# Module-IV

Fundamentals of Polymer Chemistry

A polymer in its simplest form can be regarded as comprising molecules of closely related composition of molecular weight at least 2000, although in many cases typical properties do not become obvious until the mean molec-ular weight is about 5000. There is virtually no upper end to the molecular weight range of polymers since giant three-dimensional networks may produce crosslinked polymers of a molecular weight of many millions.

Polymers (macromolecules) are built up from basic units, sometimes referred to as 'mers'. These units can be extremely simple, as in addition polymerisation, where a simple molecule adds on to itself or other simple molecules, by methods that will be indicated subsequently. Thus ethylene $CH_2:CH_2$ can be converted into polyethylene, of which the repeating unit is —CH_2CH_2—, often written as —$(CH_2CH_2)_n$, where n is the number of repeating units, the nature of the end groups being discussed later.

The major alternative type of polymer is formed by condensation polymerisation in which a simple molecule is eliminated when two other molecules condense. In most cases the simple molecule is water, but alternatives include ammonia, an alcohol and a variety of simple substances.

The product of condensation can continue to react through its end groups of hexamethylenediamine and adipic acid and thus a high molecular weight polymer is prepared.

Monomers such as adipic acid and hexamethylenediamine are described as bifunctional because they have two reactive groups. As such they can only form linear polymers. Similarly, the simple vinyl monomers such as ethylene $CH_2:CH_2$ and vinyl acetate $CH_2:CHOOCCH_3$ are considered to be bifunctional. If the functionality of a monomer is greater than two, a branched structure may be formed. Thus the condensation of glycerol $HOCH_2CH(OH)CH_2OH$ with adipic acid $HOOC(CH_2)_4COOH$ will give a branched structure.
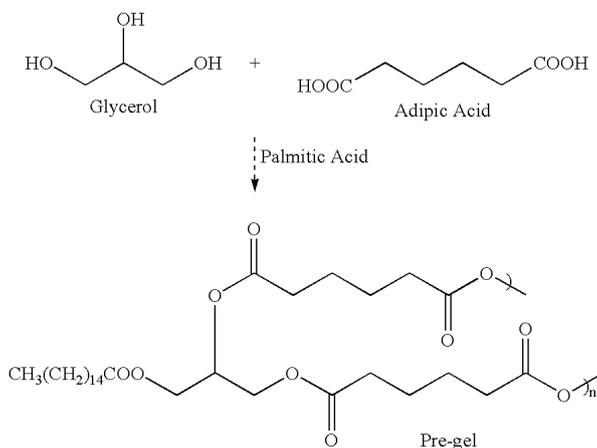
The condensation is actually three dimensional, and ultimately a three- dimensional structure is formed as the various branches link up. Although this formula has been idealised, there is a statistical probability of the various hydroxyl and carboxyl groups combining. This results in a network being built up, and whilst it has to be illustrated on the plane of the paper, it will not necessarily be planar. As functionality increases, the probability of such networks becoming interlinked increases, as does the probability withincrease in molecular weight. Thus a gigantic macromolecule will be formed which is insoluble and infusible before decomposition. It is only comparatively recently that structural details of these crosslinked or 'reticulated' polymers have been elucidated with some certainty.

Addition polymers are normally formed from unsaturated carbon-to-carbon linkages. This is not necessarily the case since other unsaturated linkages including only one carbon bond may be polymerized.

Addition polymerisation of a different type takes place through the opening of a ring, especially the epoxide ring in ethylene oxide. This opens as—CH_2CH_2O—; ethylene oxide thus acts as a bifunctional monomer forming a polymer as $H(CH_2CH_2O)_n$ CH_2CH_2OH, in this case a terminal water molecule being added. A feature of this type of addition is that it is much easier to control the degree of addition, especially at relatively low levels, than in the vinyl polymerisation described above.

Addition polymerisations from which polymer emulsions may be available occur with the silicones and diisocyanates. These controlled addition poly- merisations are sometimes referred to as giving 'stepwise' addition polymers. This term may also refer to condensation resins.

ADDITION POLYMERISATION

Addition polymerisation, the main type with which this volume is concerned, is essentially a chain reaction, and may be defined as one in which only a small initial amount of initial energy is required to start an extensive chain reaction converting monomers, which may be of different formulae, into polymers. A well-known example of a chain reaction is the initiation of the reaction between hydrogen and chlorine molecules. A chain reaction consists of three stages, initiation, propagation and termination, and may be represented simply by the progression:

$$\text{Activation} \quad +M \quad +M \quad +nM$$
$$M{-}M^*{-}M_2^*{-}M_3^*{-}M_{n+3}{-}\text{etc.}$$
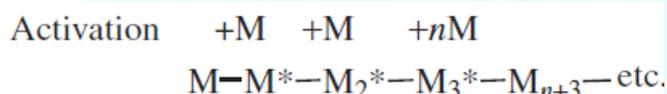
The mechanism of polymerisation can be divided broadly into two main classes, free radical polymerisation and ionic polymerisation, although there are some others.[†] Ionic polymerisation was probably the earliest type to be noted, and is divided into cationic and anionic polymerisations. Cationic poly- merisation depends on the use of catalysts which are good electron acceptors. Typical examples are the Friedel– Crafts catalysts such as aluminium chloride $AlCl_3$ and boron trifluoride BF_3.

Monomers that polymerise in the presence of these catalysts have substituents of the electron releasing type. They include styrene $C_6H_5CH{:}CH_2$ and the vinyl ethers $CH_2{:}CHOC_nH_{2n+1}$.

Anionic initiators include reagents capable of providing negative ions, and are effective with monomers containing electronegative substituents such as acrylonitrile $CH_2{:}CHCN$ and methyl methacrylate $CH_2{:}C(CH_3)COOCH_3$. Styrene may also be polymerised by an anionic method. Typical catalysts include sodium in liquid ammonia, alkali metal alkyls, Grignard reagents and triphenylmethyl sodium $(C_6H_5)_3$C-Na.

Amongst other modern methods of polymerisation are the Ziegler– Natta catalysts and group transfer polymerisation catalysts. Ionic polymeri- sation is not of interest in normal aqueous polymerisation since in generalthe carbonium ions by which cationic species are propagated and the corre- sponding carbanions in anionic polymerisations are only stable in media of low dielectric constant, and are immediately hydrolysed by water.

Free radical polymerisation

A free radical may be defined as an intermediate compound containing an odd number of electrons, but which do not carry an electric charge and are not free ions. The first stable free radical, triphenylmethyl $(C_6H_4)_3C\cdot$, was isolated by Gomberg in 1900, and in gaseous reactions the existence of radicals such as methyl $CH_3\cdot$ was postulated at an early date. The decomposition of oxidizing agents of the peroxide type, as well as compounds such as azodiisobutyronitrile
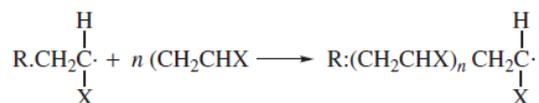
$$(CH_3)_2\underset{\underset{NC}{|}}{C}.N:N\underset{\underset{CN}{|}}{C}(CH_3)_2$$
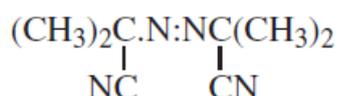
which decomposes into two radicals, $(CH_3)_2\underset{\underset{CN}{|}}{C}\cdot$ and nitrogen N_2. Thus a free radical mechanism is the basis of addition polymerisation where these types of initiator are employed. For a transient free radical the convention will be used of including a single dot after or over the active element with the odd electron.

A polymerisation reaction may be simply expressed as follows. Let R be a radical from any source. $CH_2{:}CHX$ represents a simple vinyl monomer where X is a substituent, which may be H as in ethylene $CH_2{:}CH_2$, Cl as in vinyl chloride $CH_2{:}CHCl$, $OOC.CH_3$ as in vinyl acetate $CH_2{:}CHOOCCH_3$ or many other groups, which will be indicated in lists of monomers.

The first stage of the chain reaction, the initiation process, consists of the attack of the free radical on one of the doubly bonded carbon atoms of the monomer. One electron of the double bond pairs with the odd electron of the free radical to form a bond between the latter and one carbon atom. The remaining electron of the double bond shifts to the other carbon atom which now becomes a free radical. This can be expressed simply in equation form:
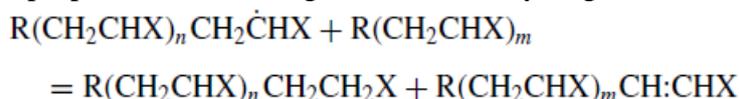
$$R + CH_2{:}CHX \longrightarrow R.CH_2\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}\cdot$$
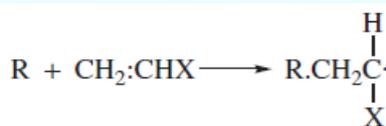
The new free radical can, however, in its turn add on extra monomer units, and a chain reaction occurs, representing the propagation stage:

$$R.CH_2\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}\cdot + n\,(CH_2CHX) \longrightarrow R{:}(CH_2CHX)_n\,CH_2\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C}}\cdot$$
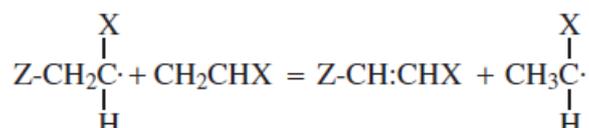
The final stage is termination, which may take place by one of several processes. One of these is combination of two growing chains reacting together:

$$R(CH_2CHX)_nCH_2\dot{C}HX + R(CH_2CHX)_mCH_2\dot{C}HX$$
$$= R(CH_2CH)_nCH_2CHXCH_2CHX(CH_2CHX)_mR$$
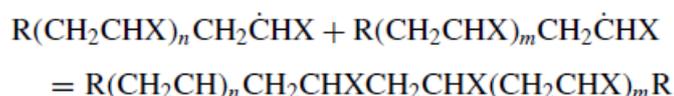
An alternative is disproportionation through transfer of a hydrogen atom:

$$R(CH_2CHX)_n CH_2\dot{C}HX + R(CH_2CHX)_m$$

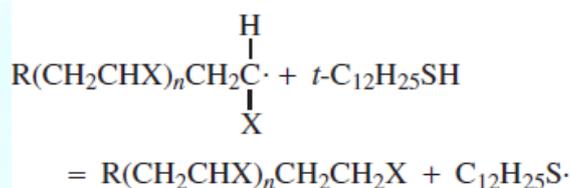$$= R(CH_2CHX)_n CH_2CH_2X + R(CH_2CHX)_m CH{:}CHX$$

A further possibility is chain transfer. This is not a complete termination reaction, but it ends the propagation of a growing chain and enables a new one to commence. Chain transfer may take place via a monomer, and may be
regarded as a transfer of a proton or of a hydrogen atom:

$$\underset{\underset{H}{|}}{\overset{\overset{X}{|}}{Z{-}CH_2C\cdot}} + CH_2CHX = Z{-}CH{:}CHX + \underset{\underset{H}{|}}{\overset{\overset{X}{|}}{CH_3C\cdot}}$$

where Z is a polymeric chain.
Chain transfer takes place very often via a fortuitous impurity or via a chain transfer agent which is deliberately added. Alkyl mercaptans with alkyl chains C_8 or above are frequently added for this purpose in polymerisation
formulations. A typical reagent is t-dodecyl mercaptan, which reacts as in the following equation:

$$R(CH_2CHX)_n CH_2\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C\cdot}} + t{-}C_{12}H_{25}SH$$

$$= R(CH_2CHX)_n CH_2CH_2X + C_{12}H_{25}S\cdot$$

Chlorinated hydrocarbons are also commonly used as chain transfer agents, and with carbon tetrachloride it is a chlorine atom rather than a hydrogen atom

$$R(CH_2CHX)_n CH_2\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C\cdot}} + CCl_4 = R(CH_2CHX)_n CHXCl + Cl_3C\cdot$$
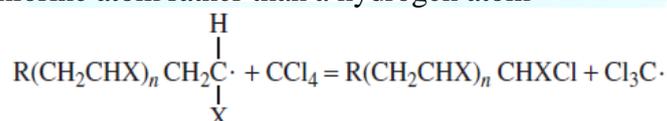
Most common solvents are sufficiently active to take part in chain transfer termination, the aliphatic straight-chain hydrocarbons and benzene being amongst the least active. The effect of solvents is apparent in the following equation, where SolH denotes a solvent:

$$R(CH_2CHX)_n CH_2\underset{\underset{X}{|}}{\overset{\overset{H}{|}}{C\cdot}} + SolH = RCH_2CHX)_n CH_2X + Sol\cdot$$
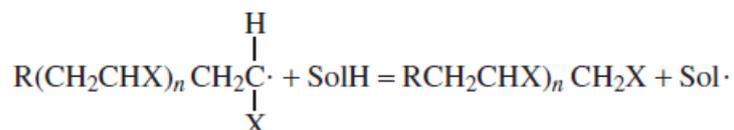
In all the cases mentioned, the radicals on the right-hand side of the equations must be sufficiently active to start a new chain; otherwise they act as a retarder or inhibitor.

Retardation and inhibition

If the addition of a chain transfer agent to a polymerising system works efficiently, it will both slow the polymerisation rate and reduce the molecular weight. This is because the free radical formed may be much less active than the original radical in starting new chains, and when these are formed, they are terminated after a relatively short growth.

Free radical initiation

Initiators of the type required for vinyl polymerisations are formed from compounds with relatively weak valency links which are relatively easily broken thermally. Irradiation of various wavelengths is sometimes employed to generate the radicals from an initiator, although more usually irradiation will generate radicals from a monomer as in the following equation:

$$CH_2CHX \xrightarrow{\eta v} CH_2CHX^*$$
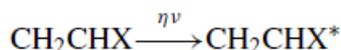
The activated molecule then functions as a starting radical. Since, however, irradiation is not normally a method of initiation in emulsion polymerisation, it will only be given a brief mention. Another well-known initiator is dibenzoyl peroxide, which decomposes in two stages:

$$C_6H_5CO.OO.OCC_6H_5 \longrightarrow 2\ C_6H_5COO\cdot$$
$$C_6H_5COO. \longrightarrow C_6H_5\cdot + CO_2$$
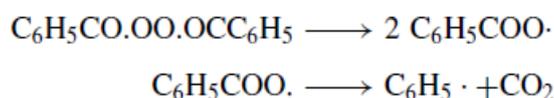
Studies have shown that under normal conditions the decomposition proceeds through to the second stage, and it is the phenyl radical C_6H_5. that adds on to the monomer. Dibenzoyl peroxide decomposes at a rate suitable for
most direct polymerisations in bulk, solution and aqueous media, whether in emulsion or bead form, since most of these reactions are performed at 60–100 °C. Dibenzoyl peroxide has a half-life of 5 h at 77 °C.
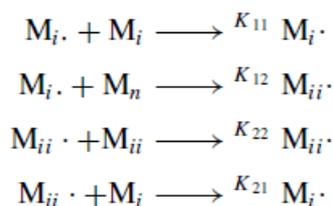
Redox polymerisation
The formation of free radicals, which has already been described, proceeds essentially by a unimolecular reaction, except in the case where ferrous ions are included. However, radicals can be formed readily by a bimolecular reaction, with the added advantage that they can be formed *in situ* at ambient or even sub ambient temperatures. These systems normally depend on the simultaneous reaction of an oxidizing and a reducing agent, and often require in addition a transition element that can exist in several valency states. The Haber–Weiss mechanism for initiation is the simplest case of a redox system.

Copolymerisation
There is no reason why the process should be confined to one species of monomer. In general, a growing polymer chain may add on most other monomers according to a general set of rules which, with some exceptions.
If we have two monomers denoted by M_i and M_n and M_i and M_n denote chain radicals having M_i and M_{ii} as terminal groups, irrespective of chain length four reactions are required to describe the growth of polymer:

$$M_i. + M_i \xrightarrow{\ K_{11}\ } M_i\cdot$$
$$M_i. + M_n \xrightarrow{\ K_{12}\ } M_{ii}\cdot$$
$$M_{ii}\cdot + M_{ii} \xrightarrow{\ K_{22}\ } M_{ii}\cdot$$
$$M_{ii}\cdot + M_i \xrightarrow{\ K_{21}\ } M_i\cdot$$

where K has the usual meaning of a reaction rate constant. These reactions reach a 'steady state' of copolymerisation in which the concentration of radicals is constant; i.e. the copolymerisation is constant and the rates of formation of radicals and destruction of radicals by chain termination are constant. Under these conditions the rates of formation of each of the two radicals remain constant and without considering any elaborate mathematical derivations we may define the monomer reactivity rations r_1 and r_2 by the expressions

$$r_1 = \frac{K_{11}}{K_{12}} \qquad \text{and} \qquad r_2 = \frac{K_{22}}{K_{21}}$$

These ratios represent the tendency of a radical formed from one monomer to combine with itself rather than with another monomer.

POLYMER STRUCTURE AND PROPERTIES

Polymer structure

The physical properties of a polymer are determined by the configuration of the constituent atoms, and to some extent by the molecular weight. The configuration is partly dependent on the main chain, and partly on the various side groups. Most of the polymers which we are considering are based on long chains of carbon atoms. In representing formulae we are limited by the plane of the paper, but a three-dimensional structure must be considered. The C—C internuclear distance is 1.54 A°, and where free rotation occurs the C—C—C bond is fixed at 109° (the tetrahedral angle). By tradition, we represent the polyethylene chain in the full extended fashion:

$$\underset{}{\overset{CH_2\quad CH_2\quad CH_2}{\diagdown\,\diagup\,\diagdown\,\diagup\,\diagdown\,\diagup}}$$
$$CH_2\quad CH_2$$
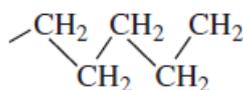
In practice the polymer is an irregular coil. The dimension most frequently used to describe an 'average' configuration is the 'root mean square', symbolised as r, which can be symbolised mathematically as

$$\frac{\left[\sum n_1 r_1{}^2\right]^{0.5}}{\left[\sum n_1\right]}$$

where there are n individual polymer molecules, and the distance apart of the chain ends is r_1, r_2, etc. This concept of root mean square is necessary in dealing with certain solution properties, and also certain properties of elasticity. No real polymer molecule can have completely free and unrestricted rotation, although an unbranched polythene $(C_2H_4)_n$ approaches closest to this ideal. (The theoretical polymethylene $(CH_2)_m$ has been prepared by the polymerisation of diazomethane CH_2N_2, with elimination of nitrogen.) The properties
of polyethylene over a wide range of molecular weights are, at ambient temperatures, those of a flexible, relatively inelastic molecule, which softens fairly readily. Chain branching hinders free rotation and raises the softening point of the polymer. Even a small number of crosslinks may, however, cause a major hindrance to the free rotation of the internal carbon bonds of the chain, resulting in a sharp increase in stiffness of the resulting product. Many side chain groups cause steric hindrance and restrictions in the free rotation about the double bonds. A typical example is polystyrene, where the planar zigzag formulation is probably modified by rotations of 180° a round alternate double bonds to produce a structure of minimum energy, such as
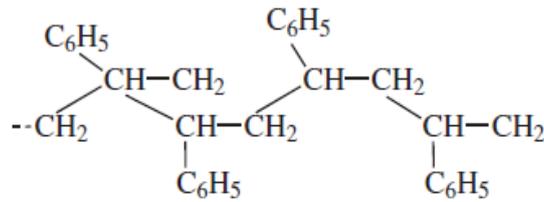
Because of the steric hindrance, polystyrene is a much harder polymer than polyethylene. Other molecular forces that effect the physical state of the polymers are the various dipole forces and the London or dispersion forces. If different parts of a group carry opposite charges, e.g. the carbonyl: C=O and hydroxyl —O—H$^+$, strong interchain attraction occurs between groups on different chains by attraction of opposite charges. This attraction is strongly temperature dependent. A special, case of dipole forces is that of hydrogen bonding,
by which hydrogen atoms attached to electronegative atoms such as oxygen or nitrogen exert a strong attraction towards electronegative atoms on other chains. The principal groups of polymers in which hydrogen bonding occurs are the hydroxyl and the amino. NHX or amide. CONH$_2$ groups and are illustrated as:
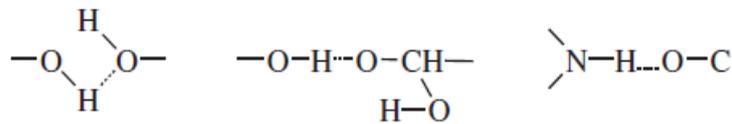
The net effect of dipole forces, especially hydrogen bonding, is to stiffen and strengthen the polymer molecules, and in extreme cases to cause crystalline polymers to be formed. Examples of polymers with strong hydrogen bonding are polyvinyl alcohol, polyacrylamide and all polymers including carboxylic acid groups, e.g. copolymers including units of acrylic acid CH$_2$:CHCOOH and crotonic acid CH$_2$:CH.CH$_2$COOH.

Molecular Weight Distribution

M_n: Number-Average Mol. Wgt.
The number-average molecular weight (molar mass) of a polymer containing N_i molecules of mass M_i is the arithmetic mean of the molar mass distribution:

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

M_w: Weight-Average Mol. Wgt.

The weight-average molecular weight (molar mass) is the sum of the products of the molar mass of each fraction multiplied by its weight fraction (w_i).
In terms of w_i or numbers of molecules, M_w is

$$M_w = \sum w_i M_i \qquad\qquad M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

M_z: Z-Average Mol. Wgt.
The z-average molecular weight (molar mass) is:

$$M_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}$$

M_z is especially sensitive to the presence of high-MW chains.

PDI: Polydispersity index
The molecular weight distribution, or polydispersity index, is the ratio of the weight- average molecular weight to the number-average molecular weight:

$$PDI = \frac{M_w}{M_n}$$

The polydispersity index of a monodisperse polymer is 1.00.
The polydispersity index increases as the polymer distribution broadens.

Molecular weight effects

The molecular weight scatter formed as a result of any polymerisation is typical of a Gaussian type. Before discussing the general effect of molecular weight on polymer characteristics, some further definitions are desirable. The number average molecular weight Mn is the simple arithmetical average of each molecule as a summation, divided by the number of molecules, the 'popular' idea of an average. Another measurement of average is the 'weight' average, and is an expression of the fact that the higher molecular weight fractions of a polymer play a greater role in determining the properties than do the fractions of lower molecular weight.
Its definition is based on multiplying the number of identical molecules of molecular weight Mn by the overall weight of molecules of that weight and dividing by the sum total of the weights. Mathematically, this is given by

$$M_w = \frac{\sum w_1 M_1}{\sum w_1}$$

where w_1 represents the overall weight of molecules of molecular weight M_1. The weight average molecular weight M_w is invariably greater than the number average as its real effect is to square the weight figure. For certain purposes, the z average is used in which M_1 in the equation above is squared, giving even higher prominence to the higher molecular weight fractions. In practice all the viscosity characteristics of a polymer solution depend on Mw rather than M_n. Thus nine unit fragments of a monomer of molecular weight 100 individually pulled off a polymer of molecular weight 1 000 000 reduces its M_n to 100 000. The Mw is just over 999 000. This corresponds to a negligible viscosity change. A number of methods of measuring molecular weight are used and are summarised here:

(a) *Osmometry*. This is a vapour pressure method, useful for polymers of molecular weight up to about 25 000; membrane osmometry is used for molecular weights from 20 000 to 1 000 000. These are number average methods.

(b) *Viscometry*. This is a relative method, but the simplest, and its application is widespread in industry. Viscometry is approximately a weight average method.

(c) *Light scattering*. This is a weight average method.

(d) *Gel permeation chromatography*. This is a direct fractionation method using molecular weight. It is relatively rapid and has proved to be one of the most valuable modern methods.

(e) *Chemical methods*. These usually depend on measuring distinctive end groups. They are number average methods.

In some cases selective precipitation can be used to fractionate a polymer according to molecular weight. This is essentially a relative method based on known standards. This method also differentiates between varying species in a copolymer.
The properties of polymers are governed to some extent by molecular weight as well as molecular structure. Properties also depend partly on the distribution of molecular weights, and in copolymers on the distribution of molecular species. The differences in solubility in solvents in exploited in fractionation where blended solvents are used, only one being a good solvent for the polymer. The added poor solvent will tend to precipitate the higher molecular weight fractions first. Thus polyvinyl acetate may be fractionated by the gradual addition of hexane C_6H_{14} to dilute solutions of the polymer in benzene.

Transition points
Although when dealing with a crystalline substance there is a sharp melting point, sometimes denoted Tm, when dealing with a polymer containing molecules with a range of molecular weights it is not possible to describe
the changes in state on heating in a similar manner. Amorphous materials, unless crosslinked or decomposing at a relatively low temperature, will soften gradually, and although a softening point or range may be quoted, this depends on an arbitrarily chosen test, usually on the time taken for a steel ball to penetrate a known thickness of the polymer.
However, an amorphous polymer has a number of physical changes of condition, the most important being the second-order transition point, usually referred to as Tg, already mentioned previously. Physically this transition point is connected with the mobility of the polymer chains. Below Tg, the chains may be regarded as substantially immobile, except for movements around an equilibrium position. Above this temperature appreciable movement of segments occurs in the polymer chains. Below the Tg, the polymer is a hard, brittle solid; above this temperature increased flexibility and possibly rubberlike characteristics are observed.