Some Themes in the Chemistry of Macromolecules.

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THE domain of colloid chemistry was once referred to as the " world of neglected dimensions." If we may judge from the volume of literature published since that challenge was issued we may now rest assured that it has more than fully been met. There is, however, another world of neglected dimensions which had indeed been severely left alone until a few years ago. This is the region of particulate matter which ranges from the dimensions usually associated with molecules, namely, about 10^{-8} cm., up to the limit where the ultramicroscope just begins to be useful, namely, 10^{-6} cm. Nevertheless, there is a valid reason for this neglect. At the lower end of the scale, chemists have been busy dealing with the properties and reactions of small molecules with considerable success; at the upper limit, the study of colloidal chemistry in its broadest sense has brought to light what effects an extensive interface has on particulate matter. The time is therefore ripe for an attack on the second world of neglected dimensions. On this occasion the attack may be begun from both ends, utilising nearly every device and method known to the chemist. But not only is this region of chemistry a fertile field for the exercise of those methods already developed; it is the region in which lie molecules of importance in biological processes; it is the region of many synthetic organic products conveniently grouped under the term of plastics.

The field of macromolecular chemistry may thus be said to have relationships with every division of the subject. It is therefore impossible in this lecture to attempt to survey it as a whole, for such a survey would merely be encyclopædic. Instead, we shall try to see, in a few illustrative examples, how it is possible to apply old methods and to develop new techniques for learning something about the formation, structure, and behaviour of large molecules. In this way the problems yet to be solved will be thrown into stronger relief.

We shall deal first with the synthetic rather than the analytical method as the easier approach of the whole problem. In the pre-macromolecular era the only way of building a large molecule consisted in joining up smaller molecules two at a time, as, for example, in Fischer's classical researches on the polypeptides. The trouble about such processes is that each growth of the molecule required a separate stage in the synthetic technique. In order to obtain say 1000 repeating units in the big molecule a most laborious and certainly impracticable synthesis would be required. If, however, matters could be so arranged that all the stages occur in one reaction system the problem of macromolecular production would be solved. As often happens, the way to accomplish this was discovered purely empirically. Suppose we consider a simple hydroxy-acid of the type $OH{\cdot}R{\cdot}CO_2H$; then, if R is of such a size that the hydroxyl and carboxyl groups can approach each other, a molecule of water may be eliminated and a lactone formed. On the other hand, if this geometrical criterion is not fulfilled, the hydroxyl group of one molecule may interact with the carboxyl group of another and so form a double molecule. Once this has happened the growth at either end of the molecule may continue indefinitely, giving a so-called linear polyester. We may further restrict the possibility of intramolecular reactions by using a dihydric alcohol and a dibasic acid. Syntheses of this kind are not, however, confined to hydroxyl and carboxyl groups. Any two groups which react with each other so as to form a covalent bond between the molecules containing them, provided there are at least two such groups in each molecule, satisfy the requirements for these polycondensations. In this way then the step-wise synthesis may be achieved in one system.

The next question that arises concerns the factors limiting super-ester formation, for in practice there is a limit to molecular growth. When a polyhydric alcohol and a polybasic acid are heated together, the degree of polymerisation of the ester is not very large; for example, 20 units is a common figure, the molecular weight being calculated by end-group determination. If, however, such super-esters have to compete in mechanical properties with naturally occurring macromolecules such as the polysaccharides, it is absolutely essential to increase the molecular weight. Suitable heat treatment in a vacuum with the elimination of more water brings about the necessary increase. The most striking outcome of these researches by the late W. H. Carothers is the production of the polyamide Nylon. Here it has been possible to obtain a fibre having superior mechanical properties to silk, by achieving a high molecular weight and orienting the individual molecules so that the maximum degree of lateral adhesion may exist between them.

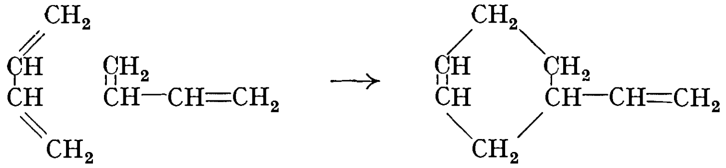
One of the interesting problems in these polycondensations is to find whether such molecular growth occurs (*a*) by the addition of a molecule of monomer, *i.e.*, alcohol or acid to a growing molecule, or (*b*) by the exclusive reaction between polymeric units themselves. Most of the evidence favours the latter type of mechanism.

The other type of reaction giving rise to big molecules is that in which molecules unite without the elimination of small molecules. This can only occur if unsaturation is present. The commonest type of unsaturation used for this purpose is that of ethylene derivatives, but the opening of a $>C{=}O$ bond in suitable circumstances may give rise to high polymers as in polyaldehydes, or even the opening of a ring as in the polymerisation of ethylene oxide. In so far as ethylene derivatives are concerned, it may be said that, apart from ethylene itself, any unsymmetrical derivative may be induced to polymerise to linear macromolecules. If, however, there is more than one double bond in the molecule, numerous complications arise, especially if the double bonds are conjugated. Such conjugation leads to strong resonance in the molecule with profound effects on its reactivity. Sometimes dienes simply undergo a Diels–Alder reaction, no polymerisation in the true sense of the word being observed.

These associations are of great importance because they do provide some definite information about the conditions for the molecule acquiring reactivity. Although butadiene may be induced to form rubber-like polymers with the repeating unit

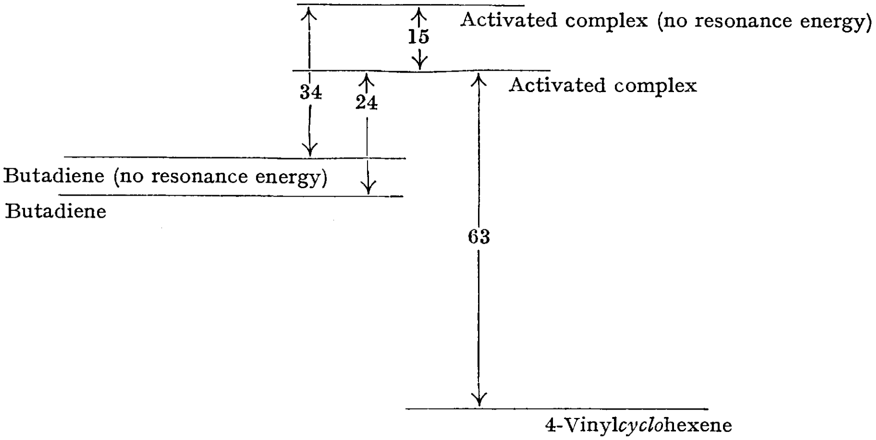
$$-CH_2-CH{=}CH-CH_2-,$$

thermal activation of the molecules in the gas phase gives rise to 4-vinyl*cyclo*hexene, thus (Kistiakowski and Ransom, *J. Chem. Physics*, 1939, **7**, 729):



One molecule of butadiene may further react with the dimer to form an octahydrodiphenyl, but there the process stops. Many such dimerisations have been studied, especially of the Diels–Alder type. The first important fact is that the energy of activation is not specially large, ranging from 15 kg.-cals. for *cyclo*pentadiene to 26 kg.-cals. for $\Delta^{\alpha\gamma}$-pentadiene (Kistiakowski and Lacher, *J. Amer. Chem. Soc.*, 1936, **58**, 123). These figures only refer to dimerisation, and the question that arises is whether the double bonds are actually opened out so as to form a diradical, with the simultaneous appearance of a double bond in the middle of the butadiene molecule. Arguing by analogy with the kinetics of homogeneous *cis-trans*-conversions which require relatively small energies of activation, *e.g.*, 30 kg.-cals., we might presume that this would be quite insufficient to open the double bonds. For ethylene, it has been estimated that the energy required to open the double bond may amount to at least 100 kg.-cals., and such a value would exclude the possibility that association would occur through the medium of diradicals. However, if the principle of resonance is invoked, these energetic considerations require drastic modification. The state of affairs can best be illustrated by an energy-level diagram (Fig. 1). It being assumed for the moment that the intermediate complex in the butadiene reaction is in fact a diradical of the structure $-CH_2-CH{=}CH-CH_2{\cdot}CH_2-CH{=}CH-CH_2-$, unstabilised by resonance, and also that butadiene has no resonance energy, the energy of activation for the association would amount to nearly 40 kg.-cals. The resonance energy of butadiene is only 5 kg.-cals., but that of the radical is estimated to be as high as 20 kg.-cals., which means that the activation energy of the reaction is reduced to 24 kg.-cals. Thus resonance reduces activation energy. Now it is important to observe that nearly all vinyl compounds exhibit resonance in a marked degree; *e.g.*, in the ketone $CH_2{:}CH\cdot CO\cdot CH_3$, the acrylate $CH_2{:}CH\cdot CO\cdot OEt$, and styrene $CH_2{:}CHPh$. In considering the mechanism of the polymerisation of such molecules it is tempting to speculate how far resonance may reduce the energy of activation so as to make practicable energetically the postulation of a free-radical mechanism.

FIG. 1.



Dimerisation of butadiene, showing effect of resonance energy on the energy of activation. Numerals represent kg.-cals.

Although resonance may speed up a reaction, another factor tends to reduce reactivity. When two simple molecules collide, the main criterion that reaction should occur is that the necessary energy of activation should be present at the time of collision. On the other hand, when more complicated molecules are under consideration this simple picture is inadequate. In this case, the molecules do not always react. A tentative explanation was that, since such large molecules would only react at a relatively small region, it was essential that the geometry of the colliding system should also satisfy certain conditions. This explanation raises an important point in dealing with large polymeric molecules because it might be supposed that growth would become appreciably slower as the size increased. At present data are not sufficiently precise to enable us to say whether this effect exists. Recent developments in the theory of chemical reactivity between molecules like dienes have shown that the lack of reactivity may be ascribed to the difficulty of the conversion of the (unquantised) translational degrees of freedom of the colliding molecules into quantised vibrational degrees of freedom of the association product or complex. The quantitative theory does, in fact, account for the magnitude of this steric factor in the case of butadiene; but its extension to long linear polymeric molecules is beset with difficulty, for it is necessary to have complete information, not only about the modes of vibration of the active polymer, but also of the molecule formed when the monomer adds on to the active polymer. Again experimental data are lacking.

The Mechanism of the Polymerisation of Vinyl Compounds.

The aim of the kinetic analysis of polymerisation of vinyl compounds is simply to attempt to measure, for each molecule potentially capable of exhibiting polymerisation, the magnitude of the velocity coefficient for the reaction

$$(\text{Active polymer})_n + \text{monomer} \longrightarrow (\text{Active polymer})_{n+1}$$

where n is the number of units in the polymer. The difficulties of performing such measurements will be indicated by referring later to the methods that may be adopted for the solution of this outstanding problem. In fact, if the nature and reactivity of the active polymer can be determined, we may say that the problem of the mechanism of polymerisation is completely solved; but since this is the aim of chemical kinetics in general, it is unlikely that this desirable state of affairs will be reached in polymeric reactions for some time.

For the moment we will devote attention to monovinyl derivatives. It is now well established that all compounds of the type $CH_2{=}C{<}$ are capable of polymerisation. The nature of the substituent groups on the α-carbon atom has, of course, a profound effect, but in general it may be said that any polar group such as Cl, CO_2H, CN, $CO{\cdot}CH_3$, etc., will function in this way. In the very early days of polymer chemistry it was believed that the monomeric units were joined together by secondary valency forces; but evidence soon accumulated to show that the linkage was by primary valency forces, for the unsaturation, present in the monomer, is not apparent in the polymer. Furthermore, it is possible to alter the nature of the substituents in the monomeric unit in the polymer molecule without affecting the structure of the polymer as a whole. For example, polystyrene $(C_6H_5{\cdot}CH{:}CH_2)_n$ may be hydrogenated, polymethacrylate hydrolysed, and even polyvinyl acetate hydrolysed to polyvinyl alcohol and reacetylated to polyvinyl acetate without changing the number of monomeric units in the polymer (Blaikie and Crozier, *Ind. Eng. Chem.*, 1936, **28**, 1135; McDowell and Kenyon, *J. Amer. Chem. Soc.*, 1940, **62**, 415).

Polymerisation of these molecules may be brought about by heat, light, or catalysts such as peroxides, metallic halides, sulphuric acid—in other words, by almost any reagent which will react with a double bond. The first problem is therefore to find how the monomer is brought into a reactive state; but as a preliminary to this the following matter must be decided. (*a*) Is it necessary that each time a monomer adds on to the growing polymer this monomer should require to be activated or (*b*) when one molecule of monomer is activated do further molecules of monomer add on comparatively readily? Pictorially the two mechanisms can be represented thus:

$$\begin{array}{rcl} & (a.) & \\ M & \longrightarrow & M' \\ M' + M' & \longrightarrow & M'_2 \\ M'_2 + M' & \longrightarrow & M'_3 \end{array} \qquad\qquad \begin{array}{rcl} & (b.) & \\ M & \longrightarrow & M' \\ M' + M & \longrightarrow & M'_2 \\ M'_2 + M & \longrightarrow & M'_3 \end{array}$$

(M′ represents an active molecule)

Both mechanisms lead to the production of linear polymers. The problem is to discriminate between them in any given reaction. The first mechanism is in a way equivalent to polyester formation in that the reaction consists of a series of almost similar bimolecular reactions. The essential distinguishing feature is simply that in the second scheme one monomer so activated will bring about the polymerisation of many ordinary molecules of monomer. Although evidence for the first scheme is not entirely lacking, it would seem that in the great majority of cases the second scheme plays a predominant part. For example, minute amounts of catalyst cause the polymerisation of many molecules of monomer. One quantum of absorbed light will likewise lead to the disappearance of many molecules of monomer. Small traces of certain molecules will markedly inhibit the rate of reaction. These features are, of course, characteristic of the well-known chain reactions of ordinary kinetics. If this fact is admitted, one of the first objects of any theoretical treatment is to measure the concentration of active molecules in order that we may compute the velocity coefficient (k) of the reaction $P + M$ (P is the active polymer), for the rate of polymerisation is then given by the simple equation

$$\text{Rate} = \Sigma k_p[P][M]$$

where Σ sums the effect of all sizes of active polymer which are necessarily present in any reaction system. One method of computing this coefficient is the following. If the value of [P] is plotted against time of reaction, zero time being that point at which the catalyst was added, then [P] gradually rises to an equilibrium value. If the catalyst is removed in some way, then [P] will gradually fall to zero, since the active molecules are removed by some reaction in which they are rendered ineffective for further growth. During the period when [P] is practically constant, its rate of production must be equal to its rate of removal. Suppose these rates are k_i[M] and k_t[P], then

$$k_i[\mathrm{M}] = \Sigma k_t[\mathrm{P}]$$

or

$$\Sigma[\mathrm{P}] = k_i[\mathrm{M}]/k_t$$

If we put these values in the foregoing equation

$$\text{Rate of polymerisation} = \Sigma k_p k_i[\mathrm{M}]_2/k_t\ *$$

Proceeding in this way, we try various methods of producing and removing P and see what kinds of rate equations are obtained. These are then compared with the observed kinetics in order to find whether the assumptions are valid. But this stationary-state method can only be used provided the time of reaction be long compared with the half-life of P.

In most reactions the activated molecules, or perhaps radicals, which play a part in the rate-determining step are, on account of their extreme reactivity, of short life and consequently are present only in minute concentration—indeed, so low that any ordinary analytical device is insufficiently sensitive for the purpose. On the other hand, in polymer reactions, in which free radicals may well play a part, a radical might conceivably have a much longer life and therefore would be present in significant amounts. Triphenylmethyl and similar radicals are cases in point, where the detection is possible by simple physical methods. In such circumstances another treatment will be necessary to determine k_p. Before we can proceed, it is therefore necessary to measure the mean lifetime of the active molecule.

If polymerisation is induced by heating the monomer there is no method of determining directly the mean life. The necessary control of the activation process can most conveniently be accomplished by using ultra-violet radiation. The photoreaction is allowed to proceed steadily and then the radiation is switched off. The interesting fact emerges that in some cases the polymerisation stops in a fraction of a second, whereas in others it continues for extraordinarily long periods—for weeks in some instances. Examples of the former type are the gas-phase photopolymerisations of methyl acrylate, vinyl acetate, vinyl chloride, methyl vinyl ketone, the radical-induced polymerisation of methyl methacrylate, butadiene, vinyl acetate. Examples of the latter are not numerous but include the photopolymerisation of chloroprene, methyl methacrylate, and methyl *iso*propenyl ketone (see, *e.g.*, Melville, *Ann. Reports*, 1939, **36**, 71—77). With liquid-phase catalysed polymerisation it is much more difficult to decide between long- and short-lived molecules. The usual observation is that the reaction proceeds until all the monomer is polymerised. If, however, a catalyst is used which is rather unstable thermally, such as benzoyl peroxide, then it is possible so to arrange matters that the catalyst will decompose in a time shorter than that required for the completion of reaction. Under these conditions the reaction stops when the catalyst is destroyed. Similar behaviour is observed in the polymerisation of butadiene vapour in presence of aqueous hydrogen peroxide (Gee, Davies, and Melville, *Trans. Faraday Soc.*, 1939, **35**, 1298). The unfortunate fact is that these measurements cannot of course be made very precise, and all that can be said is that the mean life of the active polymer does not exceed a few minutes. These methods do, however, provide a guide to the type of kinetic analysis to be employed in the more detailed investigation of the reaction.

The technique of determining mean life-times may, however, be pushed a stage further. If a stationary state is established, we have

$$\text{Rate of production of P} = \text{Rate of removal of P} = [\mathrm{P}]/\tau$$

where τ is the mean life of P. The rate of production of P may be calculated in photoreactions by measuring the number of quanta absorbed, and the rate of removal by measuring the rate of consumption of an intentionally added inhibitor. The problem then is to determine τ.

* This is a very simplified treatment. In a rigorous treatment it is necessary to write down and solve stationary state equation for all sizes of P.

In many of the photochemical polymerisations it is found that the rate of reaction is proportional to the square root of the intensity of the incident light. Employing the simple considerations on p. 418, we see that such a relationship can only be explained on the assumption that the active polymer molecules disappear two at a time when they meet in a suitable collision. Use can be made of this fact in two techniques for measuring τ (Jones and Melville, *Proc. Roy. Soc.*, 1940, *A*, **175**, 392). Suppose there are projected into a long tube two pencils of light each of intensity I, then the rate of polymerisation will be proportional to $2I$. If now the two beams are superimposed the rate will be proportional to $\sqrt{2I}$. Thus the rate will vary with the distance between the two beams. At a certain distance the rate will have a mean value. On the average this will be approximately the distance d which an active polymer molecule diffuses in space before it combines with another of its kind. The lifetime of the molecule is the time for diffusion. These quantities are related by the expression $d^2 = 2Dt$, where D is the diffusion coefficient of the polymer through the monomer. A mean value for this quantity can be calculated if the molecular weight is known, and therefore τ may be computed. In the polymerisation of methyl acrylate τ may be as long as 1 sec. This is in contrast with the usual lives of radicals which are of the order of 10^{-2} sec. or even less.

Another method based upon a similar principle consists in rotating a sector between the reaction vessel and the source of light, the sector being so constructed that the light is cut off for half the time. In this case the velocity of polymerisation is dependent on sector speed. Once again the intermediate point gives approximately a measure of the lifetime of the active polymer. The reason for the rate varying with sector speed may be seen from the following argument. Suppose the sector is stopped with the reaction vessel exposed to the source of light, then

$$\text{Rate} = \text{const.} \times \sqrt{I}$$

If the sector rotates slowly compared with the life time of the active polymer, then

$$\text{Rate} = \text{const.} \times \sqrt{I}/2$$

But if the sector rotates very quickly, this condition is virtually equivalent to cutting down the intensity of the light by a factor of 2 and therefore

$$\text{Rate} = \tfrac{1}{2}\,\text{const.} \times \sqrt{I}/2$$

So far no measurements have been made to find how τ varies with molecular size, for it is difficult enough to get these methods to work, apart from extending their range of usefulness.

The unfortunate disability of these methods is that they depend upon mutual destruction of the active polymer. Some technique must be devised for dealing with reactions in which the active polymer disappears at a rate proportional to the first power of its concentration. One obvious method would be to study the distribution of deposited polymer, much in the same way as proved successful with highly dilute flames. Alternatively, attempts might be made to study the distribution of dead polymer in space by observing the intensity of scattered light produced by it. The trouble is that these methods almost invariably fail because the polymer reaction is strongly exothermic, and if, therefore, pressures of the order of 10—100 mm. are being used, the convection currents so produced upset any regular distribution of solid polymer. At low enough pressures the method may produce roughly qualitative results, as happens in the mercury-sensitised polymerisation of acetylene (*Trans. Faraday Soc.*, 1936, **32**, 258).

The next important point to be decided is the nature of the active polymer itself. There are two extreme points of view. One is that the double bond of the monomer is opened out to a diradical, and then monomer adds on at each end:

$$CH_2{=}CHX \longrightarrow -CH_2{-}CHX- \longrightarrow -CH_2{-}CHX{-}CH_2{-}CHX-, \text{etc.}$$

One slight variation of this mode of addition is that the catalyst, *e.g.*, a single radical, might add on to one end of the molecule, thus producing a single bigger free radical which would grow in precisely the same way. Such a mechanism easily accounts for the ready addition of monomer once the free radical is formed and would also account for the fact that loss of activity occurs when two free-radical ends of the molecule either unite or disproportionate. The other school of thought postulates activation of the monomer but not to the extent of opening the double bond. With this mechanism the addition of monomer means the migration of a hydrogen atom, thus :

$$\mathrm{CH_2{=}CHX + CH_2{=}CHX \longrightarrow CH_3{-}CHX{-}CH{=}CHX}\ \text{(activated).}$$

At the other extreme this mechanism might be become stepwise in character if each addition of monomer required as much activation energy as the first association of the two monomeric units or the energy required to activate one of them. The first to suggest the latter mechanism was Whitby, the evidence being that it was possible to show by bromine-absorption experiments that polymers from styrene and similar molecules possessed a terminal double bond. Although there may be no doubt about this terminal double bond in the dead polymer, it might well be produced when, say, a radical chain is ended by disproportionation, thus :

$$\begin{array}{ll} \sim\!\sim\!\sim \mathrm{CH_2{-}CHX{-}} & \mathrm{{-}CHX{-}CH_2}\!\sim\!\sim\!\sim \\ \sim\!\sim\!\sim \mathrm{CH{=}CXH} & \mathrm{X{\cdot}CH_2{-}CH_2}\!\sim\!\sim\!\sim \end{array}$$

There are two pieces of evidence which appear to support or rather to demonstrate that the polymerisation of styrene in the liquid phase may occur by way of the free-radical mechanism : (*a*) the fact that the free radicals from tetraphenylsuccinodinitrile induce styrene to polymerise (Schultz and Wittig, *Naturwiss.*, 1939, **27**, 387), and (*b*) magnetic measurements would seem to indicate the presence of free radicals during polymerisation.

All this presumes, however, that there is only one mechanism for polymerisation. There may, in fact, be at least two, if not more. A study of the photopolymerisation of methyl methacrylate, chloroprene, and methyl *iso*propenyl ketone demonstrates the duality of mechanism. For example, when hydrogen atoms or methyl radicals are added to methyl methacrylate vapour, polymerisation by the free-radical mechanisms occurs wholly in the gas phase

$$\mathrm{H + CH_2{:}CMe{\cdot}CO_2Me \longrightarrow CH_3{-}\overset{|}{C}Me{\cdot}CO_2Me}, \text{ etc.}$$

The large free radicals eventually interact with each other and the polymerisation ceases after about 10^{-2} sec. (Melville, *Proc. Roy. Soc.*, 1937, *A*, **163**, 511). It is not yet known at what end the hydrogen atom adds on, nor is it certain if all the monomer molecules add on in a regular fashion. If, however, the vapour is illuminated directly, polymer is certainly produced, but when the light is switched off polymerisation continues in the dark, growth occurring in the solid phase of polymer deposited on the walls of the reaction vessel. Here, too, the polymerisation starts in the gas phase, and it must therefore be presumed that the kind of molecule which is produced must differ considerably from a free radical. For want of a better alternative we may suppose the mechanism is of the double-bond type. Certainly the activity of the polymer has to be maintained. This is difficult to understand, but whatever its precise nature it is destroyed by reagents such as hydrogen atoms and iodine molecules for methacrylate, and even oxygen in the case of the long-lived polychloroprene.

It is curious that, although methyl acrylate behaves in much the same way as methacrylate, there is no continued growth in the dark (Melville, *Proc. Roy. Soc.*, 1938, *A*, **167**, 99). On the double-bond hypothesis, this is readily explicable because the terminal double bonds may react thus :

$$\begin{array}{c} \sim\!\sim\!\sim\mathrm{CH{=}CHX + X{\cdot}CH{=}CH}\!\sim\!\sim\!\sim \\ \sim\!\sim\!\sim\mathrm{CH_2{-}CX{=}CX{-}CH_2}\!\sim\!\sim\!\sim \end{array}$$

whereas methacrylate ends could not so react, since two methyl groups would need to be shifted simultaneously.

This long-lived type of molecule was first discovered by Carothers (Carothers *et al.*, *J. Amer. Chem. Soc.*, 1931, **53**, 4203) with chloroprene which grows rather more quickly than methyl methacrylate. Under suitable conditions methyl *iso*propenyl ketone behaves in a like manner, although again methyl vinyl ketone is like methyl acrylate in that its activity does not survive for long. It will be observed that all these long-lived molecules possess the general structure $CH_2{=}CXY$, where X might be termed the polymer-activating group and Y is a substituent which may not necessarily help polymerisation. But all these molecules may be made to polymerise without the exhibition of these long-lived characteristics, thus demonstrating that one and the same molecule may polymerise by a variety of mechanisms. In order to explain longevity, it has been suggested that if a large-polymer free radical finds itself embedded in dead polymer it would have extreme difficulty in finding another similar molecule with which to react, and so its growth would be terminated. An observation with chloroprene shows that such an explanation is unlikely (Bolland and Melville, Proc. Rubber Tech. Conf., London, 1938, 239). If live polychloroprene saturated with monomeric chloroprene is irradiated, rapid additional polymerisation occurs but this ceases immediately the light is cut off. As a matter of fact, this additional polymerisation goes at a rate proportional to the square root of the intensity, which demonstrates conclusively that the active ends of the polymer can find and react with each other even in a tangled skein of rubber molecules. It is tempting to speculate how far resonance energy might be invoked to explain the continued reactivity along the lines outlined in the section on association of dienes. The technique does, however, provide a method of making large molecules of a length without apparent limit.

The above discussion on the mechanism whereby an active polymer may lose its activity has been confined to mutual interaction of free radicals or double bonds. There are, however, other ways of destroying its activity. Molecular growth may be checked by the addition to the reaction mixture of specific inhibitors; in the liquid phase these are generally of the antioxidant type, such as quinol or pyrogallol; in the gas phase, oxygen is usually a powerful inhibitor. Sometimes the effect of the inhibitor is complicated by the fact that it reduces the concentration of the catalyst that interacts with the monomer. This makes the interpretation of the kinetics difficult. Besides this intentional termination there are a number of examples, *e.g.*, acetylene, butadiene, in which kinetic analysis shows that the monomer itself can destroy the activity of the growing polymer. The chemistry of the process is obscure, but it might be explained on the assumption that the monomer reacts in such a way that it produces a terminal structure incapable of adding on further monomer molecules (see below) (see *Ann. Reports*, 1940, **37**, 68). It may also be presumed that a molecule might lose its energy spontaneously, *e.g.*, by cyclisation of a diradical. This process would, however, only be important when the polymer is small.

Interpolymerisation.

It is a difficult enough problem adequately to deal with the polymerisation of a single monomer, but it is still more difficult to consider the behaviour of a mixture of two or three monomers. Interpolymers are, however, of great importance because they often possess unique properties which cannot be obtained by using mechanical mixtures of simple polymers. The reason for this state of affairs is that the number of vinyl derivatives which polymerise is limited. Substituents such as Cl, CO_2CH_3, $CO{\cdot}CH_3$, CN, $CH{:}CH_2$, C_6H_5, OAc are normally employed since, in general, such groups yield sufficiently reactive monomers to give large polymers. Production of interpolymers may be achieved by polymerisation of mixtures of monomers in the hope that true interpolymerisation does occur. The success of this operation can usually be gauged by an examination of the properties of the resultant resin. An alternative method consists in partly modifying the nature of groups present in a homogeneous polymer, as, for example, in the partial hydrolysis of polyvinyl acetate to polyvinyl alcohol. One of the best examples is the copolymer of vinyl acetate and vinyl chloride. Polyvinyl chloride is not easy to mould or dissolve, but it is tough and has in general good mechanical properties, whereas polyvinyl acetate has roughly the opposite characteristics. A mechanical mixture of the two does not achieve the desired result, which is only attained by interpolymerisation. Another incidental use of interpolymerisation is the inducement of certain molecules to form products of high molecular weight. Butadiene does not form such products, yet by interpolymerisation with methyl methacrylate or acrylonitrile the requisite molecular size may readily be obtained. Similarly, methyl *iso*propenyl ketone may be induced to polymerise much more readily if it is mixed with methyl vinyl ketone. Here the most surprising result is that in the photopolymerisation the rate of interpolymerisation is greater than that of methyl vinyl ketone itself (T. T. Jones, private communication). On the other hand, in the liquid-phase interpolymerisation of styrene and methyl methacrylate the rate is rather less than the mean value of the polymerisation rates of the pure monomer (Norrish and Brookman, *Proc. Roy. Soc.*, 1939, *A*, **171**, 147). Again, butadiene functions as an inhibitor for the photopolymerisation of methyl acrylate and vinyl acetate (unpublished experiments). These are only random observations, but when they are extended and sufficiently systematised it will be possible to treat the problem upon a proper kinetic basis and thus permit predictions to be made regarding the speed of such interpolymerisations and the structure of the resulting products.

Another interesting way of making mixed molecules utilises the observation that, if the vapour of methyl methacrylate or of chloroprene is illuminated, a polymer is deposited on the walls of the reaction vessel which continues to grow for a considerable time after the light is cut off. If, *e.g.*, chloroprene vapour is admitted to a vessel containing live polymethacrylate, polychloroprene will be formed on top of the methacrylate. Similarly, if the chloroprene is withdrawn and methacrylate vapour substituted, a layer of polymethacrylate will grow on top of the polychloroprene; a molecular sandwich is thereby built up, and this process may be repeated many times. Again, we may start with live polychloroprene and go through the same cycle of processes. If a mixture of vapours is admitted, then a rather different type of composite polymer may be built up. Methyl *iso*propenyl ketone likewise may be induced to grow on live polymethacrylate. Limitation of this kind of molecular growth is readily done by destroying the activity at the end of the macromolecule. Iodine and atomic hydrogen are effective for methacrylate, and oxygen and gentle heat suffice for chloroprene. Once destroyed, the activity cannot be restored (Bolland and Melville, *Osterreich. Chem.-Ztg.*, 1939, No. 10).

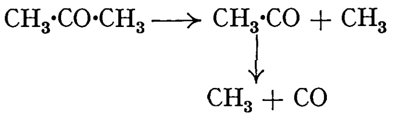
Molecular Weight of Polymers.

It might be supposed that if the molecular weight of the inactive polymer is determined by viscosimetric, end-group determinations or by the ultracentrifuge there is no necessity to devise any method of measuring the chain length of the active polymer just before its activity is destroyed. If the polymer chain is branched or even crosslinked, both determinations are a prerequisite for the elucidation of the structure of the polymer. Even if the polymer is linear the information is useful.

First of all, the possible kinetic methods may be mentioned. In catalysed liquid-phase polymerisations the chain length of the polymer might be expected to be given by the ratio of the number of monomeric molecules polymerised to the number of molecules of catalyst used up. The most extraordinary observation made in the benzoyl peroxide-catalysed polymerisation of styrene or of vinyl acetate is that the chain length so defined is greater than that determined by osmotic or viscosimetric methods. This means that one catalyst molecule must be capable in some way of starting the growth of several polymer molecules. How this is done is rather a mystery, although several transfer mechanisms have been postulated to explain how the active molecule may transfer its activity to a normal monomer molecule.

Another method of attempting to measure the rate of production of active polymer consists in adding an inhibitor to the reaction mixture such that all growing polymers are ultimately poisoned. Under these conditions the rate of consumption of inhibitor molecules is exactly equal to the rate of production of active molecules. Since the rate of disappearance of monomer in the uninhibited reaction is also known, the chain length is easily computed. Examples of this method are found in the butadiene-inhibited polymerisation of methyl acrylate (*Proc. Roy. Soc.*, 1938, *A*, **167**, 99) and the stannic chloride-catalysed, hydrogen chloride-inhibited, liquid-phase polymerisation of styrene (Williams, J., 1938, 246, 1046).

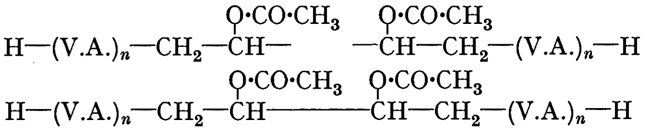
The quantum yield in a photo-reaction cannot unfortunately be taken as a measure of the chain length because it is usually difficult to say whether each quantum of light absorbed starts off a polymer chain. Any chain length so obtained is thus a minimum value. In the acetone-sensitised polymerisation of ethylene, vinyl acetate, and methyl vinyl ketone the rate of carbon monoxide production from the primary dissociation



$$\begin{array}{c}\mathrm{CH_3{\cdot}CO{\cdot}CH_3 \longrightarrow CH_3{\cdot}CO + CH_3}\\ \qquad\qquad\quad\downarrow\\ \qquad\qquad\quad\mathrm{CH_3 + CO}\end{array}$$

affords a measure of the rate of production of methyl radicals all of which can be shown to start off polymerisation. This method has the great merit that small amounts of carbon monoxide may readily be estimated in presence of large excess of monomer and acetone simply by freezing out the latter molecules with liquid air. In this way very long chain lengths can be measured (see, *e.g.*, *Chem. and Ind.*, 1940, **59**, 267).

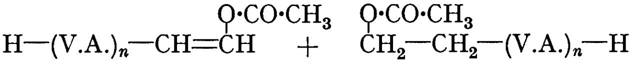
Yet another method of measuring molecular weights kinetically consists in using hydrogen atoms to start polymerisation. Provided the hydrogen atom reaction can be studied to the exclusion of any other reaction—as it can with vinyl acetate—then the ratio of the number of molecules of monomer consumed to the number of hydrogen atoms which disappear is a direct measure of the chain length. In such a case it may be possible to discriminate between the two ways in which free radicals are destroyed, *i.e.*, (i) by combination :



$$\mathrm{H{-}(V.A.)_n{-}CH_2{-}\overset{O\cdot CO\cdot CH_3}{\overset{|}{C}H}{-}} \qquad \mathrm{{-}\overset{O\cdot CO\cdot CH_3}{\overset{|}{C}H}{-}CH_2{-}(V.A.)_n{-}H}$$

$$\mathrm{H{-}(V.A.)_n{-}CH_2{-}\overset{O\cdot CO\cdot CH_3}{\overset{|}{C}H}{-\!-\!-\!-}\overset{O\cdot CO\cdot CH_3}{\overset{|}{C}H}{-}CH_2{-}(V.A.)_n{-}H}$$

or (ii) by disproportionation :

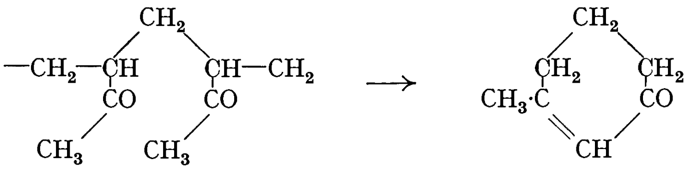


$$\mathrm{H{-}(V.A.)_n{-}CH{=}\overset{O\cdot CO\cdot CH_3}{\overset{|}{C}H}} \quad + \quad \mathrm{\overset{O\cdot CO\cdot CH_3}{\overset{|}{C}H_2}{-}CH_2{-}(V.A.)_n{-}H}$$

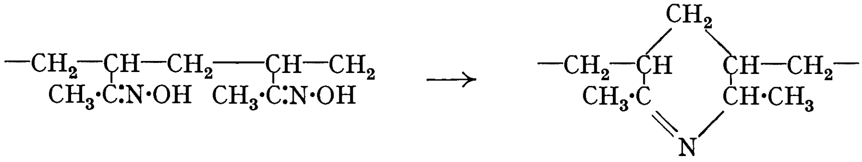
In the latter case the molecular weight of the resultant polymer will be identical with the kinetic chain length multiplied by the molecular weight of the monomer. The difficulty of making an exact discriminating test is that the polymers are not all of the same size, being in fact distributed about a mean molecular size. The kinetic method gives essentially a number-average molecular weight whereas if the viscosimetric method is employed a weight-average molecular weight is obtained. Exact statistical calculations for this kind of polymerisation have indicated that the relationship between the two is rather complicated but the latter is larger than the former. With the vinyl acetate reaction the viscosimetric molecular weight is about three times that of the kinetic weight based upon the assumption of combination. It is therefore difficult to say which type of termination mechanism is predominant (Tuckett and Melville, unpublished observations).

The Structure of Vinyl Polymers.

The problem here is apparently simple. Suppose we consider a vinyl molecule A–B, then the question arises as to whether the polymer is built up regularly, ABAB, etc., or whether the structure ABBAAB occurs in any part of the polymer molecule. Generally, it would seem to be safe to say that the majority of such molecules are constructed according to the former plan. For example, polyvinyl alcohol prepared by hydrolysing polyvinyl acetate gives all the characteristics of 1 : 3-diols : periodic acid does not react with it, nitric acid oxidises it to oxalic acid, and the absorption spectrum is similar to that of 1 : 3-diols (Marvel, *J. Amer. Chem. Soc.*, 1938, **60**, 1045). Similarly (Marvel and Levesque, *ibid.*, p. 280), in the products of pyrolysis of polymethyl vinyl ketone, 3-methyl*cyclo*hexenone may be isolated, and this can only be derived from an ABAB structure thus :



Also (*ibid.*, 1939, **61**, 3234) if the polyketone is converted into the ketoxime and this is treated with alcoholic hydrogen chloride a cyclic product is formed, not in 100% but only in 86·5% yield:



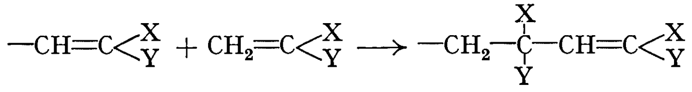
The reason for this small yield will be explained below. Suffice it to say that it supports the ABAB structure.

Again, comparison of the absorption spectra of polyvinyl chloride solutions with those of 2 : 3- and 2 : 4-dichloropentane shows that the latter molecule is the more similar to the polymer. When zinc removes halogen from polyvinyl chloride the resultant polymer is not unsaturated, which would happen if any halogen atoms were in the 1 : 2-positions (Marvel *et al.*, *J. Amer. Chem. Soc.*, 1939, **61**, 3241). On the other hand, there is some evidence to indicate that methyl α-bromoacrylate is an ABAB product, for it exhibits reactions of a 1 : 2-dihalogenated molecule; *e.g.*, 97% of halogen is removed by zinc (Marvel and Cowan, *ibid.*, p. 3156).

It was mentioned above that removal of halogen by zinc from a polymer is not quantitative. The explanation of this behaviour suggests another way of tackling the problem of the structure of vinyl polymers, namely, by considering the statistics of the removal of halogen. The cardinal point is that, provided that crosslinking does not occur between chains as a result of halogen removal, *two* halogen atoms must be removed simultaneously—a single atom is necessarily unreactive. Consider polyvinyl chloride as an example. If the structure is that of a 1 : 3-dichloro-compound, then on reaction with zinc the first and second and fourth and fifth halogens might be removed and the third left. The problem is to calculate what fraction of chlorine is left isolated. Without going into details it can be shown that a fraction $1/e^2$ is so left, *i.e.*, 13·5% (Flory, *ibid.*, p. 1518). On the other hand, if the polymer is a random mixture of ABAB and ABBAAB and it is assumed that two chlorines in the 1 : 4-position do not react at all, then there are three possibilities: (*a*) 1 : 2- and 1 : 3-positions react equally quickly, (*b*) 1 : 2 reacts much more quickly than 1 : 3, and (*c*) vice versa. As a matter of fact each case gives rise to the same result, namely, that the fraction remaining is $1/2e$ or 18·4%. It will be seen that the discrimination cannot easily be made but the result shows that the proportion of chlorine left is less than 16% and may be as small as 13%, which would provide strong additional support for the ABAB structure.

In the copolymer of vinyl acetate and vinyl chloride the presence of the acetate groups complicates the analysis but the results are substantially the same, favouring the ABAB pattern.

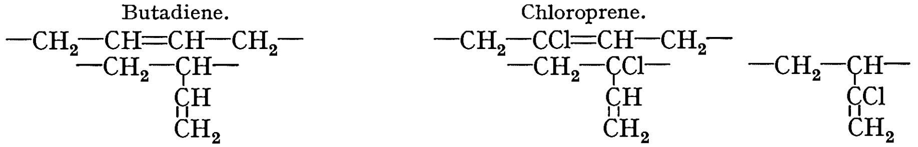
In this connection it may be noted that if a monovinyl molecule of the structure $CH_2{=}C{<}^{X}_{Y}$ polymerises by a mechanism involving the migration of a hydrogen atom each time a monomeric molecule adds on to the live polymer, thus:



$$-CH{=}C{<}^{X}_{Y} + CH_2{=}C{<}^{X}_{Y} \longrightarrow -CH_2-\overset{X}{\underset{Y}{C}}-CH{=}C{<}^{X}_{Y}$$

then the addition can only occur in such a way as to produce an ABAB polymer. Otherwise either an X or a Y group must be shifted. Even if hydrogen atom migration does not take place as in the free-radical polymerisation, it is probable that the polar nature of X or of Y is sufficient to ensure that the monomer will add on in a regular manner. Although it would be unsafe to generalise from these few examples, it would seem probable that most polymers are of the ABAB type.

Matters are a good deal more complicated when dienes polymerise, for there are two possible structures for butadiene and three for chloroprene :



Butadiene.

$$-CH_2-CH{=}CH-CH_2-$$

$$\begin{array}{l} -CH_2-CH- \\ \qquad\quad | \\ \qquad\; CH \\ \qquad\quad \| \\ \qquad\; CH_2 \end{array}$$

Chloroprene.

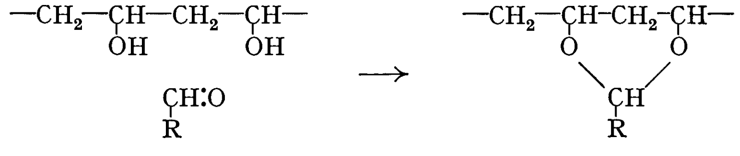
$$-CH_2-CCl{=}CH-CH_2-$$

$$\begin{array}{l} -CH_2-CCl- \\ \qquad\quad | \\ \qquad\; CH \\ \qquad\quad \| \\ \qquad\; CH_2 \end{array} \qquad \begin{array}{l} -CH_2-CH- \\ \qquad\quad | \\ \qquad\; CCl \\ \qquad\quad \| \\ \qquad\; CH_2 \end{array}$$

The most that can be said is that both 1 : 2- and 1 : 4-addition can occur. For example, the product from the sodium-catalysed polymerisation of butadiene gives on ozonolysis a polyaldehydic carboxy-acid, which would imply 1 : 2-addition (Kummener, *Kautschuk*, 1934, **10**, 149). On the other hand, polymerisation in emulsion gives a polymer which on ozonolysis gives succinic acid and aldehyde and also butane-1 : 2 : 4-tricarboxylic acid. This would mean that both 1 : 2- and 1 : 4-addition occur. Curiously enough, if interpolymerised with methyl methacrylate, butadiene appears to add on in the 1 : 4-position, 1 : 2 being entirely absent (Hill, Lewis, and Simonsen, *Trans. Faraday Soc.*, 1939, **35**, 1067). There is some evidence that chloroprene may behave in the same versatile manner. This polymer is self-vulcanising, *i.e.*, it may be cross-linked without the need for the addition of sulphur. This cross-linking, for example by radiation, would seem to require that a vinyl side chain takes part in the reaction.

Three-dimensional Molecules.

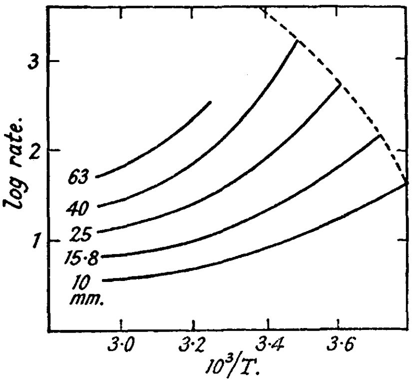
The above remarks have been restricted to linear macromolecules. It is, however, possible to visualise molecules which branch like a tree or form three-dimensional networks of atoms. The question arises as to the identification of such types and the types of monomer from which they tend to be derived. The three-dimensional network is obviously a system which, if big enough, will not be broken up by immersion in any solvent. This fact precludes much work on its structure. At present there is no way in which the magnitude of the mesh of the net can be determined. Since such networks cannot be orientated by mechanical methods, any attempt at the determination of structure is not possible by *X*-ray technique. Furthermore, swelling characteristics are so qualitative that this mode of approach is not very helpful. Fortunately, it is easy to recognise those monomeric systems which are likely to give rise to crosslinked molecules. In the vinyl molecule all that is necessary is the existence of two vinyl groups in the monomer—whether they are separately or simultaneously activated does not at present matter. In the polycondensation type of reaction it is necessary to have at least three similar reactive groups in one of the molecules, as, *e.g.*, the three hydroxyl groups in glycerol if this molecule is caused to react with a dibasic acid. There is, however, more in the problem that is implied by these simple statements. Geometrical criteria must also be satisfied. For example, aldehydes react readily with linear polyvinyl alcohol, but the resulting molecule is not crosslinked (unpublished observations). We must conclude, therefore, that although the following reaction can occur



the aldehyde cannot simultaneously react with two hydroxyl groups from different polyvinyl alcohol molecules.

Another way of tackling the problem of crosslinking consists in examining the kinetics of the reaction for abnormal features. Such crosslinking depends primarily on branching of chains of atoms. In this connection it may be recalled that a similar hypothesis was put forward many years ago to account for the transition of slow to explosive combustion in a very narrow pressure and temperature range. Chemically the difference between the two reactions is simply that in the polymer reactions the active patch on the growing molecule sometimes gives rise to two active patches in the bigger molecule, whereas in the explosive reaction two active centres or chain carriers emerge from a collision into which one entered in the first place. Kinetically the assumptions lead to precisely the same kind of mathematical expression for the reaction velocity. It is unnecessary here to enter into the algebra of the question : suffice it to say that the characteristics of such branching are (*a*) an abnormally high variation of rate with pressure, *i.e.*, high reaction orders which do not have any other rational explanation, and (*b*) a non-exponential relationship between rate and temperature in the sense that the rate varies with temperature even more rapidly than would be predicted by the usual Arrhenius relation. Another characteristic by means of which branching might be recognised is based on a small variation of rate with incident light intensity, if the reaction is photochemical.

FIG. 2.



Photopolymerisation of methyl vinyl ketone at different temperatures and pressures. Broken line shows limit of vapour pressure.

So far, only one reaction has been discovered which exhibits these anomalies, namely, the photochemical polymerisation of methyl vinyl ketone (*Chem. and Ind.*, **1940**, **59**, 267 and unpublished results). The results are most readily summarised in a diagram (Fig. 2) in which the logarithm of the rate is plotted as is usual against the reciprocal of absolute temperature for a number of different pressures. Apart from the interesting fact that the reaction possesses a negative temperature coefficient, as do many photopolymerisations, the most marked feature is the abnormal increase in rate with decreasing temperature. Indeed, it would seem that the rate might become indefinitely large were it not for the fact that the vapour pressure puts a limit on the temperature that may be used at any one pressure. Similarly, we find that if the logarithm of the rate is plotted against that of the pressure, the slope of the resultant curve indicates not only a high order but a rapidly increasing order with pressure. These are just the characteristics associated with branching, and it is therefore interesting to find that the polymer is completely insoluble in all solvents. The problem of determining the precise reaction which causes branching and the frequency with which it occurs has not yet been solved. However, some guidance may be given by the following facts. Methyl vinyl ketone polymerises by rather an indirect method, in that the molecule first breaks up into radicals. These radicals then start off free-radical polymerisation, thus :

$$\mathrm{R{-}CH_2{-}\overset{CO\cdot CH_3}{CH}{-}} + \mathrm{CH_2{=}\overset{CO\cdot CH_3}{CH}} \longrightarrow \mathrm{R{-}CH_2{-}\overset{CO\cdot CH_3}{CH}{-}\quad {-}CH_2{-}\overset{CO\cdot CH_3}{CH}{-}}$$

If therefore the molecular chain is to branch by interaction with a monomer, three free valencies will have to be produced. This may happen in the following manner (provided the free radical collides with a ketone molecule which has just been activated photochemically) :

$$\mathrm{R{-}} + \mathrm{CH_2{:}CH\cdot CO\cdot CH_3} \longrightarrow \mathrm{R\cdot CH_2\cdot \underset{|}{C}H\cdot \underset{|}{C}O} + \mathrm{CH_3{-}}\ \cdot$$

The kinetics of the reaction show very clearly that the free radicals so produced mutually saturate each other and lead to a three-dimensional polymer. Incidentally, the fact that such a three-dimensional network is produced demonstrates that in this particular case when free radicals interact they combine and do not disproportionate.

This review has been mainly confined to a particular class of macromolecules. No apology is made for such a one-sided view. The reason is simply that a little progress has recently been made in this branch of macromolecular chemistry.