

Fundamentals of Polymer Chemistry

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1 THE CONCEPT OF A POLYMER

1.1 Historical introduction

The differences between the properties of crystalline organic materials of low molecular weight and the more indefinable class of materials referred to by Graham in 1861 as 'colloids' has long engaged the attention of chemists. This class includes natural substances such as gum acacia, which in solution are unable to pass through a semi-permeable membrane. Rubber is also included among this class of material.

The idea that the distinguishing feature of colloids was that they had a much higher molecular weight than crystalline substances came fairly slowly. Until the work of Raoult, who developed the cryoscopic method of estimating molecular weight, and Van't Hoff, who enunciated the solution laws, it was difficult to estimate even approximately the polymeric state of materials. It also seems that in the nineteenth century there was little idea that a colloid could consist, not of a product of fixed molecular weight, but of molecules of a broad band of molecular weights with essentially the same repeat units in each.

Vague ideas of partial valence unfortunately derived from inorganic chemistry and a preoccupation with the idea of ring formation persisted until after 1920. In addition chemists did not realise that a process such as ozonisation virtually destroyed a polymer as such, and the molecular weight of the ozonide, for example of rubber, had no bearing on the original molecular weight.

The theory that polymers are built up of chain formulae was vigorously advocated by Staudinger from 1920 onwards [1]. He extended this in 1929 to the idea of a three-dimensional network copolymer to account for the insolubility and infusibility of many synthetic polymers, for by that time technology had by far outstripped theory. Continuing the historical outline, mention must be made of Carothers, who from 1929 began a classical series of experiments which indicated that polymers of definite structure could be obtained by the use of classical organic chemical reactions, the properties of the polymer being controlled by the starting compounds [2]. Whilst this was based on research in condensation compounds (see Section 1.2) the principles hold good for addition polymers.

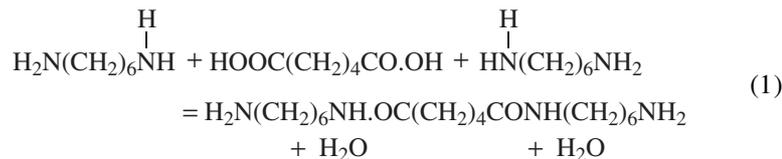
The last four decades have seen major advances in the characterisation of polymers. Apart from increased sophistication in methods of measuring molecular weight, such as the cryoscopic and vapour pressure methods, almost the whole range of the spectrum has been called into service to elucidate polymer structure. Ultraviolet and visible spectroscopy, infrared spectroscopy, Raman and emission spectroscopy, photon correlation spectroscopy, nuclear magnetic resonance and electron spin resonance all play a part in our understanding of the structure of polymers; X-ray diffraction and small-angle X-ray scattering have been used with solid polymers. Thermal behaviour in its various aspects, including differential thermal analysis and high-temperature pyrolysis followed by gas-liquid chromatography, has also been of considerable value. Other separation methods include size exclusion and hydrodynamic chromatography. Electron microscopy is of special interest with particles formed in emulsion polymerisation. Thermal and gravimetric analysis give useful information in many cases. There are a number of standard works that can be consulted [3–6].

1.2 Definitions

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 molecular 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 $\text{CH}_2\text{:CH}_2$ can be converted into polyethylene, of which the repeating unit is $\text{—CH}_2\text{CH}_2\text{—}$, often written as $\text{—(CH}_2\text{CH}_2)_n$, 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 formation of a condensation polymer can best be illustrated by the condensation of hexamethylenediamine with adipic acid to form the polyamide best known as nylon®:



Addition polymerisation of a different type takes place through the opening of a ring, especially the epoxide ring in ethylene oxide CH_2CH_2 .

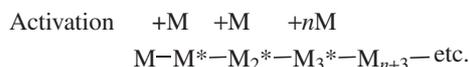


This opens as $-\text{CH}_2\text{CH}_2\text{O}-$; ethylene oxide thus acts as a bifunctional monomer forming a polymer as $\text{H}(\text{CH}_2\text{CH}_2\text{O})_n \text{CH}_2\text{CH}_2\text{OH}$, in this case a terminal water molecule being added. A feature of this type of addition is that it is 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 polymerisations are sometimes referred to as giving 'stepwise' addition polymers. This term may also refer to condensation resins. Further details are given in Chapter 7.

2 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:



The termination reaction depends on several factors, which will be discussed later.

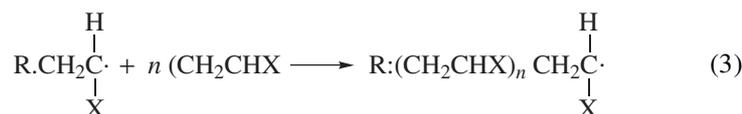
The mechanism of polymerisation can be divided broadly into two main classes, free radical polymerisation and ionic polymerisation, although there are some others.[†] Ionic polymerisation was probably the earliest type to be noted, and is divided into cationic and anionic polymerisations. Cationic polymerisation 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 $\text{C}_6\text{H}_5\text{CH}:\text{CH}_2$ and the vinyl ethers $\text{CH}_2:\text{CHOC}_n\text{H}_{2n+1}$ [7].

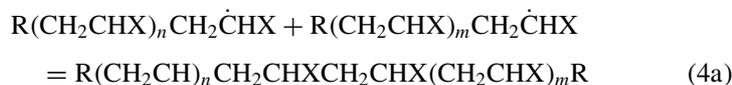
Anionic initiators include reagents capable of providing negative ions, and are effective with monomers containing electronegative substituents such

[†] Some modern sources prefer to refer to addition polymerisation and stepwise polymerisation.

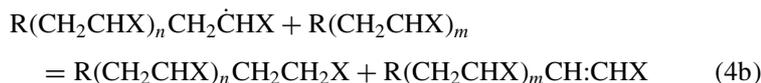
The new free radical can, however, in its turn add on extra monomer units, and a chain reaction occurs, representing the propagation stage:



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:



An alternative is disproportionation through transfer of a hydrogen atom:

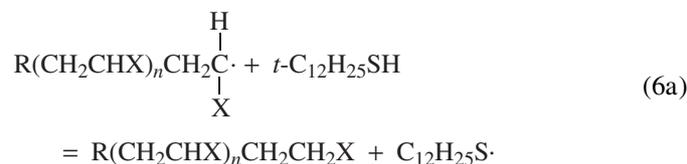


A further possibility is chain transfer. This is not a complete termination reaction, but it ends the propagation of a growing chain and enables a new one to commence. Chain transfer may take place via a monomer, and may be regarded as a transfer of a proton or of a hydrogen atom:



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 C₈ 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:

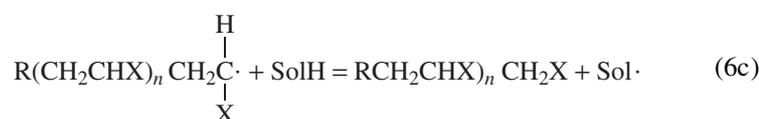


Chlorinated hydrocarbons are also commonly used as chain transfer agents, and with carbon tetrachloride it is a chlorine atom rather than a hydrogen atom

that takes part in the transfer:



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:

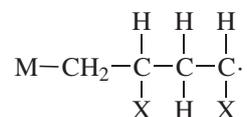


In all the cases mentioned, the radicals on the right-hand side of the equations must be sufficiently active to start a new chain; otherwise they act as a retarder or inhibitor (see the next section)

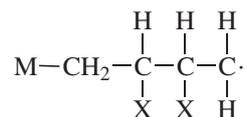
Derivatives of allyl alcohol $\text{CH}_2\text{:CHCH}_2\text{OH}$, although polymerisable by virtue of the ethylenic bond, have marked chain transfer properties and produce polymers of low molecular weight relatively slowly (see also Section 2.1.2). Stable intermediate products do not form during a polymerisation by a free radical chain reaction, and the time of formation of each polymer molecule is of the order of 10^{-3} s.

Kinetic equations have been deduced for the various processes of polymerisation. These have been explained simply in a number of treatises [10–13]. The classic book by Flory [10] derives these equations in greater detail.

A useful idea which may be introduced at this stage is that of the order of addition of monomers to a growing chain during a polymerisation. It has been assumed in the elementary discussion that if a growing radical $\text{M-CH}_2\text{C}\cdot$ is considered, the next unit of monomer will add on to produce



It is theoretically possible, however, for the next unit of monomer to add on, producing



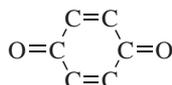
The latter type of addition in which similar groups add in adjacent fashion is known as 'head-to-head' addition in contrast to the first type above, known as 'head-to-tail' addition. The head-to-tail addition is much more usual in polymerisations, although in all cases head-to-head polymerisation occurs at least to some extent.

There are various ways of estimating head-to-head polymerisation, both physical and chemical. Nuclear magnetic resonance data should be mentioned amongst the former. The elucidation of polyvinyl acetate $(\text{CH}_2\text{CH}(\text{OOCCH}_3)_n)$ may be taken as representative of a chemical investigation. A head-to-tail polymer when hydrolysed to polyvinyl alcohol would typically produce units of $(\text{CH}_2\text{CHOHCH}_2\text{CHOH})$. A head-to-head unit is $(\text{CH}_2\text{CHOHCHOHCH}_2)$. In the latter case there are two hydroxyl groups on adjacent carbon atoms, and the polymer is therefore broken down by periodic acid HIO_4 , which attacks this type of unit. It is possible to estimate the amount of head-to-head addition from molecular weight reduction or by estimation of the products of oxidation.

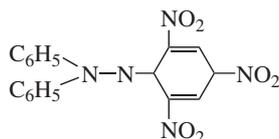
2.1.1 Retardation and inhibition

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 in the equivalent of equation (6a) 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.

In some cases, however, polymerisation is completely inhibited since the inhibitor reacts with radicals as soon as they are formed. The most well known is *p*-benzoquinone.



This produces radicals that are resonance stabilised and are removed from a system by mutual combination or disproportionation. Only a small amount of inhibitor is required to stop polymerisation of a system. A calculation shows that for a concentration of azodiisobutyronitrile of $1 \times 10^{-3} \text{ mole}^{-1}$ in benzene at 60°C , a concentration of $8.6 \times 10^{-5} \text{ mole L}^{-1} \text{ h}^{-1}$ of inhibitor is required [10]. *p*-Hydroquinone $\text{C}_6\text{H}_4(\text{OH})_2$, probably the most widely used inhibitor, only functions effectively in the presence of oxygen which converts it to a quinone-hydroquinone complex giving stable radicals. One of the most effective inhibitors is the stable free radical 2 : 2-diphenyl-1-picryl hydrazyl:



This compound reacts with free radicals in an almost quantitative manner to give inactive products, and is used occasionally to estimate the formation of free radicals.

Aromatic compounds such as nitrobenzene $C_6H_5NO_2$ and the dinitrobenzenes (*o*-, *m*-, *p*-) $C_6H_4(NO_2)_2$ are retarders for most monomers, e.g. styrene, but tend to inhibit vinyl acetate polymerisation, since the monomer produces very active radicals which are not resonance stabilised. Derivatives of allyl alcohol such as allyl acetate are a special case. Whilst radicals are formed from this monomer, the propagation reaction (equation 3) competes with that shown in the following equation:



In this case the allylic radical is formed by removal of an alpha hydrogen from the monomer, producing an extremely stable radical which disappears through bimolecular combination. Reaction (7) is referred to as a degradative chain transfer [11–14].

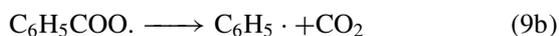
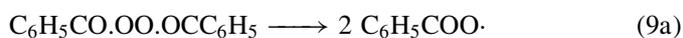
2.1.2 Free radical initiation

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:



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. The decomposition of azodiisobutyronitrile has already been mentioned (see Section 2.1), and it may be noted that the formation of radicals from this initiator is accelerated by irradiation.

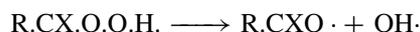
Another well-known initiator is dibenzoyl peroxide, which decomposes in two stages:



Studies have shown that under normal conditions the decomposition proceeds through to the second stage, and it is the phenyl radical $C_6H_5\cdot$ 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.

A number of other diacyl peroxides have been examined. These include *o*-, *m*- and *p*-bromobenzoyl peroxides, in which the bromine atoms are useful as markers to show the fate of the radicals. Dilauroyl hydroperoxide $C_{11}H_{23}CO.OO.OCC_{11}H_{23}$ has been used technically.

Hydroperoxides as represented by *t*-butyl hydroperoxide $(CH_3)_3C.O.O.H$ and cumene hydroperoxide $C_6H_5C(CH_3).O.O.H$ represent an allied class with technical interest. The primary dissociation



is by secondary decompositions, which may include various secondary reactions of the peroxide induced by the radical in a second-order reaction and by considerable chain transfer. These hydroperoxides are of interest in redox initiators (see Section 2.1.3).

Dialkyl peroxides of the type di-*t*-butyl peroxide $(CH_3)_3C.O.O.C(CH_3)_3$ are also of considerable interest, and tend to be subject to less side reactions except for their own further decomposition, as shown in the second equation below:



These peroxides are useful for polymerisations that take place at 100–120 °C, whilst di-*t*-butyl peroxide, which is volatile, has been used to produce radicals for gas phase polymerisations.

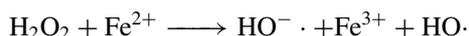
A number of peresters are in commercial production, e.g. *t*-butyl perbenzoate $(CH_3)_3C.O.O.O.C_6H_5$, which acts as a source of *t*-butoxy radicals at a lower temperature than di-*t*-butyl hydroperoxide, and also as a source of benzyloxy radicals at high temperatures. The final decomposition, apart from some secondary reactions, is probably mainly



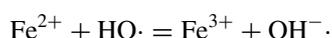
For a more detailed description of the decomposition of peroxides a monograph by one of the current authors should be consulted [15]. Whilst some hydroperoxides have limited aqueous solubility, the water-soluble initiators are a major type utilised for polymerisations in aqueous media. In addition, some peroxides of relatively high boiling point such as *tert*-butyl hydroperoxide are sometimes added towards the end of emulsion polymerisations (see Chapter 2) to ensure a more complete polymerisation. These peroxides are also sometimes included in redox polymerisation (see Section 2.1.3), especially to ensure rapid polymerisation of the remaining unpolymerised monomers.

Hydrogen peroxide H_2O_2 is the simplest compound in this class and is available technically as a 30–40 % solution. (This should not be confused with the 20–30 volume solution available in pharmacies.) Initiation is not

caused by the simple decomposition $\text{H}_2\text{O}_2 = 2 \text{OH}\cdot$, but the presence of a trace of ferrous ion, of the order of a few parts per million of water present, seems to be essential, and radicals are generated according to the Haber–Weiss mechanism:



The hydroxyl radical formed commences a polymerisation chain in the usual manner and is in competition with a second reaction that consumes the radical:



When polymerisations are performed it seems of no consequence whether the soluble iron compound is in the ferrous or ferric form. There is little doubt that an equilibrium exists between the two states of oxidation, probably due to a complex being formed with the monomer present.

The other major class of water-soluble initiators consists of the persulfate salts, which for simplicity may be regarded as salts of persulfuric acid $\text{H}_2\text{S}_2\text{O}_8$. Potassium persulfate $\text{K}_2\text{S}_2\text{O}_8$ is the least soluble salt of the series, between 2 and 4 % according to temperature, but the restricted solubility facilitates its manufacture at a lower cost than sodium persulfate $\text{Na}_2\text{S}_2\text{O}_8$ or ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The decomposition of persulfate may be regarded as thermal dissociation of sulfate ion radicals:



A secondary reaction may, however, produce hydroxyl radicals by reaction with water, and these hydroxyls may be the true initiators:



Research using ^{35}S -modified persulfate has shown that the use of a persulfate initiator may give additional or even sole stabilization to a polymer prepared in emulsion. This may be explained by the polymer having ionised end groups from a persulfate initiator, e.g. ZOSO_3Na , where Z indicates a polymer residue.

A general account of initiation methods for vinyl acetate is applicable to most monomers [16].

2.1.3 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 subambient temperatures. These systems normally depend on the simultaneous reaction of an oxidizing and a reducing agent, and often require in addition a

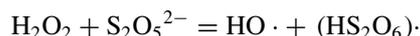
transition element that can exist in several valency states. The Haber–Weiss mechanism for initiation is the simplest case of a redox system.

Redox systems have assumed considerable importance in water-based systems, since most components in systems normally employed are water soluble. This type of polymerisation was developed simultaneously during the Second World War in Great Britain, the United States and Germany, with special reference to the manufacture of synthetic rubbers. For vinyl polymerisations, as distinct from those where dienes are the sole or a major component, hydrogen peroxide or a persulfate is the oxidizing moiety, with a sulfur salt as the reductant. These include sodium metabisulfite $\text{Na}_2\text{S}_2\text{O}_5$, sodium hydrosulfate (also known as hyposulfite or dithionite) $\text{Na}_2\text{S}_2\text{O}_4$, sodium thiosulfate $\text{Na}_2\text{S}_2\text{O}_3$ and sodium formaldehyde sulfoxylate $\text{Na}(\text{HSO}_3\cdot\text{CH}_2\text{O})$. The last named is one of the most effective and has been reported to initiate polymerisations, in conjunction with a persulfate, at temperatures as low as 0°C . In almost all of these redox polymerisations, a complete absence of oxygen seems essential, possibly because of the destruction by oxygen of the intermediate radicals that form.

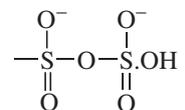
However, in redox polymerisations operated under reflux conditions, or in otherwise unsealed reactors, it is often unnecessary in large-scale operations to continue the nitrogen blanket after polymerisation has begun, probably because monomer vapour acts as a sealant against further oxygen inhibition.

There have been relatively few detailed studies of the mechanisms of redox initiation of polymerisation. A recent survey of redox systems is available [17]. The review already quoted [15] gives a number of redox initiators, especially suitable for vinyl acetate, most of which are also suitable for other monomers.

Since almost all such reactions take place in water, a reaction involving ions may be used as an illustration. Hydrogen peroxide is used as the oxidizing moiety, together with a bisulfite ion:



The HS_2O_6 represented here is not the dithionate ion, but an ion radical whose formula might be



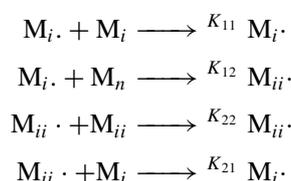
Alternatively, a hydroxyl radical may be formed together with an acid dithionate ion. Some evidence exists for a fragment of the reducing agent rather than the oxidizing agent acting as the starting radical for the polymerisation chain. This seems to be true of many phosphorus-containing reducing agents; e.g. hypophosphorous acid with a diazonium salt activated by a copper salt when used as an initiating system for acrylonitrile shows evidence of a direct phosphorus bond with the polymer chain and also shows that the phosphorus is present as one

atom per chain of polymer [18]. Many of the formulations for polymerisation quoted in the various application chapters are based on redox initiation.

2.2 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, will be enunciated later.

If we have two monomers denoted by M_i and M_n and $M_i\cdot$ and $M_n\cdot$ 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:



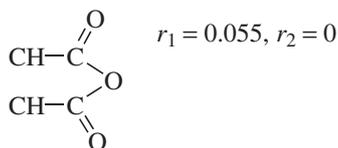
where K has the usual meaning of a reaction rate constant. These reactions reach a 'steady state' of copolymerisation in which the concentration of radicals is constant; i.e. the copolymerisation is constant and the rates of formation of radicals and destruction of radicals by chain termination are constant. 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 ratios r_1 and r_2 by the expressions

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

These ratios represent the tendency of a radical formed from one monomer to combine with itself rather than with another monomer. It can be made intelligible by a practical example. Thus, for styrene $C_6H_5CH:CH_2$ (r_1) and butadiene $CH_2:CHCH:CH_2$ (r_2), $r_1 = 0.78$ and $r_2 = 1.39$. These figures tend to indicate that if we start with an equimolar mixture, styrene radicals tend to copolymerise with butadiene rather than themselves, but butadiene has a slight preference for its radicals to polymerise with each other. This shows that if we copolymerise an equimolar mixture of styrene and butadiene, a point occurs at which only styrene would remain in the unpolymerised state. However, for styrene and methyl methacrylate, $r_1 = 0.52$ and $r_2 = 0.46$ respectively. These two monomers therefore copolymerise together in almost any ratio. As the properties imparted to a copolymer by equal weight ratios of these two monomers are broadly similar, it is often possible to replace one by the other on cost alone, although the inclusion of styrene may cause yellowing of copolymer films exposed to sunlight.

Nevertheless, if an attempt is made to copolymerise vinyl acetate with styrene, only the latter will polymerise, and in practice styrene is an inhibitor for vinyl acetate. The reactivity ratios, r_1 and r_2 for styrene and vinyl acetate respectively have been given as 55 and 0.01. However, vinyl benzoate $\text{CH}_2\text{:CHOCC}_6\text{H}_5$ has a slight tendency to copolymerise with styrene, probably because of a resonance effect. If we consider the case of vinyl acetate and *trans*-dichlorethylene (TDE) *trans*- $\text{CH}_2\text{Cl:CH}_2\text{Cl}$, $r_1(\text{vinyl acetate}) = 0.85$ and $r_2 = 0$. The latter implies that TDE does not polymerise by itself, but only in the presence of vinyl acetate. Vinyl acetate, on the other hand, has a greater tendency to copolymerise with TDE than with itself, and therefore if the ratios are adjusted correctly all of the TDE can be copolymerised.

Let us consider the copolymerisation of vinyl acetate and maleic anhydride:



Sometimes a very low r_2 is quoted for maleic anhydride, e.g. 0.003. Vinyl acetate thus has a strong preference to add on to maleic anhydride in a growing radical rather than on to another vinyl acetate molecule, whilst maleic anhydride, which has practically no tendency to add on to itself, readily adds to a vinyl acetate unit of a growing chain. (Note that homopolymers of maleic anhydride have been made by drastic methods.) This is a mathematical explanation of the fact that vinyl acetate and maleic anhydride tend to alternate in a copolymer whatever the starting ratios. Excess maleic anhydride, if present, does not homopolymerise. Surplus vinyl acetate, if present, forms homopolymer, a term used to distinguish the polymer formed from a single monomer in contradistinction to a copolymer. Styrene also forms an alternating copolymer with maleic anhydride.

Only in one or two exceptional cases has both r_1 and r_2 been reported to be above 1. Otherwise it is a general principle that at least one of the two ratios is less than 1. It will be readily seen that in a mixture of two monomers the composition of the copolymer gradually changes unless an 'azeotropic' mixture is used, i.e. one balanced in accord with r_1 and r_2 , provided that r_1 and r_2 are each < 1 .

Polymers of fixed composition are sometimes made by starting with a small quantity of monomers, e.g. 2–5 % in the desired ratios, and adding a feedstock which will maintain the original ratio of reactants. This is especially noted, as will be shown later, in emulsion polymerisation. If it is desired to include the more sluggishly polymerising monomer, and an excess is used, this must be removed at the end, by distillation or extraction.

However, as a general principle it should not be assumed that, because two or more monomers copolymerise completely, the resultant copolymer is reasonably homogeneous. Often, because of compatibility variations amongst the constantly varying species of polymers formed, the properties of the final copolymer are liable to vary very markedly from those of a truly homogeneous copolymer.

The term ‘copolymer’ is sometimes confined to a polymer formed from two monomers only. In a more general sense, it can be used to cover polymers formed from a larger number of monomers, for which the principles enunciated in this section apply. The term ‘terpolymer’ is sometimes used when three monomers have been copolymerised.

When copolymerisation takes place in a heterogeneous medium, as in emulsion polymerisation (see Chapter 2), whilst the conditions for copolymerisation still hold, the reaction is complicated by the environment of each species present. Taking into account factors such as whether the initiator is water or monomer soluble (most peroxidic organic initiators are soluble in both), the high aqueous solubility of monomers such as acrylic acid $\text{CH}_2\text{:CHCOOH}$ and, if partition between water-soluble and water-insoluble monomers is significant, the *apparent* reactivities may differ markedly from those in a homogeneous medium. Thus, in an attempted emulsion polymerisation, butyl methacrylate $\text{CH}_2\text{:C}(\text{CH}_3)\text{COOC}_4\text{H}_9$ and sodium methacrylate $\text{NaOCC}(\text{CH}_3)\text{:CH}_2$ polymerise substantially independently. On the other hand, methyl methacrylate and sodium methacrylate will copolymerise together since methyl methacrylate has appreciable water solubility [19, 20].

More unusually vinyl acetate and vinyl stearate $\text{CH}_2\text{:CHOCC}_{17}\text{H}_{35}$ will only copolymerise in emulsion if a very large surface is present due to very small emulsion particles (of order $<0.1 \mu\text{m}$) or a class of emulsifier known as a ‘solubiliser’ is present, which has the effect of solubilising vinyl stearate to a limited extent in water, increasing the compatibility with vinyl acetate which is about 2.3 % water soluble.

Problems relating to copolymerisation in emulsion will be found in Chapter 3 and Sections 2.2.1 and 8.5. For more advanced texts, see the Appendix, Section 8.

2.2.1 The *Q, e* scheme

Several efforts have been made to place the relative reactivities of monomers on a chemical–mathematical basis. The chief of these has been due to Alfrey and Price [21]. Comparison of a series of monomers with a standard monomer is most readily made by using the reciprocal of r with respect to that monomer; i.e. the higher the value of $1/r$ the poorer the copolymerisation characteristics. Thus, taking styrene as an arbitrary 1.0, methyl methacrylate 2.2 and acrylonitrile 20, vinyl acetate is very high on this scale. However, the relative scale of reactivities is not interchangeable using different radicals as references [22].

It has been observed that the product $r_1 r_2$ tends to be smallest when one of the two monomers concerned has strongly electropositive (electron-releasing) substituents and there are electronegative (electron-attracting) substituents on the other. Thus alternation tends to occur when the polarities of the monomers are opposite.

Alfrey and Price therefore proposed the following equation:

$$K_{12} = P_1 Q_2 \exp(-e_1 e_2)$$

where P_1 and Q_2 are constants relating to the general activity of the monomers M_1 and M_2 respectively and e_1 and e_2 are proportional to the residual electrostatic charges in the respective reaction groups. It is assumed that each monomer and its corresponding radical has the same reactivity. Hence, from the reactions in Section 2.2,

$$r_1 r_2 = \exp[-(e_1 - e_2)^2]$$

The product of the reactivity ratios is thus independent of Q . The following equation is also useful:

$$Q_2 = \frac{Q_1}{r_1} \exp[-e_1(e_1 - e_2)]$$

A series of Q and e values has been assigned to a series of monomers by Price [23]. Typical e values are -0.8 for butadiene, -0.8 for styrene, -0.3 for vinyl acetate, $+0.2$ for vinyl chloride, $+0.4$ for methyl methacrylate and $+1.1$ for acrylonitrile.

Whilst the Q, e scheme is semi-empirical, it has proved highly useful in coordinating otherwise disjointed data.

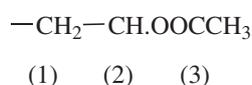
3 CHAIN BRANCHING; BLOCK AND GRAFT COPOLYMERS

3.1 Chain branching

Occasionally chain transfer (Section 2.1) results in a hydrogen atom being removed from a growing polymer chain. Thus in a chain that might be represented as $(\text{CH}_2\text{CHX})_n$, the addition of further units of $\text{CH}_2:\text{CHX}$ might produce an intermediate as $(\text{CH}_2\text{CHX})_n \cdot \text{CH}_2\dot{\text{C}}\text{X.C.CH}_2\text{CHX}$. A short side chain is thus formed by hydrogen transfer. For simplicity, this has been shown on the penultimate unit, but this need not be so; nor is there any reason why there should only be one hydrogen abstraction per growing chain. From the radicals formed branched chains may grow.

Chain branching occurs most readily from a tertiary carbon atom, i.e. a carbon atom to which only one hydrogen atom is attached, the other groupings depending on a carbon to carbon attachment, e.g. an alkyl or an aryl group. The mechanism is based on abstraction of a hydrogen atom, although of

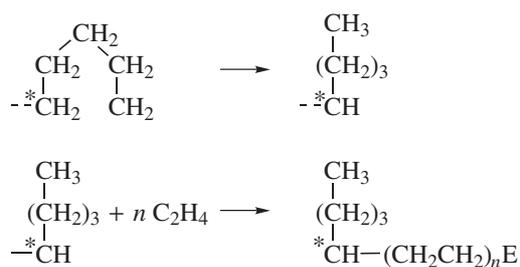
course abstraction can also occur with a halogen atom. With polyvinyl acetate, investigations have shown that limited chain transfer can occur through the methyl grouping of the acetoxy group $\cdot\text{OOCCH}_3$. The result of this type of branching is a drastic reduction of molecular weight of the polymer during hydrolysis, since the entire branch is hydrolysed at the acetoxy group at which branching has occurred, producing an extra fragment for each branch of the original molecule. It has also been shown that in a unit of a polyvinyl acetate polymer the ratio of the positions marked (1), (2) and (3) is 1 : 3 : 1.



It is now known that there is significant chain transfer on the vinyl H atoms of vinyl acetate [24].

Another method of forming branched chains involves the retention of a vinyl group on the terminal unit of a polymer molecule, either by disproportionation or by chain transfer to monomer. The polymer molecule with residual unsaturation could then become the unit of a further growing chain. Thus a polymer molecule of formula $\text{CH}_2\text{CHX}-(\text{Mp})$, where Mp represents a polymer chain, may become incorporated into another chain to give a structure $(\text{Mq})\cdot\text{CH}_2\cdot\text{CX}-(\text{Mp})(\text{Mr})$, where Mq and Mr represent polymer chains of various lengths, that may be of the same configuration or based on different monomers, depending on conditions.

Ethylene, $\text{CH}_2:\text{CH}_2$, which is normally a gas (b.p. 760 mm Hg: -104°C , critical temperature 9.5°C) is prone to chain branching when polymerised by the free radical polymerisation process at high temperatures and pressures, most branches having short chains. In this case intramolecular formation of short chains occurs by chain transfer, and is usually known as 'back biting'.



where E represents an end group. The carbon with the asterisk is the same throughout to illustrate the reaction.

Excessive chain branching can lead to crosslinking and insolubility (Chapter 5). It is possible for chain branching to occur from completed or 'dead' molecules by hydrogen abstraction, and although this impinges on grafting, it is treated as a chain branching phenomenon if it occurs during a polymerisation.

3.2 Graft copolymers

The idea of a graft copolymer is a natural extension of the concept of chain branching and involves the introduction of active centres in a previously prepared chain from which a new chain can grow. In most cases this is an added monomer, although two-polymer molecules can combine directly to form a graft. The graft base need not be an ethylene addition polymer. Various natural products, including proteins and water-soluble gums, have been used as a basis for graft copolymers by formation of active centres.

A block copolymer differs from a graft in only that the active centre is always at the end of the molecule. In the simplest case, an unsaturated chain end arising from a chain transfer can act as the basis for the addition of a block of units of a second monomer, whilst successive monomers or the original may make an additional block. Another possibility is the simultaneous polymerisation of a monomer which is soluble only in water with one which is water insoluble, provided that the latter is in the form of a fine particle size emulsion. Whether the initiator is water soluble or monomer soluble, an extensive transfer through the surface is likely, with the continuation of the chain in the alternate medium.

There are a number of ways of achieving active centres, many of which depend on an anionic or cationic mechanism, especially the former. However, since in water-based graft polymerisation only free radical polymerisations and possibly a few direct chemical reactions involving an elimination are of interest, the discussion here will be confined to these topics.

Graft centres are formed in much the same manner as points of branching, with the difference that the graft base is preformed. It may be possible to peroxidise a polymer directly with oxygen, to provide hydroperoxide O.OH groups directly attached to carbon. This is facilitated, particularly, where numerous tertiary carbon occur as, for example, in polypropylene $(-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-)$. In

other cases the direct use of a peroxide type of initiator encourages the formation of free radicals on existing polymer chains. Particularly useful in this respect is *tert*-butyl hydroperoxide, *tert*-C₄H₉.O.OH, because of the strong tendency of the radical formed from it to abstract hydrogen atoms. Dibenzoyl peroxide (C₆H₅CO.O)₂ is also frequently used as a graft initiator. In aqueous systems initiators such as *tert*-butyl hydroperoxide may be used in conjunction with a salt of a sulfur-reducing acid to lower the temperature at which radicals are generated.

Graft methods make it possible to add to polymers such as butadiene–styrene chains of a monomer that is not normally polymerisable, such as vinyl acetate. The polymerisation medium in which a graft can take place is in general not restricted; the process may take place fairly readily in emulsion. There is a vast amount of literature available on the formation and properties of graft copolymers [25].

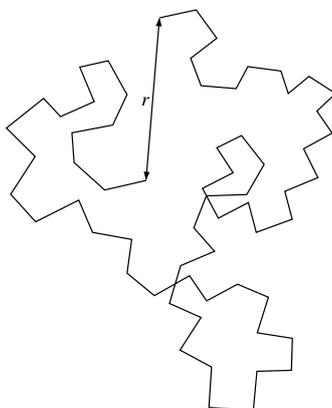


Figure 1.1 Diagrammatic molecular coil. (Reproduced from Moore [27].)

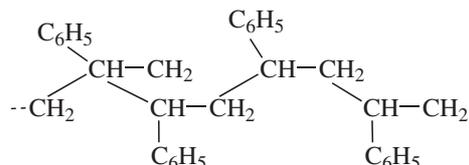
In practice the polymer is an irregular coil, as shown in Figure 1.1. The dimension most frequently used to describe an 'average' configuration is the 'root mean square', symbolised as r , which can be symbolised mathematically as

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

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.

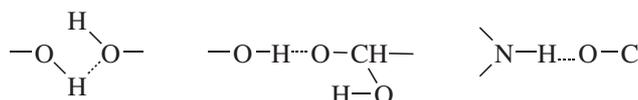
No real polymer molecule can have completely free and unrestricted rotation, although an unbranched polythene $(C_2H_4)_n$ approaches closest to this ideal. (The theoretical polymethylene $(CH_2)_m$ has been prepared by the polymerisation of diazomethane CH_2N_2 , with elimination of nitrogen.) The properties 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° around 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 by the following:



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 (see below). Examples of polymers with strong hydrogen bonding are polyvinyl alcohol $(\text{—CH}_2\text{CHOH—})_n$, polyacrylamide $(\text{CH}_2\text{CH—})_n$ and all polymers including carboxylic acid



groups, e.g. copolymers including units of acrylic acid $\text{CH}_2\text{:CHCOOH}$ and crotonic acid $\text{CH}_2\text{:CH.CH}_2\text{COOH}$.

The London forces between molecules come from time-varying dipole moments arising out of the continuously varying configurations of nuclei and electrons which must, of course, average out to zero. These forces, which are independent of temperature, vary inversely as the seventh power of the distance between the chains, as do dipole forces, and only operate at distances below 5 \AA .

Forces between chains lead to a cohesive energy, approximately equal to the energies of vapourisation or sublimation. A high cohesive energy is associated with a high melting point and may be associated with crystallinity. A low cohesive energy results in a polymer having a low softening point and easy deformation by stresses applied externally.

Whilst inorganic materials often crystallise and solid organic polymers generally possess crystallinity, X-ray diffraction patterns have shown that in some polymers there are non-amorphous and crystalline regions, or crystallites. Whilst crystallinity is a characteristic of natural products such as proteins and synthetic condensation products such as the polyamide fibres, crystallinity sometimes occurs in addition polymers. Even if we discount types prepared by special methods, such as use of the Ziegler–Natta catalysts [8], which will not

be discussed further here since they are not formed by classical free radical reactions, a number of polymers prepared directly or indirectly by free radical methods give rise to crystallinity.

One of these already mentioned is polyvinyl alcohol, formed by hydrolysis of polyvinyl acetate. It must, however, be almost completely hydrolysed, of the order of 99.5 %, to be effectively crystalline, under which conditions it can be oriented and drawn into fibres. If hydrolysis is partial, the resulting disorder prevents crystallinity. This is the case with the so-called 'polyvinyl alcohol' of saponification value about 120, which is used for emulsion polymerisation. This polymer consists, by molar proportions, of about 88 % of vinyl alcohol and 12 % of vinyl acetate units.

Polymers of vinylidene chloride CH_2CCl_2 are strongly crystalline. Polymers of vinyl chloride CH_2CHCl and acrylonitrile CH_2CHCN are partially crystalline, but crystallinity can be induced by stretching the polymer to a fibre structure to induce orientation. Polyethylene, when substantially free from branching, is crystalline and wax-like because of the simple molecular structure. It does not, of course, have the other properties associated with crystallinity caused by hydrogen bonding, such as high cohesive strength.

Another type of crystallinity found in polymers is side chain crystallinity, e.g. in polyvinyl stearate $(-\text{CH}_2\text{CH}-)_n$ or polyoctadecyl acrylate

$(-\text{CH}_2\text{CH}-)_n$ $\begin{matrix} \text{OOC.C}_{17}\text{H}_{35} \\ | \\ \text{COOC}_{16}\text{H}_{37} \end{matrix}$ This type of crystallinity has relatively little application,

since the products tend to simulate the crystalline properties of a wax. However, this property may be useful in connection with synthetic resin-based polishes, the subject of a later chapter.

In considering the effect of side chains on polymer properties, it is convenient to take a series of esters based on acrylic acid and compare the derived polymers. These are most readily compared by the second-order transition points (T_g). Technical publications show some variation in these figures, probably because of variations in molecular weight. However, polymers prepared under approximately the same conditions have much the same degree of polymerisation (DP), and emulsion polymers are preferred as standards in this connection.

Figure 1.2 shows the variations in T_g of a series of homologous polymers based on acrylic acid $\text{CH}_2\text{:CHCOOH}$ and methacrylic acid $\text{CH}_2\text{:C}(\text{CH}_3)\text{COOH}$. The striking difference in T_g of the polymers based on the methyl esters should be noted, being almost 100 °C. This is due to the steric effect of the angular methyl .CH_3 group on the carbon atom to which the carboxyl group is attached. Polymethyl methacrylate is an extremely hard solid, used *inter alia* for 'unbreakable' glass.

The effect of the angular methyl group slowly diminishes as the alcohol side chains become longer; these latter keep the chains apart and reduce the polar

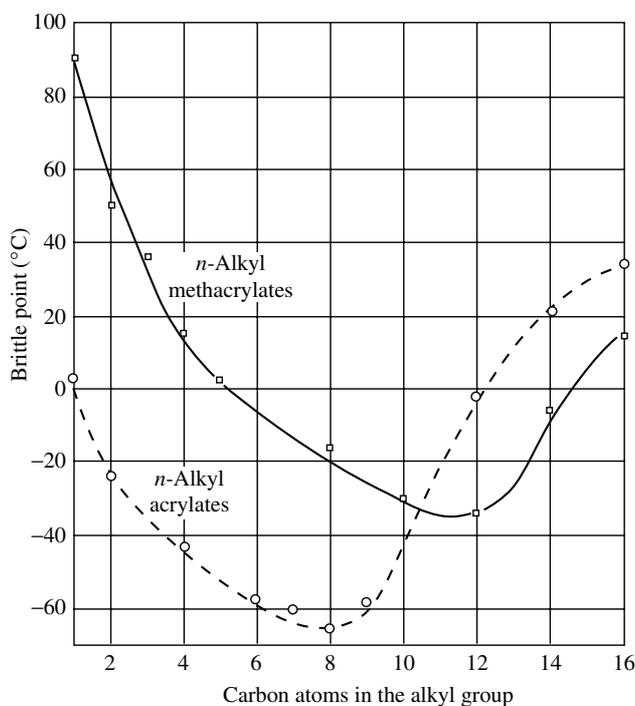


Figure 1.2 Brittle points of polymeric *n*-alkyl acrylates and methacrylates. (Reproduced with permission from Riddle [28].)

forces. In consequence the T_g diminishes in the case of alkyl ester polymers of acrylic acid until the alkyl chain reaches about 10 carbon atoms. It then increases again with side chain crystallinity. The methacrylate ester polymers, however, continue to drop in T_g , usually until a C_{13} alkyl group is reached, since the steric effect of the angular methyl group on the main chain also prevents side chain crystallinity at first.

Similar conditions prevail in the homologous series of vinyl esters of straight chain fatty acids based on the hypothetical vinyl alcohol $CH_2.CHOH$. From polyvinyl formate $(-CH_2CH-)_n$ through polyvinyl acetate $(-CH_2CH-)_n$ to vinyl laurate $(-CHCH-)_n$ there is a steady fall in T_g , the polymers varying

from fairly brittle films derived from a latex at ambient temperature to viscous sticky oils as the length of the alcohol chain increases. Note, however, that the polymerisation and even copolymerisation of monomers with long side chains, above about C_{12} , becomes increasingly sluggish.

The above examples, in both the acrylic and the vinyl ester series, have considered the effect of straight chains inserted as side chains in polymer molecules. The effect of branched chains, however, is different. As chain branching increases, the effect of the overall size of the side chain diminishes. An example of this will be illustrated in Chapter 9 when considering specific examples of monomers that might be the basis of emulsions for paints. Thus polyisobutyl methacrylate has a higher T_g than polybutyl methacrylate. Polymers based on *tert*-butyl acrylate or *tert*-butyl methacrylate have a higher softening point than the corresponding *n*-butyl esters.

Another interesting example of the effect of branched chains is that of the various synthetic branched chain acids in which the carbon atom in the α position to the carbon of the carboxyl is quaternary, corresponding to a general formula $\text{HOOC.C(R}_1\text{)(R}_2\text{)(R}_3\text{)}$, where R_1 is CH_3 , R_2 is CH_3 or C_2H_5 and R_3 is a longer chain alkyl group, which may be represented as $\text{C}_{4-6}\text{H}_{9-13}$. These form vinyl esters which correspond in total side chain length to vinyl caprate $\text{CH}_2\text{:CHOOC C}_9\text{H}_{19}$ but do not impart the same flexibility in copolymers [29].

It is often more practical to measure the effect of monomers of this type by copolymerising them with a harder monomer such as vinyl acetate and measuring the relative effects. Thus the vinyl esters of these branched chain acids, although they are based on C_{10} acids on average, are similar to a C_4 straight chain fatty acid as far as lowering of the T_g is concerned. It is also interesting to note that polymers and copolymers of these acids afford much greater resistance to hydrolysis than polymers of vinyl esters of *n*-alkyl acids. In copolymers these highly branched groups have a shielding effect on neighbouring ester groups, reducing their ease of hydrolysis by alkali [30, 31]. In this connection the angular methyl group in methacrylate ester polymers has the effect of making hydrolysis of these products extremely difficult.

4.2 Molecular weight effects

The molecular weight scatter formed as a result of any polymerisation is typical of a Gaussian type. Thus a fractionation of polystyrene is shown in Figure 1.3, in which the distribution and cumulative weight totals are shown as a percentage.

Before discussing the general effect of molecular weight on polymer characteristics, some further definitions are desirable. The number average molecular weight M_n 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 M_n by the overall weight of molecules of that weight and

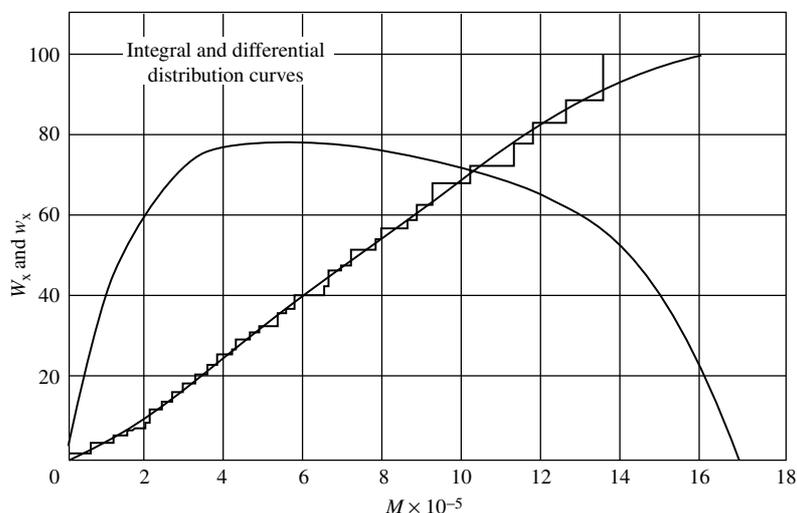


Figure 1.3 Molecular weight distribution for thermally polymerised polystyrene as established by fractionation. (From the results of Merz and Raetz [32].)

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 M_w 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 M_w 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:

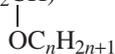
- (a) *Osmometry*. This is a vapour pressure method, useful for polymers of molecular weight up to about 25 000; membrane osmometry is used for molecular weights from 20 000 to 1 000 000. These are number average methods.
- (b) *Viscometry*. This is a relative method, but the simplest, and its application 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 is 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.

In some cases molecular weight variations have an extreme effect on polymer properties. This is particularly significant in the polyvinyl ethers ($-CH_2CH$)



in which a polymer can vary from an oil at a molecular weight of about 5000 to a rubbery material if the molecular weight is above 100 000. The polyvinyl ethers, however, are not prepared as homopolymers by a free radical mechanism. The differences are usually illustrated by the change in the second-order transition point (see the next section). The softening points, which correspond approximately to melting ranges, and which are estimated by standard methods [33], are also affected by molecular weight.

The overall effect of solvents on polymers is too complex to be considered here. However, the reader is referred to the treatise by Flory [10] or the simpler treatment as shown in references [3] to [6], [11] and [12].

4.3 Transition points

Although when dealing with a crystalline substance there is a sharp melting point, sometimes denoted T_m , 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 T_g , already mentioned previously. Physically this transition point is connected with the mobility of the polymer chains. Below T_g , 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 T_g , the polymer is a hard, brittle solid; above this temperature increased flexibility and possibly rubber-like characteristics are observed.

The second-order transition point may be measured in various ways; e.g. the rate of change of polymer density varies with temperature, as does the rate of change of other properties such as specific heat. Most useful is differential thermal analysis (DTA), which indicates the differential in the heating capacity of a substance. Modern DTA instruments are extremely sensitive.

The significance of T_g in emulsion polymers is indicated in Chapter 4 (Section 4.4). It may be noted that an alternative temperature, known as the minimum film formation temperature (MFT) is frequently a substitute for T_g . This is the lowest temperature at which a drying emulsion containing polymer particles will form a continuous film. Because of the conditions of film formation, this temperature is usually 3–5 °C higher than the T_g . DTA results have shown that many polymers have transition points other than T_g . These are associated with the thermal motion of the molecules.

In many cases where a polymer has practical utility, it may be desirable that T_g should be reduced to achieve reasonable flexibility for the polymer. This is accomplished by plasticisation which reduces T_g to a level below ambient, or below the MFT in the case of a latex. As an example of plasticisation, about 40 parts of di-2-ethylhexyl phthalate are required to transform 60 parts of polyvinyl chloride from a hard, horny material to a flexible sheet. 'Internal plasticisation' is a term used for the formation of a copolymer, the auxiliary monomer of which gives increased flexibility to the polymer formed from the principal monomer.

5 TECHNOLOGY OF POLYMERISATION

Monomers may be polymerised by free radical initiation by one of five methods: polymerisation in bulk, in solution, dispersed as large particles in water or occasionally in another non-solvent (suspension polymerisation), or dispersed as fine particles, less than 1.5 μm , usually less than 1 μm in diameter. The last-named process is usually known as emulsion polymerisation. As the applications of polymers in emulsion is the basis of this series of volumes, emulsion polymerisation is the subject of Chapter 3. A variant of suspension polymerisation may be described as solution precipitation. It is often applied to copolymers, e.g. a copolymer of methyl methacrylate and methacrylic acid. In concentrated solution, the acid solubilises the methyl methacrylate. On

polymerisation a fine water-insoluble powder is produced, which, depending on the monomer ratios, is usually alkali soluble.

In the past two decades a variation of emulsion polymerisation has been introduced, the polymers being known as 'dispersymers'. To form dispersymers, a liquid monomer forms an emulsion-like product in an organic liquid, usually a liquid hydrocarbon, in which the polymer is insoluble. The final emulsion closely resembles an aqueous polymer emulsion in physical appearance [34].

5.1 Bulk polymerisation

Whilst in most cases laboratory experiments may be performed on undiluted monomers, or on controlled dilutions with solvents do not affect the polymerisation seriously, this process produces difficulties in large-scale production, which may be of the order of 5 tonnes in a single batch. Problems are caused by an increase in viscosity of the mass during polymerisation, and in particular the removal of the heat of polymerisation, which for most monomers is of the order of $20 \text{ kg cal gm}^{-1} \text{ mole}^{-1}$. Special equipment with a high surface-volume ratio is desirable, as with the polymerisation of methyl methacrylate which is polymerised in thin sheets with a very low initiator ratio. Bulk polymerisation of vinyl acetate was described in reports of German factory production after the Second World War [35]. In this case the hot polymer is sufficiently fluid to be discharged directly from a cylindrical reactor. In an alternative continuous process the monomer is passed down a polymerisation tower [36]. Processes have been developed for the bulk polymerisation of vinyl chloride which is insoluble in its own monomer [37].

5.2 Solution polymerisation

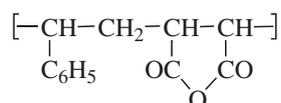
Polymerisation with a solvent diluent can be readily accomplished as the major problems of bulk polymerisation are overcome with increasing dilution. Some practical problems persist, however. Commercial solvents are seldom pure and the impurities may have an inhibiting or retarding effect on polymerisation; this is especially so with monomers such as vinyl acetate which are not resonance stabilised. In addition, many solvents have a chain transfer effect (Section 2.1). Towards the end of a polymerisation the degree of dilution of the monomer is extremely high; the efficiency of initiator therefore falls, and it is lost by chain transfer with the solvent or by mutual destruction of the radicals. Thus several repeat initiations are necessary towards the end of a practical polymerisation in solvent to achieve the 99+ % polymerisation generally desired.

Practical experience has shown that molecular weights in solution polymerisation are also susceptible to a number of other factors, such as the type and nature of stirring, and the type and nature of the reactor, including its shape and the surface-volume ratio. There is likely to be a 'wall effect', which may terminate growing radicals. In addition, stirring conditions affect the rate

of attainment of equilibrium, whilst the amount of reflux, where present, also affects the nature of the final polymer. Since it is not usually desirable and may be difficult to distill unpolymerised monomer, even if a satisfactory azeotrope with the solvent exists, direct solvent polymerisation has limited practical application and is of principal interest where the solutions are used directly, either as solvent-based coatings or as adhesives [37]. Solvent polymerisation can normally be used only to prepare polymers of relatively low molecular weight.

5.3 Suspension polymerisation

Suspension polymerisation may be described as a water-cooled bulk polymerisation, although initiators that are water soluble may create some variations. The fundamental theory is simple and depends on the addition to the water of a dispersing agent. This may be a natural water-soluble colloid such as gum acacia, gum tragacanth, a semi-synthetic such as many cellulose derivatives (see Chapter 2) or a fully synthetic polymer. These include polyvinyl alcohol, or alternatively a water-soluble salt derived from a styrene/maleic anhydride 1 : 1 copolymer



These dispersing agents may be mixed; occasionally a small quantity of surfactant of the order of 0.01 % is added. The normal concentration of dispersing agents is about 0.1 %, based on the water present. Monomer or monomers are added so that overall concentration is 25–40 %, although occasionally specific formulations claim 50 %.

The function of the dispersing agent is that of forming an ‘envelope’ around the beads as formed by stirring and preventing their coagulation and fusion during polymerisation. An intermediate or ‘sticky’ state occurs in almost all polymerisations in which a solution of polymer in monomer of high viscosity is formed, and the beads would fuse together very readily, except for the energy supplied by the stirring in keeping them apart and the stabilising action of the dispersing agent. Certain monomers, e.g. vinyl chloride, which are not solvents for their own monomers are an exception to this rule, but the same principle applies to the dispersant acting as a particle stabiliser. This type of polymerisation is sometimes referred to as ‘bead’ polymerisation.

There is a very clear distinction between suspension polymerisation and emulsion polymerisation. Whilst emulsion polymerisation produces particles usually $\leq 1 \mu\text{m}$ in diameter, occasionally up to $2.5 \mu\text{m}$, suspension particles are at least ten times larger in diameter, often of the order of 1 mm, although they are not necessarily spherical in shape. The kinetics of polymerisation of the two types are often quite different. To ensure that beads or ‘pearls’ (another

term used) are formed, the second-order transition point T_g (see Chapter 4, Section 4.4.2) must be below the ambient temperature; otherwise the beads will flow together as soon as stirring is stopped. This tendency can be reduced somewhat, e.g. by coating a bead dispersion of low molecular weight polyvinyl acetate with cetyl alcohol, which is present during the polymerisation. Bead polymerisation is only practicable as a general rule, where the T_g is above about 25 °C and preferably above 35 °C. A summary of some suspension polymerisation processes for vinyl chloride is available [38].

It is possible to perform suspension polymerisation using solid dispersants. Thus styrene may be polymerised in suspension with organic peroxidic initiators with a tricalcium ortho-phosphate dispersant and sodium dodecylbenzene sulfonate [39].

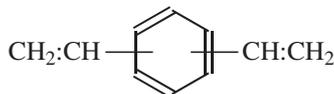
6 THE PRINCIPAL MONOMERS AND THEIR POLYMER

6.1 Hydrocarbons

The simplest hydrocarbon capable of free radical addition polymerisation is ethylene C_2H_4 , which as a gas is treated under pressure. Higher aliphatic hydrocarbons such as propylene $CH_3CH:CH_2$, 1-butene $CH_3CH_2CH:CH_2$ and a number of longer chain aliphatic ethenes cannot in general be polymerised by themselves by free radical, as distinct from ionic methods, because of their allylic character. However, they are capable of copolymerisation, and some specifications have claimed their copolymerisation with vinyl acetate in emulsion. Only hydrocarbons with their unsaturation in the 1-position can be copolymerised satisfactorily in this manner.

Styrene $C_6H_5CH:CH_2$ is the simplest aromatic hydrocarbon monomer. Others are vinyl-toluene and *o*-, *m*- and *p*-methylstyrene $CH_3C_6H_4CH:CH_2$. α -Methylstyrene $C_6H_4C(CH_3):CH_2$ is also a technical product, but its polymerisation has problems because it has a low ceiling temperature; i.e. the propagation and depropagation rates during formation tend to become equal and hence no polymer is formed unless a low-temperature initiator system is used.

The divinyl-benzenes, written



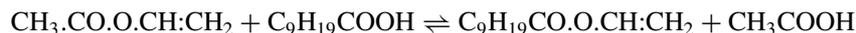
a notation used when it is desired to leave the positions of the substituents undecided, are a by-product of styrene manufacture and are used for crosslinking.

The dienes are described in Section 6.8. There have been a few other specialised monomers based on condensed rings, but as they are generally solids their use in emulsion systems is very limited, if at all.

6.2 Vinyl esters

Vinyl esters are derived from the hypothetical vinyl alcohol, $\text{CH}_2\text{:CHOH}$, an isomer of acetaldehyde CH_3CHO , which is normally formed when an attempt is made to prepare the monomer. The esters, however, whether derived from acetylene or ethylene (see later), are of major importance in many latex applications. The principal ester of commerce is vinyl acetate $\text{CH}_2\text{:CHOOCCH}_3$, a liquid which is fairly readily hydrolysed, of b.p. 73°C . Vinyl acetate has the advantage of being one of the cheapest monomers to manufacture.

Vinyl propionate $\text{CH}_3\text{CH}_2\text{COOCH:CH}_2$ is fairly well established as a monomer, probably by direct acetylene preparation. Other esters are encountered less frequently, and in most cases are probably prepared by vinylolysis rather than directly, using vinyl acetate as an intermediate [40–42]. Vinylolysis is not the same as *trans*-esterification and involves a mercury salt such as *p*-toluene sulfonate as an intermediate. Thus vinyl caprate is prepared by reacting vinyl acetate with capric acid in the presence of a mercuric salt, using an excess of vinyl acetate; the reaction is reversible:



The capric acid can be conveniently removed with sodium carbonate after removal of excess acetic acid with sodium bicarbonate, which does not react with the higher fatty acids. The vinyl esters of mixed C_8 , C_{10} and C_{12} fatty acids have been used technically in forming copolymers with vinyl acetate [43].

Vinyl butyrate $\text{CH}_3\text{CH}_2\text{CH}_2\text{OOCCH:CH}_2$ is referred to in the literature, but is probably not in commercial production. Vinyl laurate $\text{CH}_3(\text{CH}_2)_8\text{COOCH:CH}_2$ has been in technical production in Germany. Of other esters of fatty acids, only vinyl stearate $\text{C}_{17}\text{H}_{35}\text{COOCH:CH}_2$, a solid, has been manufactured on a technical scale. The most interesting vinyl esters have been derivatives of pivalic acid $(\text{CH}_3)_3\text{C.COOH}$, the simplest branched chain fatty acid in which the carbon atom adjacent to the carboxyl group is quaternary. In these vinyl esters, one methyl group may be replaced by ethyl, and a second by a longer alkyl chain, and thus the general formula for the esters is $\text{CH}_3\text{C}_{7-8}\text{H}_{14-16}\text{C}(\text{CH}_3)(\text{C}_{1-2}\text{H}_{2-4})\text{OOCCH:CH}_2$ [44].

Vinyl chloroacetate $\text{CH}_3\text{CICOOCH:CH}_2$ is occasionally quoted. Because of the relatively labile atom, copolymers including this monomer take part in a number of crosslinking reactions.

Vinyl benzoate $\text{C}_6\text{H}_5\text{COOCH:CH}_2$ is the only aromatic vinyl ester that finds some application if relatively hard polymers with some alkali resistance are required [43].

6.3 Chlorinated monomers

Vinyl chloride $\text{CH}_2\text{:CHCl}$, a gas, is the cheapest monomer of the series, and has widespread commercial use. It may be polymerised in bulk with specialised

apparatus, but it is also polymerised both in suspension and in emulsion. It is frequently copolymerised, especially with vinyl acetate.

Vinylidene chloride $\text{CH}_2:\text{CCl}_2$, a low boiling liquid, is also a relatively low cost monomer. It forms a polymer with a marked tendency to crystallise because of its relatively symmetrical structure. In most cases it is copolymerised, especially with vinyl chloride or methyl acrylate.

The corresponding symmetrical compound in the *trans* form, *trans*-dichloroethylene $\text{CHCl}:\text{CHCl}$, has been used in limited quantities as a comonomer with vinyl acetate [45]. Trichloroethylene $\text{CHCl}:\text{CCl}_2$, although not normally considered as a monomer, may take part in some copolymerisations, especially with vinyl acetate.

Chloroprene $\text{CH}_2:\text{CCl}.\text{CH}:\text{CH}_2$ a diene (see Section 5.8), is mainly used in the formulation of elastomers, but occasionally a polymer containing chloroprene is used as an alternative to a hydrocarbon diene.

Vinyl bromide $\text{CH}_2:\text{CHBr}$ is technically available, and finds some application in specialist polymers with fire-resistant properties. The boiling point is 15.8°C . A number of highly chlorinated or brominated alcohol esters of acrylic and methacrylic acids have been described, and are probably in limited production, often for captive use for the production of fire-resistant polymers.

Vinyl fluoride CH_2CHF , vinylidene fluoride $\text{CH}_2:\text{CF}_2$, tetrafluoroethylene $\text{F}_2\text{C}:\text{CF}_2$ and hexafluoropropylene $\text{CF}_3\text{CF}:\text{CF}_2$ have found industrial applications in recent years. The monomers are gaseous. For perfluoroalkyl acrylates see the next section.

6.4 Acrylics

6.4.1 Acrylic and methacrylic acids

The most numerous class of monomers are the acrylics, viz. esters of acrylic acid $\text{CH}_2:\text{CHCOOH}$ and methacrylic acid $\text{CH}_2:\text{C}(\text{CH}_3)\text{COOH}$. Both are crystalline solids at low ambient temperatures, becoming liquid at slightly higher temperatures (see Figure 1.2). These acids polymerise and copolymerise extremely readily, being frequently employed in copolymers to obtain alkali-soluble polymers. Whilst both acids are water soluble, methacrylic acid, as might be expected because of its angular methyl group, is more soluble in ester monomers, and to some extent in styrene, and as such is more useful in copolymerisation, especially if water based.

Whilst esters of acrylic acid give soft and flexible polymers, except for those with long alkyl chains, methyl methacrylate polymerises to an extremely hard polymer. The polymers in this series become softer with increasing alkyl chain lengths up to C_{12} . The highest alkyl chain acrylics in both series tend to give side chain crystallisation.

6.4.2 Individual acrylic and methacrylic esters

A range of esters of acrylic acid are available commercially from methyl acrylate through ethyl acrylate to *n*-heptyl acrylate and 2-ethylhexyl acrylate $\text{CH}_2\text{:COOCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$. They vary from the fairly volatile, pungent liquids of the lowest member of the series to characteristic, but not necessarily unpleasant, odour of the higher members of the series. The highest members require distillation under reduced pressure to avoid simultaneous decomposition and polymerisation.

The methacrylic ester series closely parallels the acrylics, but boiling points tend to be somewhat higher, especially with the short chain esters (Table 1.1). Methyl methacrylate $\text{CH}_2\text{:C}(\text{CH}_3)\text{COOCH}_3$ is by far the most freely available and least costly of the monomers of the series.

As an alternative to the simple alkyl esters, several alkoxyethyl acrylates are available commercially, e.g. ethoxyethyl methacrylate $\text{CH}_3\text{:C}(\text{CH}_3)\text{COOC}_2\text{H}_4\text{OC}_2\text{H}_5$ and the corresponding acrylate. The ether oxygen which interrupts the chain tends to promote rather more flexibility than a simple carbon atom.

Some technical perfluorinated alkyl acrylates have been described. They include *N*-ethylperfluorooctanesulfonamidoethyl acrylate $\text{C}_n\text{F}_{2n+1}\text{SO}_2\text{N}(\text{C}_2\text{H}_5)\text{-CH}_2\text{O-C(O)-CH=CH}_2$ (*n* approximately 7.5, fluorine content 51.7%), the corresponding methacrylate and the corresponding butyl derivatives. The ethyl derivatives are waxy solids, the ethyl acrylate and the corresponding methacrylate derivative having a melting range of 27–42 °C. The butyl acrylic derivative is a liquid, freezing at –10 °C.

Various glycol diacrylates and dimethacrylates are available. Ethylene glycol dimethacrylate $\text{CH}_2\text{:C}(\text{CH}_3)\text{COOC}_2\text{H}_4\text{OOC}(\text{CH}_3)\text{:CH}_2$ is extremely reactive, and is sometimes marketed as a solution in methyl methacrylate. It polymerises extremely readily and acts as a powerful crosslinking agent. The dimethacrylates of triethylene glycol and higher glycols, some of which are also readily available, are less reactive, retain better flexibility and are more controllable in their polymerisation characteristics.

Glycidyl methacrylate $\text{CH}_2\text{CHCH}_2\text{OOCC}(\text{CH}_3)\text{:CH}_2$ has two reactive groups, the epoxide group being distinct in nature from the vinyl double bond (see also Chapters 5 and 7). The epoxide group is only slowly reactive in water, and even in emulsion polymerisation does not hydrolyse excessively. However, the presence of the group makes the methacrylate moiety much more prone to ready polymerisation.

The half esters of both ethylene glycol and propylene glycol are now monomers of commerce, propylene glycol monoacrylate $\text{CH}_3\text{CHOHCH}_2\text{OOCCH:CH}_3$ being typical (the primary alcohol unit is the

active one in the formula). These monomers provide a source of the mildly reactive and hydrophilic groups on polymer chains. A problem with these monomers is that traces of a glycol dimethacrylate may be present as impurities at a low level.

6.4.3 Acrylics based on the amide group

Acrylamide $\text{CH}_2\text{:CHCONH}_2$ and methacrylamide $\text{CH}_2\text{:C(CH}_3\text{)CONH}_2$ are articles of commerce, especially the former. Polymers of the former are water soluble, but the solubility of the latter depends on conditions of preparation, e.g. molecular weight of the polymers. Both are very frequently used in copolymerisation. Polyacrylamide is often used as a flocculating agent. Certain derivatives, viz. methylolacrylamide $\text{CH}_2\text{:CHCONHCH}_2\text{OH}$, methoxymethylacrylamide $\text{CH}_2\text{:CHCONHCH}_2\text{OCH}_3$ and isobutoxyacrylamide $\text{CH}_2\text{:CHCONHCH}_2\text{OC}_4\text{H}_9\text{-iso}$, are of interest in crosslinking. The last named has the advantage of being monomer soluble but water insoluble, making it more amenable to handling in emulsion polymerisation. Diacetoneacrylamide *N*-(1,1-dimethyl-3-oxobutyl) acrylamide [also known as 1-dimethyl-3-oxobutyl)acrylamide] $(\text{CH}_2\text{:CHNHC(O)(CH}_3\text{)}_2\text{CH}_2\text{COCH}_3)$ has the advantage of both water and monomer solubility [46].

6.4.4 Cationic acrylic monomers

If a compound such as dimethylaminoethyl alcohol $(\text{CH}_3)_2\text{NC}_2\text{H}_4\text{OH}$ is esterified via the hydroxyl groups with acrylic or methacrylic acids instead of neutralising the amino group, a cationic monomer, e.g. $(\text{CH}_3)_2\text{NC}_2\text{H}_4\text{OOCCH:CH}_2$, is formed. At acid pH levels this monomer is cationic, with the amino group forming salts that polymerise and copolymerise in the normal way via the acrylic double bond. Another typical monomer is *t*-butylaminoethyl methacrylate *t*- $\text{C}_4\text{H}_9\text{NHC}_2\text{H}_4\text{OOC(CH}_3\text{):CH}_2$. At neutral or higher pH levels, ionisation of this weak base is suppressed, and it acts as a nonionic monomer. However, hydrolysis tends to be rapid in aqueous media at high pH, forming the alkanolamine salts of the acids. Cationic monomers from the corresponding aminopropyl compound are also known.

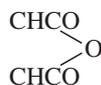
6.4.5 Acrylonitrile

Acrylonitrile $\text{CH}_2\text{:CHCN}$, and the less frequently used methacrylonitrile $\text{CH}_2\text{:C(CH}_3\text{)CN}$, give extremely hard polymers and are employed as comonomers to give solvent resistance. Acrylonitrile monomer, like vinyl chloride, is not a solvent for its own polymer and is about 7 % soluble in water, although its polymer is insoluble, making it of interest in theoretical studies. These monomers are unusually toxic because of the nitrile group.

6.5 Polymerisable acids and anhydrides

Besides acrylic and methacrylic acid, crotonic acid (strictly the *cis* acid) $\text{CH}_3\text{CH}:\text{CHCOOH}$, a white powder, often takes part in copolymerisations, especially with vinyl acetate, but it only self-polymerises at low pH and with great difficulty. Itaconic acid (methylenesuccinic acid) $\text{CH}_2:\text{C}(\text{CH}_3\text{COOH})\text{COOH}$, a water-soluble solid, also readily takes part in copolymerisation, although it will only homopolymerise at about pH2.

Maleic acid *cis*- $\text{HOOCCH}:\text{CHCOOH}$, the simplest dibasic acid, is rarely copolymerised on its own, but frequently as the anhydride, maleic anhydride:



which is much more reactive. However, it cannot be directly polymerised in water, although its rate of hydrolysis is slow. It readily forms copolymers, e.g. with styrene, ethylene or vinyl acetate, most readily as alternating (equimolar) copolymers, irrespective of the initial molar ratios. These copolymers are water soluble in their alkaline form after hydrolysis and frequently occur as stabilisers in emulsion polymerisation.

Fumaric acid *trans*- $\text{HOOCCH}:\text{CHCOOH}$, the isomer of maleic acid and thermodynamically the most stable form, is occasionally used as a comonomer, although there is some doubt as to its reactivity, and it may do little more than provide end groups, thus acting as a chain transfer agent.

Aconitic acid, an unsaturated carboxylic acid of formula $\text{HOOCCH}_3\text{C}(\text{COOH}):\text{CHCOOH}$, obtained by removing the elements of water from citric acid, is occasionally quoted as a monomer in patents and theoretical studies. Citraconic acid (methylmaleic acid) $\text{CH}_3\text{C}(\text{COOH}):\text{CHCOOH}$, its isomer mesaconic acid (methylfumaric acid) and citraconic anhydride are also occasionally used for copolymerisation. The acids in this paragraph are not articles of commerce as far as has been ascertained.

Various alkyl and alkoxy diesters of itaconic acid have been introduced, but as far as is known, production has not been sustained, although they are extremely good internal plasticisers for polyvinyl acetate. Their relatively high cost mitigated against their use.

6.6 Self-emulsifying monomers

A number of monomers have the property of stabilising emulsions without the assistance of emulsifiers (see Chapter 2) or with a minimal quantity. Their polymers are generally water soluble and often so are their copolymers, depending on monomer ratios. These monomers contain strongly hydrophilic groups, the sulfonate $\cdot\text{SO}_3\text{Na}$ being the most usual. They usually copolymerise readily with most of the standard monomers used in emulsion polymerisation.

Amongst the earliest was sodium vinyl sulfonate $\text{CH}_2\text{:CHSO}_3\text{Na}$, which was in use in Germany in the 1940s. Other monomers of this class include sodium sulfoethyl methacrylate $\text{CH}_2\text{:CHC}(\text{:O})\text{NH}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{Na}$.

Of unusual interest is 2-acrylamido-2-methylpropanesulfonic acid (AMPS monomer[®]) $\text{CH}_2\text{:CHC}(\text{:O})\text{NHC}(\text{CH}_3)_2\text{CH}_2\text{SO}_3\text{H}$, normally used as the sodium salt. This monomer also copolymerises readily. A monograph describes these compounds in greater detail [47].

The salts of the polymerisable acids have appreciable self-emulsifying powers when used as comonomers, especially when they are about 10 % or more by weight. The alkylolamine unsaturated esters (Section 6.4.3), when used in the form of their alkali or amine salts, come into this category [48].

6.7 Esters for copolymerisation

Esters of maleic and fumaric acids are often used in copolymerisation, both the diesters and more unusually the monoesters being reacted. The fumarate diesters, which are rather non-volatile liquids, have a feeble tendency to form homopolymers on prolonged heating with initiators, but little, if any, evidence exists to suggest that maleic esters can homopolymerise. Copolymerisation characteristics of fumarate esters are more favourable than those of maleate esters, and they are mainly copolymerised with vinyl acetate to impart internal plasticisation. It has been suggested that maleate and fumarate esters isomerise to identical products during a polymerisation reaction, but this has not been proved. Although in theory the units entering a polymer should become identical with the disappearance of the double bond, there are many steric factors associated with the polymer molecules as a whole.

The principal esters are those of *n*-butyl alcohol, 2-ethylhexyl alcohol, a technical mixture of C9–11 alcohols and ‘nonyl alcohol’, which is 1,3,3-trimethylhexanol.

The half esters of maleic acid and their salts are occasionally quoted in patents and other technical literature, and seem, probably because of their polar–non-polar balance to polymerise fairly readily. The methyl half ester *cis*- $\text{CH}_3\text{OOCCH:CHCOOH}$ is a solid; some of the higher alkali half esters are liquids. Half esters of other polymerisable acids such as fumaric and itaconic acids have been reported, but are more difficult to prepare. The half esters tend to disproportionate fairly readily, especially in the presence of water, to the free acid and the diester:



A number of successful copolymerisations in emulsion of half esters of long-chain alcohol and sterically hindered alcohols have been disclosed [49].

6.8 Monomers with several double bonds

Unsaturated hydrocarbons containing two double bonds constitute a special class of monomer. The principal representatives of this class are butadiene $\text{CH}_2:\text{CH}:\text{CH}:\text{CH}_2$, isoprene $\text{CH}_2:\text{C}(\text{CH}_3):\text{CH}:\text{CH}_2$ and chloroprene $\text{CH}_2\text{CCl}:\text{CH}:\text{CH}_2$.

When a monomer contains more than one double bond which can polymerise approximately equally freely, crosslinking can occur readily, and small quantities of this type of monomer are added to other polymerising systems to obtain controlled crosslinking. Examples are *p*-divinyl benzene (see Section 6.1), and ethylene glycol dimethacrylate $\text{CH}_2:\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{OOC}(\text{CH}_3):\text{CH}_2$.

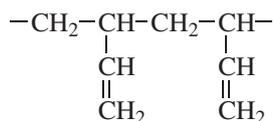
In these cases the radicals formed are resonance stabilised, so that two chains can form simultaneously, and when a biradical is added to a growing chain, two points occur from which the chain can continue, resulting in rapid branching and crosslinking.

The dienes are a special class in distinction to monomers such as the divinyl benzenes and the diesters such as a glycol acrylate. If a monomer such as butadiene is polymerised, the monoradical formed is highly stabilised by resonance. The two resonance forms can be represented as

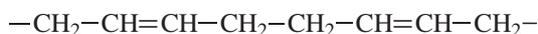


where R represents a residual monovalent group.

As a result, two methods of addition are possible, one being known as 1 : 2 addition, the other as 1 : 4 addition, and may be represented by the following:



Bi-unit of a 1 : 2 addition

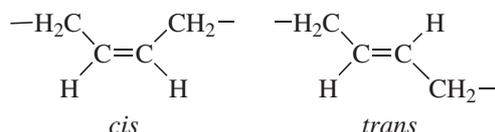


Bi-unit of 1 : 4 addition

During a free radical polymerisation in emulsion, about 20 % of a 1 : 2 polymer addition and 80 % of 1.4 addition takes place. Copolymerisation with other monomers such as styrene tends to increase 1 : 2 units at the expense of 1 : 4 units.

A further possibility of variation occurs because the 1 : 2 unit possesses an asymmetric carbon atom, while due to the double bond, 1 : 4 addition may

occur in the *cis* or *trans* positions, giving the following isomers:



It has been found possible to deduce various structures by infrared absorption bands, *trans* formation having been shown to decrease with temperature.

During a polymerisation including butadiene, there is a greater than usual tendency for side reactions to occur. These involve the residual double bonds in completed molecules or growing chains. This often causes gel formation, as measured by the insoluble fractions in acetone, or another standard solvent. Gel formation and other crosslinking reactions occur with increasing frequency as the degree of polymerisation increases. In consequence, when solid products of controlled properties are required, polymerisations and copolymerisations involving butadiene are not taken to completion. The reaction is inhibited before polymerisation is complete and surplus monomer is removed by distillation. Possibilities for isomerism in the polymerisation of chloroprene and isoprene are even more complex than with butadiene.

The application of diene polymers and copolymers is largely associated with synthetic rubber, but these copolymers have other applications; e.g. copolymers with a styrene content of 40 % and above have been used for coatings and for carpet backing. In these copolymers the residual double bonds render them prone to degradative oxidation.

The structure of butadiene copolymers is interesting and accounts for their physical properties. A polymer molecule may be considered to be a randomly coiled chain—an irregular spiral—in the unstretched state. Elastomers in the fully stretched state, particularly natural rubber, i.e. polyisoprene (C_5H_8)_n, tend to crystallise, this crystallisation being lost when the stress causing the extension is removed. Ideally a limited number of crosslinks is desirable for elastic recovery to occur. Because of their less regular structure, copolymers of butadiene do not tend to crystallise.

Modern work has shown that where polymerisation takes place by methods that produce a highly stereoregular or stereospecific products, the tendency is for crystallisation to occur on stretching. In most copolymers that we will consider in these volumes, the high quantity of comonomer causes the normal plastic type of property to predominate, rather than the rubber-like extensibility. Thus the bulky phenyl C_6H_5 groups in the styrene copolymers effectively prevent crystallisation, and the copolymers in film form tend to approximate more closely in properties to other vinyl-type polymers.

The double bonds in polymers involving dienes facilitate crosslinking, which in rubber technology is known as vulcanisation. The utilization of the double bonds for crosslinking has increased in recent years.

6.9 Allyl derivatives

Allyl alcohol $\text{CH}_2\text{:CHCH}_2\text{OH}$ and its simple derivatives, such as allyl acetate $\text{CH}_2\text{:CH}_2\text{OOCCH}_3$, have little practical application in vinyl polymerisation, because of their powerful tendency to degradation chain transfer (p. xx). Similar considerations apply to methallyl alcohol $\text{CH}_2\text{:C(CH}_3\text{)CH}_2\text{OH}$ and its derivatives. A practical difficulty also arises with allyl alcohol and its more volatile derivatives because of their extreme lachrimatory character.

Certain other allyl derivatives, however, are of greater utility. Diallyl *o*-phthalate $\text{CH}_2\text{:CHCH}_2\text{OOC}_6\text{H}_4\text{OOCCH}_2\text{CH:CH}_2$ contains two vinyl groups, and as such the tendency to crosslink is in competition with that of chain transfer. Whilst this diester is not normally used in emulsion polymerisation, it is frequently included in the thermosetting polyesters, especially in conjunction with a monomer such as styrene, which will reduce the tendency to premature crosslinking. These derivatives find particular application in reinforced polyesters, viz. those reinforced with glass fibres.

Allyl derivatives containing epoxide groups seem to copolymerise somewhat more readily, probably because the nucleophilic epoxide group reduces the tendency to resonance. These derivatives are of interest as they are potentially crosslinking monomers. They include allyl glycidyl ether



and allyl dimethyl glycidate



which is formed by Darzen's reaction.

This little-known reaction would repay further study, at any rate as far as polymer production is concerned. It is fundamentally the reaction of a chlorinated ester, such as allyl chloroacetate with acetone in the presence of a stoichiometric quantity of alkali near 0 °C, sodium hydride being particularly effective [49].

Monomers such as allyl methacrylate $\text{CH}_2\text{:CHCH}_2\text{OOC(CH}_3\text{):CH}_2$ are occasionally quoted, having mild crosslinking properties. A useful volume describing allyl compounds is available [14].

6.10 Vinyl ethers

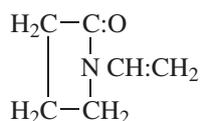
Whilst the vinyl ethers have long been known as monomers, they have been unimportant in aqueous polymerisation. By themselves they only form copolymers, not homopolymers under free radical conditions, and ionic catalysts are

used when a homopolymer is required. Although the vinyl ethers copolymerise readily with many vinyl monomers under free radical conditions, difficulty arises during polymerisation in the presence of water since they hydrolyse readily to acetaldehyde and alcohols below a pH of about 5.5. This makes emulsion polymerisation with a monomer such as vinyl acetate difficult, except under careful control of pH.

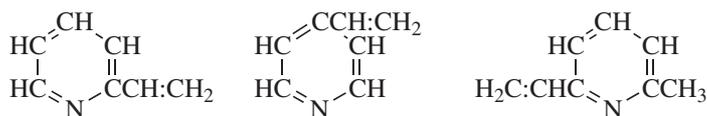
Except for the tendency to hydrolysis, the physical properties of the vinyl ether monomers closely resemble that of the corresponding saturated compounds. Available monomers, including vinyl methyl ether $\text{CH}_2\text{CHOCH}_3$, vinyl ethyl ether $\text{CH}_2\text{:CHOC}_2\text{H}_5$, both *n*- and isobutyl vinyl ethers $\text{CH}_2\text{:CHOC}_4\text{H}_9$ and a long-chain alkyl ether, vinyl cetyl ether $\text{CH}_2\text{:CHOC}_{16}\text{H}_{33}$, have been available.

6.11 Miscellaneous monomers containing nitrogen

N-Vinylpyrrolidone is a completely water-miscible cyclic monomer which can be regarded as a cyclic imide. It readily forms polymers and copolymers, the water soluble types being used as protective colloids. The monomer is

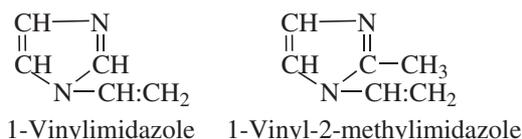


2-Vinylpyridine, 4-vinylpyridine and to a lesser extent 2-methyl-5-vinylpyridine have been prepared commercially, and polymerise to give products that are the basis of polymeric cationic electrolytes. They are most frequently in copolymers with butadiene and styrene in tyre cord adhesives (see Chapter 8). The physical properties of the polymers tend to resemble those of styrene. The formulae of the monomers are shown below:

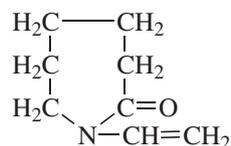


2-Vinylpyridine 4-Vinylpyridine 2-Methyl-5-vinylpyridine

1-Vinyl imidazole and the allied 1-vinyl 2-methylimidazole are basic monomers produced on a small scale, and their major function is improvement of adhesion:

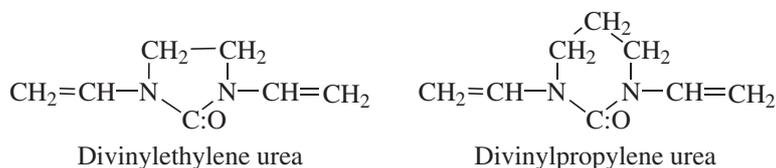


Vinyl caprolactam is occasionally used as a reactive thinner:



It has a melting point of 34 °C, and may be distilled under reduced pressure. It also has the property of improving adhesion.

Divinylethylene urea and divinylpropylene urea, with melting points of 66 and 65 °C respectively, find utilization as reactive thinners:



6.12 Toxicity and handling

As a general rule, all the quoted monomers should be handled with at least the precautions associated with the corresponding saturated compounds. In some cases, e.g. the acrylic esters, the toxicity, in particular the vapour, is more toxic than the corresponding saturated esters. The lower acrylic esters, but not the methacrylic esters, have an extremely unpleasant odour, but the level of intolerance is well below the maximum safety level recommended. Some precautions are advised in handling acrylamide.

Acrylonitrile and methacrylonitrile have the characteristic toxicity of cyanides. On the laboratory scale they should be handled in well-ventilated fume cupboards and prevented from coming into direct contact with the skin. Special precautions, including the wearing of oilskins and fresh air breathing apparatus, are required for large-scale manufacturing processes.

Allyl alcohol and some of its derivatives are lachrimatory.

The above comments are of a general character only. In all cases manufacturers' literature and official literature should be consulted, safety information being obligatory in many countries.

The following are synthetic monomers based on the vinyl esters of mixed branched chain acids, known as Versatic[®] acids, the feature being that the carbon atom is in the alpha position of quaternary:

Veova 9 is the vinyl ester of acids averaging 9 carbon atoms; b.p. 185–200 °C, s.g. 0.89. The T_g of the homopolymer is 60 °C. Veova 10 is the vinyl ester of acids averaging 10 carbon atoms and is less branched than Veova 9; b.p. 133–136 °C, s.g. 0.875–0.885. Some perfluorinated acrylic derivatives are described in Section 6.4.

Table 1.1 Physical properties of the principal monomers

Monomer	Formula	<i>b.p.</i> (°C)	<i>m.p.</i> (°C)	<i>s.g. Pressure</i> (mm) (<i>d</i> _{20/20})
Ethylene	CH ₂ :CH ₂	-104		
Propylene	CH ₂ :CHCH ₃	-31		0.5139 (<i>d</i> _{20/4})
I-Butene	CH ₂ :CHCH ₂ CH ₃	-6.3		0.5951 (<i>d</i> _{20/4})
I-Hexene	CH ₂ :CHC ₃ H ₆ CH ₃	+63.5		0.6734 (<i>d</i> _{20/4})
I-Octene	CH ₂ :CHC ₅ H ₁₀ CH ₃	121.3		0.7194(<i>d</i> _{15.5/15.5})
Styrene	C ₆ H ₅ :CH:CH ₂	145.2		0.905 (<i>d</i> _{25/25})
Vinyl toluene	CH ₃ C ₆ H ₄ :CH:CH ₂	167.7		0.8930
<i>o</i> -Methyl styrene	C ₆ H ₄ C(CH ₃):CH ₂	163.4		0.9062 (<i>d</i> _{25/25})
Divinyl benzene	C ₆ H ₄ (CH:CH ₂) ₂	195		
(55 % technical product)				
<i>m</i> -Diisopropenylbenzene	<i>m</i> -C ₆ H ₄ [C(CH ₃):CH ₂] ₂	231		0.925
<i>p</i> -diisopropenylbenzene	<i>p</i> -C ₆ H ₄ [C(CH ₃):CH ₂] ₂			0.965
(sublimes at 64.5 °C)				
Butadiene 1:3	CH ₂ :CHCH:CH ₂	-4.7		0.6205 ^a
Isoprene	CH ₂ :C(CH ₃)CH:CH ₂	34.07		0.686(<i>d</i> _{15.6/15.6})
Vinyl chloride	CH ₂ :CHCl	-14		0.912
Vinylidene chloride	CH ₂ :CCl ₂	31.7		1.1219(<i>d</i> _{20/4})
<i>trans</i> -Dichloroethylene	CHCl:CHCl	49		1.265(<i>d</i> _{15/4})
Chloroprene	CH ₂ :CClCH:CH ₂	59.4		0.9583
Vinyl fluoride	CH ₂ :CHF	-57		
Vinylidene fluoride	CH ₂ :CF ₂	-84		
Tetrafluoroethylene	CF ₂ :CF ₂	-76		
Vinyl formate	CH ₂ :CHOOCH ₃	46.6		0.9651
Vinyl acetate	CH ₂ :CHOOCCH ₃	72.7		0.9338

^aunder own vapour at 21 °C

Vinyl propionate	CH ₂ :CHOOCC ₂ H ₅	94.9		0.9173
Vinyl butyrate	CH ₂ :CHOOCC ₃ H ₇	116.7		0.9022
Vinyl caprate	CH ₂ :CHOOCC ₉ H ₁₉	148/50		
Vinyl laurate	CH ₂ :CHOOCC ₁₁ H ₂₃	142/10		
Vinyl stearate	CH ₂ :CHOOCC ₁₇ H ₃₅	187-188/4.3	35-36 44-46/20	1.1888
Vinyl chloroacetate	CH ₂ :CHOOCC ₂ Cl	203		1.0703
Vinyl benzoate	CH ₂ :CHOOCC ₆ H ₅	141.3	12.3	1.0472
Acrylic acid	CH ₂ :CHCOOH	161	15	1.015
Methacrylic acid	CH ₂ :C(CH ₃)COOH	80		0.950
Methyl acrylate	CH ₂ :CHCOOCH ₃	99.6		0.9230
Ethyl acrylate	CH ₂ :CHCOOC ₂ H ₅	148.8		0.9015
n-Butyl acrylate	CH ₂ :CHCOOC ₄ H ₉	106/25		0.8794(<i>d</i> _{25/4})
n-Heptyl acrylate	CH ₂ :CHCOOC ₇ H ₁₅	128/50		0.8869
2-Ethylhexyl acrylate	CH ₂ :CHCOOC ₈ H ₁₇			
Lauryl acrylate	CH ₂ :CHCOOC ₁₁ H ₂₃			
Methyl methacrylate	CH ₂ :C(CH ₃)COOCH ₃	100.5		0.939
Ethyl methacrylate	CH ₂ :C(CH ₃)COOC ₂ H ₅	118.4		0.909
n-Butyl methacrylate	CH ₂ :C(CH ₃)COOC ₄ H ₉	166		0.893
Lauryl methacrylate	CH ₂ :C(CH ₃)COOC ₁₂ H ₂₃			
Ethoxyethyl acrylate	CH ₂ :CHCOOC ₂ H ₄ OC ₂ H ₅	174.1	-8	0.868(<i>d</i> _{25/15.6})
Ethoxyethyl methacrylate	CH ₂ :C(CH ₃)COOC ₂ H ₄ OC ₂ H ₅	91-93/35		0.9834
Ethylene glycol dimethacrylate	CH ₂ :C(CH ₃)COOC ₂ H ₄ OOCC(CH ₃):CH ₂	96-98/4		1.06(<i>d</i> _{15.5/15.5})
(96 % technical)	CH ₂ :CHCOOCH ₂ CHCH ₂ O	57/2		1.1074
Glycidyl acrylate				

(continued overleaf)

Table 1.1 (continued)

Monomer	Formula	b.p. (°C)	m.p. (°C)	s.g. Pressure (mm) ($d_{20/20}$)
Glycidyl methacrylate	$\text{CH}_2\text{:C}(\text{CH}_3)\text{COOCH}_2\text{CHCH}_2$ O	75/10		1.073(25)
Ethylene glycol monoacrylate	$\text{CH}_2\text{:CHCOOC}_2\text{H}_4\text{OH}$	76/8		1.11
Ethylene glycol monomethacrylate	$\text{CH}_2\text{:C}(\text{CH}_3)\text{COOC}_2\text{H}_4\text{OH}$	84/5		1.07
Propylene glycol monoacrylate	$\text{CH}_2\text{:CHCOOC}_3\text{H}_6\text{OH}$	85/9		1.05
Propylene glycol monomethacrylate	$\text{CH}_2\text{:C}(\text{CH}_3)\text{COOC}_3\text{H}_6\text{OH}$	92/8		1.03
Acrylamide	$\text{CH}_2\text{:CHCONH}_2$	125/25	85	1.222(30°)
Methacrylamide	$\text{CH}_2\text{:C}(\text{CH}_3)\text{CONH}_2$		110	
Acrylonitrile	$\text{CH}_2\text{:CHCN}$	77.3		0.8060
Methacrylonitrile	$\text{CH}_2\text{:C}(\text{CH}_3)\text{CN}$	90.3		0.8001($d_{20/4}$)
Methylolacrylamide (available as 60 % solution)	$\text{CH}_2\text{:CHCONHCH}_2\text{OH}$			
Methylenediacylamide	$(\text{CH}_2\text{CHCONH})_2\text{CH}_2$	97.5/40		0.933($d_{25/4}$)
Diethylaminoethyl methacrylate	$(\text{C}_2\text{H}_5)_2\text{NC}_2\text{H}_4\text{OOC}(\text{CH}_3)\text{:CH}_2$	103/12		0.914($d_{20/4}$)
<i>t</i> -Butyl aminoethyl methacrylate	$t\text{-C}_4\text{H}_9\text{NH}_2\text{C}_2\text{H}_4\text{OOCCH}(\text{CH}_3)\text{:CH}_2$	97.5/40		0.933
<i>trans</i> -Crotonic acid	$\text{CH}_2\text{CH:CHCOOH}$	72		0.963($d_{80/4}$)
Itaconic acid	$\text{CH}_2\text{:C}(\text{CH}_2\text{COOH})\text{COOH}$	167		1.6
Maleic acid	<i>cis</i> - $(\text{:CHCOOH})_2$	200	130	1.609($d_{20/4}$)
Fumaric acid	<i>trans</i> - $(\text{:CHCOOH})_2$	290	286	1.635($d_{20/4}$)
Aconitic acid	$\text{HOOCCH}_2\text{C}(\text{COOH})\text{:CHCOOH}$		191	
Maleic anhydride	$(\text{:CHCO})_2\text{O}$	202	52.5	1.48
Di- <i>n</i> -butyl maleate	$(\text{:CHCOOC}_4\text{H}_9)_2$	280.6		0.9964
Di-2-ethylhexyl maleate	$(\text{:CHCOOC}_8\text{H}_{17})_2$	209/10		0.9436($d_{15.5/15.5}$)
Dinonyl maleate	$(\text{:CHCOOC}_9\text{H}_{19})_2$			0.9030($d_{15.5/15.5}$)
Di- <i>n</i> -butyl fumarate	$(\text{:CHCOOC}_4\text{H}_9)_2$	138/8		0.9869($d_{20/4}$)

Di-2-ethylhexyl fumarate	(:CHCOOC ₈ H ₁₇) ₂		
Methyl acid maleate	HOOCCH:CHCOOCH ₃		
Butyl acid maleate	HOOCCH:CHCOOC ₄ H ₉		
Dimethyl itaconate	CH ₃ OOCCH ₂ C(:CH ₂)COOCH ₃	91.5/10	1.27(<i>d</i> _{2/4})
Dibutyl itaconate	C ₄ H ₉ OOCCH ₂ C(:CH ₂)COOC ₄ H ₉	140/10	0.9833(<i>d</i> _{2/2})
Allyl alcohol	CH ₂ :CHCH ₂ OH	96	0.8540(<i>d</i> _{20/4})
Allyl chloride	CH ₂ :CHCH ₂ Cl	45	0.9397(<i>d</i> _{20/4})
Allyl acetate	CH ₂ :CHCH ₂ OOCCH ₃	103.5	0.928
Diallyl phthalate	(CH ₂ :CHCH ₂ OOC) ₂ C ₆ H ₄	290(150/1)	
Allyl glycidyl ether	CH ₂ :CHCH ₂ OCH ₂ CHCH ₂ O	50-52/15	0.967(<i>d</i> _{20/4})
Allyl dimethyl glycidate	CH ₂ :CHCH ₂ OCCOC(CH ₃) ₂	89/8	
Vinyl methyl ether	CH ₂ :CHOCH ₃	6	0.7500
Vinyl ethyl ether	CH ₂ :CHOC ₂ H ₅	35.5	0.7541
Vinyl n-butyl ether	CH ₂ :CHOC ₄ H ₉	94	0.7803
Vinyl isobutyl ether	CH ₂ :CHOC ₄ H ₉	83	0.7706
Vinyl cetyl ether	CH ₂ :CHOC ₁₆ H ₃₃		
N-Vinyl pyrrolidone	CH ₂ C(O)N(CH ₂)CH ₂ CH ₂	148/100	1.04
2-Vinyl pyridine	CHCHCHC(CH:CH ₂)N	110/150	0.9746
4-Vinyl pyridine	CHCHC(CH:CH ₂)CHCN	121/150	0.988
2-Methyl 5-vinylpyridine	CHC(CH:CH ₂)CHCHC(CH ₃)N	75/15	

7 PHYSICAL PROPERTIES OF MONOMERS

Table 1.1 is not intended to be exhaustive, but gives the b.p and m.p. values where they are above about -5°C and density (s.g.) of the principal monomers. The order in which they are given is that of previous sections.

8 APPENDIX

This section is devoted to a list of references to which the reader may refer if more information is required on the subjects listed in this chapter, with special, but not exclusive, reference to monomers and their general and polymerisation properties. It is not intended to be exhaustive, and as far as possible is based on monographs and surveys, to avoid the necessity of obtaining copies of numerous original works.

There have been few, if any, publications in English or other Western languages in the quarter century specifically devoted to monomers. A few earlier works, still useful, are quoted here. For a general account of monomers, the following is suggested:

C.E. Schildknecht, *Vinyl and Related Monomers*, Wiley, New York, 1952

Although more than 40 years old, this volume is still very valuable.

R.H. Boundy and R.F. Boyer (eds.), *Styrene, Its Polymers, Copolymers and Derivatives*, Reinhold, New York, 1952

E.H. Riddle, *Monomeric Acrylic Esters*, Reinhold, New York, 1954

S.A. Miller (ed.), *Acetylene, Its Properties, Manufacture and Uses*, Vol. 1, Ernest Benn, London, 1965

S.A. Miller (ed.), *Ethylene and Its Industrial Derivatives*, Chapters 6 and 11, Ernest Benn, London, 1969

J.V. Koleske and L.H. Wartman (eds.), *Polyvinyl Chloride, Its Preparation and Properties*, Gordon and Breach, New York, and Macdonald Technical and Scientific, London, 1969

Many of the major producers issue bulletins on properties and polymerisation of the various monomers. The following multivolume Encyclopaedias have many articles of interest:

Encyclopedia of Polymer Science, 2nd edn, eds. H.F. Mark, G. Gaylord and N.M. Bikales, Wiley, New York

Comprehensive Polymer Science, eds. C. Booth and C. Price, Pergamon Press, Oxford, 1989

Handbook of Polymer Science and Technology, eds. G. Allen and J.C. Bevington, Marcel Dekker, New York

P.A. Lovell, M.S. El-Aasser, eds, *Emulsion Polymerisation, and Emulsion Polymers*, John Wiley, 1997.

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