing material, and specific processing procedures, spheres of widely varying porosity are available. The motion in and out of the stationary phase is dependent on a number of factors including Brownian motion, chain size, and conformation. The latter two are related to the polymer chain's hydrodynamic volume—the real, excluded volume occupied by the polymer chain. Since smaller chains preferentially permeate the gel particles, the largest chains are eluted first. As noted earlier, the fractions are separated on the basis of size.

The resulting chromatogram is then a molecular size distribution. The relationship between molecular size and molecular weight is dependent on the conformation of the polymer in solution. As long as the polymer conformation remains constant, which is generally the case, molecular size increases with increase in molecular weight. The precise relationship between molecular size and molecular weight is conformation dependent. For random coils, molecular size as measured by the polymer's radius of gyration,  $R$ , and molecular weight,  $M$ ,  $R$  is proportional to  $M^{1/2}$ , where "b" is a constant dependent on the solvent, polymer concentration,

and temperature. Such values are known and appear in the literature for many polymers allowing the ready conversion of molecular size data collected by SEC into molecular weight and MWD.

There is a wide variety of instrumentation ranging from simple manually operated devices to completely automated systems. Briefly, the polymer-containing solution and solvent alone are introduced into the system and pumped through separate columns at a specific rate. The differences in refractive index between the solvent itself and polymer solution are determined using a differential refractometer. This allows calculation of the amount of polymer present as the solution passes out of the column.

The unautomated procedure was first used to separate protein oligomers using Sephadex gels. Today, there are a wide variety of specialized and general gels used as column packing. The efficiency of these packed columns can be determined by calculating the height in feet equivalent to a theoretical plate, which is the reciprocal of the plate count per feet (P). P is directly proportional to the square of the elution volume ( $V_c$ ) and inversely proportional to the height of the column in feet and the square of the baseline (D) as follows:

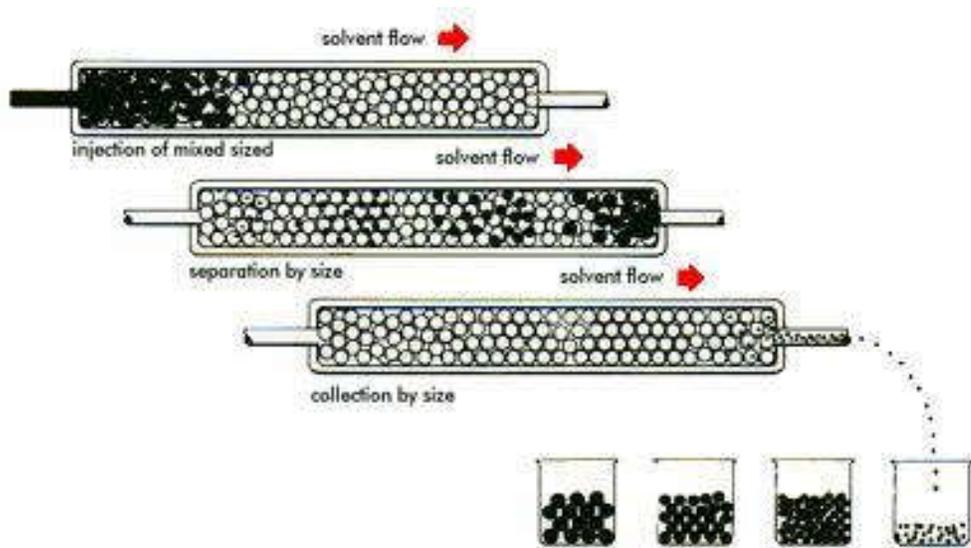
$$(3.7) \quad P = \left( \frac{16}{f} \right) \left[ \left( \frac{V_c}{D} \right)^2 \right]$$

Conversion of retention volume for a given column to molecular weight can be accomplished using several approaches including peak position, universal calibration, broad standard, and actual molecular weight determination by coupling the SEC to an instrument that gives absolute molecular weight.

In the peak position approach, well-characterized narrow fraction samples of known molecular weight are used to calibrate the column and retention times determined. A plot of  $\log M$  versus retention is made and used for the determination of samples of unknown molecular weight. Unless properly treated, such molecular weights are subject to error. The best results are obtained when the structures of the samples used in the calibration and those of the test polymers are the same.

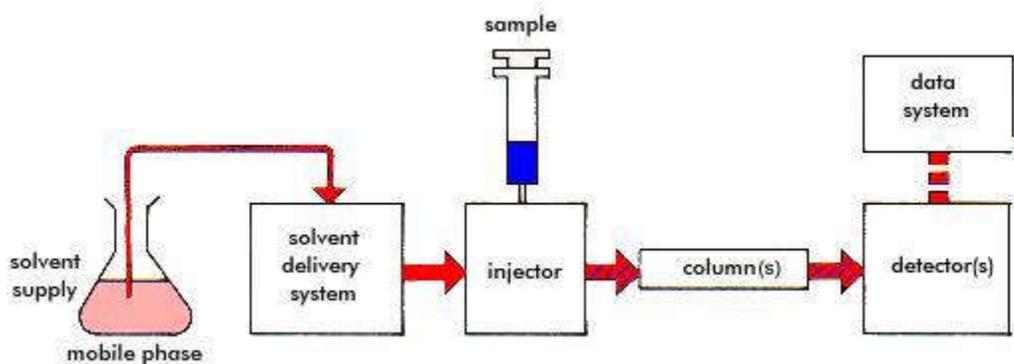
The universal calibration approach is based on the product of the limiting viscosity number (LVN) and molecular weight being proportional to the hydrodynamic volume. Benoit showed that for different polymers, elution volume plotted against the log LVN times molecular weight gave a common line. In one approach molecular weight is determined by constructing a universal calibration line through plotting the product of log LVN for polymer fractions with narrow MWDs as a function of the retention of these standard polymer samples for a given column. Molecular weight is then found from retention time of the polymer sample using the calibration line.

Probably the most accurate approach is to directly connect, couple, the SEC to a device, such as a light-scattering photometer, that directly measures the molecular weight for each elution fraction. Here, both molecular weight and MWD are accurately determined.



Molecules of various sizes elute from the column at different rates. The column retains low molecular weight material (small black dots) longer than the high molecular weight material (large black dots). The time it takes for a specific fraction to elute is called its "retention time"

## Schematic of a basic Gel Permeation Chromatograph



This diagram illustrates how the sample is injected into the mobile phase and the path the sample takes to the detector.

### **Components of GPC:**

#### **A. Pump**

Pumps the polymer in solution through the system.

Always be sure you have enough mobile phase for your run. Do not let the column run dry.

#### **B. Injector**

**Introduces the polymer solution into the mobile phase.**

250 $\mu$ l sample loop. Inject 100 to 200  $\mu$ l.

#### **C. Column Set**

**Efficiently separates sample components from one another.**

High efficiency columns give maximum separating capability and rapid analyses. Every column must provide reproducible information over extended periods for both analytical and fraction collecting purposes. We have 3 Styragel HR columns from Waters.

#### **D. Detector**

**Monitors the separation and responds to components as they elute from the column.**

In addition, the detectors must be sensitive and have a wide linear range in order to respond to both trace amounts and large quantities of material if necessary. Since all compounds refract light, the differential refractometer (RI) is referred to as a "universal" detector. As a result it is the most widely used detector to monitor molecular weight distribution. The refractive index of polymers is constant above approximately 1000 MW. Therefore, the detector response is directly proportional to concentration. We have a Waters 410 RI detector. Besides information about molecular weight averages and distribution obtained with RI, the use of UV absorbance detectors may provide information about composition. We have a Waters 2996 PDI detector.

#### **E. Automatic data processing equipment**

Automatically calculates, records, and reports numerical values for  $M_z$ ,  $M_w$ ,  $M_v$ ,  $M_n$ , and MWD.

### **Solubility**

Solubility of biologically important macromolecules as some proteins and nucleic acids is not straightforward since they often behave micelle or colloid-like and are said to be soluble in water. These essential molecules have a different hydrophobic inner structure and hydrophilic outer structure designed allowing them to function within an aqueous environment yet maintain the essential inner structure retaining the critical geometries necessary to perform various activities.

Polymer mobility is important in a number of aspects. Most processing procedures require a polymer to be fluid enough, either through application of heat and/or pressure or with the polymer present in a solution, to be processed. Here, we will focus on the general topic of polymer solubility and factors that influence polymer solubility.

Polymer mobility is an important aspect helping determine a polymer's physical, chemical, and biological behavior. Lack of mobility, either because of interactions that are too swift to allow the segments within the polymer chain some movement or because there is not sufficient energy (such as a high enough temperature) available to create mobility or because of a lack of available free volume, results in a brittle material. Many processing techniques require the polymer to have some mobility. This mobility can be achieved through application of heat and/or pressure and through dissolving the polymer. Because of its size, the usual driving force of entropy increase for the mixing and dissolving of materials is smaller for polymers in comparison to small molecules. Traditional molecular weight determinations require that the polymer be dissolved.

The physical properties of polymers, including solubility, are related to the strength of covalent bonds, the stiffness of the segments in the polymer backbone, the amount of crystallinity/amorphous, and the intermolecular forces between the polymer chains. The strength of the intermolecular forces is equal to the Cohesive Energy Density (CED), which is the molar energy of vaporization per unit volume. Since intermolecular attractions of solvent and solute must be overcome when a solute (here the polymer) dissolves, CED values may be used to predict solubility.

When a polymer dissolves, the first step is often a slow swelling process called solvation in which the polymer molecules swell by a factor  $\nu$ , which is related to CED. Linear and branched polymers dissolve in a second step, but network polymers remain in a swollen condition.

In order for a material to be dissolved, it is essential that the free energy difference which is the driving force in the solution process, decrease to below zero, that is, be negative.  $H$  and  $S$  are equal to the change in enthalpy and change in entropy, and for constant temperature, the relationship is the classical Gibbs equation:

$$G = H - TS$$

“Like-likes-like best of all” is a description that is useful at appropriate times in science. It is true of solubility. Thus, water-likes-water best of all and is infinitely soluble in itself. Hexane-likes-hexane best of all and is infinitely soluble in itself. Hexane and water are not soluble in one another because hexane is nonpolar and water is polar; thus, they are not like one another. In

solubility, and in fact all mixing, the H term is always unfavorable when mixing or solubility occurs. (Shortly, we will deal with attempts such as the CED and solubility parameter to minimize the unfavorable aspect of the H term.) Thus, it is the S term that allows mixing and solubility to occur. As seen in Figure 3.3, the amount of randomness or disorder gain is great when pure materials such as water and ethanol are changed from the ordered pure materials to the disordered mixture.

By comparison, the increase in randomness, S, is much smaller if one of the materials is a polymer since the possible arrangements of the polymer chains is much more limited because the polymer units are attached to one another and not free to simply move about on their own. Figure 3.4 illustrates this with water and poly(ethylene glycol) (PEG). We notice several aspects. First, as noted earlier, the number of arrangements of the PEG units is limited. Second, as in the case of an onion, each layer of PEG chains must be peeled back allowing water molecules to approach inner layers before entire solubility occurs and causes swelling. This results in polymer solubility often requiring a longer period of time, sometimes hours to weeks to months, in comparison to the solubility of smaller molecules where solubility can occur in seconds.

Polymer solubility, in comparison to small molecules, is:

- a. More limited with respect to the number of solvents as a result of the lower increase in randomness that must overcome the unfavorable enthalpy term
- b. More limited with respect to the extent of solubility
- c. Takes a longer time to occur
- d. The theta temperature is the lowest temperature at which a polymer of infinite molecular weight is completely miscible with a specific solvent. The polymer coil expands above the theta temperature and contracts at lower temperatures.

## **Rheology**

In the melt state thermoplastics show varying resistance (viscosity) to applied flow stress.

Viscosity (resistance to flow):

1. decreases with increasing temperature
2. increases with increasing pressure

3. decreases with increasing shear strain rate (shear thinning, pseudoplastic)
4. increases with increasing molecular size (MW)
5. decreases with increasing lubricant content
6. increases with increasing filler content

Polymer dispersions (latex, plastisols) can exhibit both shear thinning (pseudoplasticity) and shear thickening (dilatancy). Because of their high viscosities, thermoplastic melts rarely show turbulent flow. In most situations it can be assumed that flow is laminar.

In an isothermal channel, such as an extrusion die where the wall is at the same temperature as the melt, the flow front will be parabolic, with the highest velocity at the centre of the channel and reducing to zero at the wall. In injection moulding, where a hot melt flows into cooler channels, a “frozen” skin layer is established at the wall with the melt flowing inside the skin in an unfolding melt front (“fountain flow”).

# Unit III. Characterization and Processing of Polymers

## Characterization

### Spectral characterization of polymers

This section of the thesis includes the IR and NMR spectral characterization of the monomers, epoxy resins, bisbenzoxazines and polySchiff bases.

#### **IR spectral characterization**

IR spectroscopy is an excellent technique for the qualitative analysis because except for optical isomers, the spectrum of compound is unique. Information about the structure of a molecule could frequently be obtained from its absorption spectrum. An infrared spectrum is obtained by passing infrared radiation through a sample. A detector generates a plot of % transmission of radiation versus the wave number or wavelength of the radiation transmitted. At 100% transmission, all the energy of radiation passes through the molecule. At lower values of % transmission, some of the energy is being absorbed by the compound. Each spike in the infrared (IR) spectrum represents absorption of energy. These spikes are called absorption bands. Electromagnetic radiation with wave numbers from 4000 to 400  $\text{cm}^{-1}$  has just the right energy to correspond to stretching and bending vibrations in molecules. Electromagnetic radiation with this energy is known as infrared radiation because it is just below the “red region” of visible light. (Infra is Latin word meaning “below”).

The intensity of an absorption band depends on the size of dipole moment change associated with the vibration. In other words, depends on polarity of the vibrating bond. Intensity of the absorption band also depends on number of bonds responsible for the absorption. The concentration of the sample used to obtain an IR spectrum also affects the intensity of absorption bands. Concentrated samples have greater wave numbers and therefore more intense absorption bands.

IR spectral analysis of uncured and cured epoxy resins

IR spectra of epoxy resins (ESB4HCy, ESB4HM and ESB4HE) are presented in Figs. 3.4 to 3.6 and IR absorption peaks in Table 3.7. Observed

characteristic absorption peaks are 3423-3386 (OH str.), 1678-1654 (N=CH str.), 1254-1248 (C-O-C str.), 1384-1308 (O-H def.) and 1166-1109 (C-OH def.) besides alicyclic and aromatic groups, confirming formation of epoxy resins.

IR spectra of epoxy resins cured using phthalic anhydride (ECyP-5, ECyP-10, ECyP-15, EMP-5, EMP-10, EMP-15, EEP-5, EEP-10 and EEP-15) are presented in Figs. 3.7 to 3.15 and absorption peaks in Tables 3.8 to 3.10. Observed characteristic IR absorption peaks for ECyP-5 to ECyP-15 are 3425-3422 (O-H str.), 1717-1715 (C=O str.), 1246-1245 (C-O-C str.), 1320-1319 (O-H def.) and 1096-1080 (C-OH def.) For EMP-5 to EMP-15: 3448-3422 (O-H str.), 1711-1706 (C=O str.), 1662-1661 (N=CH str.), 1269-1234 (CO-C str.), 1317-1269 (O-H def.) and 1118-1105 (C-OH def.); and for EEP-5 to EEP-15: 3408-3360 (O-H str.), 1712-1711 (C=O str.), 1239-1236 (C-O-C str.) 1308-1307 (O-H def.) and 1102-1036 (C-OH def.)

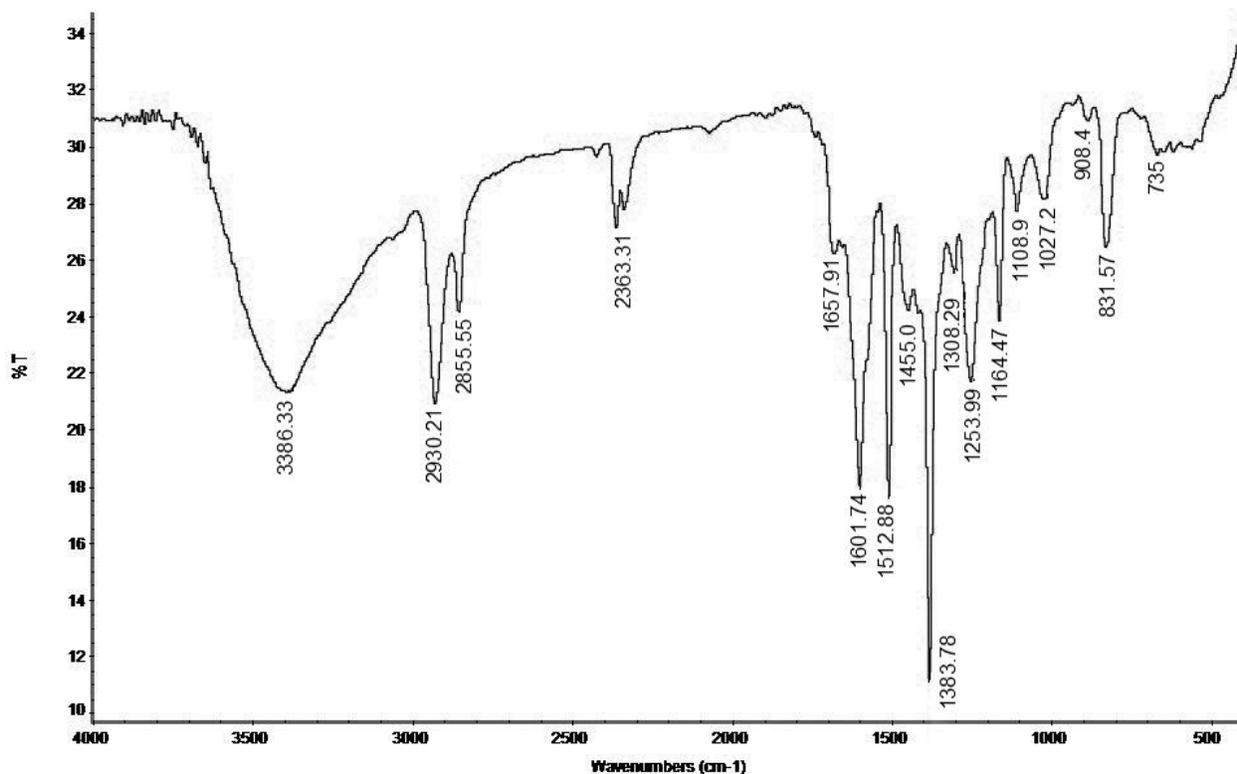


Figure 3.4 ; IR (KBr) spectrum of epoxy resin (ESB4HCy)

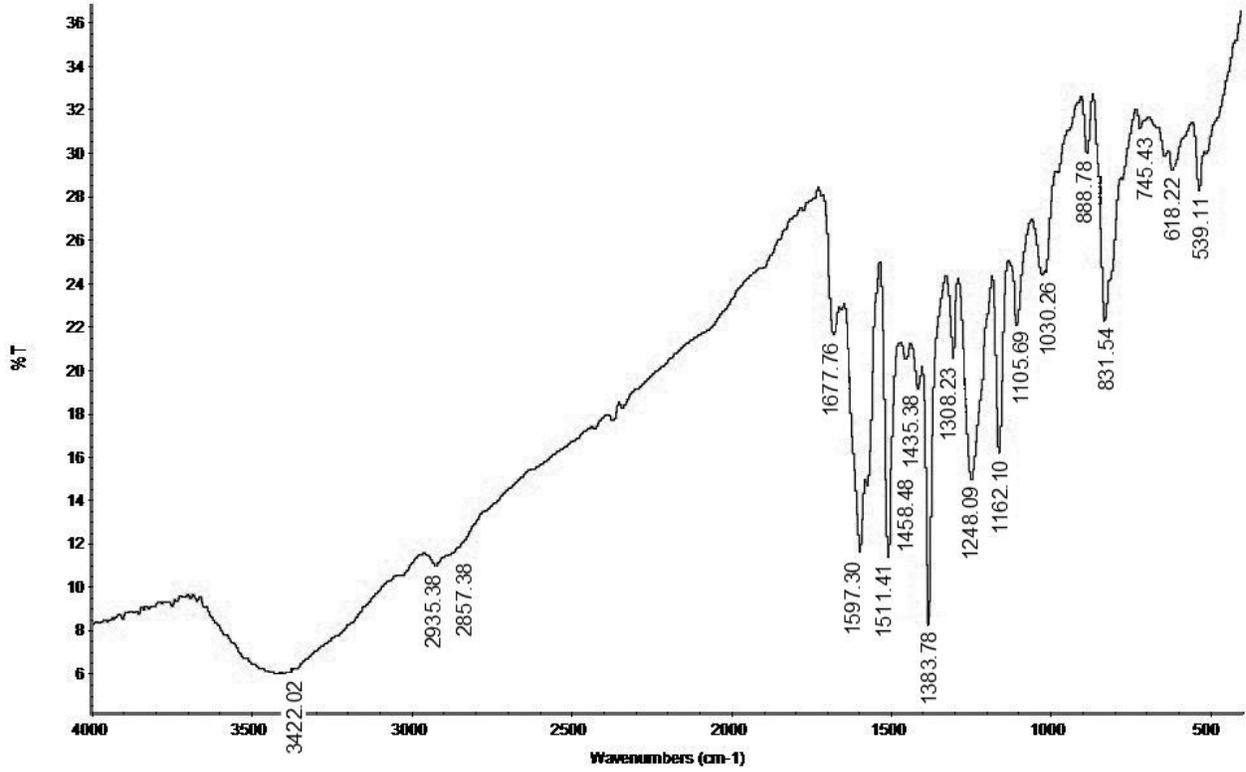


Fig. 3.5: IR (KBr) spectrum of epoxy resin (ESB4HM)

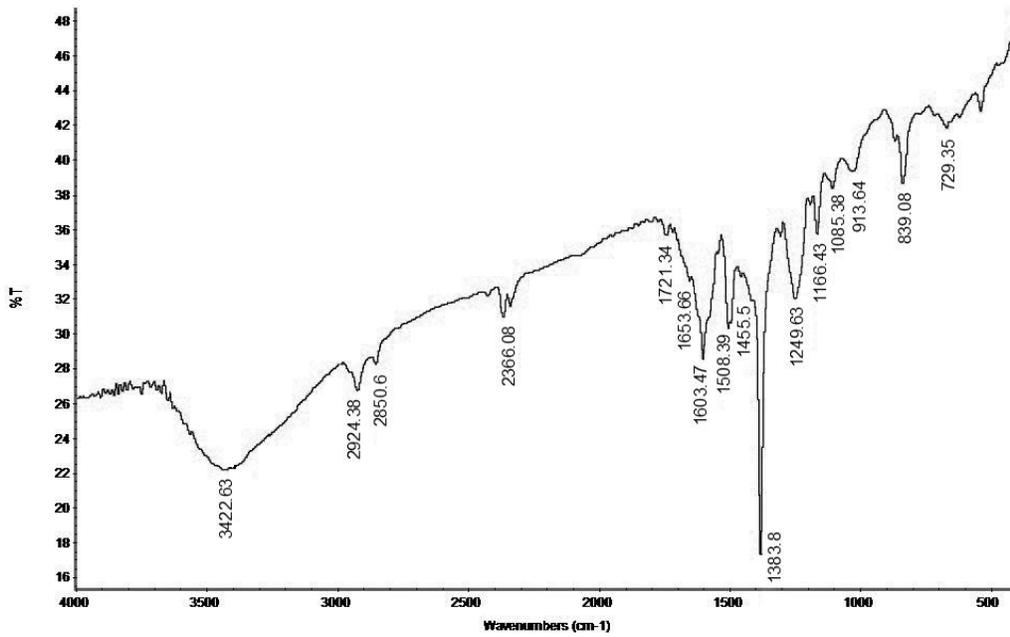


Fig. 3.6: IR (KBr) spectrum of epoxy resin (ESB4HE)

**Table-3.7:** The characteristic IR absorption frequencies of ESB4HCy, ESB4HM and ESB4HE.

Types	Group vibration mode	Observed IR frequencies, (cm <sup>-1</sup> )			Expected frequencies, (cm <sup>-1</sup> )
		ESB4HCy	ESB4HM	ESB4HE	
Alkane -CH <sub>2</sub> -	C-H (v <sub>as</sub> )	2930.2	2935.4	2924.4	2975-2950
	C-H (v <sub>s</sub> )	2855.6	2857.4	2850.6	2880-2860
	C-H def	1455.0	1458.5	1456	1470-1435
	Twisting & Wagging	1254.0	1248.1	1249.6	~1250
	Skeletal CH <sub>2</sub>	735.0	745.4	729.4	750-720
Arom- atic	C=C str.	1601.7	1597.3	1603.5	1600-1400
		1512.9		1508.4	
		1455.0			
	C-H (i.p.d.)	1254.0	1248.1	1249.6	1258±11, 1175±6, 1117±7, 1013±5 (1,4 sub.)
1164.5		1162.1	1166.4		
1108.9		1105.7	1108.1		
1027.2		1030.3	1085.4		
C-H (o.p.d.)	831.6	831.5	839.1	817±15 (1,4 sub.)	
Schiff base	N = CH str.	1657.9	1677.8	1653.7	1690-1635
	C – N vib.	1383.8	1308.2	1333.8	1360-1310
Ether	C-O-C	1254.0	1248.1	1249.6	1275-1200
-OH	O-H str.	3386.3	3422.0	3422.6	3400-3200
	O-H def.	1383.8	1308.2	1383.8	1350-1260
	C-O-H def.	1108.9	1105.7	1166.4	1120-1030

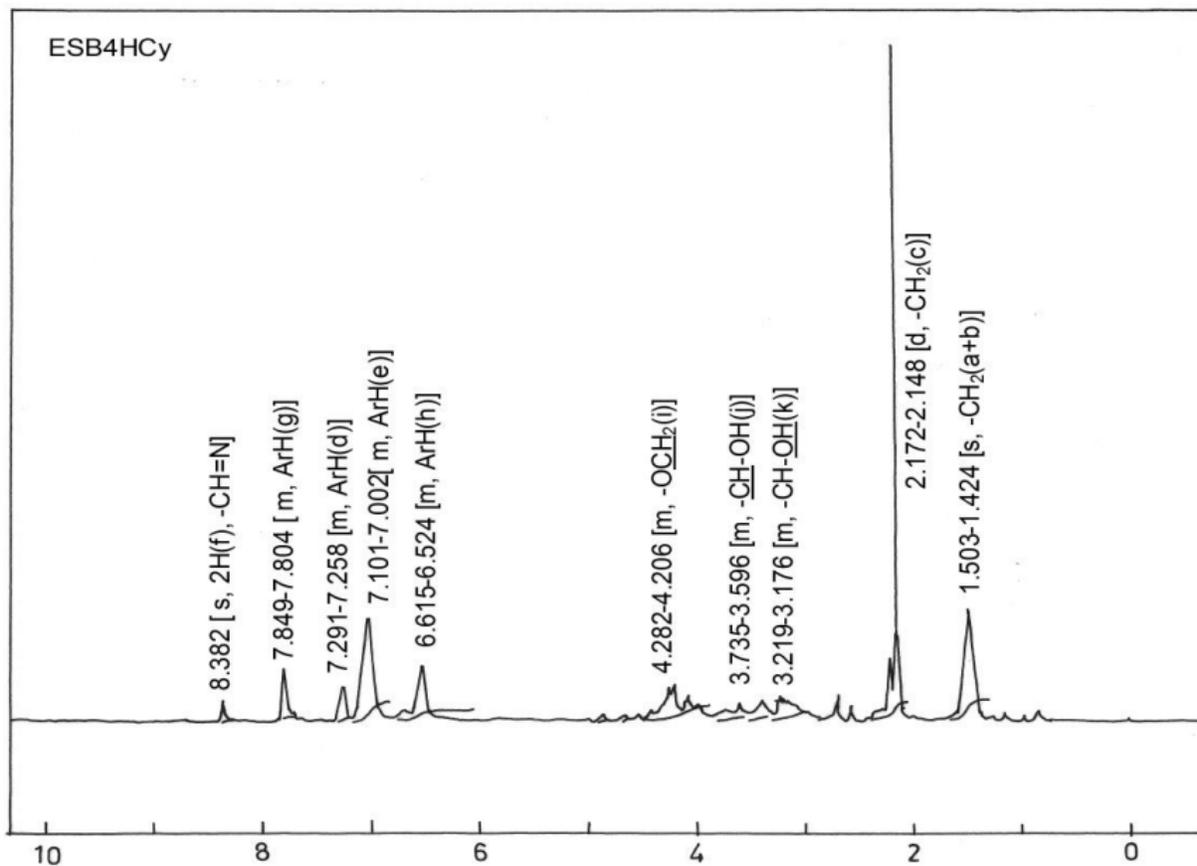
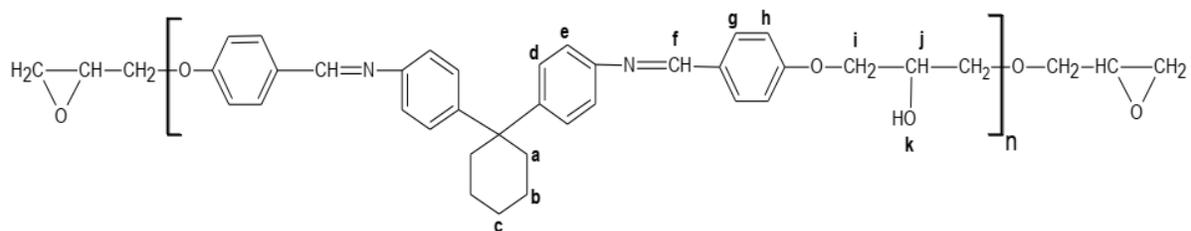
## NMR spectral characterization

Some nuclei spin about their axes in a manner to that electrons spin. In the presence of an externally applied magnetic field, a spinning nucleus can only assume a limited number of stable orientations. Nuclear magnetic resonance occurs, when a spinning nucleus in a lower energetic orientation in a magnetic field absorbs sufficient electromagnetic radiation to be excited to a higher energetic orientation. The excitation energy varies with the type and environment of the nucleus. NMR spectroscopy can be used for the quantitative chemical analysis.

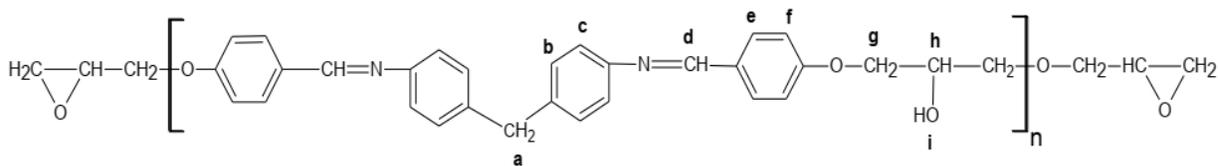
NMR spectroscopy consists of measuring the energy that is required to change a spinning nucleus from a stable orientation to a less stable orientation in the magnetic field. Different spinning nuclei absorb at different frequencies of radiation to change their orientations. The frequencies at which absorption occur can be used for qualitative analysis. The decrease in intensity of incident radiation owing to absorption during a particular transition is related to the different spinning nuclei at different frequencies in the magnetic field.

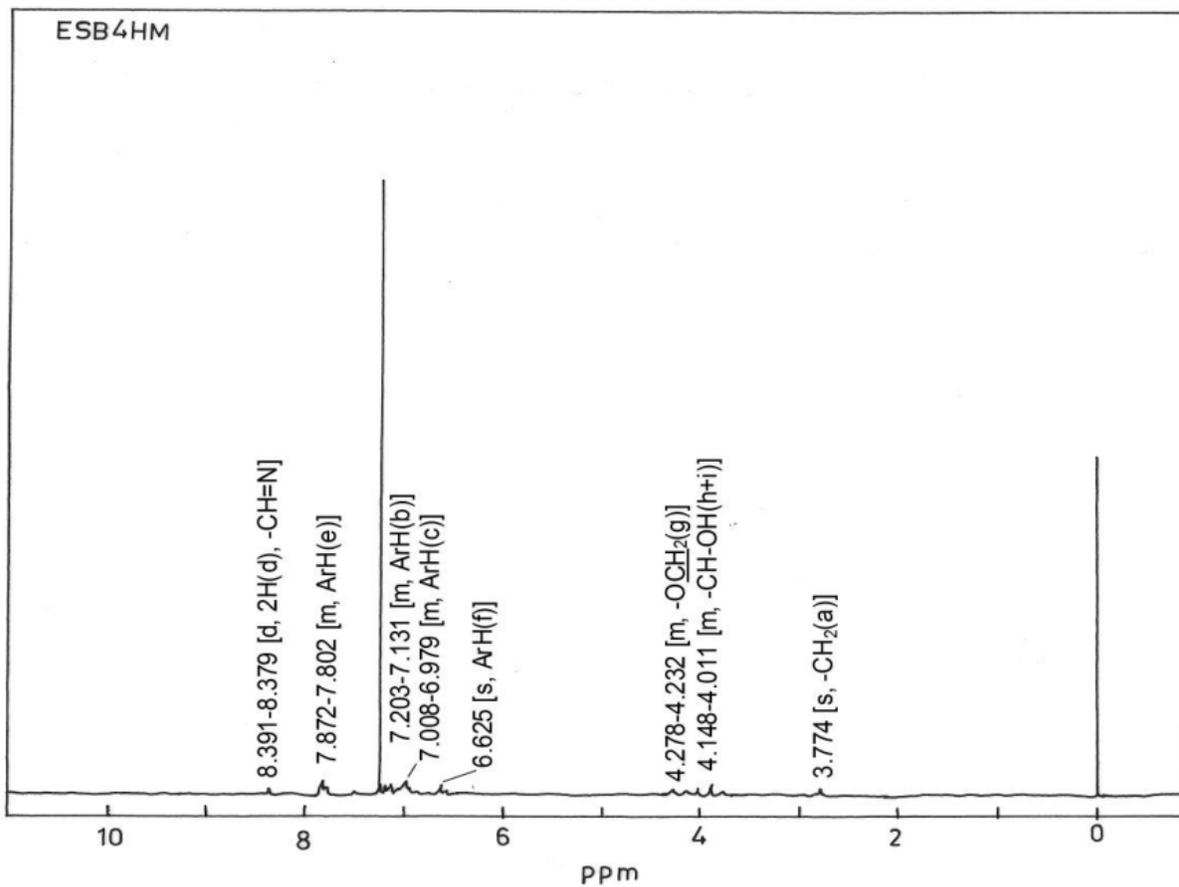
The decrease in intensity of incident radiation owing to absorption during a particular transition is related to the number of nuclei in the sample that undergo the transition and can be used for quantitative analysis. NMR spectrometer was invented in 1945 by Felix Bloch (Stanford University) and Edward Purcell. They shared the Nobel Prize (1952) in Physics for their work.

<sup>1</sup>HNMR spectral analysis of epoxy resins  
<sup>1</sup>HNMR spectra of ESB4HCy, ESB4HM and ESB4HE were scanned on a Bruker AVANCE II 400 MHz spectrometer by using CDCl<sub>3</sub>/DMSO-d<sub>6</sub> as a solvent and TMS as an internal standard. <sup>1</sup>HNMR spectra of ESB4HCy, ESB4HM and ESB4HE are presented in Figs. 3.36 to 3.38, respectively. Chemical shifts (ppm) and multiplicities of different types of protons of the resins are assigned in corresponding spectrum itself. Residual chloroform is appeared at about 7.25 ppm.

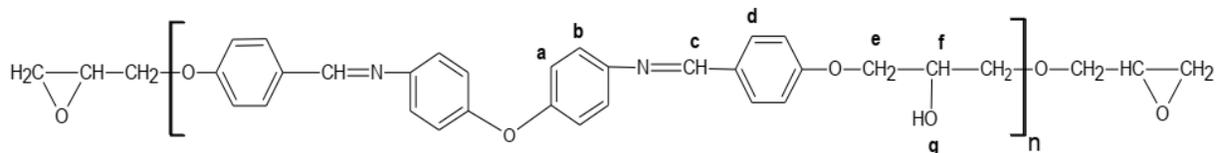


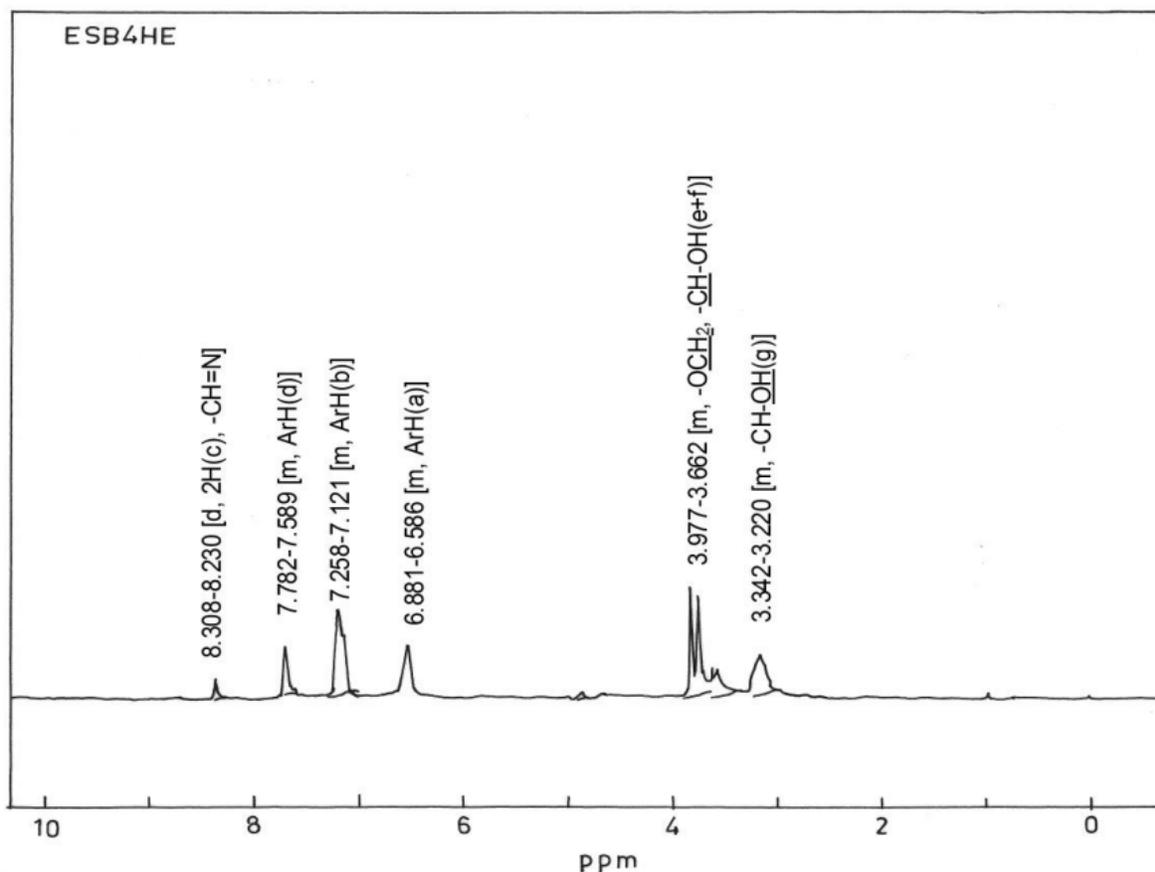
**Fig. 3.36:** NMR (400MHZ) spectrum of epoxy (ESB4HCy) in CDCl<sub>3</sub>





**Fig. 3.37:** NMR (400MHZ) spectrum of epoxy (ESB4HM) in DMSO-d<sub>6</sub>





**Fig. 3.38:** NMR (400MHz) spectrum of epoxy (ESB4HE) in DMSO-d6

## Thermal analysis

Synthetic polymers are highly useful in the rapidly developing fields such as space exploration, terrestrial transportation, modern communications, energy saving, environmental protection, public health, microbiology, medicine, etc. A major driving force for the growth and interest in the studies of thermally stable polymers is attributed to their extensive applications in aeronautics and in supersonic appliances. Considerable research work has been undertaken on the thermal stability of polymers to derive the polymers, which may be useful for high temperature applications.

Data on thermal characteristics are important tool for evaluating product performance as well as processability of polymeric materials. Thermal properties like specific heat and thermal

conductivity are the determining factors in selection of processing parameters as well as designing the machines and tools for shaping of plastics. The data are also useful in screening the materials for specific applications. On practical side, thermal analysis of polymers not only explains the behavior of polymers under conditions of high temperatures but also helps in selecting the right kind of material for the specific uses where high temperatures are encountered. It also suggests the design and synthesis of new materials for specific requirements in polymer technology such as high temperature resistant synthetic and natural fibers, transportation industries, electrical and electronic instruments, appliances, etc.

Kinetic study of thermal decomposition of epoxy resins containing flame retardant components was reported by Wang and Shi. Hyperbranched polyphosphate ester (HPPE) and phenolic melamine (PM) were blended in different ratios with a commercial epoxy resin to obtain a series of flame retardant resins. The thermal decomposition mechanism of cured ester was studied by thermogravimetric analysis and in situ Fouriertransform infrared spectroscopy.

The processing characteristics, thermal cure and catalytic cure behavior for both resins were investigated mainly by means of viscosity measurements and non-isothermal differential scanning calorimetry (DSC). The effect of propargyl and methylol content of PN and MPN, the molecular weight and the configuration of the parent novolac, on the processing and cure behavior was studied in details. Processing parameters and curing kinetic parameters were obtained. Both resins exhibit excellent processing properties. Thermal cure of PN resins possessed one cure mechanism and that of MPN resins possessed two cure mechanisms according to DSC analysis. The dual-cure-type mechanism made MPN resins superior to PN resins in terms of a mild and controllable cure process. Compared with thermal cure, catalytic cure of PN resins showed lower initiation temperature and cure temperature by about 60 °C. These novel resins have a bright prospect of application as matrix for thermal-structural composite materials.

## **Effect of various operating parameters**

### **1. Atmosphere**

The atmosphere associated with any thermal analysis, which is composed of gases that are introduced from outside and those are evolved from the samples. The presence or absence of such gases may have strong influence on the results. These gases may react with the sample or with each other and change the reaction mechanism or product composition. Inert atmosphere and vacuum will influence the decomposition processes as well. In vacuum the primary decomposition of gases will tend to be pumped away from the sample before the molecules collide with the surface and undergo secondary reactions. When these molecules collide with inert gas molecules, they may undergo homogeneous reactions or may be reflected back to the sample surface and react there.

### **2. Container geometry**

The container geometry influences the gaseous environment and heat transfer to the samples. Even with a flowing gaseous atmosphere, a deep narrow container will limit the contact between the sample surface and gas, whereas a shallow, broad container will promote the contact.

### **3. Container material**

It is reasonable to expect that in some cases the container material will react with material being tested or some of the products.

### **4. Sample size**

Two major effects are associated with the sample size, namely surface and bulk effects. In carrying out degradation studies, it is customary to reduce film thickness or particle size until the rate of the decomposition becomes independent of size.

## **5. Rate of heating**

In the case where only kinetic considerations are significant, an increase in rate of temperature rise will cause the process to be displayed to a higher temperature because they will be at the lower temperature for a shorter length of time. The rate of change of the measured parameter will also be greater for faster heating

## **Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA)**

Physical transformation such as glass transition, cold crystallization and crystallization from melts, crystalline disorientation, and melting can be studied by differential scanning calorimetry (DSC) and differential thermal analysis (DTA). Glass transition involves the motion of short segments in the amorphous region and is related to the brittleness of the polymer. Crystallization from the melt is of great practical importance. A number of properties of polymers like melting range, heat of fusion and melting point depression, degree of crystallinity, random copolymer structure and stereo regularity and identification of composition of a mixture may be studied through melting. DSC is a method where by the energy necessary to establish a zero temperature difference between a substance and a reference material is recorded as a function of temperature or time. The energy input to the sample is compensated by an increased energy input to the sample in order to maintain a zero temperature difference because this energy input is precisely equivalent in magnitude to the energy absorbed during the transition in direct calorimetric measurement. The combination of programmed and isothermal techniques has been used for characterizing unresolved multistep reactions in polymers. DSC provides useful informations about crystallinity, stability of crystallites, glass transition temperature, cross linking, kinetic parameters such as the activation energy, the kinetic order, frequency factor, entropy change and heat of polymerization.

## **Thermo Gravimetric Analysis (TGA)**

Thermogravimetry is a useful analytical technique for recording weight loss of a test sample as a function of the temperature or time, which may be useful for understanding the chemical nature of the polymer. Thus, the weight of a substance in an environment heated or cooled at a controlled rate is recorded as a function of time or temperature. There are three types of thermogravimetry namely

1. Static or isothermal thermogravimetry,
2. Quasistatic thermogravimetry and
3. Dynamic thermogravimetry

Most of the studies of polymers are generally carried out with dynamic thermogravimetry. Normally sample starts losing weight at a very slow rate up to a particular temperature and thereafter, the rate of loss becomes large over narrow range of temperature. After this temperature the loss in weight levels off. TGA curves are characteristic for given polymers because of unique sequence of physico-chemical reactions, which occur over definite temperature ranges and at the rates that are function of the polymer structures. The change in weight is a result of the rupture and/or formation of various physical and chemical bonds at elevated temperatures that lead to the evaluation of volatile products in the formation of heavier reaction products. Pyrolysis of many polymers yields TG curves, which follow relatively simple sigmoidal curves. In such a case weight of sample decreases slowly as reaction begins and then decreases rapidly over a comparatively narrow range of temperature and finally levels off as the reaction gets completed. The shape of the curve depends on the kinetic parameters: reaction order ( $n$ ), frequency factor ( $A$ ) and activation energy ( $E_a$ ). The values of these parameters have been shown to be of major importance to elucidate the mechanism in polymer degradation.

Reich and Levi have described several temperature characteristics for qualitative assessment of relative thermal stability of polymers:

1. Initial decomposition temperature ( $T_0$ )

2. Temperature of 10% weight loss (T10)
3. Temperature of maximum rate of decomposition (Tmax)
4. Half volatilization temperature (Ts)
5. Differential decomposition temperature
6. Integral procedural decomposition temperature (IPDT)

For the estimation of kinetic parameters from TG traces, several so called exact methods have been proposed. All these methods involve the two assumptions that thermal and diffusion barriers are negligible and that Arrhenius equation is valid. Since small quantities of materials are employed in TG studies, thermal and diffusion barriers would be negligible. Since the shape of any TG curve is dependent on the nature of apparatus and the way in which it is used. Most kinetic treatments are based on relationship of the type.

$$\frac{dC}{dt} = k f(C) \quad \dots 3.1$$

Where C = Degree of conversion, t = time; k=rate constant, and f(C) = temperature independent function of C

The constant k is generally assumed to have the Arrhenius form

$$k = A e^{-Ea/RT} \quad \dots 3.2$$

C is defined as the conversion with respect to initial material

$$C = 1 - \frac{W}{W_o} \quad \dots 3.3$$

where  $W_o$  = Initial weight of the material and W = weight of the material at any time.

The residual weight fraction is given by

$$\frac{W}{W_o} = (1-C)$$

and the rate of conversion is given by

$$\frac{dC}{dt} = - \left( \frac{1}{W_o} \right) \frac{dW}{dt}$$

For homogeneous kinetics, the conversion would be assumed to have the form

$$f(C) = (1-C)^n \quad \dots 3.5$$

Where n = order of the reaction

Upon substituting Eqns. 3.2 and 3.5 into Eqn. 3.1

$$\frac{dC}{dt} = A e^{-Ea/RT} (1-C)^n$$

OR

$$\frac{dC}{dT} = \left( \frac{A}{\beta} \right) (e^{-Ea/RT}) (1-C)^n \quad \dots 3.6$$

Where  $\beta$  = Rate of heating

## **X-ray spectroscopy**

X-ray diffraction is a widely used tool for structural identification for almost all solids under the right conditions. X-ray diffractometers are generally either single crystal or powder. Single crystal studies allow the absolute configurational determination of polymeric materials that have high degrees of crystallinity. Such determinations are costly with respect to time because of the complexity of polymeric materials.

Powder x-ray spectroscopy can employ smaller crystalline samples from one to several hundred nanometers. These crystallites have broadened peak profiles as a result of incomplete destructive interference at angles near the Bragg angle defined as

$$n\lambda = 2d \sin \theta$$

where  $n$  is the order of a reflection

$\lambda$  the wavelength

$d$  the distance between parallel lattice planes

$\theta$  the angle between the incident beam and a lattice plane known as the Bragg angle  
This broadening allows determination of crystallite size and size distribution. (Note that this is not particle size.)

X-ray analysis of proteins and nucleic acids is especially important as the absolute structure is needed for many advances in the field of medicine and biochemistry.

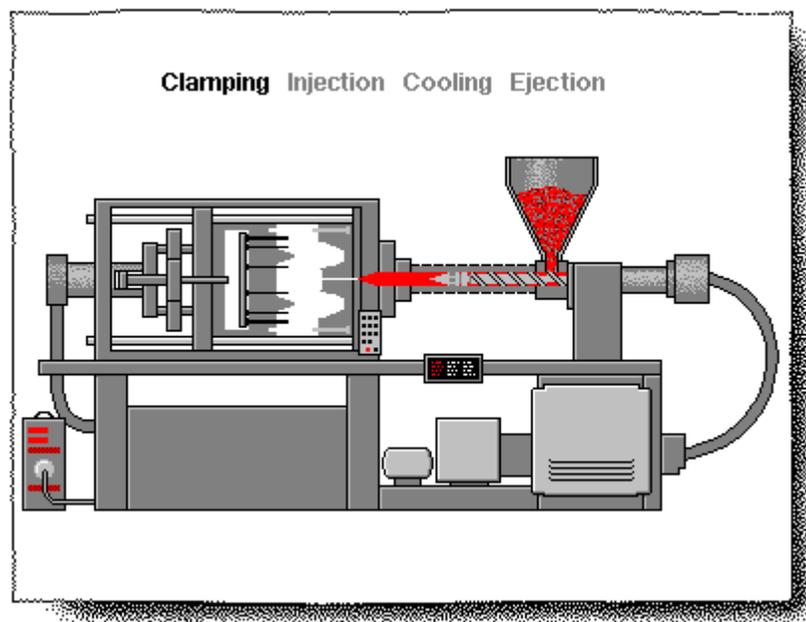
## **Polymer Processing**

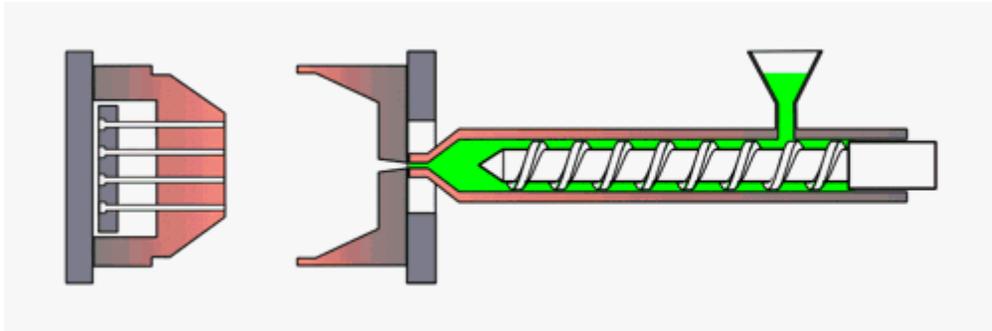
Plastics are mainly organic polymers of high molecular mass, but they sometimes contain other substances as well. Plastics are usually synthetic, most commonly derived from petrochemicals, but many are partially natural. Plastics are usually classified by their chemical structure of the

polymer's backbone and side chains. Some important groups in these classifications are the acrylics, polyesters, silicones, polyurethanes, and halogenated plastics. There are a variety of methods used to process plastic. Each method has its advantages and disadvantages and are better suited for specific applications. There are various plastic processing techniques featured with their relevant animations.

## **Injection molding**

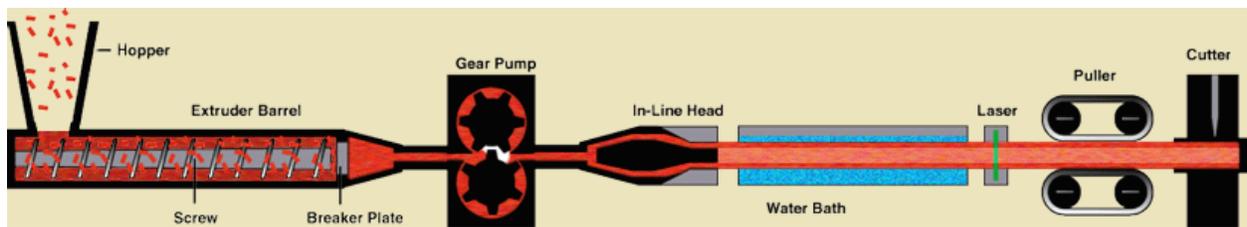
Injection molding is a manufacturing process for producing parts by injecting material into a mold. The main method used for processing plastic is injection molding. With this process, the plastic is placed into a hopper. The hopper then feeds the plastic into a heated injection unit, where it is pushed through a long chamber with a reciprocating screw. Here, it is softened to a fluid state. A nozzle is located at the end of the chamber. The fluid plastic is forced through the nozzle into a cold, closed mold. The halves of the mold are held shut with a system of clamps. When the plastic is cooled and solidified, the halves open and the finished product is ejected from the press.





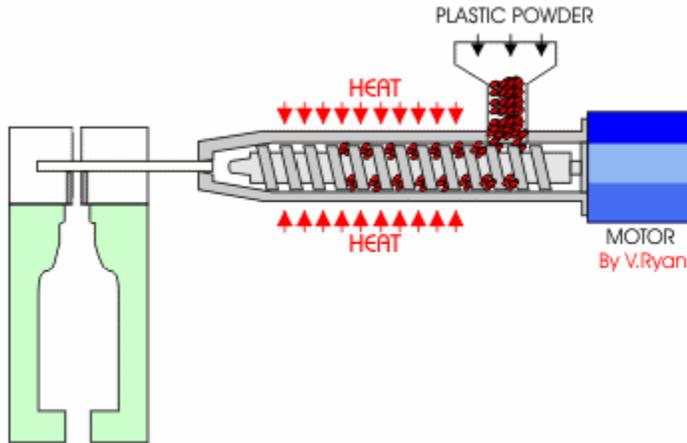
## **Plastics extrusion**

Plastics extrusion is a high volume manufacturing process in which raw plastic material is melted and formed into a continuous profile. The process of extrusion is usually used to make products such as film, continuous sheeting, tubes, profile shapes, rods, coat wire, filaments, cords, and cables. As with injection molding, dry plastic material is placed into a hopper and fed into a long heating chamber. At the end of the chamber, however, the material is forced out of a small opening or a die in the shape of the desired finished product. As the plastic exits the die, it is placed on a conveyor belt where it is allowed to cool. Blowers are sometimes used to aid in this process, or the product may be immersed in water to help it cool.



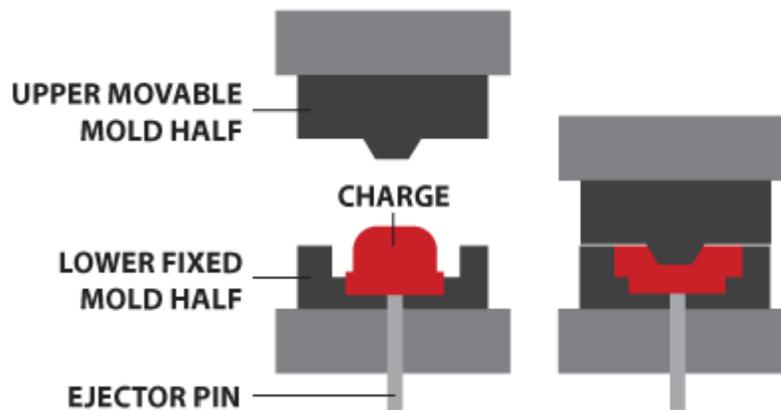
## **Blow Molding**

Stretch Blow Molding process is mainly used when the plastic product that needs to be created should be hollow. A molten tube is created with blow molding by using compressed air, which blows up the tube and forces it to conform to the chilled mold. Variations of blow molding include injection, injection-stretch, and extrusion blow molding.



## Compression molding

Compression molding is the most common process used with thermosetting materials and is usually not used for thermoplastics. With this process, the material is squeezed into its desired shape with the help of pressure and heat. Plastic molding powder and other materials are added to the mix in order to create special qualities or to strengthen the final product. When the mold is closed and heated, the material goes through a chemical change that causes it to harden into its desired shape. The amount temperature, amount of pressure, and length of time utilized during the process depends on the desired outcome.



## Additives, fillers, and reinforcements

Additives, fillers, and reinforcements are used to change and improve the physical and mechanical properties of plastics. In general, reinforcing fibers increase the mechanical properties of polymer composites while particular fillers of various types increase the modulus.

<b>TABLE 1. Effects of additives, fillers, and reinforcements on polymer properties</b>		
<b>Additive / Filler / Reinforcement</b>	<b>Common materials</b>	<b>Effects on polymer properties</b>
<b>Reinforcing fibers</b>	<b>Baron, carbon, fibrous minerals, glass, Kevlar</b>	<ul style="list-style-type: none"> <li>■ <b>Increases tensile strength.</b></li> <li>■ <b>Increases flexural modulus.</b></li> <li>■ <b>Increases heat-deflection temperature (HDT).</b></li> <li>■ <b>Resists shrinkage and warpage.</b></li> </ul>
<b>Conductive fillers</b>	<b>Aluminum powders, carbon fiber, graphite</b>	<ul style="list-style-type: none"> <li>■ <b>Improves electrical and thermal conductivity.</b></li> </ul>
<b>Coupling agents</b>	<b>Silanes, titanates</b>	<ul style="list-style-type: none"> <li>■ <b>Improves interface bonding between polymer matrix and the fibers.</b></li> </ul>
<b>Flame retardants</b>	<b>Chlorine, bromine, phosphorous, metallic salts</b>	<ul style="list-style-type: none"> <li>■ <b>Reduces the occurrence and spread of combustion.</b></li> </ul>
<b>Extender fillers</b>	<b>Calcium carbonate, silica, clay</b>	<ul style="list-style-type: none"> <li>■ <b>Reduces material cost.</b></li> </ul>
<b>Plasticizers</b>	<b>Monomeric liquids, low-molecular-weight materials</b>	<ul style="list-style-type: none"> <li>■ <b>Improves melt flow properties.</b></li> <li>■ <b>Enhances flexibility.</b></li> </ul>
<b>Colorants (pigments and dyes)</b>	<b>Metal oxides, chromates, carbon blacks</b>	<ul style="list-style-type: none"> <li>■ <b>Provides colorfastness.</b></li> <li>■ <b>Protects from thermal and UV degradation (with carbon blacks).</b></li> </ul>
<b>Blowing agents</b>	<b>Gas, azo compounds, hydrazine derivatives</b>	<ul style="list-style-type: none"> <li>■ <b>Generates a cellular form to obtain a low-density material.</b></li> </ul>

## **Modifying polymer properties**

Electrical properties can be affected by many fillers. For example, by adding conductive fillers, an electromagnetic shielding property can be built into plastics, which are normally poor electrical conductors. Anti-static agents can be used to attract moisture, reducing the build-up of static charge.

Coupling agents are added to improve the bonding of the plastic matrix and the reinforcing fibers. Different fillers are used to lower the cost of materials. Other additives include flame retardants to reduce the likelihood of combustion, lubricants to reduce the viscosity of the molten plastic, plasticizers to increase the flexibility of the materials, and colorants to provide colorfastness.

## Low-aspect fillers

Fillers modify the properties and molding of the compound to which they are added. If the fillers are characterized with a low aspect ratio between the longest and the shortest dimensions, the basic properties will be less changed from those of the unfilled polymer. Fillers benefit plastics parts in the following ways:

- Shrinkage will be less.
- Thermal resistance may be improved.
- Strength, especially compressive strength, will be improved.
- Impact resistance will often be lower than for the unfilled polymer.
- Solvent resistance will often be improved.

## High-aspect fillers: fibers

When the aspect ratio between the longest and the shortest dimension of the filler is large, for example, greater than 25, the filler can be characterized as a fiber. Fiber reinforcements will significantly affect the properties of the compounds to which they are added.

### ▶ **Fibers impact strength**

- ▶ Assuming good bonding between the fiber and the polymer matrix, the strength in the fiber direction will be significantly increased. If many fibers are oriented in the same direction, large differences will be noted between the modulus in the orientation direction and in the direction perpendicular to the orientation. The latter will be very close to that for the unfilled polymer.

### ▶ **Fibers affect shrinkage**

The fibers will also have a significant effect on the shrinkage properties of the compound: shrinkage in the orientation direction will be much less than the shrinkage in the cross direction.

### ▶ **Importance of predicting fiber orientation**

Because the fiber orientation varies with the flow direction, in the thickness direction, and at weld line locations, it is important to be able to predict these orientations, in order to predict the properties of the molded article.

# **Polymer stabilizers**

**Stabilizers** are a class of chemical additives commonly added to polymeric materials, such as plastics, to inhibit or retard their degradation. Polymers can be subject to various degradation processes, including oxidation, UV-damage, thermal degradation, ozonolysis, or combinations thereof like photo-oxidation.<sup>[2]</sup> These processes all degrade the polymer on a chemical level, leading to chain scission that can adversely affect its mechanical properties such as strength and malleability, as well as its appearance and colour.

A vast number of chemically distinct polymers exist, with their degradation pathways varying according to their chemical structure, as such an equally wide range of stabilizers exists. The market for antioxidant stabilisers alone was estimated at US\$1.69 billion for 2017.

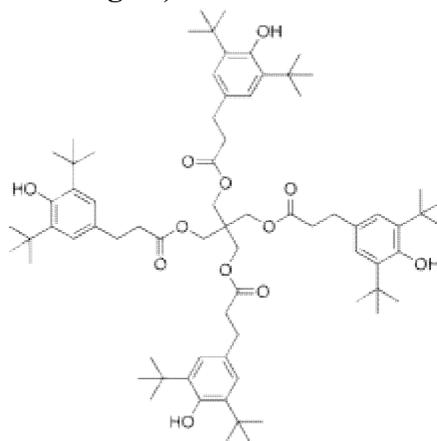
Most carbon-based materials deteriorate over time due to the effects of light, atmospheric oxygen and other environmental factors. In plastics this can cause discoloration and embrittlement, which can reduce the useful lifespan of the object. Stabilizers are used to prevent this by inhibiting the various degradation processes such as oxidation, chain scission and uncontrolled recombinations and cross-linking. Typically a number of different stabilizers will be needed in combination, each inhibiting a particular degradation pathway. The effectiveness of the stabilizers depends on solubility, distribution within the plastic, ability to stabilize, and rate of loss during processing and use. The effect on the viscosity on the plastic is also an important concern for processing.

## **Antioxidants**

Antioxidants inhibit autoxidation that occurs when polymers reacts with atmospheric oxygen. For some compounds this can happen gradually at room temperature but almost all polymers are at risk of thermal-oxidation when they are processed at high temperatures. The molding or casting of plastics (e.g. injection molding) require them to be above their melting point or glass transition temperature (~200-300 °C) and under these conditions reactions with oxygen occur much more rapidly. Once initiated, autoxidation proceeds via a free radical chain reaction which can be autocatalytic. As such, even though efforts are usually made to reduce oxygen levels, total exclusion is often not achievable and even exceedingly low concentrations of oxygen can be

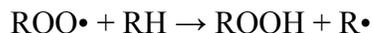
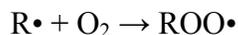
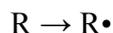
sufficient to initiate degradation. Sensitivity to oxidation varies significantly depending on the polymer in question; without stabilizers polypropylene and unsaturated polymers such as rubber will slowly degrade at room temperature where as polystyrene can be stable even at high temperatures. Antioxidants are of great importance during the process stage, with long-term stability at ambient temperature increasingly being supplied by hindered amine light stabilizers (HALs). Antioxidants are often referred to as being primary or secondary depending on their mechanism of action.

### Primary antioxidants (radical scavengers)

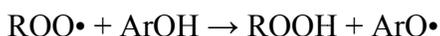


Pentaerythritol tetrakis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate): A primary antioxidant consisting of sterically hindered phenols with para-propionate groups.

Primary antioxidants act as radical scavengers and remove peroxy radicals ( $\text{ROO}\cdot$ ), as well as to a lesser extent alkoxy radicals ( $\text{RO}\cdot$ ), hydroxyl radicals ( $\text{HO}\cdot$ ) and alkyl radicals ( $\text{R}\cdot$ ). Oxidation begins with the formation of alkyl radicals, which react very rapidly with molecular oxygen (rate constants  $\approx 10^7\text{--}10^9 \text{ mol}^{-1} \text{ s}^{-1}$ ) to give peroxy radicals, these in turn abstract hydrogen from a fresh section of polymer in a chain propagation step to give new alkyl radicals. The overall process is exceedingly complex and will vary between polymers but the first few steps are shown below in general:

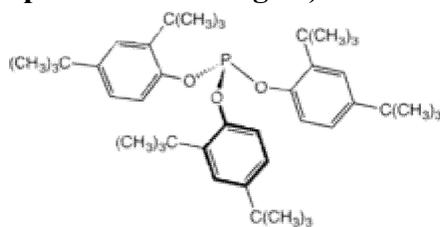


Due to its rapid reaction with oxygen the scavenging of the initial alkyl radical (R•) is exceedingly difficult and can only be achieved using specialised antioxidants bearing reactive groups, such as acryloyls, the majority of primary antioxidants react instead with the longer lasting peroxy radicals (ROO•). Hydrogen abstraction is usually the rate determining step in the polymer degradation and the peroxy radicals can be scavenged by hydrogen donation from an alternative source, which converts them into organic hydroperoxides (ROOH). The most important commercial stabilizers for this are hindered phenols such as BHT or analogues thereof and secondary aromatic amines such as alkylated-diphenylamine. Amines are typically more effective, but cause pronounced discoloration, which is often undesirable (i.e., in food packaging, clothing). The overall reaction with phenols is shown below:



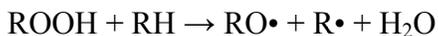
The end products of these reactions are typically quinones, which may also impart unwanted colour. Modern phenolic antioxidants often have complex molecular structures, often including a propionate-group at the para position of the phenol (i.e. they are ortho-alkylated analogues of phloretic acid). The quinones of these can rearrange once to give a hydroxycinnamate, regenerating the phenolic antioxidant group and allowing further radicals to be scavenged.<sup>[11]</sup> Ultimately however, primary antioxidants are sacrificial and once they are fully consumed the polymer will begin to degrade.

### Secondary antioxidants (hydroperoxides scavengers)



Tris(2,4-di-tert-butylphenyl)phosphite, a phosphite widely used as a secondary antioxidant in polymers.

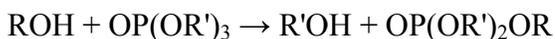
Secondary antioxidants act to remove organic hydroperoxides (ROOH) formed by the action of primary antioxidants. Hydroperoxides are less reactive than radical species but can initiate fresh radical reactions:



As they are less chemically active they require a more reactive antioxidant. The most commonly employed class are phosphite esters, often of hindered phenols e.g. Tris(2,4-di-tert-butylphenyl)phosphite. These will convert polymer hydroperoxides to alcohols, becoming oxidized to organophosphates in the process:

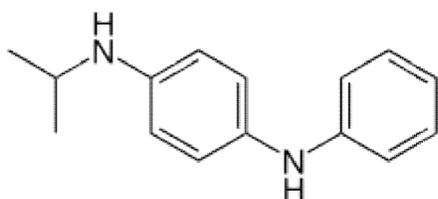


Transesterification can then take place, in which the hydroxylated polymer is exchanged for a phenol:



This exchange further stabilizes the polymer by releasing a primary antioxidant, because of this phosphites are sometimes considered multi-functional antioxidants as they can combine both types of activity. Organosulfur compounds are also efficient hydroperoxide decomposers, with thioethers being particularly effective against long-term thermal aging, they are ultimately oxidised up to sulfoxides and sulfones.

### Antiozonant

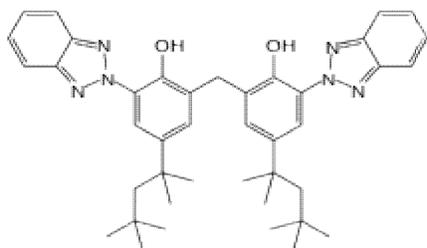


N-Isopropyl-N'-phenyl-1,4-phenylenediamine (IPPD) a p-phenylenediamine based antiozonant

Antiozonants prevent or slow down the degradation of material caused by ozone. This is naturally present in the air at very low concentrations but is exceedingly reactive, particularly towards unsaturated polymers such as rubber, where it causes ozone cracking. The mechanism of ozonolysis is different from other forms of oxidation and hence requires its own class of antioxidant stabilizers. These are primarily based on p-phenylenediamine and work by reacting

with ozone faster than it can react with vulnerable functional groups in the polymer (typically alkene groups). They achieve this by having a low ionization energy which allows them to react with ozone via electron transfer, this converts them into radical cations that are stabilized by aromaticity. Such species remain reactive and will react further, giving products such as 1,4-benzoquinone, phenylenediamine-dimers and aminoxyl radicals.<sup>[17][18]</sup> Some of these products can then be scavenged by antioxidants.

## Light stabilizers



Bisotrizole: A benzotriazole-phenol based UV absorber

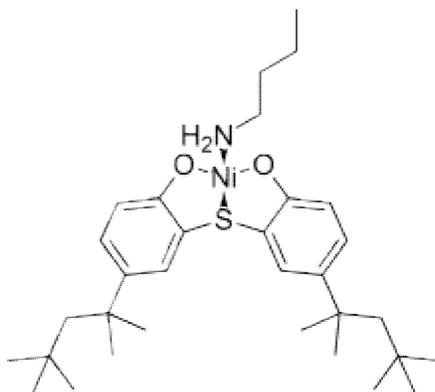
Light stabilizers are used to inhibit polymer photo-oxidation, which is the combined result of the action of light and oxygen. Like autoxidation this is a free radical process, hence the antioxidants described above are effective inhibiting agents, however additional classes of additives are also beneficial, such as UV absorbers, quenchers of excited states and HALS.

## UV absorbers

The UV absorbers dissipate the absorbed light energy from UV rays as heat by reversible intramolecular proton transfer. This reduces the absorption of UV rays by the polymer matrix and hence reduces the rate of weathering. Typical UV-absorbers are benzotriazoles and hydroxyphenyltriazines for polycarbonates and acrylics,<sup>[19]</sup> oxanilides for polyamides and benzophenones for PVC.

Strongly light-absorbing PPS is difficult to stabilize. Even antioxidants fail in this electron-rich polymer. The acids or bases in the PPS matrix can disrupt the performance of the conventional UV absorbers such as HPBT. PTHPBT, which is a modification of HPBT are shown to be effective, even in these conditions.

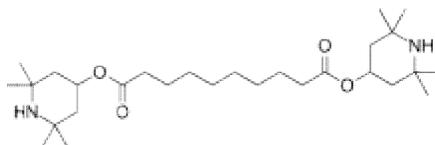
## Quenchers



A nickel-phenoxide quencher. CAS No 014516-71-3

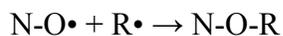
Photo-oxidation can begin with the absorption of light by a chromophore within the polymer (which may be a dye or impurity) causing it to enter an excited state. This can then react with ambient oxygen, converting it into highly reactive singlet oxygen. Quenchers are able to absorb energy from excited molecules via a Förster mechanism and then dissipate it harmlessly as either heat or lower frequency fluorescent light. Singlet oxygen can be quenched by metal chelates, with nickel phenolates being a common example.

## Hindered amine light stabilizers



Example structure of a HAL

The ability of hindered amine light stabilizers (HALS or HAS) to scavenge radicals produced by weathering, may be explained by the formation of aminoxyl radicals through a process known as the Denisov Cycle. The aminoxyl radical (N-O•) combines with free radicals in polymers:



Although they are traditionally considered as light stabilizers, they can also stabilize thermal degradation.

Even though HALS are extremely effective in polyolefins, polyethylene and polyurethane, they are ineffective in polyvinyl chloride (PVC). It is thought that their ability to form nitroxyl radicals is disrupted. HALS act as a base and become neutralized by hydrochloric acid (HCl) that is released by photooxidation of PVC. The exception is the recently developed NOR HALS, which is not a strong base and is not deactivated by HCl.

# Polymer Chemistry

## UNIT II and UNIT IV

### The Addition-Condensation System

This system divides polymerizations into two kinds

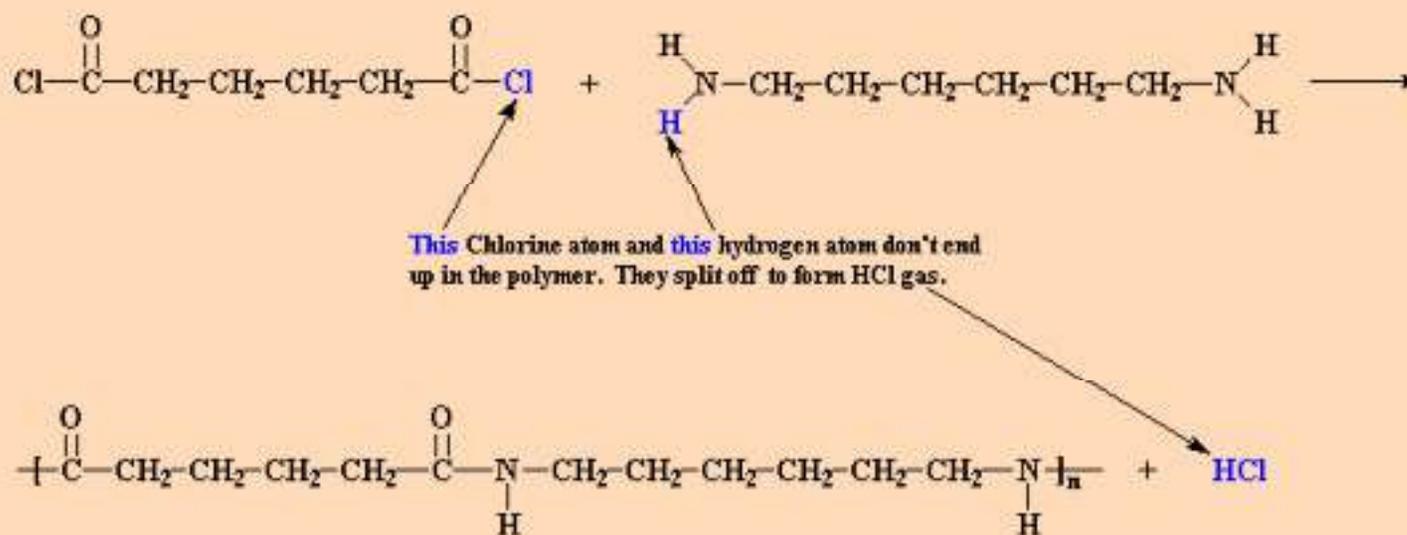
#### *Addition Polymerization* and *Condensation Polymerization*

we call a polymerization an *addition polymerization* if the entire monomer molecule becomes part of the polymer. We call a polymerization a *condensation polymerization* if part of the monomer molecule is kicked out when the monomer becomes part of the polymer. The part that gets kicked out is usually a small molecule like water, or HCl gas. Such small molecules *condense* on things as tiny droplets, hence the name. Let's look at some examples to illustrate the point.

When ethylene is polymerized to make polyethylene, then every atom of the ethylene molecule becomes part of the polymer. The monomer is *added* to the polymer outright. You might say that an addition polymer is like a good friend who accepts everything about you, the pleasant and the unpleasant alike.

But a condensation polymer is more like a snotty social club that says, "Sure you can join, but only if you ditch those friends of yours". You see, in a condensation polymerization, some atoms of the monomer don't

end up in the polymer. When nylon 6,6 is made from adipoyl chloride and hexamethylene diamine, the chlorine atoms from the adipoyl chloride, each along with one of the amine hydrogen atoms, are expelled in the form of HCl gas.



Because there is less mass in the polymer than in the original monomers, we say that the polymer is *condensed* with regard to the monomers. The byproduct, whether it's HCl gas, water, or whatnot, is called a *condensate*.

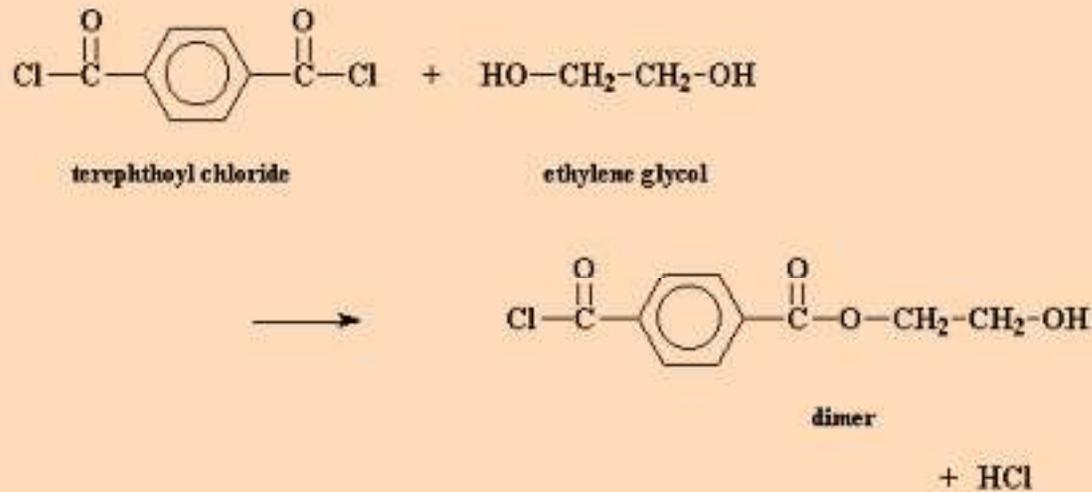
The Bottom Line

Want the short version? Condensation polymerizations give off byproducts. Addition polymerizations don't.

Now let's talk about the next system of classification: The Chain Growth - Step Growth system.



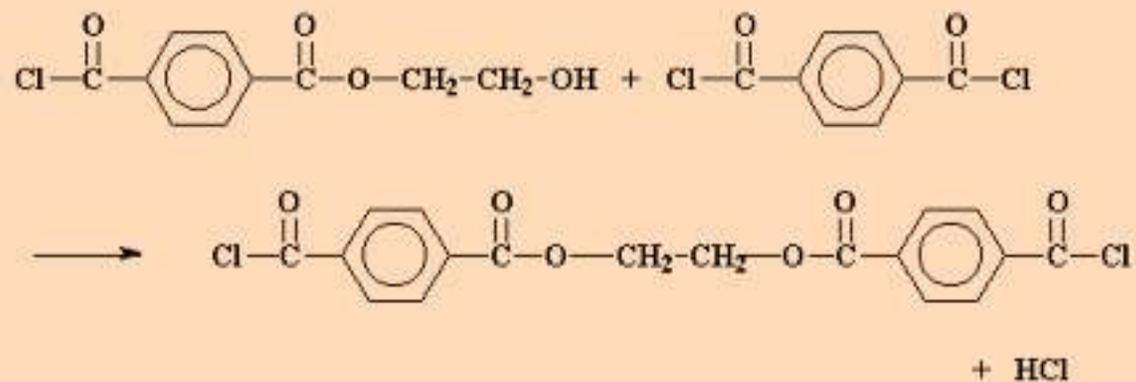
poly(ethylene terephthalate). The first thing that happens is that the two monomers will react to form a dimer. Sounds simple enough.



**Terephthoyl chloride and ethylene glycol react to form an ester dimer**

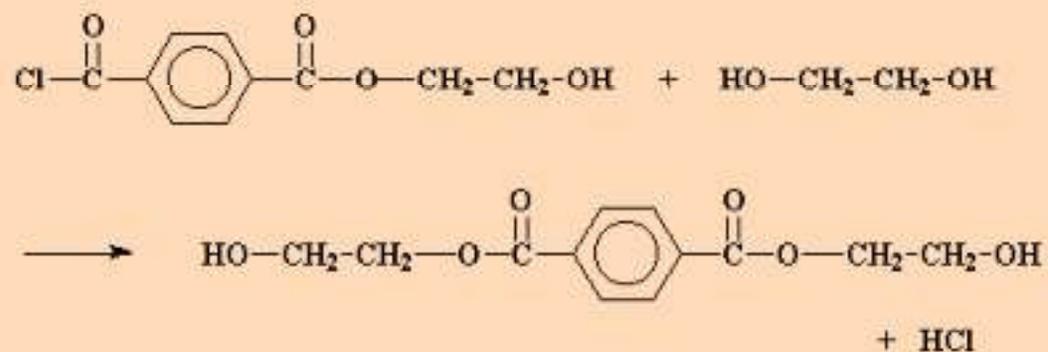
Now at this point in a chain growth system, only one thing could happen: a third monomer would add to the dimer to form a trimer, then a fourth to form a tetramer, and so on. But here, in the free land of step growth polymerization, that dimer can do a lot of different things. It can of course react with one of the monomers to form a trimer:

Our little dimer can react with a molecule of terephthoyl chloride...

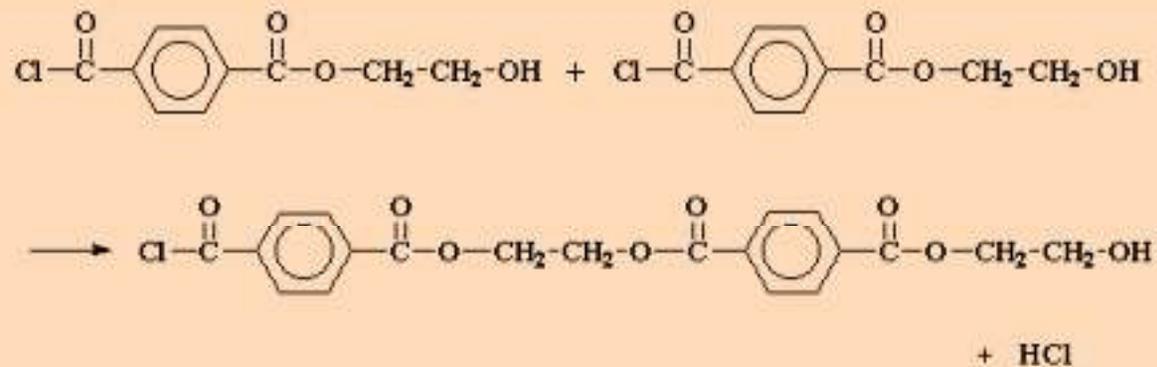


Or...

It can react with a molecule of ethylene glycol.

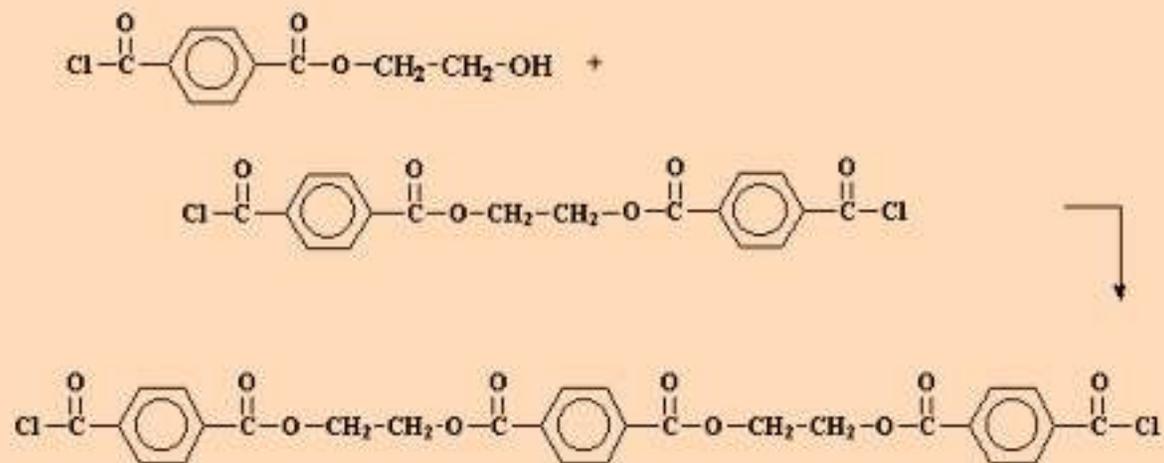


But it can do other things, too. It may react with another dimer to form a tetramer:



Two of our dimers are ganging up to form a tetramer.

Or it may even get really crazy and react with a trimer to form a pentamer.



**Merger Mania!**

The dimer joins the trimer to form a pentamer. Will the madness never stop?

Making things more complicated, these tetramers and pentamers can react to form even bigger oligomers. And so they grow and grow until eventually the oligomers are big enough to be called polymers.

Just think of the way your bank keeps merging with other banks and getting bigger and bigger, and you'll get the idea.

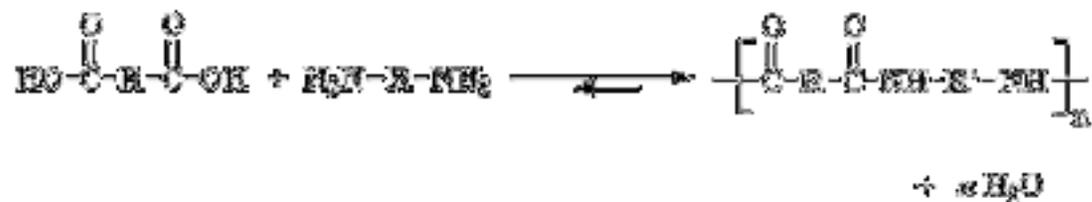
### The Bottom Line

The main difference is this: In a step growth reaction, the growing chains may react with each other to form even longer chains. This applies to chains of all lengths. The monomer or dimer may react in just the same way as a chain hundreds of monomer units long. But in an addition polymerization, only monomers react with growing chains. Two growing chains can't join together the way they can in a step growth polymerization.

### *Polycondensations*

There is another way to describe polymerizations other than the step-growth/chain-growth system. The most important thing you need to know about this system is that it classifies all polymerizations as polycondensations or polyadditions. Polycondensations are polymerizations in which a small molecule by-product is produced. The by-product is usually something like water, HCl, or once in awhile NaCl. Polyadditions on the other hand are polymerizations in which no by-product is produced.

The simplest polycondensation for making nylons is the polymerization of a diacid and a diamine. This reaction might not normally go to high conversions, but by removing the water by-product (usually by carrying out the reaction under vacuum so the water evaporates), we can force this reaction go to higher conversions.



Removing water makes the reaction go to high conversion thanks to LeChatlier's Principle. The self-condensation of an amino acid is a simple modification of the above reaction. Again, this reaction is forced to high conversion by removing the water formed with a vacuum.



Take a look at the above two reactions. Because the first one uses two different types of monomers, one which has two amine groups and one with two acid group, we call this an AA-BB system. Think of the amine groups as A's and the acid groups as B's, and you can figure out why. Likewise, the second reaction, the one using the amino acid, is called an AB system. This is obviously because the monomer contains both an amine group (A) and an acid group (B) in the same molecule.

AB systems have an advantage over AA-BB systems. The advantage is that in an AB system, one always has the same amount amine groups and acid groups. As we all know, stoichiometric balance of amine and acid groups is absolutely critical when making nylons. With AA-BB systems, the amounts of the two monomers must be measured very carefully to ensure perfect stoichiometric balance.

### *Interfacial Polymerizations*

Making nylon 6,6 is even easier if you use a diamine and a diacid chloride instead of a diacid. This is because acid chlorides are much more reactive than acids. The reaction is done in a two-phase system. The amine is dissolved in water, and the diacid chloride in an organic solvent. The two solutions are placed in the same beaker. Of course, the two solutions are immiscible, so there will be two phases in the beaker. At the interface of the two phases, the diacid chloride and

diamine can meet each other, and will polymerize there. There is special way to do this called the "Nylon Rope Trick"<sup>4</sup>, and we'll show you how to do that in just a minute.

While this is a neat party trick, it isn't used commercially because, first, acid chlorides are a lot more expensive than acids, and second, acid chlorides stink horribly, and are much more toxic than acids. And third, the fibers produced by this trick aren't very strong, anyway.

### ***Ring-Opening Polymerization***

The ring opening-polymerization of lactams is a chain-growth polymerization. It is also a polyaddition reaction, that is, no byproducts are produced. The thermodynamic driving force for ring-opening polymerizations is ring strain. Cyclic molecules polymerize in order to relieve the strain. Take a look at Table 3, and you'll see that 5- and 6-membered rings don't have very much ring strain, so they don't polymerize well. But 7-membered rings, like  $\epsilon$ -caprolactam, are much more strained and polymerize easily. As you can see in Table 3, so do many larger cyclic monomers.

Table 3

#### Polymerizability of Lactams<sup>5</sup>

Type of Polymerization	Order of Polymerizability (ring sizes)
anionic (strong base)	7 > 5 > 6
hydrolytic (water initiated)	7 > 8 > 9 >> 5 > 6
Cationic	8 > 7 > 11 > 5 > 6

There are two ways to carry out a ring-opening polymerization of  $\epsilon$ -caprolactam.

The second way to make nylon 6 is to use a strong base as an initiator.<sup>6</sup> How strong a base? Very strong. A normal strong base like NaOH isn't going to work here. We'll need an extra strong base like sodium hydride (NaH). The hydride anion

is an incredibly strong base, and when it sees caprolactam, it runs straight to the amide hydrogen and pulls it right off, as you can see in Figure 1.

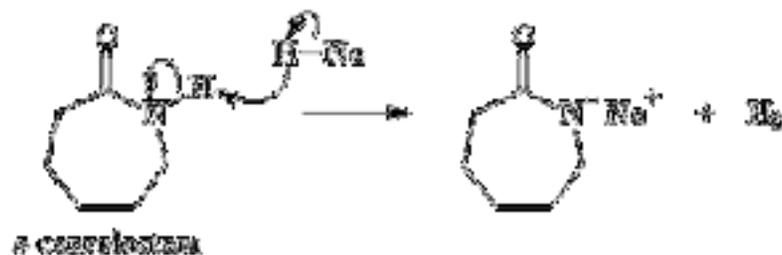
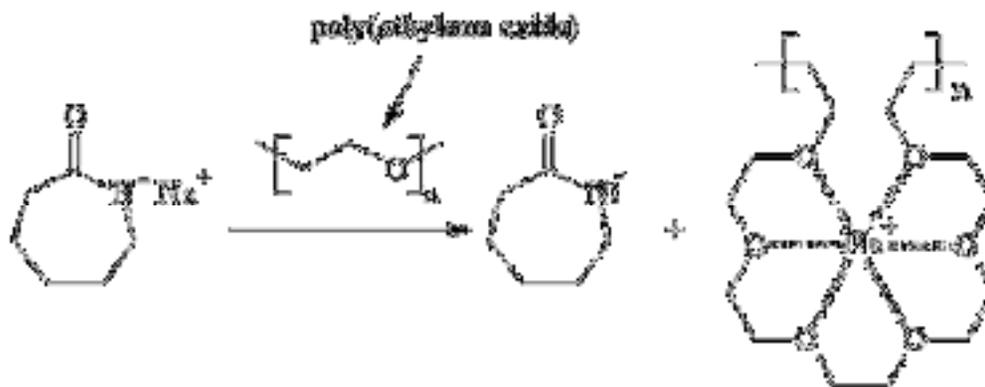


Figure 1

Now the leftover sodium cation can form a salt with the negatively charged nitrogen that is left behind when the hydrogen is extracted. But we don't want that. We want the nitrogen to be a free anion, because it will be more reactive that way. So we're going to throw some poly(ethylene oxide) into the reaction mixture. This will complex the sodium cation, keeping it from associating with the anionic nitrogen. You can see this in Figure 2.

Figure 2



So the nitrogen, free to react, will donate an unshared pair of electrons to the carbonyl carbon of another caprolactam molecule. (Remember, carbonyl carbons are electron deficient, and are easily attacked by anions.) After some electron-shuffling in which the electrons in the bond between the carbonyl carbon and the amide nitrogen shift to the nitrogen, the second caprolactam molecule ring-opens, as you can see in Figure 3.



Figure 3

The new molecule formed also has a negatively-charged nitrogen, an amine anion. This is an unstable species, so the activation energy is high for this step. This makes this the slow step of the reaction. For this reason, there is an induction period at the beginning of the reaction before polymerization begins.

Being unstable, that anionic nitrogen will abstract a proton from *another* molecule of  $\epsilon$ -caprolactam, as Figure 4 clearly shows.

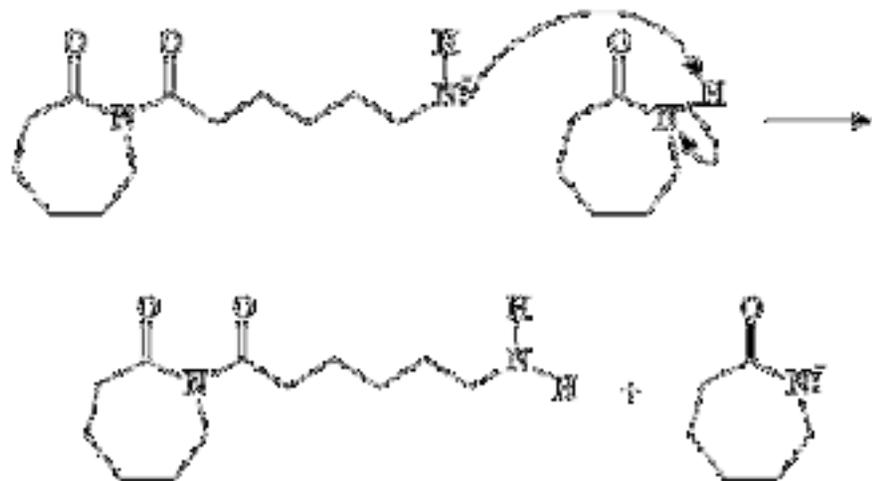


Figure 4

We have an anion of gamma -caprolactam once again, and the negatively charged nitrogen attacks the ring carbonyl carbon of the species we just formed. Take a look at Figure 5 and you'll see what's happening.

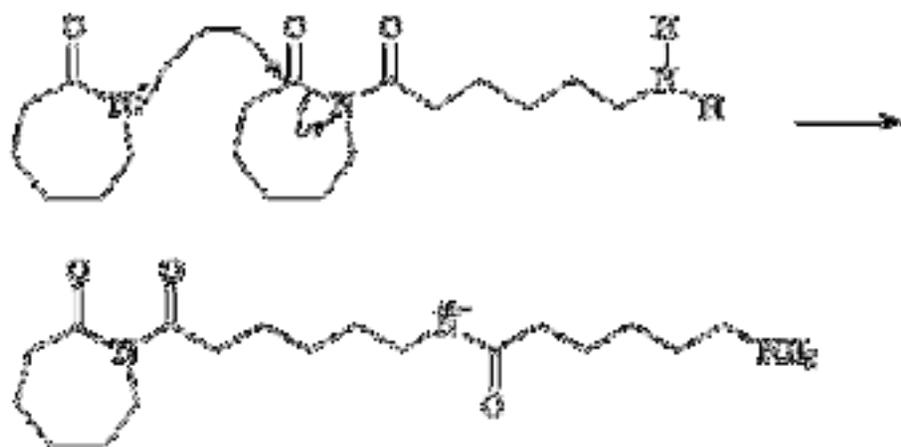


Figure 5

This step is faster than the first ring opening step, the one in Figure 3, because the starting species involved this time is much more reactive. You see, the reacting compound this time is an *imide*, a compound with a nitrogen atom bonded to *two* carbonyl carbons. The last time we were reacting an *amide*, which is a compound with a nitrogen bonded to only one carbonyl carbon. Imides are much more reactive than amides.

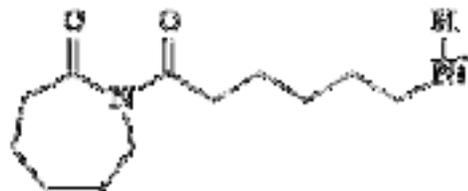


This is a reactive imide.

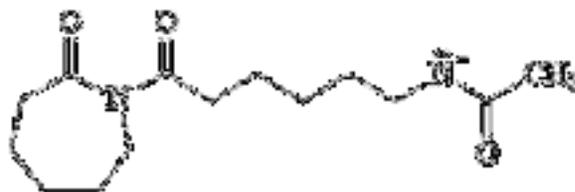


$\alpha$ -Chloroimide is an unreactive imide.

Part of the reason why imides are more reactive than amides is the fact that when an imide ring-opens we get an *amide* anion, whereas the product of an amide ring-opening is an *amine* anion. Amine anions are very unstable, but amide anions are more stable because the negative charge is stabilized by the carbonyl group bonded to the nitrogen atom.



This is an unstable amine anion. We get this when we make ring-open.



This is a relatively stable amide anion. We get this when we make ring-open.

Of course, this gives us another unstable nitrogen negative charge, and it takes a proton from another  $\epsilon$ -caprolactam molecule, which then adds to the growing chain in the same way as we saw before. This keeps happening over and over until we get high molecular weight nylon 6.

Just one more thing...remember that the first ring-opening step was so slow? We can get around this slow step by throwing a little bit of *N*-acetylcaprolactam into the reaction mixture. Not only is this a reactive imide, just like the rings in our growing chain, but it produces an amide anion when it ring-opens rather than an unstable amine anion. It takes the place of  $\epsilon$ -caprolactam in the first step, so the slow step is eliminated, and so is that annoying induction period.



*N*-acetylcaprolactam

This reaction won't work well without poly(ethylene oxide) or *N*-acetylcaprolactam. But add both of them and you can get high molecular weight nylon 6 after heating the mixture for 2-3 minutes. Just don't heat it longer, because your polymer will thermally degrade. The molecular weight will drop, and then you won't be able to draw good fibers from your polymer. Your fibers will be hard to draw and they will also be brittle, so don't let it cook for too long!

## COPOLYMERS

When a polymer is made by linking only one type of small molecule, or monomer, together, it is called a *homopolymer*. When two different types of monomers are joined in the same polymer chain, the polymer is called a copolymer. Let's imagine now two monomers, which we'll call *A* and *B*. *A* and *B* can be made into a copolymer in many different ways.

When the two monomers are arranged in an alternating fashion, the polymer is called, of course, an *alternating copolymer* (below). One interesting fact about this type is that the ratio of the two monomers is exactly 1:1. Very few copolymerizations give this type of structure, however.



### alternating copolymer

In a *random copolymer*, the two monomers may follow in any order (figure below). The ratio of the monomers incorporated into the copolymer is a result of a combination of the properties of the monomers, the polymerization conditions and the conversion of the polymerization, to name a few variables. For example, unless the two monomers have exactly the same reactivity, both with the other comonomer and with their own monomers, the ratio in the product will NOT be exactly 1-to-1. In fact, in most cases it's not, and this results in a change in the copolymer composition as the reaction proceeds. At the beginning, the more reactive monomer is incorporated more than the less reactive one.

But things change as monomers are used up and the concentration of the more reactive one decreases faster/more than that of the less reactive one. Things even out at some ratio of concentrations, giving polymer that is about 1-to-1 in composition. But now there's less of the more reactive one so it's used up faster as the reaction continues, causing the ratio of concentrations to change further till there's mostly just the less reactive monomer present. Copolymers made at this point will have more of the less reactive monomer. While you might measure an "average" composition of monomers in the final product (using NMR or FTIR or some other method), the composition of individual chains may (will) be much different than that average. And here's the kicker: the total combination of all those copolymer chains, varied in composition as they are, determines the final properties of the material made. So as they say nowadays: "It's complicated..."



**random copolymer**

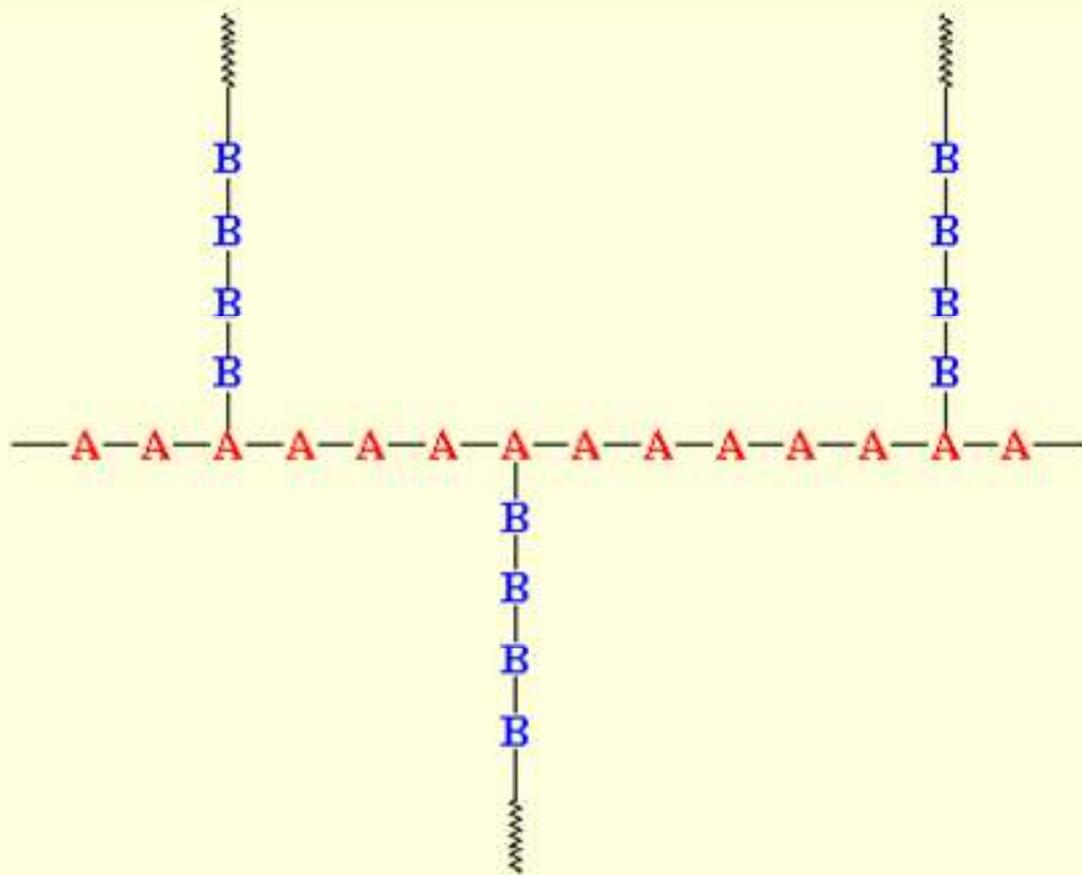
In a *block copolymer*, all of one type of monomer are incorporated together in one part of the chain, and then all of the other are reacted in somehow. A block copolymer can be thought of as two homopolymers joined together at one of the ends (below). Not surprisingly, it's not easy or cheap to make such a copolymer, so in fact, there aren't many commercial examples.



**block copolymer**

A blocky copolymer that you know very well, that is, if you wear shoes, is SBS rubber. It's used for the soles of shoes and for tire treads, too. "Blocky" means it has some of the characteristics of a true block copolymer but isn't as uniform in composition.

When chains of a polymer made of monomer *B* are grafted onto a polymer chain of monomer *A* we have a *graft copolymer* (see the figure). There are a number of ways to do this: grafting from; grafting to; or the most controlled way of using a "macromonomer." Say what? Yeah, sounds a little strange, but we're talking about a long polymer chain with a single functional group at the end that can react with the small comonomer molecules present to give the grafted structure.



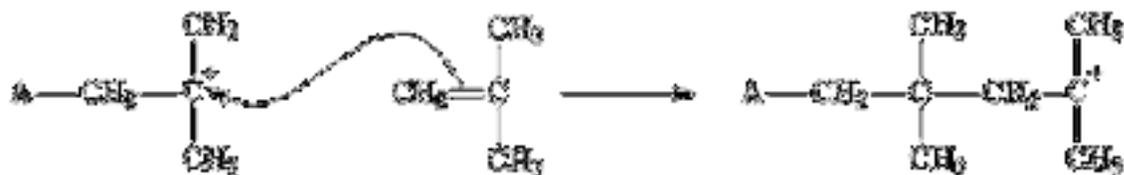
graft copolymer

One kind of commercial graft copolymer is high-impact polystyrene, or HIPS for short. It's a polystyrene backbone with chains of polybutadienegrafted onto the backbone. The polystyrene gives the material strength, but the rubbery polybutadiene chains give it resilience to make it tough and less brittle.

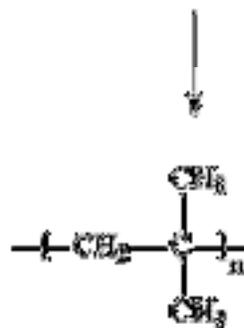
## **Ionic polymerization**

Cationic polymerization is a way of making polymers from small molecules, or monomers, which contain carbon-carbon double bonds. Its primary commercial use is for making polyisobutylene.

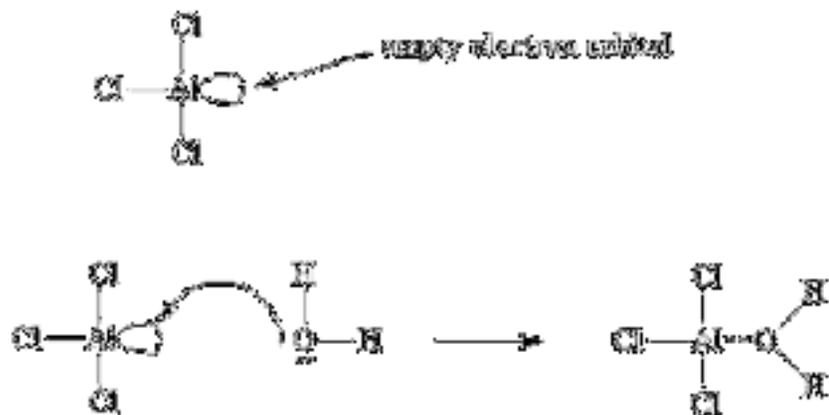
In cationic vinyl polymerization, the initiator is a cation, which is an ion with a positive electrical charge. It is shown as  $A^+$  in the picture. A pair of electrons, negatively charged, from the carbon-carbon double bond will be attracted to this cation, and will leave the carbon-carbon double bond to form a single bond with the initiator, as shown. This leaves one of the former double bond carbons at a loss for electrons, and carrying a positive charge. This new cation will react with a second monomer molecule in the same manner as the initiator reacted with the first monomer molecule. This happens over and over until a high molecular weight is reached, that is, a molecular weight at which the polymer is useful for something.



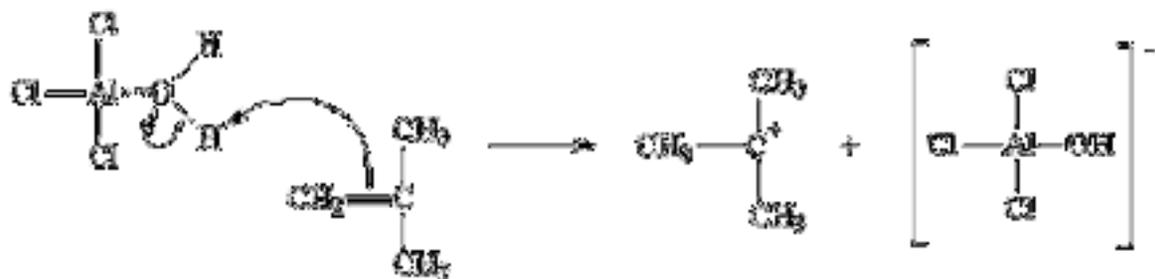
Note: When a line is drawn between two atoms, this represents a pair of electrons the atoms share. Showing one pair of electrons makes a single bond. Showing two pairs makes a double bond, shown by two lines. The curved arrows show the motion of a pair of electrons.



Many times, though, it starts off in little bit more complicated manner than that. Normally, the initiator used is something like aluminum trichloride, or  $\text{AlCl}_3$ . If you know the octet rule, you'll know that all atoms on the second row of the periodic table like to have eight electrons in their outermost shell, or level. The aluminum atom in  $\text{AlCl}_3$  is sharing electron pairs with only three other atoms, leaving it with only six electrons, two short of the magical octet. As it sits, it has a whole orbital (that is, a vacant slot where a pair of electrons should be) empty and ready for something to come along and fill it. It just so happens, much to the delight of that aluminum atom, that a very small amount of water is usually present in the system. Now the oxygen atom in water has two unshared pairs of electrons, and it most graciously donates a pair to the aluminum atom, forming an  $\text{AlCl}_3$  and  $\text{H}_2\text{O}$  complex.

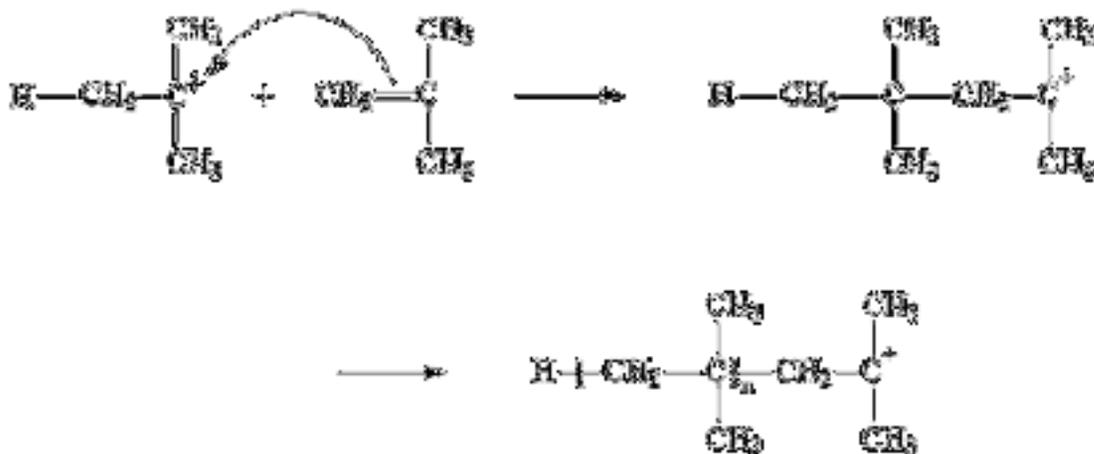


Oxygen, being very electronegative, will tend to pull the electrons it shares with the hydrogens atoms toward itself, leaving the hydrogen atoms with a slight positive charge. This leaves them ripe for attack by a pair of electrons from the double bond of a monomer molecule. The monomer in this way can swipe the hydrogen, making itself a cation, and the  $\text{AlCl}_3/\text{H}_2\text{O}$  complex becomes its complement anion,  $\text{AlCl}_3\text{OH}^-$ . This whole process by which the  $\text{AlCl}_3/\text{H}_2\text{O}$  complex forms and reacts with the first monomer molecule is called *initiation*.



You can see we've got a new cation after all this is done. Not just a cation, a *carbocation*. That's what we call a cation where the positive charge is on a carbon atom (duh!). Carbocations are very unstable. They're unstable because the carbon atom in a carbocation only has six electrons in its outermost shell. Six! That's *two* electrons short of the eight that all carbon atoms want to have in their outermost shells. So a carbocation will do just about anything to get two more electrons and reach the magic octet.

So the carbocation looks around, and finds a pair of electrons in the double bond of a nearby monomer molecule. (Remember there are two pairs of electrons in a double bond.) So the carbocation swipes those electrons, and in doing so forms a single bond with the monomer molecule. It also generates another carbocation, as you can see in the picture below. This can react with another monomer, and then another, and so on. Eventually we get a long polymer chain.

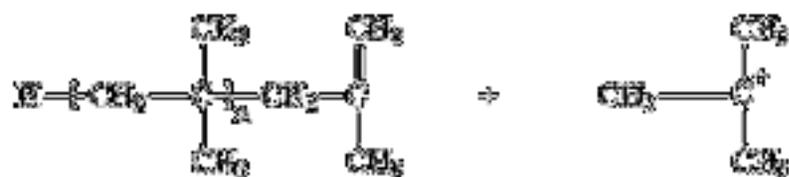


This process, by which monomer after monomer is added to form a polymer, is called *propagation*.

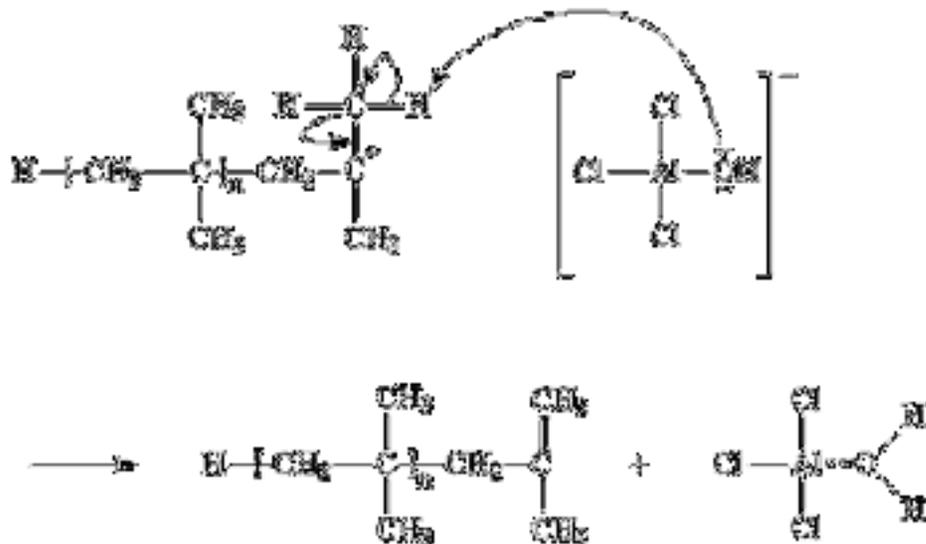
But how does it end? How does this cycle of adding more monomer molecules to the growing polymer stop? The most common way goes something like this... Imagine the growing chain of polyisobutylene. The methyl groups attached to

the cationic carbon atom have a little problem: they've got hydrogen trouble. The hydrogens on these methyl groups will, without a whole lot of persuasion, break away and join other molecules. This is just what can happen when they come close to a molecule of monomeric isobutylene. Starved for electrons as they are, being part of a cation, these hydrogens are easily attacked by a pair of electrons from the carbon-carbon bond in the isobutylene molecule. When all the electrons are through rearranging themselves, as shown by the arrows, we're left with a neutral polymer chain with a double bond at its end, and a new cation, formed from the isobutylene molecule. The polymer chain end is now neutral, and can no longer react and grow. But the new cation can start a new chain growing, in the same way as our initiator molecule did. This process is called *chain transfer*. It also happens in free radical polymerization, and other kinds of polymerization as well.

These hydrogen atoms  
like to split off and join  
other molecules



That particular kind of chain transfer is called *chain transfer to monomer*. But there's another kind of chain transfer. To understand, it helps to remember that for every cation, there is an anion lurking somewhere in the same beaker. Remember that  $\text{AlCl}_3\text{OH}^-$  ion? As we all know, cations and anions have this nasty tendency to react with each other, which can be troublesome when we want our cation to react with something else, like a monomer molecule. Let's take a look at how this happens.



When the cationic initiator reacts, and forms a growing cationic chain, the old anion of the initiating cation becomes the anion of the growing polymeric cation. Remember that anions tend to have pairs of electrons floating around with nothing to do, and, what did mother always say, idle hands do the devil's work? That's just what happens here. The electrons of the anion will, from time to time, attack the hydrogen atoms on the methyl groups adjacent to the cationic carbon. Remember these hydrogen atoms? They're the ones that were so eager to be snatched away by a nearby monomer molecule. Sometimes, not often but sometimes, these hydrogens will very easily react with the unshared electrons of the oxygen atom in the anion in the exact same manner, leaving the same dead polymer chain with a double bond at its end. But on the bright side, the  $\text{AlCl}_3/\text{H}_2\text{O}$  complex is regenerated, and it can start new polymers growing just as it did earlier. Yet another case of the villainous chain transfer.

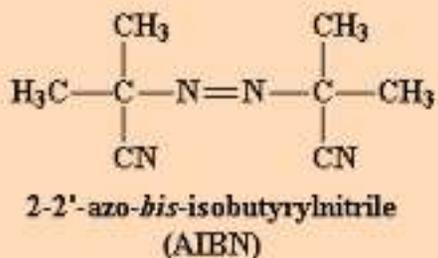
Of course, it doesn't always turn out so well. At times it is the unshared pairs of electrons from a chlorine atom which will react, not with one of the hydrogen atoms, but with the cationic carbon atom itself. It leaves the counterion, and joins the polymer. We're then left with a different kind of dead polymer, ending in a chlorine atom, and  $\text{AlCl}_2\text{OH}$ , which won't start a new polymer chain growing

This process is called *termination*, because no new chains are started. It's the last of the three major steps in any chain growth polymerization, the first two being initiation and propagation, of course. When termination happens, the polymerization is over.

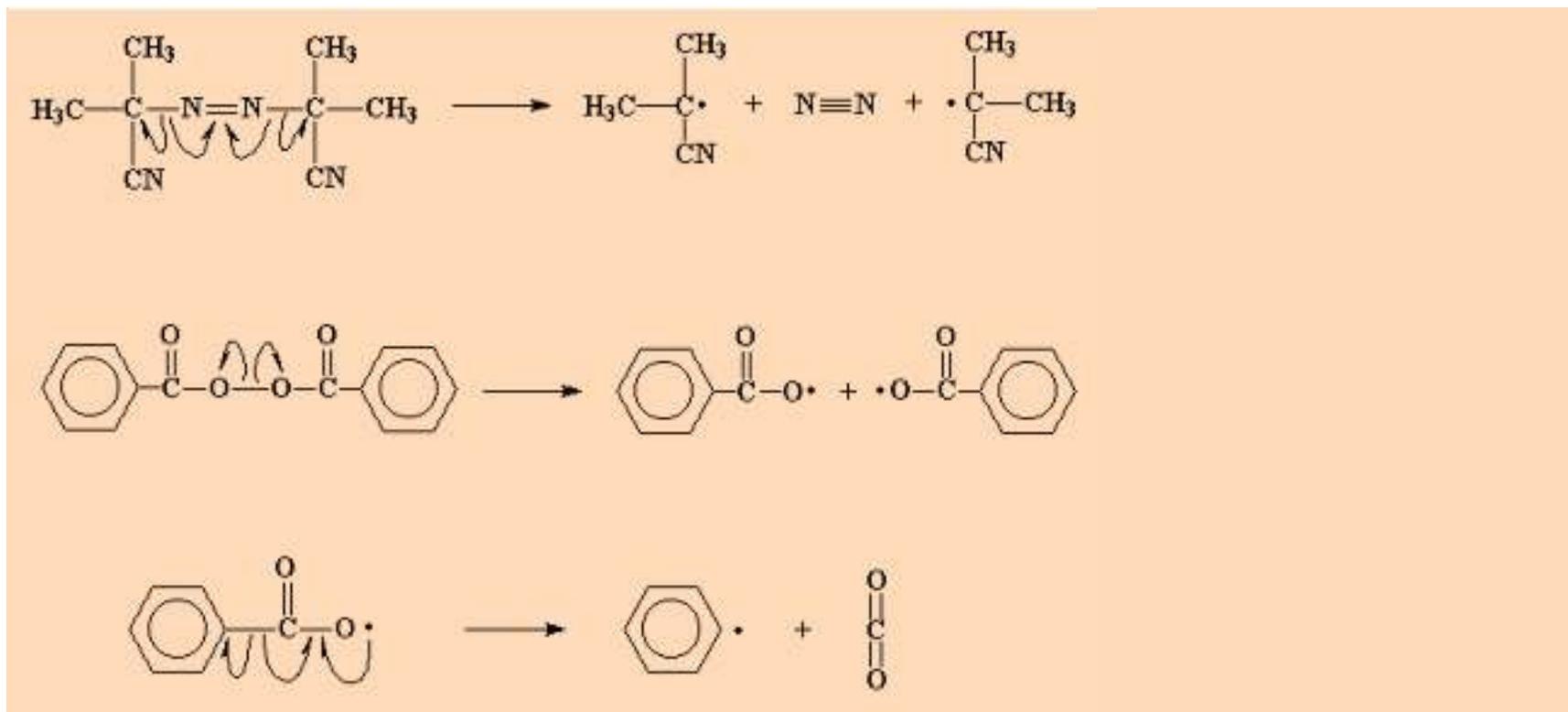
## **Free radical polymerization**

One of the most common and useful reactions for making polymers is free radical polymerization. It is used to make polymers from vinyl monomers; that is, from small molecules containing carbon-carbon double bonds. Polymers made by free radical polymerization include polystyrene, poly(methyl methacrylate), poly(vinyl acetate) and branched polyethylene.

This is the same benzoyl peroxide that rids teenage faces of zits and transforms angst-ridden adolescents into popular, happy, and attractive young citizens, or so the ads claim.

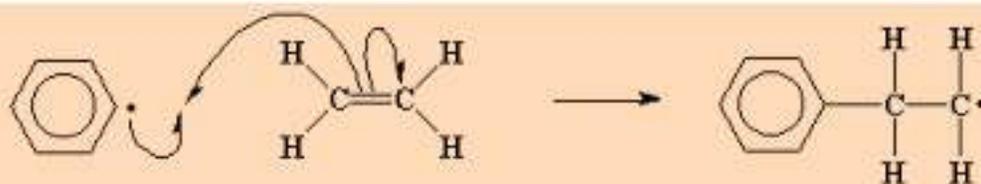


The whole process starts off with a molecule called an initiator. This is a molecule like benzoyl peroxide or 2,2'-azo-bis-isobutyronitrile (AIBN). What is special about these molecules is that they have an uncanny ability to fall apart, in a rather unusual way. When they split, the pair of electrons in the bond which is broken, will separate. This is unusual as electrons like to be in pairs whenever possible. When this split happens, we're left with two fragments, called *initiator fragments*, parts of the original molecule, each of which has one unpaired electron. Molecules like this, with unpaired electrons are called *free radicals*.



these unpaired electrons will be quite discontent with being alone and still want to be paired. If they can find ANY electrons to pair up with, they will do so. The carbon-carbon double bond in a vinyl monomer, like ethylene, has a pair of electrons which is very easily attacked by the free radical. The unpaired electron, when it comes near the pair of electrons, can't help but swipe one of them to pair with itself. This **new** pair of electrons forms a new chemical bond between the initiator fragment and one of the double bond carbons of the monomer molecule. This electron, having nowhere else to go, associates itself with the carbon atom which is not bonded to the initiator fragment. You can see that this will lead us back where we started, as we now have a **new** free radical when this unpaired electron comes to roost on that carbon atom. This whole process, the breakdown of the initiator molecule to form radicals, followed by the radical's reaction with a monomer

molecule is called the *initiation* step of the polymerization.

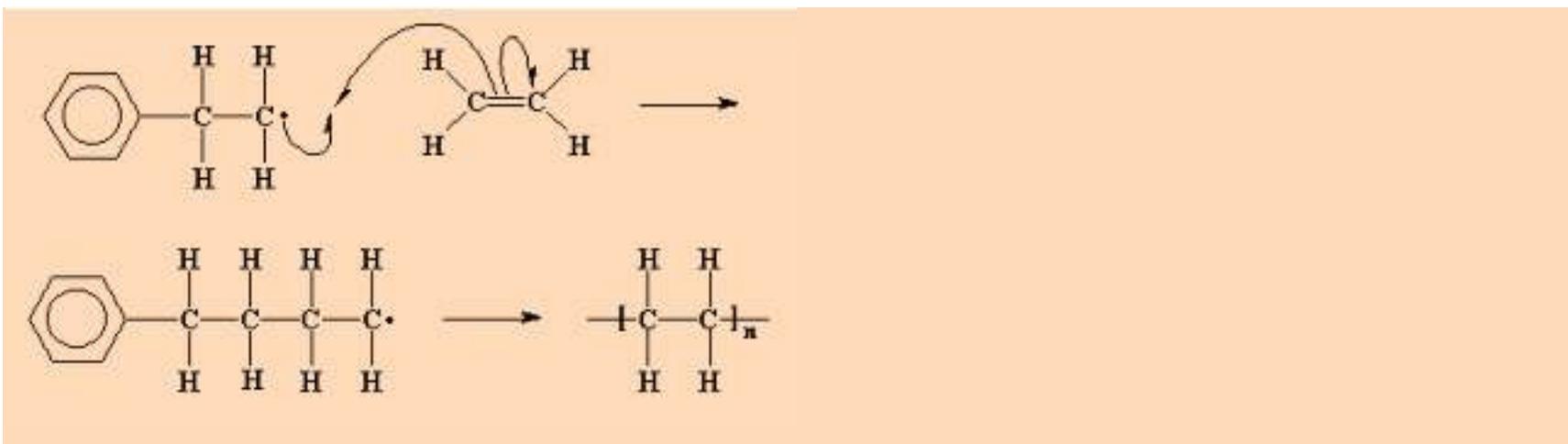


If you want to see a movie of benzoyl peroxide breaking down to form radicals and then reacting with ethylene

Wouldn't you know it, this new radical reacts with **another** ethylene molecule in the exact same way as the initiator fragment did. Of course, as we can see, this gets us nowhere as far as pairing electrons goes, because we always form another radical when this reaction takes place over and over again.

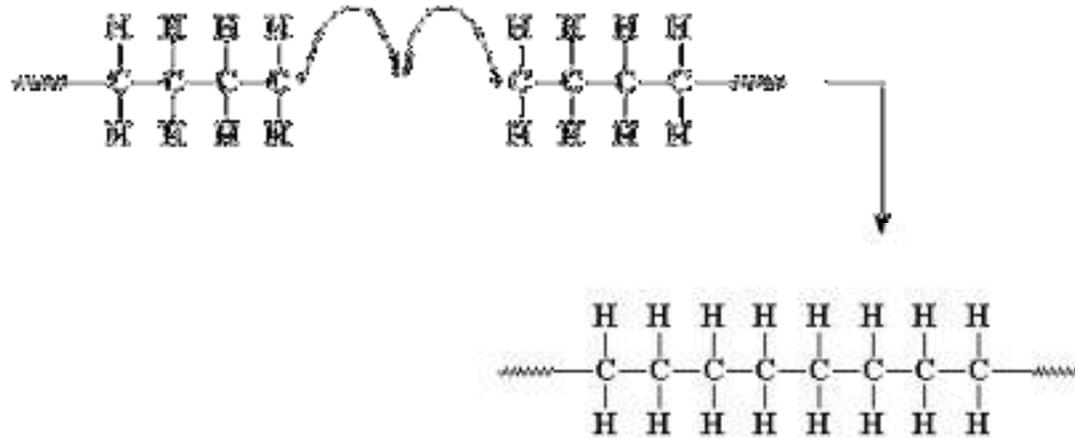
This process, the adding of more and more monomer molecules to the growing chains, is called *propagation*.

Because we keep remaking the radical over and over again, we can keep adding more and more ethylene molecules, and build a long chain of them. Self-perpetuating reactions like this one are called *chain reactions*. So as long as the chain keeps growing, who really cares if a few electrons remain unpaired?



Fortunately, the electrons care. Radicals are unstable, and eventually they are going to find a way to become paired without generating a new radical. Then our little chain reaction will come grinding to a halt. This happens in several ways. The simplest way is for two growing chain ends to find each other. The two unpaired electrons then join to form a pair, and a new chemical bond joining their respective chains. This is called *coupling*.

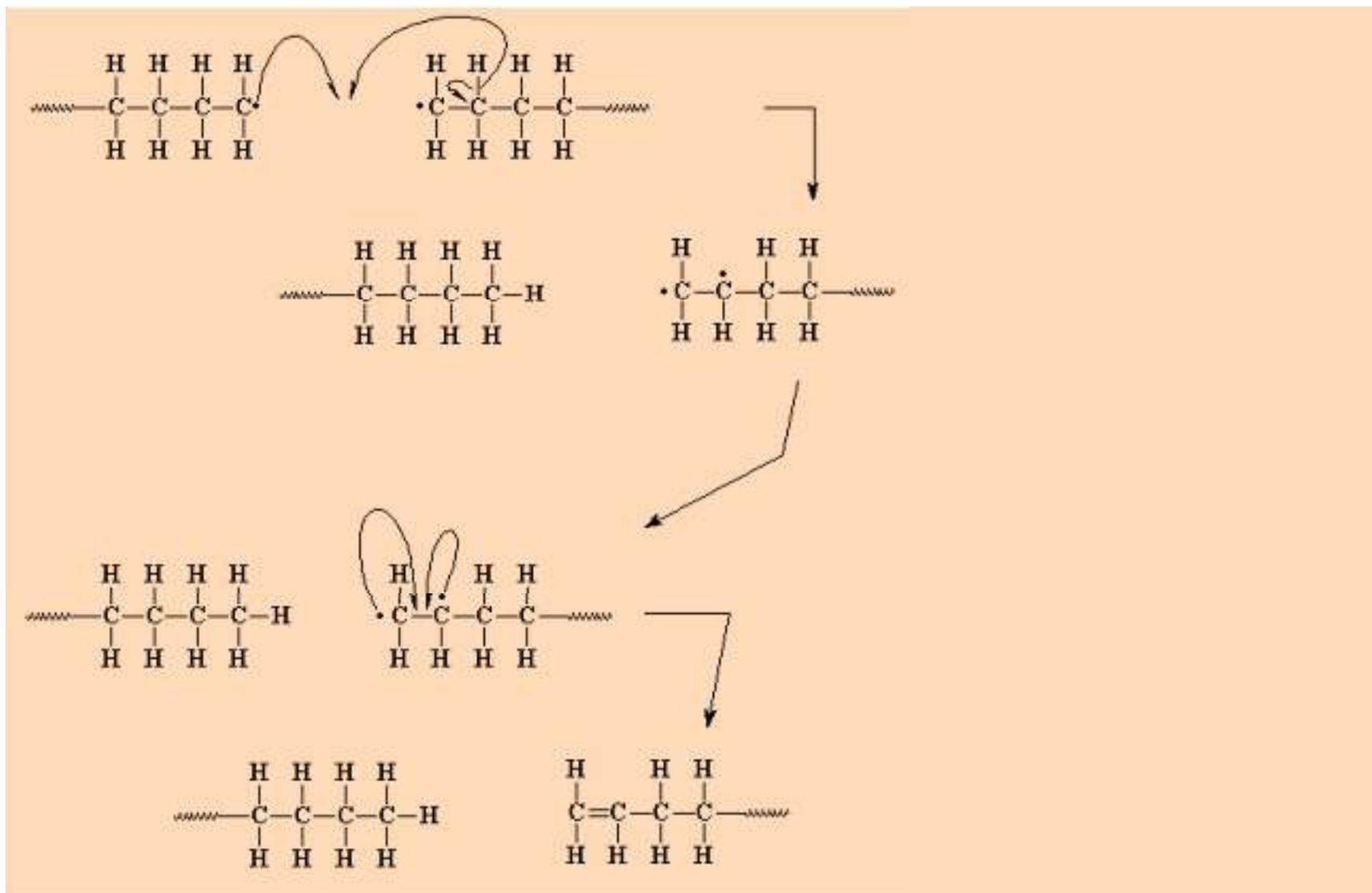
Coupling is one of two main types of *termination reaction*. Termination is the third and final step of a chain-growth polymerization. Initiation and propagation are the first two steps, of course.



Now here comes the other termination reaction in which our unpaired electrons can shut down the polymerization: it's called *disproportionation*. This is a rather complicated way in which two growing polymer chains solve the problem of their unpaired electrons. In disproportionation, when two growing chain ends come close together, the unpaired electron of one chain does something strange. Rather than simply joining with the unpaired electron of the other chain, it looks elsewhere for a mate. It finds one in the carbon-hydrogen bond of the carbon atom *next* to the other carbon radical. Our unpaired electron grabs not only one of the electrons from this bond, but the hydrogen atom as well. Now our first chain has no unpaired electrons, the end carbon now shares eight electrons with carbons and hydrogens, so everyone is happy.

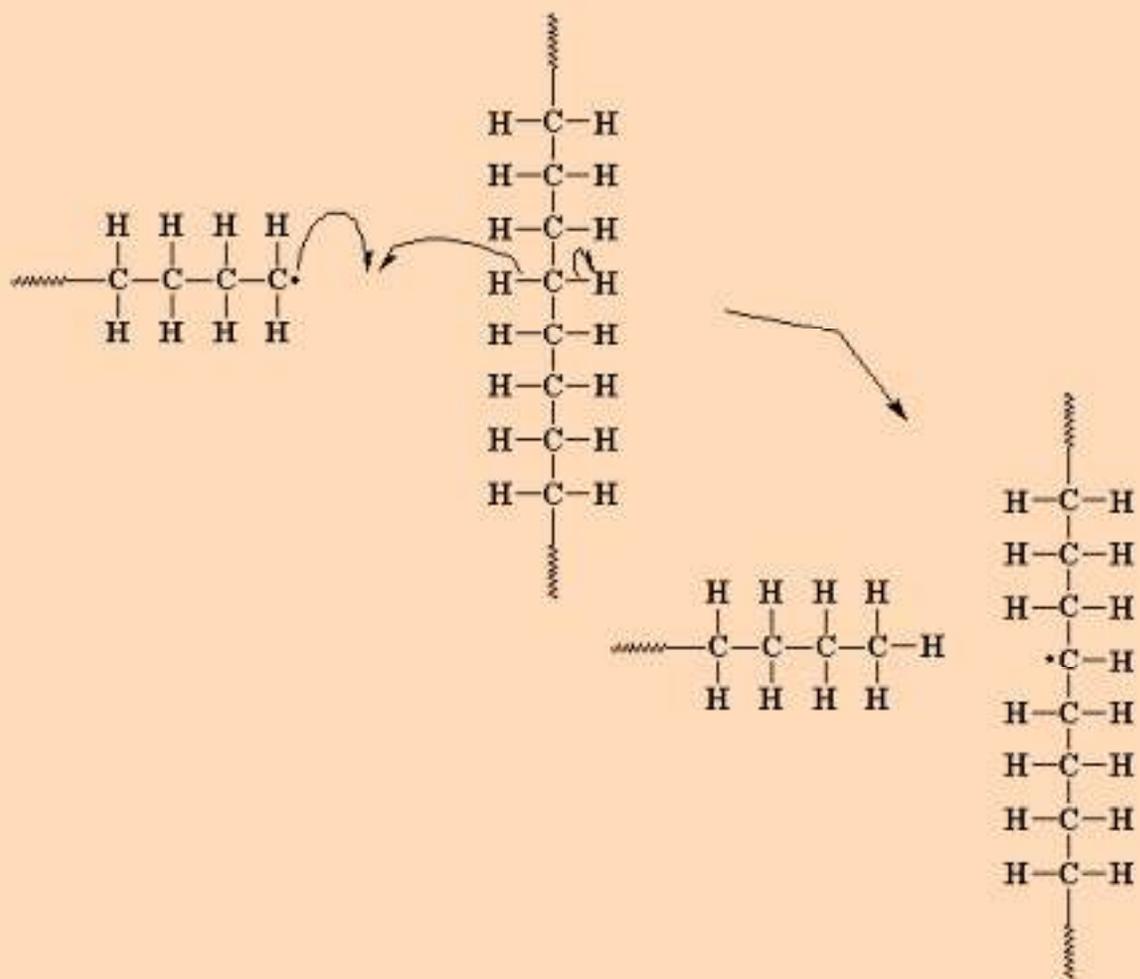
This electron can find a mate  
by swiping an electron from the  
pair of electrons which makes  
up this bond.



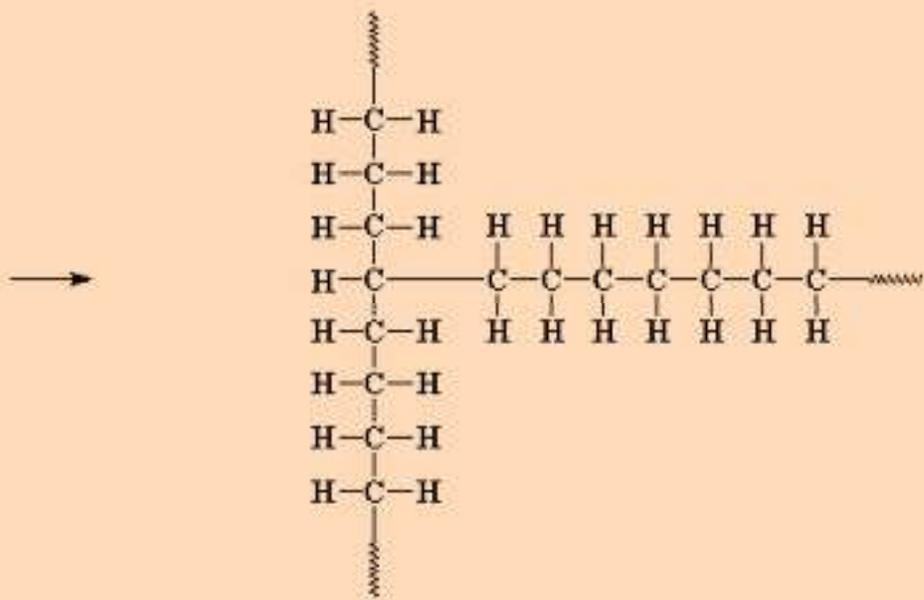
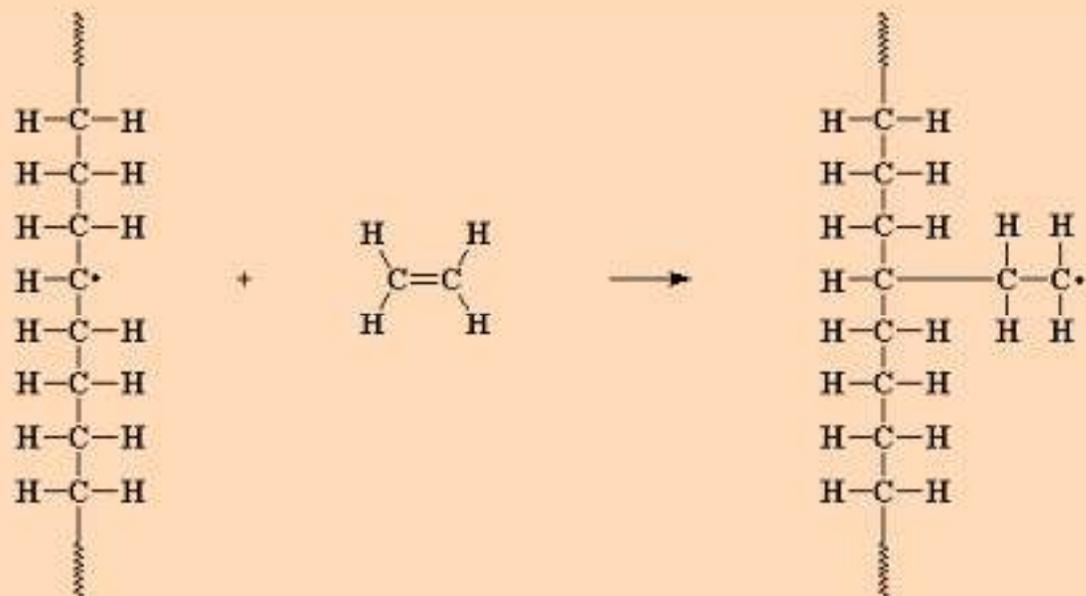


Everyone, that is, except for the polymer chain which lost its hydrogen atom. It now has not only one carbon atom with an unpaired electron, but two! Now this looks bad but it's really not too difficult a problem, as it

turns out. The two carbon radicals, being right next to each other, can easily join their unpaired electrons to form a pair, and thus form a chemical bond between the two carbon atoms. Now the two atoms already shared one pair of electrons, and the second shared pair creates a *double bond* at the end of the polymer chain.



Sometimes, the unpaired electron at the end of a growing chain is so unhappy that it will pair itself with an electron from a carbon-hydrogen bond along the backbone of another polymer chain. This leaves an unpaired electron which is nowhere near the propagating chain end. This electron can't form a double bond the way the electron from the last example did, but it can and will react with a monomer molecule, just the way the initiator fragment did. This starts a new chain growing out of the middle of first chain! This is called *chain transfer to polymer*, and the result is a *branched polymer*. It is especially a problem with polyethylene, so much so that linear non-branched polyethylene can't be made by free radical polymerization.



Such branching reactions have a big effect on how polyethylene behaves. To find out how, and how getting rid of branching helped make lowly polyethylene better than Kevlar® for use in bullet proof vests, visit the fun-filled, fact-filled and just plain fascinating polyethylene page.

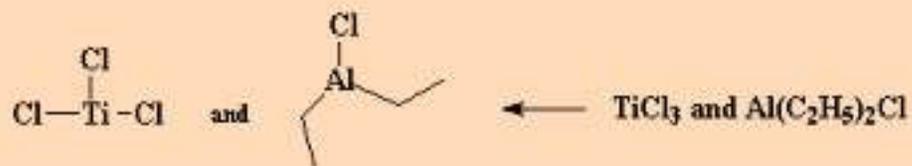
## **Ziegler natta polymerization**

Ziegler-Natta polymerization is a method of vinyl polymerization. It's important because it allows one to make polymers of specific tacticity. It was discovered by two scientists, and I think we can all figure out what their names were. Ziegler-Natta catalysis is especially useful, because it can make polymers that can't be made any other way, such as linear unbranched polyethylene and isotactic polypropylene. Free radical vinyl polymerization can only give branched polyethylene, and propylene won't polymerize at all by free radical polymerization. So this is a pretty important polymerization reaction, this Ziegler-Natta stuff.

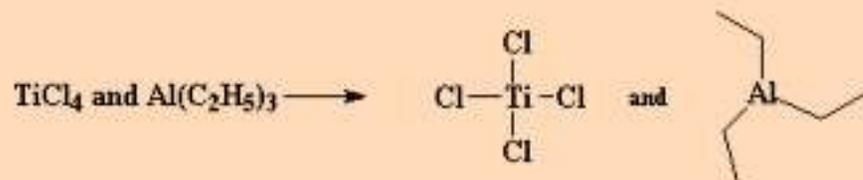
So then how does it work? Well, it's something like this: Take your Ziegler-Natta catalyst, usually  $TiCl_3$  or  $TiCl_4$ , along with an aluminum based co-catalyst, and place in the monomer at midnight on the night of the full moon. Then place the beaker on the ground in a circle of lighted candles. Now write the word "isotactic" or "syndiotactic", depending on the tacticity you desire, in runic letters on the side of the beaker with the blood of a freshly slain goat. The goat must be less than one year old, and without blemish. Then one must recite aloud the Ziegler-Natta incantation seven times, followed by the tacticity dance. If the polymerization is successful, a cold and violent wind will quickly arise and extinguish the candles, and then die away as quickly as it arose. It is important that one fast for three days before and after carrying out the ceremony. Following this little procedure usually does the trick.

Ok, so that's not really how it works, but our knowledge of how Ziegler-Natta polymerization works, and why one initiator system will work better than another, is rather limited. Picking the right conditions to make a Ziegler-Natta polymerization work often feels more like magic than science. But we do know a little bit.

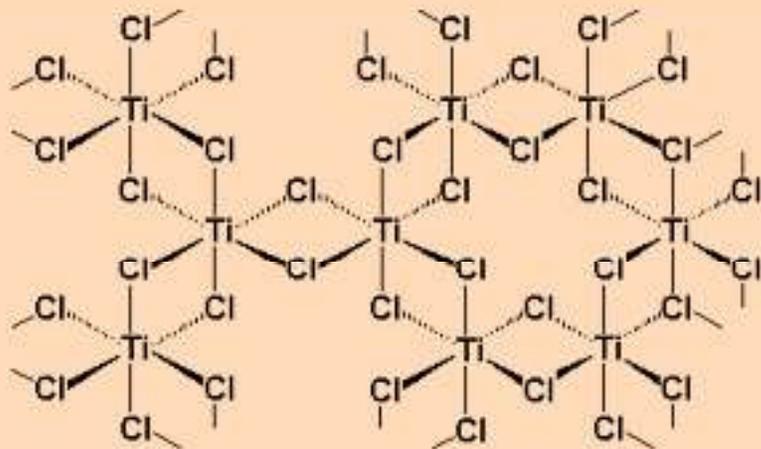
We know that it involves transition metal catalyst, like  $\text{TiCl}_3$ . We also know that co-catalysts are involved, and these are usually based on group III metals like aluminum. Most of the time our catalyst/co-catalyst pair are  $\text{TiCl}_3$  and  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ , or  $\text{TiCl}_4$  with  $\text{Al}(\text{C}_2\text{H}_5)_3$ .



These are two sets of Ziegler-Natta catalyst/co-catalyst systems. Either way, we have four chlorine atoms.

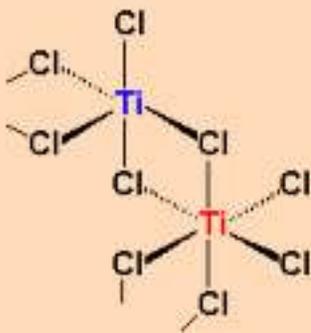


To make things simple, we'll worry about the  $\text{TiCl}_3$  and  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  system. It helps to know something about  $\text{TiCl}_3$  to know how the system works to make polymers.  $\text{TiCl}_3$  can arrange itself into a number of crystal structures. The one that we're interested in is called  $\alpha\text{-TiCl}_3$ . It looks something like this:



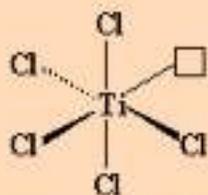
a crystal of  $\alpha$ -TiCl<sub>3</sub>

As we can see, each titanium atom is coordinated to six chlorine atoms, with octahedral geometry. That's how titanium is happiest, when it's coordinated to six other atoms. This presents a problem for the titanium atoms at the surface of the crystal. In the interior of the crystal, each titanium is surrounded by six chlorines, but on the surface, a titanium atom is surrounded on one side by five chlorine atoms, but on the other side by empty space!



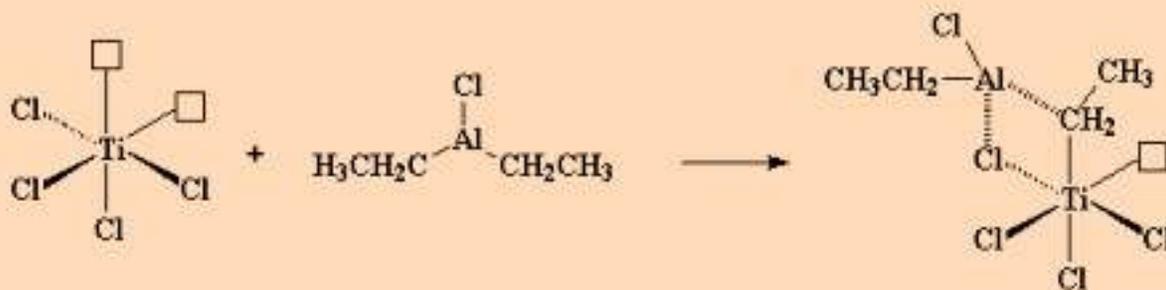
While the titanium on the interior (in red) has six chlorine neighbors, the surface titanium (blue) only has five.

This leaves poor titanium a chlorine short. Can't it just deal with it and get on with its life? Well, no. You see, titanium is one of those transition metals, and what do we know about transition metals? We know that they have six empty orbitals (resulting from one  $4s$  and five  $3d$ -orbitals) in their outermost electron shells. To be happy, titanium has to be coordinated with enough atoms to put two electrons in each of the orbitals. The titanium atom on the surface of the crystal has enough neighbor atoms to fill five of the six orbital. We're left with an empty orbital, shown as an empty square in the picture below.



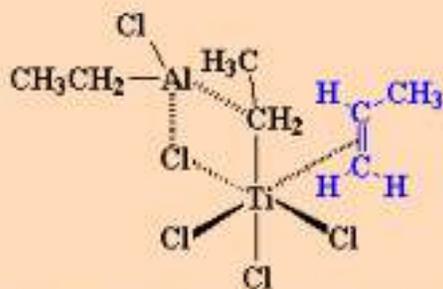
**A surface titanium has an empty orbital.**

Now this state of affairs can't go on. That titanium wants to fill its orbitals. But first,  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  enters the picture. It donates one of its ethyl groups to the impoverished titanium, but kicks out one of the chlorines in the process. We still have an empty orbital. But more about that in a moment.



As you can see in this picture, the aluminum has a hard time letting go. It stays coordinated, though not covalently bonded, to the CH<sub>2</sub> carbon atom of the ethyl group it just donated to the titanium. Not only that, but it also coordinates itself to one of the chlorine atoms adjacent to the titanium. But titanium still has one empty orbital left to be filled.

So then a vinyl monomer like propylene comes along. There are two electrons in the  $\pi$ -system of a carbon-carbon double bond. Those electrons can be used to fill the empty orbital of the titanium. We say that the propylene and the titanium form a *complex*, and we draw it like this:

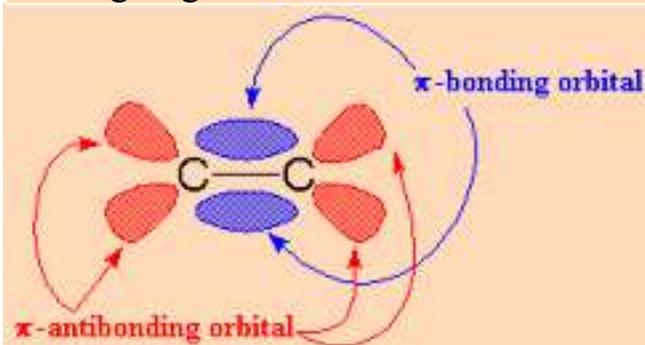


The  $\pi$ -electrons from propylene end up filling titanium's empty orbital.

But complexation is a rather complicated process, not nearly as simple as this picture implies. Those who want the whole story can read how this complexation works, and those who want the short version, can skip straight to the polymerization:

## Alkene-metal complexes

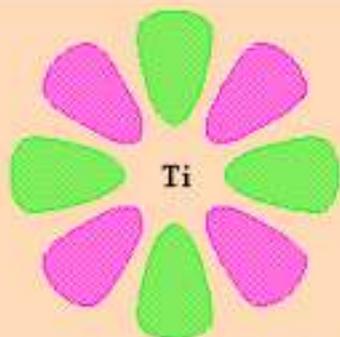
This is where it starts to get interesting. Suppose at this point that a vinyl monomer showed up, let's say, a molecule of propylene. The titanium is going to enjoy this. To understand why, let's take a look at vinyl monomer, specifically, its double bond. A carbon-carbon double bond, is made up of a  $\sigma$  bond and a  $\pi$  bond. We're going to take a closer look at that  $\pi$  bond.



The  $\pi$ -orbitals of an alkene monomer

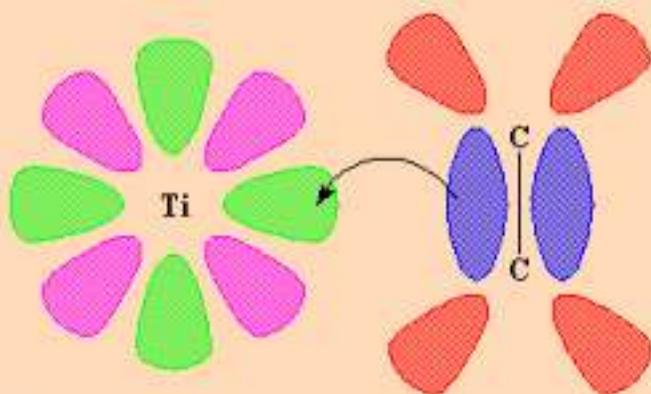
Take a look at the picture and you'll see that the  $\pi$  bond consists of two  $\pi$ -orbitals. One is the  $\pi$ -bonding orbital (shown in blue) and the other is the  $\pi$ -antibonding orbital (shown in red). The  $\pi$ -bonding orbital has two lobes sitting between the carbon atoms, and the  $\pi$ -antibonding orbital has four lobes, sticking out away from the two carbon atoms. Normally the pair of electrons stays in the  $\pi$ -bonding orbital. The  $\pi$ -antibonding orbital is too high in energy, so under normal circumstances it's empty.

Let's look again at titanium for a moment. This picture shows titanium and two of its outermost orbitals. (Yes, it has more than two, but we're only going to show two right now for clarity.)



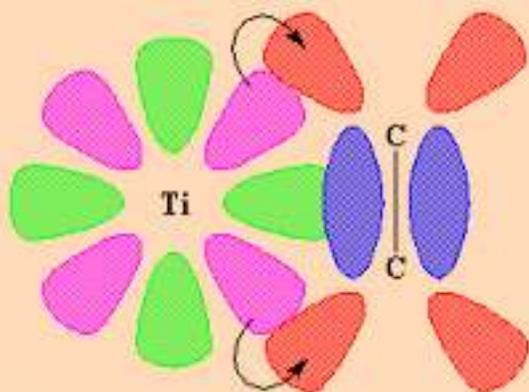
Titanium has six orbitals (one  $4s$  and five  $3d$ ) in its outermost shell, but we're only going to show two: a filled one is in pink and the empty one we've been talking about is shown in green.

One of the titanium orbitals that we've shown is that empty orbital. It's made of the green lobes. The pink lobes are one of the filled orbitals. That empty orbital is going to look for a pair electrons, and it knows just where to look. It knows that the alkene's  $\pi$ -bonding orbital has a pair that it will share. So the alkene's  $\pi$ -bonding orbital and the titanium's  $d$ -orbital come together and share a pair of electrons.



The electrons from the alkene's  $\pi$ -bonding orbital fit nicely into the empty orbital of the titanium.

But once they're together, that other orbital (the pink one) comes mighty close to that empty  $\pi$ -antibonding orbital. So the titanium orbital and the  $\pi$ -antibonding orbital share a pair of electrons, too.



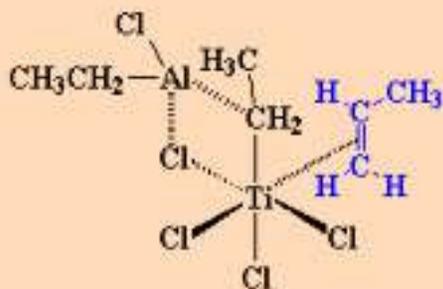
**Then electrons from one of the filled orbitals can slip into the alkene's  $\pi$ -antibonding orbital, making the titanium alkene complex stronger.**

This additional sharing of electrons makes the complex stronger. This complexation between the alkene and the titanium sets things up for the next step of the polymerization.

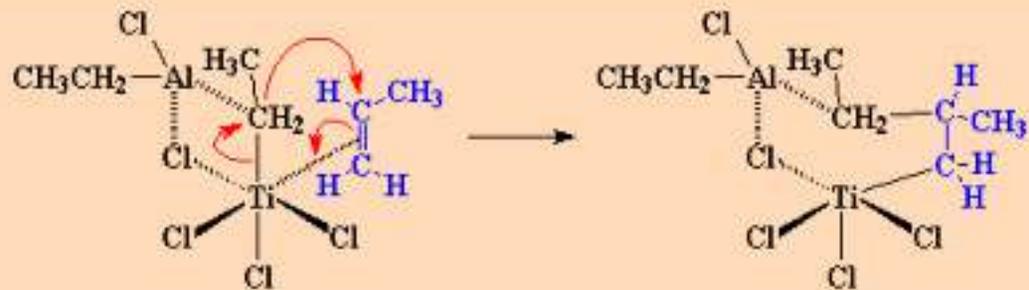
## The Polymerization

### Part One: Isotactic Polymerization

The precise nature of the complex between the titanium and the propylene is complicated. So to make things simple we're going to just draw it like we did earlier from now on, like this:

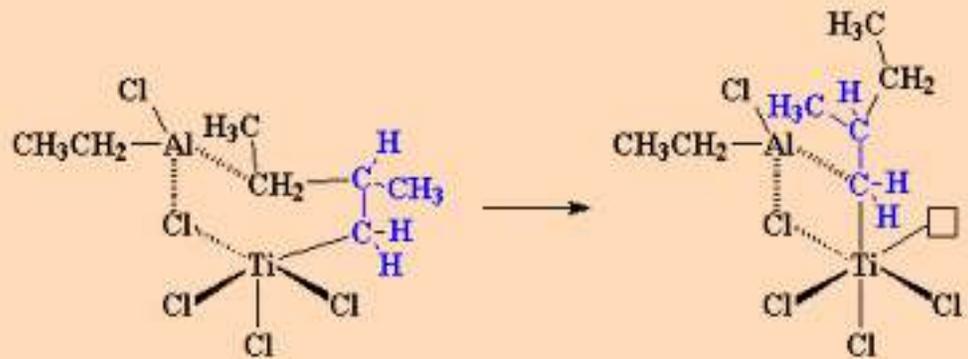


This is a nice complex, neatly solving the problem titanium had with its *d* orbitals not having enough electrons. But it can't go on like this. You see, that complex isn't going to stay that way forever. Some electron shuffling is going to happen. Several pairs of electrons are going to shift positions. You can see the shifting in the picture below:



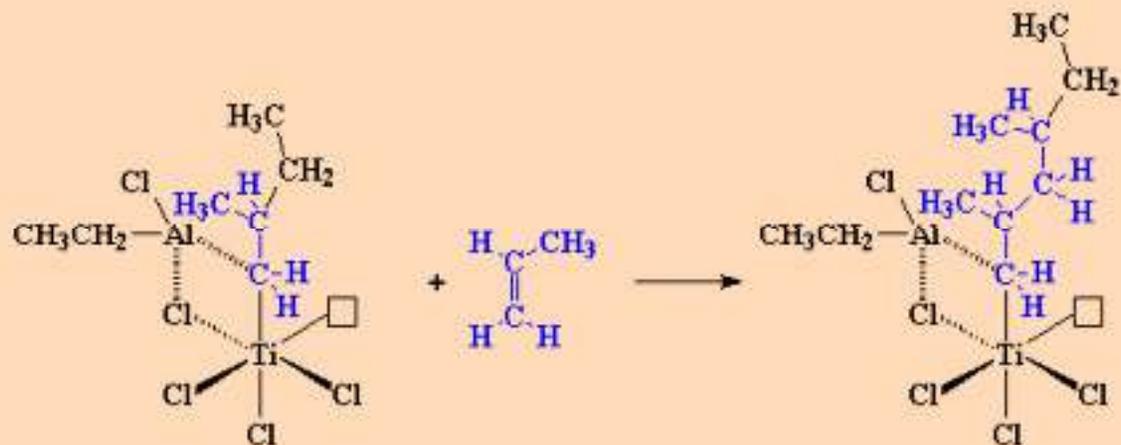
We don't know exactly which pairs shifts first, but we think the first to move is that pair from the carbon-carbon  $\pi$ -bond that is complexed with the titanium. It's going to shift to form simple titanium-carbon bond. Then the electrons from the bond between the titanium and the carbon of the ethyl group that titanium got from  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ . This pair of electrons is going to shift to form a bond between the ethyl group and the methyl-substituted carbon of the propylene monomer. Got that? It's kind of tricky to put into words, but we end up with the structure you see on the right side of the picture up there.

What happens next is what we call a *migration*. We don't know why this happens, we just know it happens. But the atoms rearrange themselves to form a slightly different structure, like this:



The aluminum is now complexed with one of the carbon atoms from our propylene monomer, as you can see. As you can also see, titanium is back where it started, with an empty orbital, needing electrons to fill it.

So when another propylene molecule comes along, the whole process starts all over, and the end result is something like this:

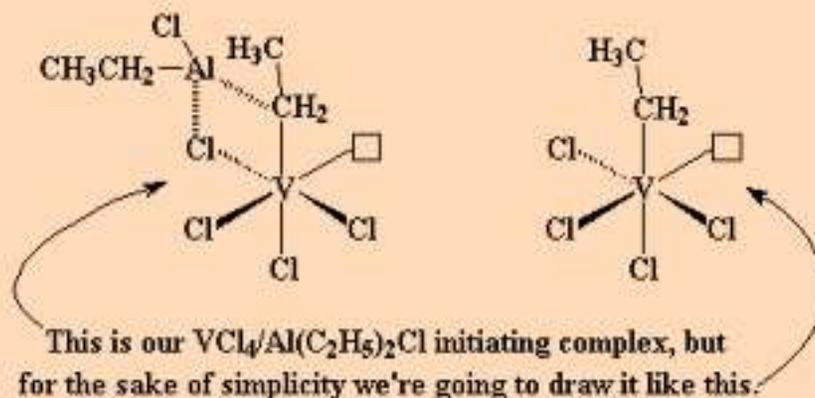


and of course, more and more propylene molecules react, and our polymer chain grows and grows. Take a look at the picture, and you'll see that all the methyl groups on the growing polymer are on the same side of the chain. With this mechanism we get isotactic polypropylene. For some reason, the incoming propylene molecule can only react if it's pointed in the right direction, the direction that gives isotactic polypropylene. We're not sure why this happens, we just know that it happens.

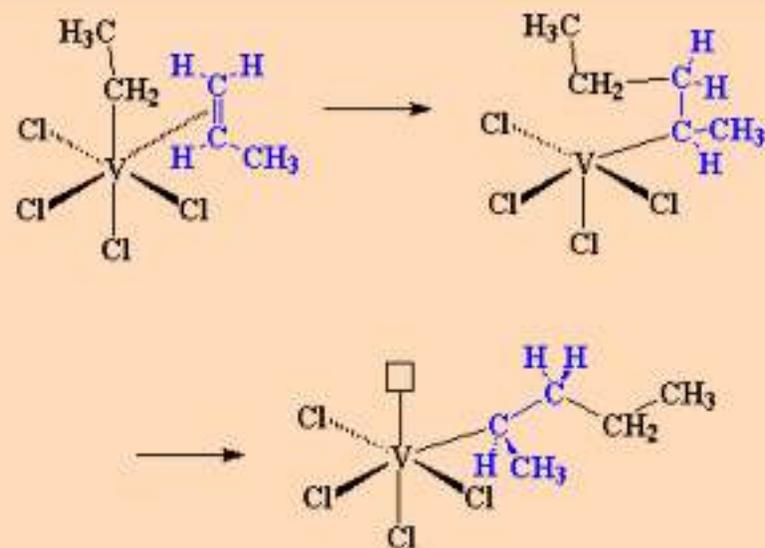
If you want to see a movie of isotactic Ziegler-Natta polymerization, [click here!](#)

*Part Two: Syndiotactic Polymerization*

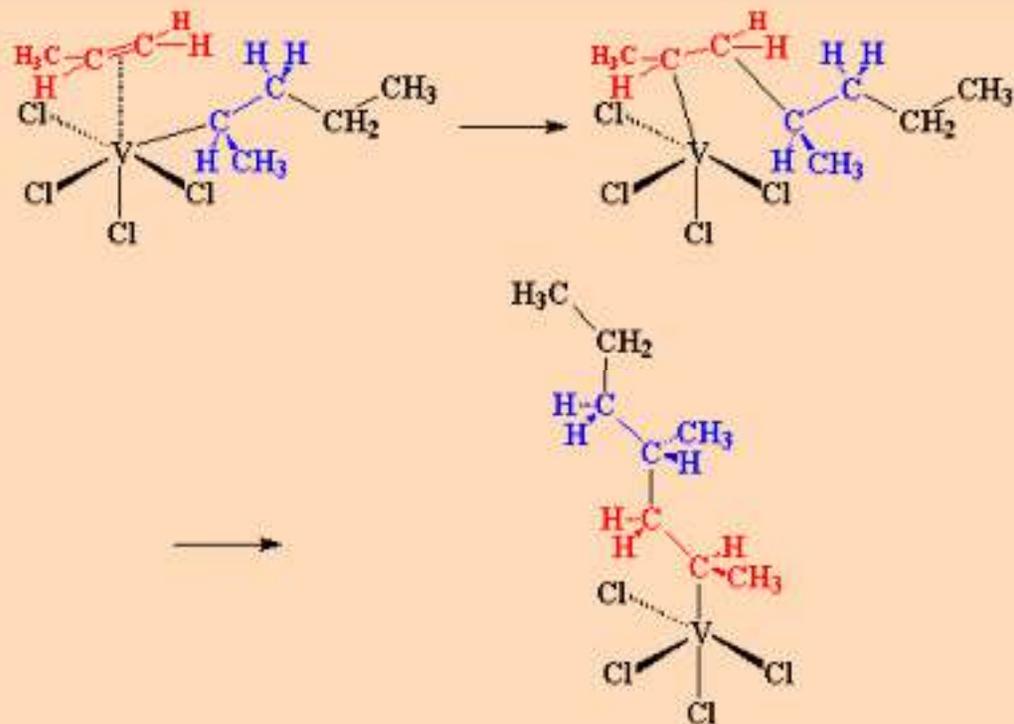
The catalyst system we just looked at gives isotactic polymers. But other systems can give syndiotactic polymers. The one we're going to look at is based on vanadium rather than titanium. That system is  $\text{VCl}_4/\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ . It looks like the picture you see on the left, not too different from the titanium system we just looked at. But to simplify things, during this little discussion we're going to just draw what you see on the right.



This complex will act pretty much the same way as the titanium system does when a propylene molecule comes its way. First the propylene complexes with the vanadium, then the electrons shift just like before, and the propylene is inserted between the metal and the ethyl group, just like before. This is all shown in the picture below.



But you can also see an important difference in this picture. Remember how with the titanium system, the growing polymer chain shifts positions on the titanium atom? You'll notice that doesn't happen here. The growing polymer chain stays in its new position. That is, until another propylene molecule comes along. This second propylene reacts while the growing chain is still in its new position, just like you see below:



But notice that when the second propylene adds to the chain, the chain changes position again. It's back in the position where it started. Take a look at the methyl groups of the first monomer, in blue, and the second monomer, in red. Notice that they're on opposite sides of the polymer chain. When the growing polymer chain is in one position the propylene monomer can only add so that the methyl group is on one side of the chain. When the chain is in the other position, propylene can only add so that the methyl group hangs off the other side. We're not exactly sure why this is. But we do know that because the growing polymer chain switches positions with each propylene monomer added, the methyl groups end up on alternating sides of the chain, giving us a syndiotactic polymer.

If you'd like to see a movie of how syndiotactic Ziegler-Natta polymerization takes place, [click here!](#)

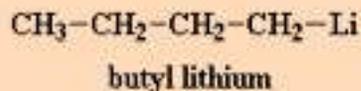
## Limitations

Ziegler-Natta polymerization is a great way to make polymers from hydrocarbon monomers like ethylene and propylene. But it doesn't work for some other kinds of monomers. For example, we can't make poly(vinyl chloride) by Ziegler-Natta polymerization. When the catalyst and cocatalyst come together to form the initiating complex, radicals are produced during intermediate steps of the reaction. These can initiate free radical polymerization of the vinyl chloride monomer. Acrylates are out, too, because Ziegler-Natta catalysts often initiate anionic vinyl polymerization in those monomers.

## ANIONIC POLYMERIZATION

Anionic vinyl polymerization is a method of making polymers from small molecules containing carbon-carbon double bonds. It is a type of vinyl polymerization. In anionic polymerization, the process is begun by an *initiator*. In this case, the initiator is an anion; that is, an ion with a negative electrical charge.

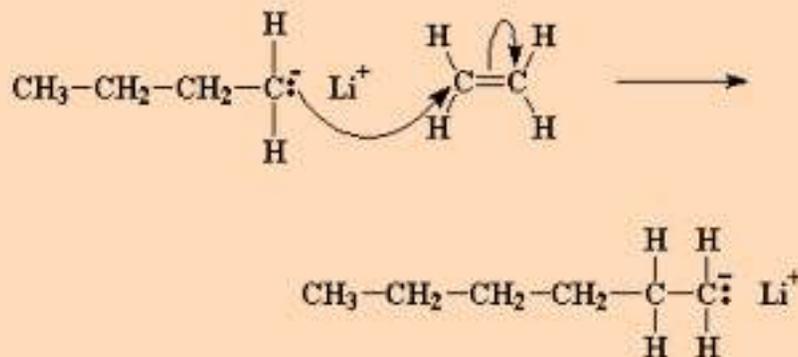
There are a lot of different initiators used in anionic vinyl polymerization, but the most often used is an unassuming little molecule called butyl lithium.



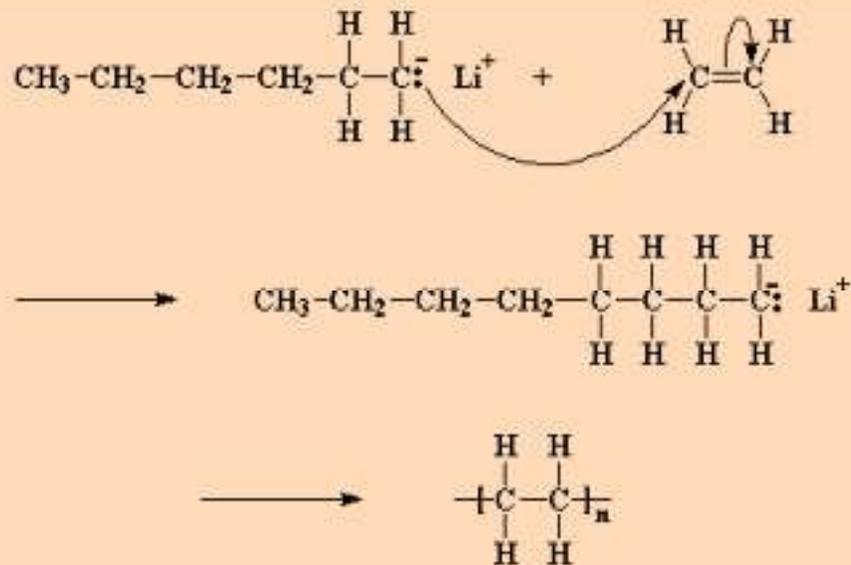
Now a little bit of the butyl lithium will always fall apart. Not a lot, but some. It falls apart to form a positive lithium cation and a negative butyl anion. We call an anion like this where the negative charge is on a carbon atom a *carbanion*



A pair of electrons from the butyl anion will be donated to one of the double bond carbon atoms of the monomer. Now this carbon atom already has eight electrons in its outer shell which it shares with the atoms to which it is bonded, so one pair of these electrons, specifically a pair in the carbon-carbon double bond, will leave the carbon atom, and settle on the other carbon atom of the carbon-carbon double bond. This forms a new carbanion, with the negative charge resting on that carbon. The process in which the butyl lithium falls apart, and the butyl anion reacts with a monomer molecule is called *initiation*.



The carbanion now reacts with another monomer molecule in just the same manner as the initiator reacted with the first monomer molecule; another carbanion is generated. This keeps happening, and each time another monomer is added to the growing chain, a new anion is generated allowing another monomer to be added. In this way the polymer chain grows. This adding of monomer after monomer is called *propagation*.



### The Chain That Wouldn't Die

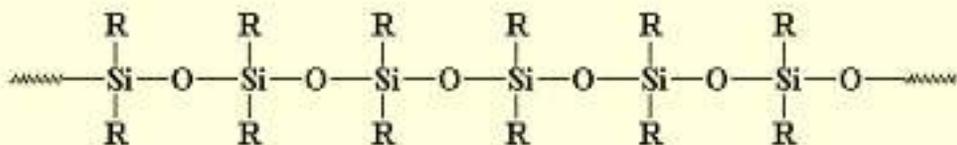
Now while you may get this nagging feeling that this can't go on forever, that something has to put a stop to this convenient process. Funny thing, though: it doesn't stop! In many cases, the only thing that stops monomers from adding to the growing chain, is that eventually there are no more monomer molecules in the beaker left to add! And even then, if someone came along some time later and dumped *more* monomer into the beaker, they would add to the chain and the chain would grow some more! Some chains of polystyrene have been known to stay active like this for years. In order to stop them, something like water, which reacts with the carbanions, has to be added to the polymer. Systems like this are called *living* anionic polymerizations. This allows us to do some interesting tricks...



## Inorganic polymers

### Silicones

Silicones are the most common of the inorganic polymers. They look like this:



They really should be called *polysiloxanes*. The bond between silicon and oxygen is very strong, but very flexible. So silicones can stand high temperatures without decomposing, but they have very low glass transition temperatures. You've probably seen rubber or caulking made of silicones somewhere before.

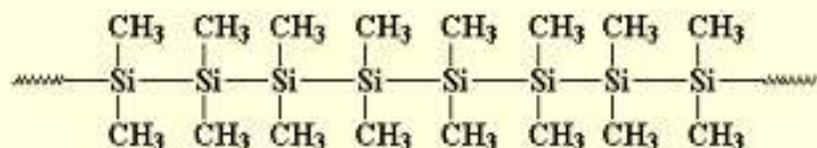
### Polysilanes

Let's take a look at the element silicon for a moment. You can see that it's right beneath carbon in the periodic chart. As you may remember, elements in the same column or *group* on the periodic chart often have very similar properties. So, if carbon can form long polymer chains, then silicon should be able to as well.

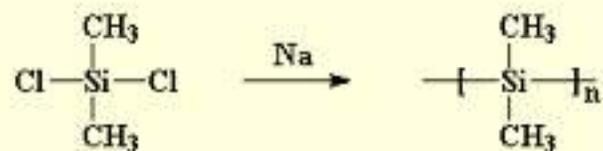
Right?

Right. It took a long time to make it happen, but silicon atoms have been made into long polymer chains. It was in the 1920's and 30's that chemists began to figure out that organic polymers were made of long carbon chains, but serious investigation of *polysilanes* wasn't carried out until the late seventies.

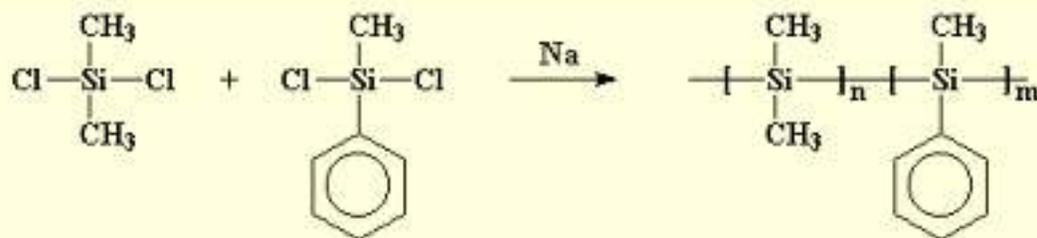
Earlier, in 1949, about the same time that novelist Kurt Vonnegut was working for the public relations department at General Electric, C.A. Burkhard was working in G.E.'s research and development department. He invented a polysilane called polydimethylsilane, but it wasn't much good for anything. It looked like this:



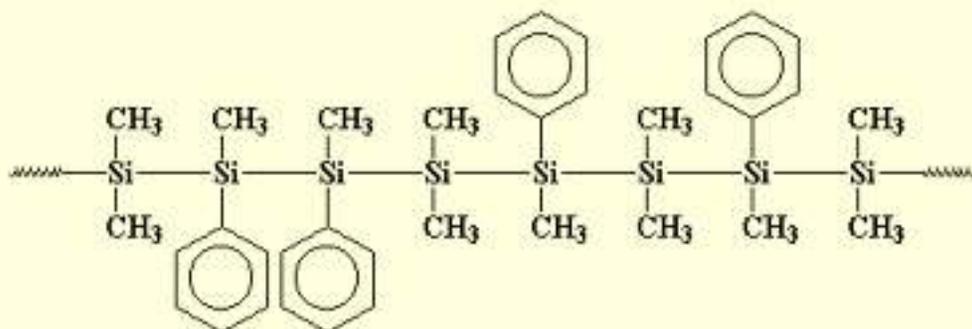
It formed crystals that were so strong that nothing could dissolve them. Burkhard tried to heat it, but it wouldn't melt below 250°C, when it decomposed, without melting. That made polydimethylsilane pretty much useless. He made it by reacting sodium metal with dichlorodimethylsilane like this:



This is important, because in the seventies, some scientists got the notion that they were going to make small rings of silicon atoms. So unwittingly did something similar to what Burkhard had done. They reacted sodium metal with dichlorodimethyl silane, but they also added some dichloromethylphenylsilane to the brew. And guess what happened! I'll give you a hint: they didn't get the rings they wanted. What they got was a copolymer, like this:



Maybe that polymer is more clearly drawn like this:

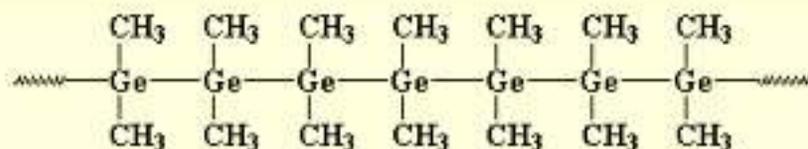


You see, those phenyl groups get in the way when the polymer tries to crystallize, so it isn't as crystalline as polydimethylsilane. This means it is soluble and can be processed and played with and studied.

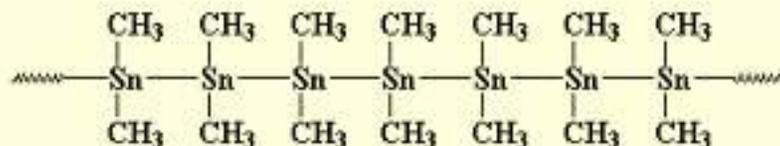
So what are these good for? Polysilanes are interesting because they can conduct electricity. Not as well as copper, mind you, but a lot better than you'd expect for a polymer, and worth investigating. They're also very heat resistant, almost up to 300 °C, but if you heat them a lot higher you can make silicon carbide out of them, which is a useful abrasive material.

### Polygermanes and Polystannanes

Okay, so if silicon can make long polymer chains, what about the other elements in Group IV? Can you make polymers out of germanium? You'd better believe you can! Not only can you make polymer chains out of germanium, but you can even make a polymer chain out of tin atoms. These polymers are called polygermanes and polystannanes, respectively.



polydimethylgermane

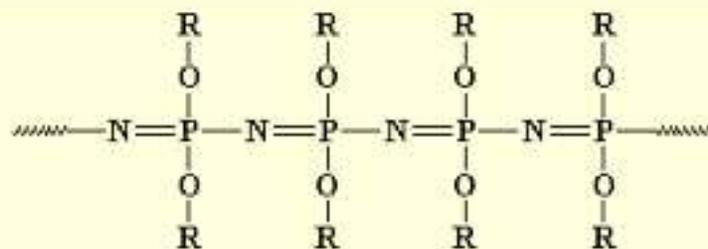


polydimethylstannane

Polystannanes are unique and nifty and wonderful and fabulous because they are the only known polymers with backbones made entirely from metal atoms. Like polysilanes, polygermanes and polystannanes are being studied for use as electrical conductors.

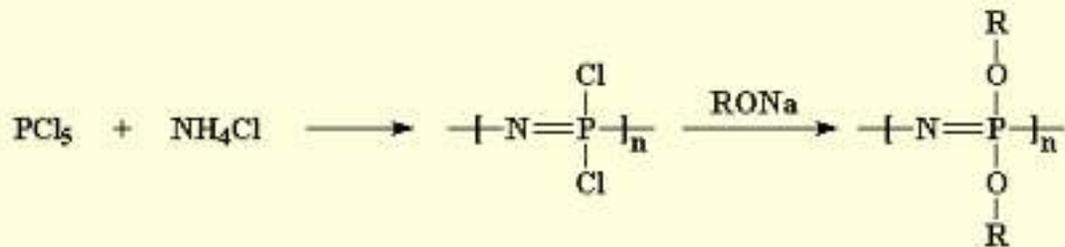
### Polyphosphazenes

I hate to break it to you folks, but we're out of Group IV elements. So the last inorganic polymer we're going to look at today is going to have to be made of something else. And that something else is phosphorus and nitrogen. Like the polysiloxanes, polyphosphazenes are made of alternating atoms, in this case, the chain is made up of alternating phosphorus and nitrogen atoms, like this:



An ether substituted polyphosphazene. (*R* is a wild card, standing for any hydrocarbon group)

This backbone is very flexible, like the polysiloxane backbone chain, so polyphosphazenes make good elastomers. They're also very good electrical insulators. Polyphosphazenes are made in two steps:



First we take phosphorus pentachloride and react it with ammonium chloride to get a chlorinated polymer. Then we treat it with an alcohol sodium salt, and that gives us an ether-substituted polyphosphazene.

Well, that's enough of this fascinating subject for now. While there may be new and exciting inorganic polymers that have been made (research marches on, of course), we can't cover everything in these pages. And don't forget, there are interesting combinations of heteroatoms (non-carbon atoms) with carbon atoms in a variety of polymer backbones and pendent groups. These could be called "semi-inorganic," although that might be too artificial for some.

## Thermosetting resins – an introduction

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The main characteristic of thermosets (literally *setting under heat*) is that they require curing, when they undergo a molecular cross-linking process which is irreversible and renders them infusible. They therefore offer high thermal stability, good rigidity and hardness, and resistance to creep.

This also means that, once cured, the resin and its laminate cannot be reprocessed except by methods of chemical breakdown, which are currently under development. For practical purposes, therefore, cured thermosetting resins can be recycled most effectively if ground to fine particles, when they can be incorporated into new laminates or other products as fillers.

Thermosetting resins have little use a pure resin, but require addition of other chemicals to render them processable. For reinforced plastics, the compounds usually comprise a resin system (with curing agents, hardeners, inhibitors, plasticisers) and fillers and /or reinforcement. The resin system provides the 'binder,' to a large extent dictating the cost, dimensional stability, heat and chemical resistance, and basic flammability. The reinforcement can influence these (particularly heat and dimensional stability) but the main effect is on tensile strength and toughness. High performance fibres, of course, have a fundamental influence on cost.

Special fillers and additives can influence mechanical properties, especially for improvement in dimensional stability, but they are mainly used to confer specific properties, such as flame retardancy, ultraviolet (UV) stability or electrical conductivity.

Thermosetting resins are normally used in the liquid state and solidify and harden on curing. With some resins it is possible to part-cure and then hold the resin in what is called the B-stage for the cure to be completed at a later time.

The most frequently used thermosetting resins are:

- polyester;
- **epoxy**;
- phenolic;
- vinyl ester;
- polyurethane;
- silicone; and
- polyamide and polyamide-imide

#### **EPOXY RESINS**

Epoxy resin is defined as a molecule containing more than one epoxide groups. The epoxide group also termed as, oxirane or ethoxyline group, is shown below,



These resins are thermosetting polymers and are used as adhesives, high performance coatings and potting and encapsulating materials. These resins have excellent electrical properties, low shrinkage, good adhesion to many metals and resistance to moisture, thermal and mechanical shock.

Viscosity, epoxide equivalent weight and molecular weight are the important properties of epoxy resins.

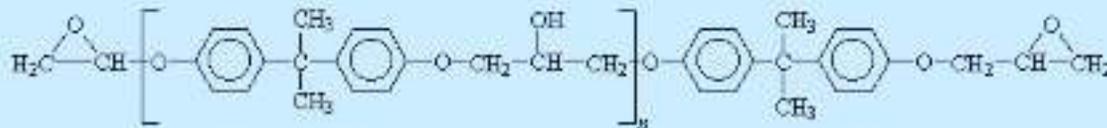
## Types of Epoxy Resins:

There are two main categories of epoxy resins, namely the glycidyl epoxy, and non-glycidyl epoxy resins. The glycidyl epoxies are further classified as glycidyl-ether, glycidyl-ester and glycidyl-amine. The non-glycidyl epoxies are either aliphatic or cycloaliphatic epoxy resins. Glycidyl epoxies are prepared via a condensation reaction of appropriate dihydroxy compound, dibasic acid or a diamine and epichlorohydrin. While, non-glycidyl epoxies are formed by peroxidation of olefinic double bond.

Glycidyl-ether epoxies such as, diglycidyl ether of bisphenol-A (DGEBA) and novolac epoxy resins are most commonly used epoxies.

### Diglycidyl Ether of Bisphenol-A (DGEBA):

Diglycidyl ether of bisphenol-A (DGEBA) is a typical commercial epoxy resin and is synthesised by reacting bisphenol-A with epichlorohydrin in presence of a basic catalyst.

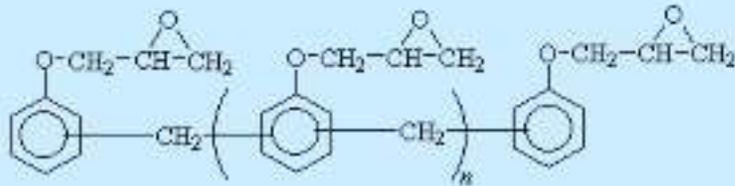


## structure of DGEBA

The properties of the DGEBA resins depend on the value of  $n$ , which is the number of repeating units commonly known as degree of polymerisation. The number of repeating units depend on the stoichiometry of synthesis reaction. Typically,  $n$  ranges from 0 to 25 in many commercial products.

## Novolac Epoxy Resins:

Novolac epoxy resins are glycidyl ethers of phenolic novolac resins. Phenols are reacted in excess, with formaldehyde in presence of acidic catalyst to produce phenolic novolac resin. Novolac epoxy resins are synthesised by reacting phenolic novolac resin with epichlorohydrin in presence of sodium hydroxide as a catalyst.



## Structure of novolac epoxy resin

Novolac epoxy resins generally contain multiple epoxide groups. The number of epoxide groups per molecule depends upon the number of phenolic hydroxyl groups in the starting phenolic novolac resin, the extent to which they reacted and the degree of low molecular species being polymerised during synthesis. The multiple epoxide groups allow these resins to achieve high cross-link density resulting in excellent temperature, chemical and solvent resistance. Novolac epoxy resins are widely used to formulate the moulding compounds for microelectronics packaging because of their superior performance at elevated temperature, excellent mouldability, and mechanical properties, superior electrical properties, and heat and humidity resistance.

## **Curing of Epoxy Resins**

The curing process is a chemical reaction in which the epoxide groups in epoxy resin reacts with a curing agent (hardener) to form a highly crosslinked, three-dimensional network. In order to convert epoxy resins into a hard, infusible, and rigid material, it is necessary to cure the resin with hardener. Epoxy resins cure quickly and easily at practically any temperature from 5-150°C depending on the choice of curing agent.

### **Curing Agents (Hardeners)**

A wide variety of curing agent for epoxy resins is available depending on the process and properties required. The commonly used curing agents for epoxies include amines, polyamides, phenolic resins, anhydrides, isocyanates and polymercaptans. The cure kinetics and the  $T_g$  of cured system are dependent on the molecular structure of the hardener. The choice of resin and hardeners depends on the application, the process selected, and the properties desired. The stoichiometry of the epoxy-hardener system also affects the properties of the cured material. Employing different types and amounts of hardener which, tend to control cross-link density vary the structure.

The amine and phenolic resin based curing agents, described below, are widely used for curing of epoxy resins.

#### **Amine based curing agents:**

Amines are the most commonly used curing agents for epoxy cure. Primary and secondary amines are highly reactive with epoxy. Tertiary amines are generally used as catalysts, commonly known as accelerators for cure reactions. Use of excessive amount of catalyst achieves faster curing, but usually at the expense of working life, and thermal stability. The catalytic activity of the catalysts affects the physical properties of the final cured polymer.

**Phenolic novolac resins:**

Epoxy resins when cured with phenolic hardener, gives excellent adhesion, strength, chemical and flame resistance. Phenolic novolac-cured epoxy systems are mainly used for encapsulation because of their low water absorption, excellent heat and electrical resistance. An accelerator is necessary for the complete cure to occur. Figure 2.4 shows cure reaction of epoxy resin with phenolic hardener.

## Rubber Toughening of Epoxy Resins

The usefulness of epoxy resins in many engineering applications is often limited by their brittle nature and poor thermal conductivity. The term toughness is a measure of material's resistance to failure i.e. the total amount of energy required to cause failure.

There are several approaches to enhance the toughness of epoxy resins which includes: (i) chemical modification of the epoxy backbone to make it more flexible structure, (ii) increasing the molecular weight of epoxy, (iii) lowering the cross-link density of matrix, (iv) incorporation of dispersed toughener phase in the cured polymer matrix, and (v) incorporation of inorganic fillers into the neat resin.

Amongst these approaches, toughening via dispersed toughener (flexibiliser) phase has been shown to be most effective. The flexibilisers can be reactive or non-reactive rubber.

## Toughening Agents

Various types of thermoplastic polymers as well as reactive rubbers are employed to enhance toughness of epoxy resin. Thermoplastic polymers, such as polyetherimide, polysulphone, polyethersulphone, and polycarbonate have been studied to modify epoxy resins. These studies show significant improvement in the toughness of epoxy resins.

The reactive rubbers used for toughening epoxy resins include, liquid acrylonitrile-butadiene copolymers with various terminal groups, polysiloxanes, polyepichlorohydrin, and polyurethanes.

Although liquid acrylonitrile-butadiene copolymers with carboxyl- (CTBN) and amine- (ATBN) terminated groups have been widely used for epoxy toughening, the relatively high glass transition temperature of the copolymer limits their low-temperature applications. In addition, these copolymers also increase the CTE value of the moulding compound. Also the presence of unsaturated structure of butadiene system is prone to thermal instability and thus unsuitable for long term use at higher temperatures.

Polysiloxanes have excellent thermal stability, moisture resistance, good electrical properties, low stress and lower  $T_g$  values. However polysiloxanes are not compatible with epoxy resins. Addition of compatibilisers such as, methylphenylsiloxane enhances the compatibility but at the same time raises the  $T_g$  of polysiloxane modifier restricting its low temperature applications.

## PHENOL FORMALDEHYDE RESIN

**Phenol formaldehyde resins (PF)** or **phenolic resins** are synthetic polymers obtained by the reaction of phenol or substituted phenol with formaldehyde. Used as the basis for Bakelite, PFs were the first commercial synthetic resins (plastics). They have been widely used for the production of molded products including billiard balls, laboratory countertops, and as coatings and adhesives. They were at one time the primary material used for the production of circuit boards but have been largely replaced with epoxy resins and fiberglass cloth, as with fire-resistant FR-4 circuit board materials.

There are two main production methods. One reacts phenol and formaldehyde directly to produce a thermosetting network polymer, while the other restricts the formaldehyde to produce a prepolymer known as **novolac** which can be moulded and then cured with the addition of more formaldehyde and heat.<sup>[1][2]</sup> There are many variations in both production and input materials that are used to produce a wide variety of resins for special purposes.

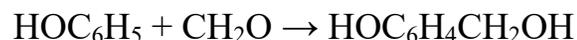


### Formation and structure

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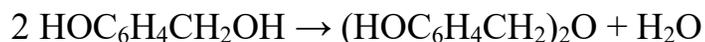
Phenol-formaldehyde resins, as a group, are formed by a step-growth polymerization reaction that can be either acid- or base-catalysed. Since formaldehyde exists predominantly in solution as a dynamic equilibrium of methylene glycol oligomers, the concentration of the *reactive* form of formaldehyde depends on temperature and pH.

Phenol reacts with formaldehyde at the ortho and para sites (sites 2, 4 and 6) allowing up to 3 units of formaldehyde to attach to the ring. The initial reaction in all cases involves the formation of a hydroxymethyl phenol:



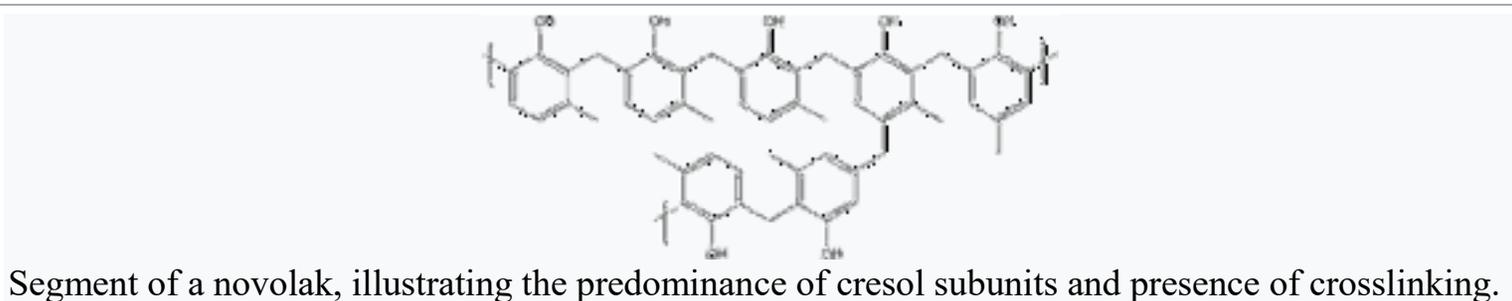
The hydroxymethyl group is capable of reacting with either another free ortho or para site, or with another hydroxymethyl group. The first reaction gives a methylene bridge, and the second forms an etherbridge:





The diphenol  $(\text{HOC}_6\text{H}_4)_2\text{CH}_2$  (sometimes called a "dimer") is called bisphenol F, which is an important monomer in the production of epoxy resins. Bisphenol-F can further link generating tri- and tetra- and higher phenol oligomers.

### Novolacs



Segment of a novolac, illustrating the predominance of cresol subunits and presence of crosslinking.

Novolaks (or novolacs) are phenol-formaldehyde resins with a formaldehyde to phenol molar ratio of less than one. In place of phenol itself, they are often produced from cresols (methylphenols). The polymerization is brought to completion using acid-catalysis such as sulfuric acid, oxalic acid, hydrochloric acid and rarely, sulfonic acids.<sup>[3]</sup> The phenolic units are mainly linked by methylene and/or ether groups. The molecular weights are in the low thousands, corresponding to about 10–20 phenol units. Obtained polymer is thermoplastic and require a curing agent or hardener to form a thermoset.

Hexamethylenetetramine is a hardener added to crosslink novolac. At a temperature greater than 90 °C, it forms methylene and dimethylene amino bridges.

Novolacs have multiple uses as tire tackifier, high temperature resin, binder for carbon bonded refractories, carbon brakes, photoresists and as a curing agent for epoxy resins. See also photolithography.

### Crosslinking and the formaldehyde/phenol ratio

When the molar ratio of formaldehyde:phenol reaches one, in theory every phenol is linked together via methylene bridges, generating one single molecule, and the system is entirely crosslinked. This is why

novolacs (F:P <1) do not harden without the addition of a crosslinking agents, and why resols with the formula F:P >1 will.

## **Applications**

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Phenolic resins are found in myriad industrial products. Phenolic laminates are made by impregnating one or more layers of a base material such as paper, fiberglass or cotton with phenolic resin and laminating the resin-saturated base material under heat and pressure. The resin fully polymerizes (cures) during this process forming the thermoset polymer matrix. The base material choice depends on the intended application of the finished product. Paper phenolics are used in manufacturing electrical components such as punch-through boards, in household laminates, and in paper composite panels. Glass phenolics are particularly well suited for use in the high speed bearing market. Phenolic micro-balloons are used for density control. Snooker balls as well as balls from many table-based ball games are also made from phenol formaldehyde resin. The binding agent in normal (organic) brake pads, brake shoes and clutch disks are phenolic resin. Synthetic resin bonded paper, made from phenolic resin and paper, is used to make countertops. Another use of phenolic resins is the making of Duroplast, used in the Trabant automobiles.

Phenolic resins are also used for making exterior plywood commonly known as *weather and boil proof* (WBP) plywood because phenolic resins have no melting point but only a decomposing point in the temperature zone of 220 °C (428 °F) and above.

Phenolic resin is used as a binder in loudspeaker driver suspension components which are made of cloth.

Billiard balls are made from solid phenolic resin.

Sometimes people select fibre reinforced phenolic resin parts because their coefficient of thermal expansion closely matches that of the aluminium used for other parts of a system, as in early computer systems and Duramold.

The Dutch painting forger Han van Meegeren mixed phenol formaldehyde with his oil paints before baking the finished canvas, in order to fake the drying out of the paint over the centuries.

## Urea-formaldehyde

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Urea-formaldehyde (UF), also known as urea-methanal, so named for its common synthesis pathway and overall structure, is a non-transparent thermosetting resin or polymer. It is produced from urea and formaldehyde. These resins are used in adhesives, finishes, particle board, medium-density fibreboard (MDF), and molded objects.

UF and related amino resins are a class of thermosetting resins of which urea-formaldehyde resins make up 80% produced globally. Examples of amino resins use include in automobile tires to improve the bonding of rubber to tire cord, in paper for improving tear strength, in molding electrical devices, jar caps, etc



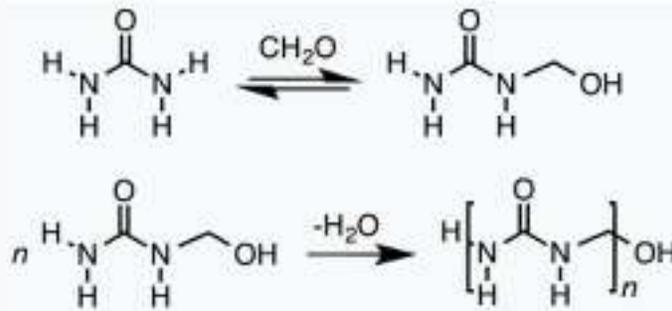
## Properties

Urea-formaldehyde resin's attributes include high tensile strength, flexural modulus, and a high heat distortion temperature, low water absorption, mould shrinkage, high surface hardness, elongation at break, and volume resistance. It has a refractive index of 1.55.

## Chemical structure

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The chemical structure of UF polymer consists of  $[(O)CNHCH_2NH]_n$  repeat units. In contrast melamine-formaldehyde resins feature  $NCH_2OCH_2N$  repeat units. Depending on the polymerization conditions, some branching can occur. Early stages in the reaction of formaldehyde and urea produce bis(hydroxymethyl)urea.



## Two steps in formation of urea-formaldehyde resin

### Production

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Approximately 1 million metric tons of urea-formaldehyde are produced annually. Over 70% of this production is then put into use by the forest products industry for bonding particleboard (61%), medium density fiberboard (27%), hardwood plywood (5%), and laminating adhesive (7%).

### General uses

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A range of objects made from urea formaldehyde

Urea-formaldehyde is pervasive. Examples include decorative laminates, textiles, paper, foundry sand molds, wrinkle resistant fabrics, cotton blends, rayon, corduroy, etc. It is also used to glue wood together. Urea formaldehyde was commonly used when producing electrical appliances casing (e.g. desk lamps). Foams have been used as artificial snow in movies.

### Polyester resin

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**Polyester resins** are unsaturated synthetic resins formed by the reaction of dibasic organic acids and polyhydric alcohols. Maleic Anhydride is a commonly used raw material with diacid functionality. Polyesterresins are used in sheet moulding compound, bulk moulding compound and the toner of laser printers. Wall panels fabricated from polyester resins reinforced with fiberglass—so-called fiberglass reinforced plastic (FRP)—are typically used in restaurants, kitchens, restrooms and other areas that require washable low-maintenance walls. They are also used extensively in cured-in-place pipe applications. Departments of Transportation in the USA also specify them for use

as overlays on roads and bridges. In this application they are known as PCO Polyester Concrete Overlays. These are usually based on isophthalic acid and cut with styrene at high levels—usually up to 50%.<sup>[1]</sup> Polyesters are also used in anchor bolt adhesives though epoxy based materials are also used.<sup>[2]</sup> Many companies have and continue to introduce styrene free systems mainly due to odor issues.

### **Unsaturated Polyester**

Unsaturated polyesters are condensation polymers formed by the reaction of polyols (also known as polyhydric alcohols), organic compounds with multiple alcohol or hydroxy functional groups, with saturated or unsaturated dibasic acids. Typical polyols used are glycols such as ethylene glycol; acids used are phthalic acid, isophthalic acid and maleic acid. Water, a by-product of esterification reactions, is continuously removed, driving the reaction to completion.

#### Advantages

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Polyester resin offers the following advantages:

1. Adequate resistance to water and variety of chemicals.
2. Adequate resistance to weathering and ageing.
3. Low cost.
4. Polyesters can withstand a temperature up to 80°C.
5. Polyesters have good wetting to glass fibres.
6. Relatively low shrinkage at between 4-8% during curing.
7. Linear thermal expansion ranges from 100-200 x 10<sup>-6</sup> K<sup>-1</sup>.

#### Disadvantages

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Polyester resin has the following disadvantages:

1. Strong styrene odor
2. More difficult to mix than other resins, such as a two-part epoxy

3. The toxic nature of its fumes, and especially of its catalyst, MEKP, pose a safety risk if proper protection isn't used

4. Not appropriate for bonding many substrates

The finished cure is most likely weaker than an equal amount of an epoxy resin

### Spinning (polymers)

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□ **Spinning** is a manufacturing process for creating polymer fibers. It is a specialized form of extrusion that uses a spinneret to form multiple continuous filaments. There are many types of spinning as enumerated below: First, the polymer being spun must be converted into a fluid state. If the polymer is a thermoplastic then it can be simply melted, otherwise it is dissolved in a solvent or chemically treated to form soluble or thermoplastic derivatives. The molten polymer is then forced through the spinneret, then it cools to a rubbery state, and then a solidified state.<sup>[1]</sup> If a polymer solution is used, then the solvent is removed after being forced through the spinneret.

#### **Wet spinning**

Wet spinning is the oldest of the five processes. This process is used for polymers that need to be dissolved in a solvent to be spun. The spinneret is submerged in a chemical bath that causes the fiber to precipitate, and then solidify, as it emerges. The process gets its name from this "wet" bath. Acrylic, rayon, aramid, modacrylic, and spandex are produced via this process.

A variant of wet spinning is **dry jet-wet spinning**, where the solution is extruded into air and drawn, and then submerged into a liquid bath. This method is used in Lyocell spinning of dissolved cellulose.

#### **Dry spinning**

A solution consisting of a fiber-forming material and a solvent is extruded through a spinneret. A stream of hot air impinges on the jets of solution emerging from the spinneret, the solvent evaporates, and solid filaments are left behind. **Solution blow spinning** is a similar technique where polymer solution is sprayed directly onto a target to produce a nonwoven fiber mat

### **Melt spinning**

Melt spinning is used for polymers that can be melted. The polymer solidifies by cooling after being extruded from the spinneret. Nylon, olefin, polyester, saran, and sulfar are produced via this process.

### **Extrusion spinning**

Pellets or granules of the solid polymer are fed into an extruder. The pellets are compressed, heated and melted by an extrusion screw, then fed to a spinning pump and into the spinneret.

