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All-Union Research Institute for
Synthetic and Natural Perfumes
(VNIISNDV)

SECONDARY REACTIONS IN RADICAL POLYMERISATION

L. M. Pyrkov and S. Ya. Frenkel'

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INTRODUCTION

In recent years detailed studies of polymerisation processes of different types have established that the main reactions in these processes are accompanied by a number of supplementary secondary processes or reactions. The distinguishing feature of these secondary reactions is the participation of previously formed polymer chains. It is therefore natural that at low degrees of conversion of monomer, *i.e.* in the range in which polymerisation kinetics, etc. are usually studied, these reactions are almost non-existent and the polymer obtained under these conditions is the product of only the main or primary reactions.

On the other hand, at high degrees of conversion, particularly when the concentration of polymer becomes comparable with the concentration of monomer, the probability of secondary reactions in polymerisation systems is considerable and these reactions have a significant effect on the polymerisation product.

The present review attempts to give a systematic account of the available data on secondary reactions in radical polymerisation.

I. INTRODUCTORY REMARKS

Study of the molecular-weight distribution (MWD) of polymer specimens obtained by bulk polymerisation under the influence of free radicals[1] shows that at low degrees of conversion, in accordance with theory, experiment gives a unimodal function for the molecular-weight distribution. On the other hand, at degrees of conversion close to 100%, experiment often gives complex distribution functions showing several maxima[1]. (In the polymerisation of diene compounds anomalous high-molecular "tails" are often observed in the MWD [2].)

The theory of radical polymerisation in bulk phase, which takes account only of the main reactions of chain initiation, growth, and rupture, never gives these complex multimodal distributions. It has been suggested[1] that MWD with a number of sharp maxima may be produced as a result of doubling, trebling, etc. of the molecular weights of individual groups of molecules as a result of certain secondary reactions accompanying polymerisation[3]. Subsequent more detailed examination of the problem showed that secondary reactions by themselves cannot be responsible for the multimodal character, which arises rather as a result of the microheterogeneity of the system at later stages of the polymerisation. Apart from any relation to the number of maxima, however, the secondary reactions may change significantly the properties of the polymer, so that it is necessary to consider these reactions.

In the work cited[1] and in a number of later papers secondary reactions were not defined sufficiently clearly, and this might lead to terminological confusion. It is shown below that the first stage in any secondary reaction is the transfer of the kinetic chain to the polymer[4]. The relative contribution of this reaction increases with the degree of conversion ψ, however, and its results differ fundamentally at high and low values of ψ. The rate of chain transfer to the polymer is

$$r_{tr,\,p} = k_{tr,\,p}[P^*]\,[P], \qquad (1)$$

where $k_{tr,p}$ is the corresponding rate constant, whose changes with change in ψ are neglected, $[P^*]$ the stationary concentration of macroradicals, and $[P]$ is the total concentration of polymer formed in the period under consideration and is proportional to ψ. In bulk polymerisation under conditions where transfer is possible chain transfer to the monomer at first competes with transfer to the polymer, but this competition progressively decreases, since with increase in ψ, $[m]$ (the concentration of the monomer) decreases and $[P]$ increases.

For the same reason, the results of chain transfer are different at high and low values of ψ. At low values of ψ, when chain growth is not diffusion-controlled, activation of any intermediate link leads to growth of a side-chain. Sometimes this reaction is also called a secondary reaction, but this is hardly appropriate, for the growth of the side-chains takes place according to the same laws as the growth of the main chains. At high values of ψ, however, when little monomer remains, the viscosity increases sharply and the growth reaction becomes diffusion-controlled; activation of intermediate links in the chains leads not only to simple growth of the side-chains, as under the conditions where large quantities of monomer are present, but also to a number of other processes. The most probable process is rupture of the chain into two fragments[5,6], one of which will have an active end. These active fragments may subsequently[7-9] (a) be depolymerised by a chain mechanism, (b) transfer their activity to another chain, (c) recombine with another similar fragment or primary "live" chain, (d) disproportionate with another fragment or primary chain, or (e) begin new growth at the expense of monomer. Since $[m]$ is small, process (e) should most probably take place at the expense of process (a).

In reaction of type (b), which is most probably accompanied by new breakdown, *two* fragments are again produced, so that a series of reactions of type (b) should lead to an increase in the total number of macromolecules in the system and to a decrease in the average weight M_n. Secondary reactions which begin with chain transfer and subsequently develop by mechanisms (b) or (d) can therefore be combined in the general class of *degradation reactions*.

Processes of types (a) and (e) (which must be considered together) or (c) involve a rearrangement of monomeric links or whole fragments between different macromolecules. These reactions can be combined under the title of *inter-chain exchange reactions*.

Let us now consider the original chain transfer reaction. Under favourable conditions, a chain activated in its centre can, without breaking down, recombine with another similar chain or with a chain having an active end. It is also possible to picture a process in which two closely adjacent chains with active intermediate links are joined together by a short bridge (two branches begin to grow towards one another and recombine). The probability of such reactions depends on the tendency of the macroradicals to recombine, and should increase sharply in diene polymerisations, the increase being greater, the greater the number of 1,2-links in the chain. Reactions of this type, leading to the formation of branched fractions, microgels, and gels, are most dangerous from the practical viewpoint; they form a third class of secondary reaction, which may conventionally be referred to as *cross-linking reactions* (conventionally, since this includes all recombinations of activated intermediate links with terminal links, leading to ordinary branching).

Reactions of the last class, like ordinary branching reactions, lead to an increase in the polydispersion, revealed as an increase in the high-molecular "tail" in the MWD. As will be shown below, however, there are insufficient grounds for assuming that particular MWD's, corresponding to "fractions" of identical degree of branching, will give separated maxima on the weight distribution curve.

Thus the term "secondary reactions" will be taken to mean the conversion of "dead" chains and macroradicals in the later stages of polymerisation, beginning with the activation of intermediate links as a result of chain transfer to the polymer. These reactions, however, are fundamentally different from ordinary branching reactions, which also result from chain transfer to the polymer. The latter reactions are nevertheless included in the discussion, for in diene polymerisations they may readily change to cross-linking reactions.

Under normal conditions, all secondary reactions should take place simultaneously, and it is impossible to observe them individually. In certain model systems (or combinations of such systems), however, it is possible to "isolate" individual reactions. This is discussed later.

II. INDIVIDUAL FORMS OF SECONDARY REACTION

a. Degradation of Polymer Chains

In recent years it has been shown that the process of radical polymerisation may be accompanied by the direct action of initiator radicals, polymer radicals, etc. on previously formed polymer chains. This usually leads to degradation, *i.e.* to rupture of the C–C bonds of the macromolecules.

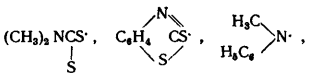
The process of C–C bond rupture is usually accompanied, to some extent, by a depolymerisation process which, as has now been shown[11,12] (Ref. 10, pp. 77–80) is also radical-initiated. Even in model systems — solutions of polymers in the presence of initiators (which are often used to study degradation in the presence of radicals) — however, the depolymerisation process plays an extremely small part[9], and in the case of "polymerisation boilers" this process cannot play a significant part, due to the actual nature of the process taking place.

The majority of the free radical reactions described in the literature relate to those cases of chemical changes in which the radical removes a hydrogen or halogen atom from an inactive molecule (Ref. 4, p. 9), *i.e.* when replacement reactions of the type

$$R_1^{\cdot} + X{-}R_2 \rightarrow R_1{-}X + R_2^{\cdot}$$

take place.

If the compound $X-R_2$ is a polymer, this reaction produces a macroradical $R_2^{\cdot}$, which, depending on its reactivity and the properties of the surrounding medium, may be stabilised in different ways, including degradation at a weakened C–C bond with the formation of inactive and active macromolecular fragments[5–9]. The degradation of polymer chains under the influence of free radicals has been described by a number of authors. Thus Dolgoplosk *et al.*[13] showed that redox systems (consisting of peroxides and hydroperoxides and different reducing agents), which are sources of free radicals at low temperatures, cause degradation of polyisobutylene and other polymers in hydrocarbon media. In particular, it was shown that at low temperatures (20°–50°) these systems initiate the vulcanisation of rubbers in the absence of oxygen and initiate a degradation process in the presence of oxygen. The rupture of the diallyl bond in complex organic molecules under the influence of free radicals was also established by Klebanskii and Fomina[14]. Dolgoplosk and coworkers[15–18] also studied the degradation of polyisobutylene in solution under the influence of a number of aliphatic radicals† (see Fig. 1), radicals with a reactive centre on nitrogen and sulphur atoms:



and radicals with a reactive centre on an oxygen atom, of the type RO· and $RO_2^{\cdot}$. The experiments were generally carried out in solutions containing 3.5 wt. % of polyisobutylene in ethylbenzene, the quantities of initiators (sources of free radicals) being equivalent to 0.45 wt. % of benzoyl peroxide. The influence of oxygen was eliminated by preparing the solutions in an atmosphere of nitrogen in Shlenk vessels, from which the ampoule-viscometers were filled. The latter were then sealed and placed in a thermostat at 90°–130°, depending on the source of free radicals used. The molecular weights before and after degradation were determined by viscosimetry. Fig. 2 shows the course of the degradation with time for a number of free radical sources.

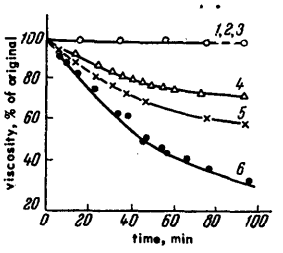


Fig. 1. Degradation of polyisobutylene in ethylbenzene solution in the presence of sources of alkyl free radicals at 110°:[16] 1) without triazene; 2) t-butylphenyltriazene; 3) azobisisobutyronitrile; 4) propylphenyltriazene; 5) ethylphenyltriazene; 6) methylphenyltriazene.

Study of the activity of different types of free radical showed that the most active in degradation are those of the type RO· and $RO_2^{\cdot}$, which are very active hydrogen-atom acceptors[19]. Radicals which are not active hydrogen-atom acceptors, such as $(CH_3)_2\dot{C}CN$, obtained by the thermal decomposition of azobisisobutyronitrile, and $(CH_3)_3\dot{C}$, obtained by the decomposition of t-butylphenyltriazene, do not cause degradation of polyisobutylene (see Fig. 1). Thus the

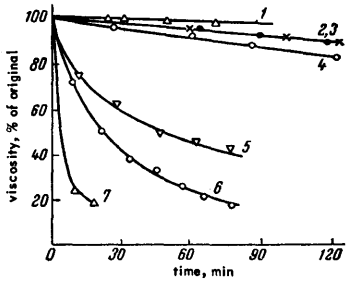
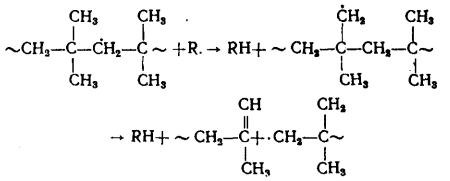


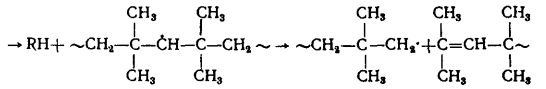
Fig. 2. Degradation of polyisobutylene in ethylbenzene solution in the presence of sources of free heteroradicals[18]: 1) without initiator, 130°; 2) mercaptobenzothiazole disulphide, 130°; 3) dimethyldiphenyltetrazene, 130°; 4) tetramethylthiuram disulphide, 130°; 5) phenylisopropyl hydroperoxide + Fe(III) naphthenate (10 mole % relative to the hydroperoxide), 110°; 6) benzoyl peroxide, 90°; 7) phenylisopropyl hydroperoxide + Co naphthenate (0.5 mole % relative to the hydroperoxide), 110°.

† These radicals were produced by the thermal decomposition of triazenes: $R{-}N{=}N{-}NHC_6H_5 \rightarrow R^{\cdot} + NHC_6H_5$, where R· is an aliphatic radical. The anilino-radical formed simultaneously is inactive.

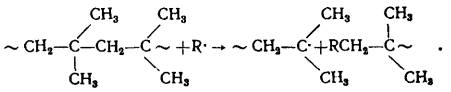
efficiency of a given radical in degradation is determined in all cases by its ability to abstract a hydrogen atom. From this it was concluded that the degradation of polyisobutylene involves the removal of an H atom from the macromolecule with the formation of a macroradical and subsequent stabilisation of the latter by degradation with the rupture of a C–C bond and the formation of a macroradical:



or



A less probable process, in the authors' opinion, is direct attack on the C–C bonds by free radicals:



These degradation steps are possible in principle, since they lead to the formation of more stable free radicals. This reaction mechanism, however, hinders the formation of the intermediate complex and increases considerably the activation energy of the process (Ref. 4, pp. 99–101). The destruction of polyisobutylene in the presence of benzoyl peroxide was also studied by Rado and Simunkova[20]. The experiments were carried out in the condensed phase at 65°–95°. It was established that the decomposition of benzoyl peroxide is a chain reaction with sensitised second-order decomposition, *i.e.* that the phenyl radicals formed by thermal decomposition of the peroxide on the one hand initiate further decomposition of the peroxide and on the other hand abstract H atoms to yield polymer radicals. It was shown that the transfer of the active centre to the polymer takes place by reaction with CH_2 groups and also with CH_3 groups, and that, since the polymer radicals of the type $\sim\dot{C}H_2$ have a high reactivity, they are stabilised by isomerisation before reaction with other radicals takes place. As a result, the reaction indicated above takes place with the formation of a new polymeric fragment radical, and the other fragment is stabilised by the formation of a double bond. It was also shown that stabilisation of the macroradicals takes place mainly by disproportionation, which is the chief means of double-bond formation in the degradation process. Recombination in the case of polyisobutylene macroradicals is complicated by steric hindrance. This mechanism for the degradation is also confirmed by experiments on the sheer degradation of polyisobutylene in the presence of I_2.[21]

It was also established that a direct relationship exists between H atom removal and C–C bond rupture[22,23], in particular in the degradation of polyisobutylene swollen in benzene in the presence of ferric naphthenate at about 100° (see Fig. 3). In this case dehydrogenation of the polymer $Fe^{3+} + RH \rightarrow Fe^{2+} + R^{\cdot} + H^+$ is the primary process, and the rupture of the C–C bond is apparently a secondary stage. The fact that polymer dehydrogenation of this type takes place was established for the case of the ferric naphthenate–isoprene system[23]. It was observed that at

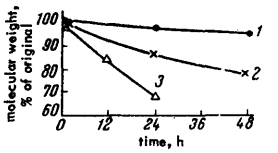


Fig. 3. Degradation of polyisobutylene in the presence of ferric naphthenate[18]: 1) in the absence of Fe(III) naphthenate; 2) 5 mole % of naphthenate relative to the polymer; 3) 20 mole %.

100° ferric naphthenate initiates the homogeneous polymerisation of isoprene. The polymerisation process was accompanied by conversion of ferric naphthenate to ferrous naphthenate. An analogous change accompanied the process of structure-formation in a 2% solution of polyisoprene in benzene at 150°. In spite of all that has been said, however, the degradation of polyisobutylene by free radicals as a result of direct attack on the main chain is also possible. Thus Thomas[24] recently showed experimentally that, in the degradation of polyisobutyelen in the condensed phase at 140° by small quantities (~1.5 wt. %) of dicumyl peroxide, 94% of the cumyloxy-radicals combined with polyisobutylene. For other rubbers under analogous conditions, deactivation of the cumyloxy-radicals takes place by removal of H atoms, and this is accompanied by structure formation. Thomas[24] and the authors[7] observed no significant depolymerisation of polyisobutylene the degradation process.

Bresler *et al.*[6] made a more detailed study of the degradation of polydienes by free radicals in solution over a wide concentration range in an atmosphere of nitrogen. The free radical sources were methylphenyltriazene, azobisisobutyronitrile, and sulphur monochloride S_2Cl_2, whose vulcanising action is apparently of the radical type[23]. The radicals used showed a wide range of activities for the removal of an H atom from organic compounds[16]. The materials studied were natural rubber containing links joined only in the 1,4-position, synthetic polyisoprene polymer containing up to 90% 1,4-links, and polydivinyl rubber containing up to 70% 1,2-links. The experiments were carried out with benzene solutions containing 0.3–10 wt. % of the polymers, the quantity of initiators (sources of free radicals) amounting to 5–50% of the weight of polymer in solution. It was established that in benzene, all the rubber specimens undergo degradation at low concentrations (0.3–1%) and gel formation at higher concentrations (3–10%). (It has recently been shown that a similar dependence on the concentration in solution is observed for the degradation and cross-linking of rubbers under the influence of the residues of complex organometallic catalysts.) The extent of the reactions in both cases, however, depends markedly on the polymer structure and the activity of the free radicals. Radicals of low activity, such as benzyl and allyl radicals, which are incapable of reacting with rupture of a C–H bond[17], were found to be ineffective in the degradation process. The most active radical (methyl) in the case of natural rubber or synthetic polyisoprene caused gel formation at concentrations of 2.7–3% and above, and degradation at lower concentrations. In the case of polybutadiene containing a large number of vinyl groups in the chain gel formation is observed at polymer concentrations of 1–3%. This agrees with the ease with

which lateral vinyl groups add on free radicals[25,26] (particularly compared with internal double bonds). The low tendency of polybutadiene to undergo degradation may be due to the fact that the polymer chain of this rubber contains a very few diallyl links with a weakened C–C bond. The comparatively inactive $(CH_3)_2\dot{C}(CN)$ radical does not cause gel formation in natural rubber and polyisoprene, even at very high concentrations of the polymer (up to 10%), but causes degradation in all cases. This agrees with the low tendency of the internal double bonds of the polymer chain to add on free radicals which are not sufficiently active. In the case of polybutadiene containing a large number of lateral vinyl groups, this radical causes gel formation at polymer concentrations above 3%. The high reactivity of the external double bonds (vinyl groups) towards $(CH_3)_2\dot{C}(CN)$ was established directly in a study of the products of the reaction of this radical with olefines[25,26]. The degradation of natural rubber and synthetic polyisoprene in the presence of $(CH_3)_2\dot{C}(CN)$ is apparently due to to the fact that the cross-linking reaction is bimolecular and requires a comparatively high concentration of polymeric radicals, which the comparatively inactive $(CH_3)_2\dot{C}(CN)$ cannot provide. On the other hand, the degradation reaction is unimolecular with respect to the macroradical concentration and can occur. The behaviour of sulphur monochloride is of particular interest. When solutions of S_2Cl_2 and natural or other rubbers (concentration 1%) are mixed, gel formation takes place in the solution. With subsequent heating, however, the gel disappears and the reduced viscosity of the solution decreases by a factor of 5–10, with a corresponding decrease in the molecular weight. The gel formed at the start of the experiment persists only in the case of comparatively concentrated solutions (2–4%) of synthetic polyisoprene and polybutadiene. Special experiments with rubber which had undergone degradation[6] showed that the relationship $\langle r^2\rangle^{1/2} = KM^a$, where $\langle r^2\rangle^{1/2}$ is the root mean square radius of the molecules, M the molecular weight, and K and a the characteristic parameters of the polymer-homologues in the given solvent, is the same for the degraded and original polymers, indicating that intramolecular cross-linking does not take place during degradation. The reaction of free radicals with polydienes can take place in two ways[27]: (a) by abstraction of a hydrogen atom with the formation of a macroradical and its subsequent decomposition:

$$\sim CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2\sim + R^{\cdot} \rightarrow RH +$$
$$+ \sim CH_2CH{=}C\dot{H}CH_2 \;\vdots\; CH_2CH{=}CH{-}\dot{C}H\sim \rightarrow$$
$$\rightarrow \sim CH_2CH{=}CHCH_2\cdot\cdot + CH_2{=}CH{-}CH{=}CH\sim;$$

(b) by addition to a double bond, which opens to form a macroradical, and subsequent degradation of the latter[24]:

$$\sim CH_2CH{=}CHCH_2{-}CH_2CH{=}CHCH_2\sim + R. \rightarrow$$
$$\rightarrow \sim CH_2CHRCHCH_2 \;\vdots\; CH_2CH{=}CHCH_2\sim \rightarrow$$
$$\sim CH_2CHRCH{=}CH_2 + \cdot CH_2CH{=}CHCH_2\sim.$$

When the concentration of polymer in the solution is sufficiently high, the recombination of macroradicals naturally leads to intermolecular cross-linking, *i.e.* to gel formation. At a sufficiently low concentration of macroradicals this recombination of intermediate activated links is hindered and the degradation process predominates.

Tasset and Smets[9] studied the degradation of poly(methyl methacrylate), polystyrene, poly(vinyl acetate), and poly-(chloroethyl acrylate) in dilute benzene solutions (1%) in the presence of similar quantities of benzoyl peroxide in the absence of oxygen at 65°–100°. The degradation was followed dynamically in sealed Mesrobian–Tobolsky viscometers and statically by determining the MWD before and after degradation, by fractionation and osmotic measurements. Special measurements were also made to determine the quantity of monomer in the product. It was shown that under these conditions, poly(α-chloroethyl acrylate), poly(methyl methacrylate), and polystyrene undergo degradation (at correspondingly decreasing velocities) whereas poly(vinyl chloride) and poly(vinyl acetate) are stable under these conditions. The influence of polymer concentration, degree of polymerisation, initiator concentration, temperature, and chemical structure on the rate of degradation were also studied. If it is assumed that the degradation of the polymer chain takes place randomly and that the number of chain ruptures is proportional to the number of links, *i.e.* to the polymer concentration, the rate of decrease in the number of bonds at time t will be

$$\frac{d(L)_t}{dt} = k_a(L)_t\,, \qquad (2)$$

where L_t is the number of bonds at time t. If we consider only degrees of degradation where $1/P_t \ll 1$, P_t being the degree of polymerisation at time t, we have[9]

$$\frac{1}{P_t} = \frac{1}{P_{t=0}} + k_a t \ddagger \qquad (3)$$

or

$$\frac{1}{M_t} = \frac{1}{M_0} + k_b t, \qquad (4)$$

where k_b, the rate constant for the degradation, is the number of moles of bond broken in 1 g of polymer in 1 min. This constant can thus be found for different polymers by measuring the molecular weights during degradation. The applicability of relationships of types (2) and (3) has been confirmed experimentally.

Fig. 4 shows the course of the degradation of poly(methyl methacrylate) fractions. Experiments at different polymer concentrations showed that the overall rate of degradation is proportional to the concentration, the value of the constant k_b remaining constant within the limits of experimental error. From Eqn. (2) it follows that $k_b = \Delta(1/M)/\Delta t$, *i.e.* after differentiation

$$\frac{dM}{dt} = k_b M^2. \qquad (5)$$

The values of k_b obtained by applying this relationship to the data given in Fig. 4 were also found to be constant within the limits of experimental error, confirming that the dependence of the degradation on molecular weight is in fact given by a relationship of type (5). Study of the dependence of the rate of degradation on the initiator concentration showed that

$$k_b = kC_{\text{init}}, \qquad (6)$$

where C_{init} is the initial concentration of added benzoyl peroxide and k a proportionality coefficient.

Fig. 5 gives the temperature dependence of the rate constants for the degradation of the three polymers studied in benzene solution at polymer concentrations of 0.8% and the

‡ In the general case, as shown by Simha[28],

$$\frac{P_t - 1}{P_t} = \frac{P_0 - 1}{P_0} e^{-k_a t},$$

from which, with the condition $1/P_t \ll 1$, we obtain Eqn. (3) as a first approximation by taking logarithms and expanding in powers of $1/P_t$.

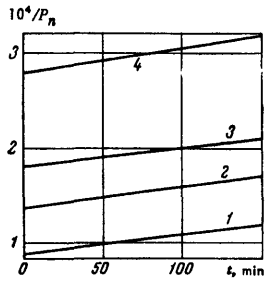


Fig. 4. Degradation of poly(methyl methacrylate) fractions of different degrees of polymerisation under the influence of benzoyl peroxide at 75°. Polymer concentration 5 wt.%, peroxide concentration 1 wt.%:[9] 1) P = 11460; 2) P = 7250; 3) P = 5500; 4) P = 3580.

same peroxide concentration. At 75° the values of k_b found under these conditions were (mole^{-1} sec^{-1}): $2.15 \times \times 10^9$, 1.04×10^9, and 25×10^9 for poly(methyl methacrylate), polystyrene, and poly(α-chloroethyl acrylate) respectively. From the data given in Fig. 5, using the Arrnhenius equation

$$k_b = Ae^{-\Delta U/RT}, \qquad (7)$$

it was found that the values of the activation energy for the degradation process were the same for all three polymers studied and amounted to 31–32 kcal, which corresponds approximately to the activation energy for the decomposition of benzoyl peroxide[29]. The difference in the absolute values of k_b for different polymers is due to differences in the chemical structure of the polymers and in the relative stability of the radicals produced during degradation.

It is suggested that degradation takes place according to the following scheme: (1) initiation of the primary radicals $(C_6H_5COO)_2 \xrightarrow{k_i} 2R^{\cdot}$; (2) transfer of an active centre to the polymer with the formation of a macroradical: $R^{\cdot}$ + + polymer $\xrightarrow{k_t} P_n^{\cdot}$; (3) rupture of a skeletal C–C bond: $P_0 \xrightarrow{k_d} P_x + P_y^{\cdot}$; (4) depolymerisation with subsequent stabilisation of the polymeric "fragment" $P_{y-1}^{\cdot}$ in different ways: $P_y^{\cdot} \underset{\sim}{\overset{k_p}{\rightarrow}} P_{y-1}^{\cdot}$. It is clear that, although the rate of degradation is determined by all the stages, the viscometric data reflect chiefly the third stage in the scheme, since it is this process that causes the sharp decrease in molecular weight. The effect of the chemical structure of the polymers is shown in (1) the different values of the energy of removal of an H atom from the polymer molecule at the second stage, and (2) the different stabilities of the $P_n^{\cdot}$ radical.

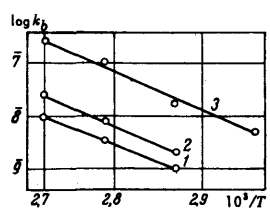
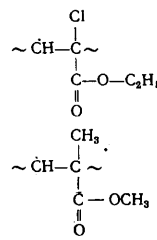


Fig. 5. Temperature dependence of the degradation rate constants[9]: 1) polystyrene; 2) poly(methyl methacrylate); 3) poly(α-chloroethyl acrylate).

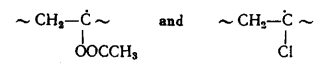
The high rate of degradation of poly(α-chloroethyl acrylate) and poly(methyl methacrylate) is due to the presence of tertiary carbon atoms in their chains, since this facilitates the degradation of the polymer chains by the radicals[21,30]



poly(α-chloroethyl acrylate) macroradical,

poly(methyl methacrylate) macroradical.

The degradation of polystyrene, on the other hand, is hindered by the high stability of the benzyl type radical $\sim CH_2-\dot{C}\sim$ (with C_6H_5), formed in the intermediate stage of the degradation. The absence of appreciable degradation in the case of poly(vinyl acetate) and poly(vinyl chloride) is due to the high activity of the radicals



since this hinders the primary stages of H atom removal. Special experiments showed that the degradation yields mainly large "fragments". As degradation proceeds there is a sharp decrease in the average molecular weight (by a factor of 4–5 after degradation for 12 h) without the presence of significant quantities of monomer in the product. (The average number of monomer molecules liberated by depolymerisation, for one chain rupture, to form a pair of "fragments" was about 30 units, when polymers with a degree of polymerisation of $5 \times 10^3 - 3 \times 10^4$ were used for the experiments.)§

The degradation of polymers under the influence of free radicals has been observed by other workers[31-36]. The displacement of the MWD towards low molecular weights as degradation proceeds, observed by Mesrobian *et al.*[31] in a study of the degradation of polystyrene in toluene under the influence of benzoyl peroxide, is shown in Fig. 6. In this work, as in earlier work by Tobolsky and Mesrobian[32,36] it was found that when the duration of the degradation process is sufficiently great and new quantities of initiator are added to the system at definite intervals to replace the initiator which has decomposed, there is a considerable decrease in the rate of degradation. By taking the monomer under analogous conditions and adding corresponding portions of initiator, however, it was possible to observe polymerisation with subsequent retardation in the same range of degrees of polymerisation as in the case of the

§ In pure depolymerisation (which is possible, for example, during degradation *in vacuo* at high temperatures) the average molecular weights and their ratios should not change at all.

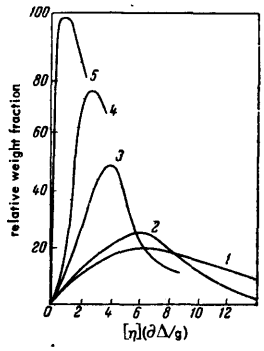


Fig. 6. Differential size distribution for polystyrene at different stages of degradation in toluene at 111°: [31] 1) initially; 2) 21 h; 3) 54 h; 4) 158 h; 5) 518 h.

polymer degradation (see Fig. 7). Analogous behaviour was observed in the case of illumination with ultraviolet light with $\lambda < 3000$ Å.

Mesrobian and Tobolsky suggested that in this case the rates of polymerisation and depolymerisation become equal and that in general thermodynamic equilibrium may be established between a polymer and its monomer. (Tobolsky and Eisenberg recently examined a general theory of equilibrium polymerisation [37].) The results obtained by Mesrobian and Tobolsky show only partial agreement with the results and conclusions of Montgomery and Winkler [33,34], who studied the same system, and with Thompson's data [35].

Mesrobian and Tobolsky obtained polymerisation and depolymerisation curves which approached a common limit. Montgomery and Winkler, and also Thompson, showed equally convincingly that this is only a special case. In general, the polymer undergoes continuous degradation, and in the case where the monomer is the starting material, the initial process is chiefly polymerisation, followed by degradation. In particular, it was shown that the molecular weight of the degradation product may be much lower than the "equilibrium" molecular weight found by Mesrobian and Tobolsky, and depends on the amount of catalyst or ultraviolet illumination. A clearer picture is obtained when we examine the distributions with respect to size of degradation product (see Fig. 6) and polymerisation product (see Fig. 8), observed at the times marked by vertical broken lines in Fig. 7, which presents Mesrobian and coworkers' data [31]. The shape of the curves in Fig. 6. indicates continuous intense breakdown of the polymer. When the monomer is the starting material (see Fig. 8), however, the polymer formed in the initial stage of the polymerisation has a comparatively high average molecular weight; subsequently, as a result of the decrease in the monomer concentration, the molecular weight of the resulting polymer decreases¶. Fig. 7 shows that, after the curves have merged, the viscosity of both solutions decreases slowly. By carrying out more prolonged experiments, Montgomery and Winkler obtained clearer proof of this decrease [33,34].

Mesrobian and coworkers do not attribute great significance to this decrease, but Montgomery and Winkler [33] and Thompson [35] consider it to be direct proof that equilibrium with respect to molecular weight is not established. They suggest that, irrespective of whether the polymer is present at the start of the reaction or appears in the system during polymerisation of the monomer, continuous degradation of the polymer takes place until radicals are formed in the system. They attribute the decrease in the rate of reduction of the viscosity for prolonged processes to the fact that in the case of the polymer with lower molecular weight, a given decrease in the viscosity requires the rupture of a higher number of bonds [34]. Montgomery and Winkler showed by special measurements that the osmotic pressure : viscosity ratio for polymers at different stages

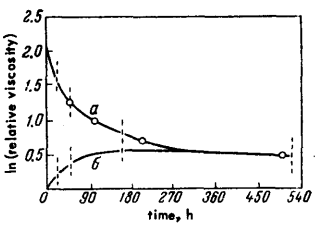


Fig. 7. Polymerisation–depolymerisation equilibrium for polystyrene–styrene in toluene at 111°: [10,31] *a*) concentration of polystyrene solution 16 g ml^{-1}, 0.5 g of benzoyl peroxide per 100 ml added every 8 h; *b*) concentration of styrene solution 16 g per 100 ml, 0.005 g benzoyl peroxide per 100 ml added every 8 h. The original polystyrene specimens consisted of the fractions with $M_n = 72 \times 10^3 - 3.6 \times 10^6$.

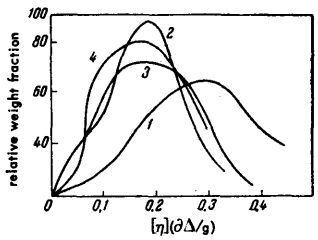


Fig. 8. Differential distribution according to the size of the macromolecules for the polymerisation of styrene in toluene at 111°: [31] 1) 21 h; 2) 54 h; 3) 158 h; 4) 518 h.

¶ In work on the high-temperature degradation of poly(methyl methacrylate) in the presence of monomer at 264° in a closed vessel [38], it was observed that at first almost complete polymerisation of the monomer took place, and this was only later followed by degradation of the newly-formed polymer and polymer added initially. Small [39] measured the equilibrium pressure of the monomer above poly(methyl methacrylate) in the presence of radicals and from the results he calculated the equilibrium concentration of monomer in the polymer, the values found being 0.3% at 100° and 2.87% at 160°.

of the degradation remains constant and that the polymer with low molecular weight (lower than the "equilibrium" molecular weight in Mesrobian and Tobolsky's terminology) cannot aggregate rapidly to polymers with higher molecular weight, although it does not follow from their data that, in the presence of agents causing degradation, its viscosity decreases with time. Grassie (Ref. 10, pp. 77–80) suggests that even in this case an increase in the molecular weight of the polymer is observed, but the increase is very slow, due to the simultaneous intense degradation. Experiment shows that in the equilibrium represented in Fig. 7, irrespective of the direction from which it is approached, approximately 80% of the polymer can be isolated from the solution. The composition of the product remaining in solution has not been established accurately (Ref. 10, pp. 77–80), but Tasset and Smets[9] showed that the quantity of monomer is small. Grassie suggests that the main fraction of the product not extractable by precipitation is a mixture of oligomers[10], and points out that the relatively rapid attainment of a state in which the system contains 80% of the polymer and the retention of this concentration during subsequent reaction indicate the existence of an equilibrium between the reactions of chain growth and of monomer removal from the chain. This equilibrium can be represented by the scheme

$$P_r + M \underset{k_d}{\overset{k_p}{\rightleftarrows}} P_{r+1}, \qquad (8)$$

where k_p and k_d are the rate constants for chain growth and rupture respectively. This also agrees with the data from the work cited above[38], since when at high temperature (264°) the depolymerisation of poly(methyl methacrylate) is accompanied by polymerisation at an appreciable velocity, *in a closed volume* quasiequilibrium should be observed, *i.e.* the attainment of a steady monomer concentration, at which the rate of polymerisation is equal to the rate of removal of monomer from the polymer. This quasiequilibrium in polymerisation–depolymerisation processes involves only the comparatively small "live" fraction of the polymer (the macroradicals or macromolecules with terminal double bonds capable of being activated at the temperature of the experiment). The thermodynamic relationships derived for true equilibria in which the system as a whole takes part cannot in principle be satisfied in the present case of high-temperature degradation and polymerisation in the poly(methyl methacrylate)–methyl methacrylate system[38]. Thus in systems in which polymerisation and degradation are taking place simultaneously, a true steady state with respect to molecular weight is in general not established. As far as Tobolsky and Mesrobian's systems are concerned, the increase in viscosity when the monomer is the starting material is due to polymerisation, but the limiting molecular weight depends on the rate of initiation and temperature. As the polymer accumulates, an ever-increasing part is played by the rupture of macromolecules, and this will not influence the above equilibrium [see Eqn. (8)]. If the pure polymer is the starting material, the removal of monomer from the chain (depolymerisation), combined with chain rupture (degradation) leads to a rapid decrease in the molecular weight of the polymer. When equilibrium of type (8) is established, however, the change in the molecular weight will be determined only by chain rupture. Thus the gradual decrease in the viscosity of a polymerised monomer or depolymerised polymer observed at the end of the reaction is due entirely to rupture (degradation) of the macromolecules, irrespective of the process described by Eqn. (8).

The merging of the polymerisation and degradation processes, observed by Mesrobian and Tobolsky (see Fig. 7) is apparently accidental (Ref. 10, Chapter IV). Mesrobian and Tobolsky's suggestion that an equilibrium molecular weight is shown by the polymer cannot be correct, particularly since the actual process which should lead to the attainment of this "equilibrium" molecular weight is not clear. The actual possibility of approaching the same molecular weight by polymerisation of the monomer or degradation of the polymer indicates merely the attainment of a certain quasisteady state (with respect to molecular weight), determined by the specific experimental conditions. This state was attained, in particular, by ultrasonic irradiation[40], and also in the work of Rossi and Bianchi[41], who irradiated solutions of styrene and polystyrene in chloroform with γ-rays from ^{60}Co. They established that there exists a quasisteady molecular weight, which can be attained either by the polymerisation of styrene in chloroform or by the degradation, also in chloroform, of polystyrene with a molecular weight higher than the quasisteady molecular weight. According to their data, $M_{\text{stationary}}$ amounts to 180×10^3 for an intensity of irradiation of 60 r min^{-1} or 300×10^3 for an intensity of 37 r min^{-1}. Rossi and Bianchi suggest that this quasisteady state of polymerisation and degradation results from an equilibrium between the energy which the macromolecule obtains from the γ-radiation and the energy which it can "remove" or, more accurately, scatter (by transfer of an exciton along the chain or by transfer to the surrounding medium) without chain rupture.

In the above discussion we have not dealt in detail with the problem of the oxidative degradation of polymers[10–12,27,42–47], since this lies outside the scope of the present article.

b. Inter-Chain Exchange

It must first of all be emphasised that inter-chain exchange cannot take place without preliminary degradation of previously formed polymer chains by free radicals, with activation of the end of one of the two resulting smaller chains. This takes place, for example, in degradation according to Tasset and Smets' scheme (see above). The resulting macroradical may begin growth again at the expense of monomer or recombine with another similar (or "normally" growing) macroradical. Thus irrespective of the specific character of the first stage (*i.e.* the reaction of the free radical with the polymer chain, leading to degradation), inter-chain exchange can take place in three ways: (1) macromolecular combination (*i.e.* recombination of the newly-formed radicals derived from different original polymer chains) with one another or with "normally" growing radicals; (2) exchange at the expense of monomer, *i.e.* repeated stages involving degradation and the new growth of activated fragments of the chain; and (3) inter-chain exchange proper, which is observed when degradation takes place as in inter-chain reactions during polycondensation[48,49]. (Such exchange may, for example, take place during the degradation of polyisobutylene by macroradicals with attack "from the side", *i.e.* directly, with rupture of C–C skeletal bonds. It has been reported[50] that in the radiolysis of a mixture of high-molecular-weight and ^{14}C-labelled low-molecular-weight polyisobutylenes, the activity appeared in the high-molecular-weight fraction, indicating inter-chain exchange.) All these three processes lead to rearrangement of the polymer segments

and this in turn, when the polymerisation process is prolonged, should lead to distributions in thermodynamic equilibrium with respect to molecular weight, of the type observed in polycondensation equilibria[48]. There is however a significant difference in the conditions of inter-chain exchange for polymerisation and polycondensation. In polycondensation, the system unavoidably contains some water, acid, amine, etc., *i.e.* materials capable of causing hydrolysis, acidolysis, aminolysis, etc.; moreover, the ends of *all* the chains are active. Thus at any moment in polycondensation, equilibrium between the process of condensation and degradation is ensured. In polymerisation there is usually a comparatively small number of agents causing degradation (free radicals), which are used up, moreover, with the passage of time. As a result, a state of thermodynamic equilibrium is never attained in polymerisation.

Finally, at different stages of the polymerisation, the probability of the above exchange reactions is not the same, and in some systems, individual reactions may not take place at all. For example, in polymerising systems where rupture of the kinetic chain takes place predominantly by disproportionation, macromolecular combination is suppressed to a considerable extent. During polymerisation, as the system becomes more viscous, the mobility of the macroradicals as a whole decreases much more rapidly than that of the microradicals†, so that in the later stages of the polymerisation, when the process becomes diffusion-controlled, exchange at the expense of the monomer becomes most probable. Since, however, the mobility of the individual active links in the macroradicals is much greater than their mobility as a whole, macromolecular recombination and inter-chain exchange proper (if the latter is possible for molecules of a given chemical structure) under these conditions cannot be completely excluded. The possibility of macromolecular recombination up to high degrees of conversion was established by a number of workers in a study of the mechanism of rupture of the kinetic chain for polystyrene and other polymers, by radioactive tracer methods. In general, however, at very high concentrations of polymer and free radicals (in particular, these may be radicals formed by decomposition of the initiator), deactivation of the latter by removal of an H atom from an intermediate link in an inactive molecule, with subsequent "cross-linking" by recombination of the macromolecules activated in this way becomes possible (this process is examined in detail below).

The process of inter-chain exchange has been studied, albeit implicitly, by a number of workers. Thus it has been established that recombination of the macroradicals of a number of polymers, in particular polystyrene, takes place during radical polymerisation[51,52]. Since polystyrene is capable of undergoing degradation by free radicals (this has been studied by Tobolsky, Mesrobian and coworkers, Tasset and Smets, Montgomery and Winkler, etc.[53]), it is clear that two aspects of the same process of inter-chain exchange were studied. It is true that Tobolsky, Mesrobian, and other authors of papers on the study of the simultaneous degradation and polymerisation of polystyrene deal only with exchange at the expense of monomer (using our terminology). These papers have been examined in detail above in the consideration of degradation. Degradation during the polymerisation of methyl methacrylate was noted by Kern *et al.*[54] It should, however, be added that there are certain indirect indications that, when the "steady state" has been established, we have to deal not only with inter-chain exchange at the expense of monomer, but also with exchange by macromolecular combination (it is possible, at least in the degradation of polystyrene, that exchange by macromolecular combination plays the chief part). Indirect proof of this, taken from papers on the study of the "steady state", is provided by the following considerations.

1. If the polystyrene + solvent + initiator systems studied by these workers showed only depolymerisation of the same type as that which takes place *in vacuo*, *i.e.* taking place, for a given macromolecule, entirely after its activation‡, appreciable quantities of monomer would be observed in these systems immediately after the start of degradation (since the viscosity decreases sharply in the first moments!), and the molecular weight would not change with time. In actual fact neither of these results is observed. Even at high degrees of degradation, the quantity of monomer remains negligible and the molecular weight decreases considerably, the MWD being displaced towards low molecular weights (see Fig. 8).

These facts indicate that depolymerisation (at any rate up to considerable degrees of degradation of polystyrene) plays almost no part, the only processes being the individual ruptures of skeletal bonds in the macromolecules with the formation of active and inactive fragments. The active fragments (macroradicals) of polystyrene are extremely stable and may recombine with one another, normally growing radicals, initiator radicals, etc.

2. Montgomery and Winkler[34] studied the efficiency of benzoyl peroxide (the number of ruptures of the polymer chain per molecule of added peroxide) in the degradation of polystyrene in different solvents by means of this radical source. The values found were 0.003, 0.001, 0.03, and 0.45 for methyl ethyl ketone, toluene, ethyl acetate, and carbon tetrachloride respectively. Carbon tetrachloride is an extremely efficient kinetic-chain carrier (one of the Cl atoms is readily given up to the macroradicals). In this solvent, therefore, the recombination of macroradicals has a much higher probability, and this is apparently revealed by the increase in the efficiency of the peroxide by a factor of 450, compared with its efficiency in toluene, which is extremely stable towards active-centre transfer.

Finally, Bresler *et al.*[7] made a special study to obtain direct proof that inter-chain reactions take place in radical polymerisation and degradation. Experiments were carried out to study the time dependence of the degradation of polystyrene under the influence of initiators (sources of primary free radicals) in solution at moderate temperatures (~100°). Since reactions of the macromolecular recombination type may be suppressed to a considerable extent at high initiator concentrations, the experiments

† At first sight it appears that the reactions between macroradicals in the presence of microradicals (formed, for example, by decomposition of the initiator) have an extremely low probability, due to the low mobility of the macroradicals. Allowance must be made, however, for the fact that (as noted in the examination of inter-chain exchange in polycondensation) individual links of the macromolecules, in particular active links (terminal groups or links with unpaired electrons), have a mobility close to that of monomer molecules.

‡ The removal of monomer from the polymer radical has an activation energy of 18–25 kcal mole^{-1}, *i.e.* this reaction may take place at a fairly high velocity even at 100°. In actual fact, thermal depolymerisation requires a temperature of ~200°, due to the high activation energy of the initiation stage.

were carried out in moderately concentrated solutions (2–4 wt. %) of polystyrene at initiator concentrations of ≤ 1% of the weight of polymer in the solution. This corresponded to a ratio of 1 molecule of initiator to 1 molecule of polymer. The experiments were carried out under strictly oxygen-free conditions§ in inert solvents (benzene and toluene). The course of the degradation was followed viscometrically. Fig. 9 shows the time dependence of the degradation of polystyrene in the presence of methylphenyltriazene. The first stage is evidently rapid decomposition of the initiator with the formation of free radicals:

$$CH_3—NH—N=NC_6H_5 \rightarrow CH_3\cdot + \cdot NHC_6H_5 + N_2.$$

Fig. 9 shows that the sharp initial decrease in viscosity mirrors the decomposition of the initiator. After about 1 h, the greater part of the initiator has decomposed and the degradation of the chains stops, after which the viscosity actually increases, apparently due to the recombination of macroradicals. It is of course possible that some part in this change in viscosity with time is played by a depolymerisation process. Control experiments show, however, that the concentration of polymer in solution before and after degradation does not change, within the limits of error (this agrees with the data of Tasset and Smets[9] and Thompson[35]). Study of the MWD of polystyrene specimens before and after degradation shows that in both cases the MWD is of the recombination type, and calculation of the number of recombinations from the values of the number-average molecular weights before and after degradation shows that ~50% of the macromolecules which have undergone degradation recombine. This provides further proof that macromolecular recombination takes place. Experiments were also carried out in the absence of oxygen and with mixed solutions of polystyrene and polyisobutylene and of polystyrene and poly(methyl methacrylate) in toluene and benzene, in which thermal decomposition of the initiators took place. The initiators used were benzoyl peroxide and methyl- and ethyl-phenyltriazene, at concentrations of 2–10% of the weight of the polymer in the solution. These systems showed the formation of

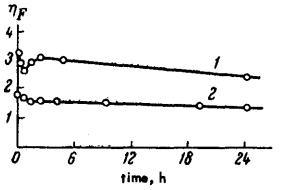


Fig. 9. Degradation of polystyrene under the influence of $CH_3^{\cdot}$ radicals[7]. Concentration of solution during degradation: 1) 4 g per 100 ml, 140°; 2) 2 g per 100 ml, 120°.

"hybrid" (*i.e.* of the block or graft type) polymers, which are evidently formed by macromolecular recombination of different macroradical fragments.

c. Kinetic-Chain Transfer to the Polymer with Subsequent Growth of a Side Chain

In bulk polymerisation, and also in solvents at high monomer concentrations, an increase in the rate of the process at high degrees of conversion is observed. An increase in the molecular weight of the product also occurs.

These phenomena are due to the increase in the viscosity of the medium, leading to a decrease in the rate constant of the rupture reaction due to recombination and disproportionation, since this depends on the rate of diffusion of the polymeric radicals to one another. Miyama[55] showed that the life-time of the polymer radicals increases in the same sense (see Fig. 10). Bresler *et al.*[56] showed by electron paramagnetic resonance in the photopolymerisation of vinyl acetate and methyl acrylate for degrees of conversion above 50–60%, that the concentration of macroradicals increases rapidly and at the end of the polymerisation process reaches 2×10^{-3} M for vinyl acetate and 0.5×10^{-3} M for methyl acrylate.

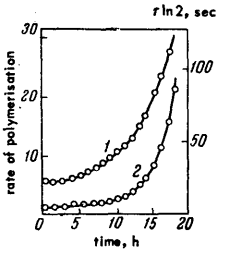


Fig. 10. Dependence of the rate of polymerisation (1) and the life-time of the polymer radicals (2) on the duration (extent) of polymerisation[55].

§ The part played by oxygen in degradation reactions depends to a considerable extent on its ability to form hydroperoxides at vulnerable points on the polymer molecule, *i.e.* tertiary carbon atoms in vinyl polymers and α-methylene groups in polydienes. Grassie considers that the hydroperoxides decompose with the formation of initiating radicals according to one of the following schemes:

$$\sim CH_2—CHX—CH_2—CHX \sim + O_2 \sim \rightarrow \sim CH_2—\underset{\displaystyle OOH}{\overset{|}{C}}X—CH_2—CHX \sim \rightarrow$$
$$\rightarrow \sim CH_2—\dot{C}X—CH_2—CHX \sim + \cdot OOH$$

or

$$\sim CH_2—\underset{\displaystyle O\cdot}{\overset{/}{C}}X—CH_2—CHX + \cdot OH.$$

Oxygen may also affect the course of a reaction by its ability to react with radicals:

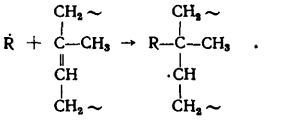
$$\sim CH_2—CX—CH_2—CHX \sim + O_2 \rightarrow$$
$$\rightarrow \sim CH_2—\underset{\displaystyle O—O\cdot}{\overset{|}{C}}X—CH_2—CHX \sim$$

These oxygen-containing radicals have a much greater tendency to decompose than the radicals from which they were formed. An example is provided by the reactions in rubber initiated by light: in the absence of oxygen these lead to the formation of cross-linkages and in the presence of oxygen to degradation. The part played by oxygen has been discussed in detail by Grassie (Ref. 10, Chapter IV).

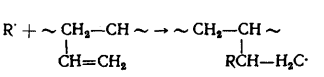
As free radicals accumulate in the polymerisation system and the concentration of the polymer increases at high degrees of polymerisation, the process of active-centre transfer to the polymer molecules with the subsequent growth of a side-chain plays an ever-increasing part. This reaction, which was described by Flory as early as 1937, is now widely used for the preparation of graft polymers. Two forms of cross-linkage formation are possible: (1) in vinyl polymerisation this reaction passes through a stage involving the abstraction of a hydrogen or halogen atom by free radicals:

$$R^{\cdot} + \sim CH_2{-}CHX \sim \rightarrow RH + \sim \dot{C}H{-}CHX \sim ,$$

where R· is a micro- or macro-radical; (2) in the case of the polymerisation of dienes, the reaction involves the abstraction of a hydrogen atom¶ or the addition of radicals to double bonds:



Kinetic-chain transfer to the polymer takes place particularly readily in the case of polymers of the 1,2-polybutadiene type with "outer" double bonds:



There are, however, data which indicate that the first type of chain transfer to the polymer also takes place for polydienes. The removal of an H atom is most probable for 1,4-polydienes. In all these cases, molecules with anomalously high molecular weights are formed.

If it is assumed that in a real polymerisation system the free radicals formed by decomposition of the initiator do not take a direct part in the reaction of active-centre transfer to the polymer, the rate of transfer to the polymer molecules $r_{tr,p}$, which is equal to the rate of formation of the side-chains in the polymeric molecules, is determined by Eqn. (1) (see above).

The experimental constant $k_{tr,p}$ is not always the constant for a definite reaction, since the polymer molecule may contain groups with different structures, reacting with the polymer radicals at different velocities. The constant is an "effective" constant. In general the primary radicals of the initiator do not act merely as initiators of the polymer chains. Their part in chain transfer to the polymer is shown by work on graft polymerisation (see below).

The absolute values of the constants for chain transfer *via* groups in the polymer molecules are usually much lower than those for transfer *via* the corresponding low-molecular-weight compounds. This is due to the fact that the inactive molecule → radical changes are associated with a change in the configuration (for example CH_4 is a tetrahedron and $CH_3^{\cdot}$ has a planar structure) and in the case of polymers this causes displacement of sections of the macromolecules. This also apparently explains the reduced reactivity of the inner double bonds of polydienes compared with that of the outer double bonds. This does not mean, however, that the transfer reaction to the polymer has a very low probability.

¶ Particularly that in the α-position with respect to a double bond.

Schulz and coworkers[57-59], in a study of the polymerisation of methyl methacrylate in the presence of low-molecular-weight poly(methyl methacrylate) prepared by a radical mechanism, found that the value of $k_{tr,p}$ decreases with increase in the molecular weight of the polymer added to the system. The authors attributed this to a difference in the rate of reaction of radicals with terminal groups (containing double bonds as a result of disproportionation) and with intermediate groups in the chain. The data obtained were used to calculate the constants for chain transfer *via* the terminal groups:

$$\left(\frac{k_{tr,p}}{k_p}\right)_{\text{terminal}} = 0.10 ,$$

where k_p is the rate constant for chain growth, and for chain transfer *via* the inner groups:

$$\left(\frac{k_{tr,p}}{k_p}\right)_{\text{inner}} = 2.2 \times 10^{-3}.$$

The fact that the terminal groups taking part in chain transfer are groups containing double bonds is confirmed by the marked decrease in the value of the ratio $k_{tr;p}/k_p$ for polymers obtained in the presence of chain carriers (butyl thioglycollate), *i.e.* containing no terminal groups with double bonds, and also by the fact that this ratio is independent of the nature of the initiator. If the added polymer contains no terminal double bond (for example, one obtained by polymerisation on metallic sodium or potassium), the value of $k_{tr,p}/k_p$ is independent of the molecular weight of the added polymer and has the value 2.2×10^{-5}. Recently, Henrici-Olive and Olive[60] used azobisisobutyronitrile labelled with ^{14}C for the polymerisation of styrene and determined the degree of conversion of the monomer and the average number of terminal groups (from the radioactivity of the polymer); they found that the resulting polystyrene is branched. They determined the ratio of the rate constants for the transfer reactions $R^{\cdot} + P \xrightarrow{k_{tr,p}} RH + P^{\cdot}$ and for initiation $R^{\cdot} + M \xrightarrow{k_{st}} RM^{\cdot}$, *i.e.* $K = k_{tr,p}/k_{st}$. For 50°, $K = 0.3 \pm 0.1$, which is fairly high. The authors derived an equation relating the constant K to the experimental values of Z (the number of terminal groups) and ψ (the percentage conversion). In the absence of the "gel effect", the equation has the form

$$\frac{1}{K-1}\ln(1+K\psi-\psi) = -\frac{Z\ln(1-\psi)}{2Z-2} , \qquad (9)$$

from which it follows that K can be determined (1) by preparing a polymer with labelled initiator, and (2) measuring ψ and Z.

The average degree of grafting (ADG), *i.e.* the number of grafts per polymer molecule, is found from the equation

$$ADG = Z-2 = \frac{-\frac{2}{K-1}\ln(1+K\psi-\psi)-2\ln(1-\psi)}{\frac{2}{K-1}\ln(1+K\psi-\psi)+\ln(1-\psi)} , \qquad (10)$$

which follows from the previous equation.

The fact that the reaction of active-centre transfer to the polymer has a high probability is also indicated by its successful application for the preparation of graft polymers.

Smets[61,62] gives the following complete scheme for the reactions accompanying the ordinary mechanism of grafting.

On the one hand, normal polymerisation takes place:

$$\text{initiator} \xrightarrow{k_d} 2R^{\cdot}, \qquad \text{(I)}$$

$$R^{\cdot} + CH_2{=}CHB \xrightarrow{k_a} R{-}CH_2{-}\dot{C}HB, \qquad \text{(II)}$$

$$R{-}CH_2{-}\dot{C}HB + n\,CH_2{=}CHB \xrightarrow{k_p} R{-}(CH_2{-}CHB)_n{-}CH_2{-}\dot{C}HB. \qquad \text{(III)}$$

These processes are accompanied by active-centre transfer to the polymer dissolved in the monomer:

$$\left.\begin{aligned} \dot{R} + {\sim}\,CH_2{-}CHA{-}CH_2{-}CHA{\sim} &\rightarrow \\ RH + {\sim}\,CH_2{-}\dot{C}A{-}CH_2{-}CHA{\sim} &\rightarrow \end{aligned}\right\}, \qquad \text{(IVa)}$$

$$\left.\begin{aligned} &R{-}(CH_2{-}CHB)_n{-}CH_2{-}\dot{C}HB + {\sim}\,CH_2{-}CHA{\sim} \rightarrow \\ &R{-}(CH_2{-}CHB)_n{-}CH_2{-}CH_2B + {\sim}\,CH_2{-}\dot{C}A{\sim} \rightarrow \end{aligned}\right., \qquad \text{(IVb)}$$

and the formation of side-chains on the molecules both as a result of "growth";

$$\left.\begin{aligned} &{\sim}\,CH_2{-}CHA{-}CH_2{-}\dot{C}A{-}CH_2{-}CHA{\sim} + n\,CH_2{-}CHB \rightarrow \\ &\rightarrow {\sim}\,CH_2{-}\underset{\displaystyle A}{\overset{\displaystyle CH_2{-}CHB{-}CH_2{-}CHB{\sim}}{\overset{|}{C}}}\!\!<_{\displaystyle CH_2{-}CHA{-}CH_2{-}CHA{\sim}} \end{aligned}\right\}, \qquad \text{(Va)}$$

and as a result of recombination with normally growing radicals:

$$\left\{\begin{aligned} &{\sim}CH_2{-}\dot{C}A{-}CH_2{-}CHA{\sim} + \dot{C}HB{-}CH_2{-}(CHB{-}CH_2)_n{\sim} \rightarrow \\ &\rightarrow {\sim}\,CH_2{-}\underset{\displaystyle A}{\overset{\displaystyle CHB{-}CH_2{-}(CHB{-}CH_2)_n{\sim}}{\overset{|}{C}}}\!\!<_{\displaystyle CH_2{-}CHA{-}CH_2{-}CHA{\sim}}. \end{aligned}\right. \qquad \text{(VIa)}$$

If active-centre transfer takes place at the terminal group of the dissolved polymer, block-copolymers are formed according to the two analogous schemes

$$\left.\begin{aligned} &{\sim}\,CH_2{-}CHA{-}CH_2{-}\dot{C}HA + n\,CH_2{=}CHB \rightarrow \\ &\rightarrow {\sim}\,CH_2{-}CHA{-}CH_2{-}CHA{-}CH_2{-}CHB{\sim} \end{aligned}\right\}, \qquad \text{(Vb)}$$

$$\left.\begin{aligned} &{\sim}\,CH_2{-}CHA{-}CH_2{-}\dot{C}HA + \dot{C}HB{-}CH_2{\sim} \rightarrow \\ &\rightarrow {\sim}\,CH_2{-}CHA{-}CH_2{-}CHA{-}CHB{-}CH_2{-}CHB{-}CH_2{\sim} \end{aligned}\right\}. \qquad \text{(VIb)}$$

As Smets points out, it was previously assumed that only reaction (IVb) can lead to the formation of macroradicals, since primary radicals should react more readily with vinyl monomers than with the polymer molecule (IVa). This hypothesis was confirmed by the higher value of the activation energy for the chain transfer reaction, compared with the reaction of attachment to the monomer. It has now been proved, however, that reaction (IVa) takes place. In analogous fashion, Allen *et al.*[63] arrived, after detailed study, at an extremely complex reaction scheme for grafting (on rubber). Smets established that, in the polymerisation of methyl methacrylate in the presence of polystyrene, a large quantity of graft polymer is formed if the initiation is brought about by benzoyl peroxide (BP) and that, on the other hand, almost no graft polymer is formed if azobisisobutyronitrile (AIN) or t-butyl peroxide are used as initiator. An analogous result was observed by a number of workers for grafting, where in the presence of benzoyl peroxide the number of graft branches was about 100 times greater than that predicted by the theory of chain transfer to the polymer, but when AIN was used as initiator, no grafting was observed.

Thus the process of chain transfer to the polymer is usually accompanied by a whole series of secondary reactions, including the direct action of initiator radicals on the macromolecules. [It is for this reason that we consider (see the Introduction) that it is inappropriate to include the chain transfer reaction to the polymer among secondary reactions without describing its consequences more precisely.] An alternative suggestion is that the activity of the macroradicals formed from the same monomer may differ considerably, depending on the initiator radical, but this is unlikely. In particular, Allen *et al.*[63] have shown that in the preparation of graft polymers by this method, the initiator used in the polymerisation has a significant influence on the side-chains.

Finally, it should be noted that intramolecular active-centre transfer is possible when a terminal radical attacks a methylene group in the same molecule:

$$\begin{array}{l} {\sim}\,CH_2{-}CH_2{-}CH_2 \\ \qquad\quad \searrow \\ \qquad\quad CH_2{-}CH_2 \end{array} \rightarrow \begin{array}{l} {\sim}\,\dot{C}H{-}CH_2{-}CH_2 \\ \qquad\quad\ \ | \\ \qquad\quad CH_2{-}CH_2 \end{array}.$$

This process leads to the appearance of a large number of short side-chains in the case of high-pressure polyethylene.

d. Cross-Linking of Macromolecules in Linear Polymerisation

In polymerisation with "insufficient" monomer (high degrees of conversion) or with a relatively large quantity of macroradicals (in diene polymerisation), where a further source of the latter is provided by the "opening" of double bonds under the influence of temperature and initiators, and also in the ω-polymerisation considered below, etc., the macroradicals active "in the centre" will recombine in two ways (see Fig. 11), *i.e.* the appearance of ordinary branched molecules will be accompanied by "cross-linking" of the molecules by means of intermediate links. This type of reaction has been examined theoretically by Flory[64], Taylor and Tobolsky[65], Case[66], and others. Cross-linking of linear polymers has been observed experimentally by a number of workers. Thus Bardwell and Winkler[67] observed cross-linking of molecules of the butadiene–styrene copolymer latex when potassium persulphate was added; the rate of cross-linking was proportional to the persulphate concentration. Baker[68] cross-linked pure polyundecanoates, containing no unsaturated bonds, and monomers with more than two functional groups, containing methylene hydrogen atoms labile towards removal by radicals; these hydrogen atoms can be removed fairly readily. Bryant *et al.*[69] showed that commercial polyethylene prepared by free-radical polymerisation often contains a small quantity (~1.5 vol.%) of microgel particles with an effective molecular weight of 10^{14}, and also a considerable quantity of highly branched macromolecules. Moore and Peck[70] made an electron microscope study of high-pressure polyethylene and observed a considerable number of molecules with $M \sim 40 \times 10^6$, which had a marked influence on the MWD. Flory[71] and Fox and Gratch[72] showed that these particles can be formed only by the recombination or cross-linking of macromolecules but not as a result of ordinary chain branching. The formation of microgel particles with a diameter of ~0.1 μ was also established by Baker. Some polymers, for example, poly(vinyl acetate), form only highly branched molecules

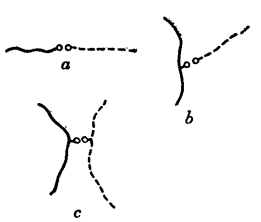


Fig. 11. The three types of macroradical recombination.

in radical polymerisation at 100°. In radical polymerisation of dienes, cross-linking of macromolecules is often observed at room temperature and above. A reaction of the type involving cross-linking of "formed" macromolecules, apparently accompanied by inter-chain exchange, was also studied by Bresler *et al.*[7] Mixed solutions of the polymers (polystyrene and polyisobutylene) with concentrations of 1–2% were kept in the presence of initiators at 80°–100°, depending on the initiator. The action of the free radicals of the initiator (methylphenyltriazene, benzoyl peroxide, etc.) led to the formation of macroradicals, which reacted partially with one another. The reaction of macroradicals of different chemical character gave "hybrid" polymers (*i.e.* of the block and graft type), which were then detected by specific sensitive methods (u.v. absorption spectra, etc.). It was found that the formation of "hybrid" polymers did in fact take place, although their yield did not exceed several per cent of the total quantity of macromolecules in the solution. It was possible to estimate the intensity of reactions of types (V) and (VI) (see above) in systems where styrene was polymerised in the presence of polyisobutylene. In these systems also, however, the yield of "hybrid" polymer for the polyisobutylene–polystyrene pair did not exceed 5%, indicating that these reactions are not rapid, apparently due to steric hindrance in the reactions between the macroradicals of polyisobutylene and polystyrene on the one hand, and the low activity of the polyisobutylene macroradicals in styrene polymerisation on the other†.

The polymerisation of styrene was also carried out in the presence of polybutadiene (5%) with ~ 20% of 1,2-linkages. The polymerisation was carried out under the influence of azobisisobutyronitrile (0.1 g per 100 ml), which has a low activity in the removal of an H atom but reacts readily with "outer" double bonds. It was established that as a result of inter-chain reaction, ~ 25% of the rubber dissolved in the monomer reacted with polystyrene at 80° and ~ 50% reacted at 120°. In both cases more than half of the resulting hybrid polymer had a gel structure, indicating high intensity of cross-linking at the double bonds of the 1,2-linked groups. The grafting of styrene on polybutadiene by secondary reactions was also carried out by Uemura *et al.*[73] with azobisisobutyronitrile and benzoyl peroxide. In the presence of the former, the styrene polymerised more rapidly but the efficiency of grafting was lower.

Recently, Miller[74] made a kinetic analysis of the cross-linking of saturated polymers by a radical mechanism in the condensed phase and verified the resulting relationships experimentally. Miller suggests that the following reactions take place:

(I) $I \xrightarrow{k_1} R^{\cdot}+R^{\cdot}$ — decomposition of initiator,

(II) $R^{\cdot}+PH \xrightarrow{k_2} RH+P^{\cdot}$ — formation of polymer radicals by H atom abstraction by the initiator radical,

(III) $R^{\cdot}+P^{\cdot} \xrightarrow{k_3} RP$

(IV) $R^{\cdot}+R^{\cdot} \xrightarrow{k_4} RR$

(V) $P^{\cdot}+P^{\cdot} \xrightarrow{k_5} PP$

— recombination of radicals of different type with one another.

Assuming further that the polymer radicals are not removed by disproportionation and do not undergo degradation, that $k_3 = \sqrt{k_4 k_5}$, and that the whole system of reactions reaches a steady state, Miller obtained the following expression for the cross-linking coefficient C (the number of cross-linkages per molecule of initiator decomposed):

$$C = \{(k_4 k_1 [I])^{1/2}/k_2[PH] + 1\}^{-2}. \quad (11)$$

At constant temperature and [PH] = const, this equation reduces to the simpler form

$$C = (K[I]^{1/2}+1)^{-2}, \text{ where } K = \{(k_4 k_1)/k_2[PH]\} = \text{const}$$

for a given polymer–initiator system. Obviously, $C \to C_{max}$ as $K[I]^{1/2} \to 0$. This is attained (a) at low values of k_1, (b) at low values of (I), and (c) at high values of k_2. (For polyethylene, for example, $C \sim 1$, due to the high value of k_2.)

The concentration of cross-linkages for any degree of decomposition of the initiator is found by integrating (11). These kinetic expressions were verified by Miller by experiments on the cross-linking of polydimethylsiloxane with benzoyl peroxide at 125° and with dicumyl peroxide at 170°.

On the basis of his experimental and theoretical studies, Miller established that ionising irradiation is much more effective in cross-linking [since of reactions (III), (IV), and (V) above, only (V) leads to cross-linking; (III) and (IV) only decrease the number of free radicals formed].

The formation of cross-linkages in polyethylene by the action of peroxides and irradiation was studied by Rado and Lazar[75–77], who calculated the number of cross-linkages from the change in the solubility of the polyethylene in boiling CCl_4, using the relationships between solubility and degree of cross-linking for polyethylene[78]. The experiments were carried out in the range 70°–90°, the quantity of peroxide added to the polymer being 0.01–0.5 mole kg^{-1}. The specimens were heated for 10^4–10^5 sec. A kinetic scheme of radical reactions was established, and, in particular, it was shown that the decomposition of the peroxide in polyethylene is a chain process, initiated by benzoate radicals produced by thermal decomposition of the peroxide. The kinetic scheme proposed by the authors for the formation of cross-linkages is identical with that given above. Increase in temperature decreased the yield of cross-linkages, since the considerable difference in the energies of activation, initiation, and transfer at higher temperatures causes the reaction of polymer radicals with primary radicals to predominate. Despite the fact that the peroxide decomposes by a chain mechanism, Rado and Lazar's experimental data correspond fairly accurately with the kinetic equation derived by Miller for the dependence of the number of cross-linkages on the peroxide concentration, if it is assumed that monomolecular decomposition of the peroxide takes place:

$$\left(\frac{[BP]}{[P-P]}\right)^{0.5} = K[BP]^{0.5}+1,$$

where [BP] and [P–P] are the concentrations of benzoyl peroxide and cross-linkages respectively, and K is a constant (at T = const).

Finally, the so-called ω-polymerisation in fact results from an intense structure-formation process which is preceded and accompanied by processes of chain transfer to the polymer and chain rupture at points corresponding to fluctuations in the concentration of polymer molecules and free radicals[79–83]. Thus Pravednikov and Medvedev[80,81] showed by labelling the "nucleus" with a radioactive tracer that, for example, the ω-polymerisation of chloroprene is accompanied by continuous rupture of the macromolecules

† The styrene was polymerised in the presence of methylphenyltriazene and benzoyl peroxide, which cause intense degradation of polyisobutylene.

of the network (due to osmotic overstrain at points of high polymer concentration) and their cross-linking by a radical mechanism, *i.e.* in our terminology, intense inter-chain exchange takes place in ω-polymerisation.

III. METHODS OF RECORDING AND STUDYING SECONDARY REACTIONS

a. Influence of Secondary Reactions on Molecular Weight Distributions

Let us examine the influence of each of the above secondary reactions on the molecular weight distributions.

Degradation. By definition, this reaction involves the rupture of single skeletal bonds of the macromolecules and obviously leads to a decrease in molecular weight. Montroll[84] and Tuckett[85] showed that with highly disordered chain rupture, irrespective of the original distribution, an equilibrium length distribution of the Kuhn–Schulz–Flory type,

$$W_x = xP^{x-1}(1-P)^2, \qquad (12)$$

is established after some time. This expression reduces to the form

$$W_x = \beta^2 x e^{-\beta x}; \qquad (13)$$

where W_x is the weight fraction of chains consisting of x links, P the probability that a given bond between two structural units remains unaffected, and $\beta = 1/\sqrt{x_n}$. Expression (12) is illustrated by Fig. 12. Thus if the initial average molecular weights and MWD are known and if the latter differed from an MWD of type (12), the decrease in average molecular weight with time and the attainment of an MWD of the Kuhn–Schulz–Flory type are a direct consequence of the disordered degradation.

Inter-chain exchange. Inter-chain exchange in radical systems, *i.e.* the recombination of macroradical "fragments", their "growth" at the expense of monomer, etc. in addition to chain degradation under the influence of radicals leads to a reduction in the rate at which the average molecular weights decrease with time, compared with that for "pure" degradation. Moreover, a quasi-steady state may be established, as has been observed by Mesrobian and Tobolsky, Rossi, and others. The influence of inter-chain exchange on the molecular weight of the polymer can be illustrated by the following example. In one of our experiments on the degradation of polystyrene in benzene solutions in the presence of methylphenyltriazene, we found the MWD of the specimen before and after degradation (both were of the recombination type[1]) and from the MWD we calculated the average molecular weights, the values being 5.06×10^5 and 3.6×10^5 respectively. Let us assume that originally there were N macromolecules with a number-average molecular weight M. Of these, n molecules underwent degradation, with the production of $2n$ chains (of which n were active) with an average molecular weight of $M/2$. If all n active chains recombine with one another, the average molecular weight after degradation $\overline{M}'_n$ will be given by

$$\overline{M}'_n = \frac{(N-n)M + nM/2 + n/2\,M}{(N-n) + n + n/2} = \frac{NM}{N + n/2}. \qquad (14)$$

If, however, all the macroradical fragments disproportionate, combine with initiator radicals, etc., *i.e.* if they are deactivated in any way other than by recombination with one another, we have

$$\overline{M}''_n = \frac{(N-n)M + 2n \times M/2}{(N-n) + 2n} = \frac{NM}{N+n}. \qquad (15)$$

The original number-average molecular weight of polystyrene in this experiment was $M_n = M = 5.06 \times 10^5$ and that after degradation was $\overline{M}_n = 3.6 \times 10^5$, *i.e.* $M_{n\,\text{init}}/\overline{M}_n = 1.4$. In case (1), $M_{\text{init}}/M' = 1 + n/2N$ and in case (2), $M_{\text{init}}/M'' = 1 + n/N$. The phenomenon is thus intermediate between cases (1) and (2), *i.e.* $1 + n/2N < 1.4 < 1 + n/N$, from which $0.8\,N > n > 0.4\,N$, *i.e.* n was about $0.6\,N$.

Assuming that $n = 0.6\,N$, it is possible to estimate the number of macroradical "fragment" recombinations which have taken place. If no recombination of radicals with one another took place, we should have, in accordance with (15),

$$\overline{M}'_{nd} = \frac{NM_{\text{init}}}{N + 0.6N} = \frac{5.06 \times 10^5}{1.6N} = 3.13 \times 10^5.$$

Experimentally, however, $\overline{M}_{nd} = 3.6 \times 10^5 > M'_{nd}$, *i.e.* recombination has taken place. Assuming that the number of recombinations was xN, we can write

$$\frac{0.4NM + 0.6N \times M/2 + (0.6-x)NM/2 + xNM}{0.4N + 0.6N + (0.6-x)N + xN} = 3.6 \times 10^5.$$

Cancelling N and substituting $M = M_{n\,\text{init}} = 5.06 \times 10^5$, we have

$$\frac{1 + 0.5\,x}{1.6} = \frac{3.6 \times 10^5}{5.06 \times 10^5} = 0.71,$$

from which

$$x = \frac{(1.6 \times 0.71) - 1}{0.5} = \frac{1.14 - 1}{0.5} = 0.28,$$

i.e. the number of recombinations was ~0.3 N. Thus the probability of inter-chain reaction was about $x/n = 0.3/0.6 = 50\%$.

It should be noted, however, that in this experiment we studied the degradation of polystyrene, whose macroradicals have a particularly strong tendency to undergo recombination. Moreover, the calculation is only approximate, since we do not make direct allowance for the cross-linking of "centres" with "ends" and of "centres" with "centres", assuming that these processes, being bimolecular, are less probable than simple degradation. In addition, if

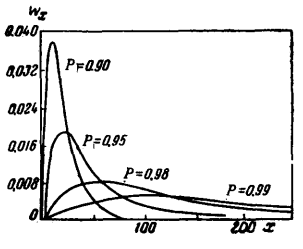


Fig. 12. Form of the Kuhn–Schulz–Flory equilibrium distribution (see text for symbols).

some "growth" of the fragments took place at the expense of monomer formed during degradation, *i.e.* exchange at the expense of monomer, this is mathematically equivalent to the above mechanism, which assumes simple recombination of macroradical "fragments".

Kinetic-chain transfer to the polymer. This process produces branched molecules, which, as Beasley[2] has shown, cause broadening of the MWD of the product and the appearance of high-molecular-weight "tails" on the distribution curve. The MWD remains unimodal, but since the longer the chain, the greater the probability that it will branch again, the MWD shows marked asymmetry (the ratio $\overline{M}_w:\overline{M}_n \to \infty$ with decrease in the most probable molecular weight $\overline{M}_{max}$). The degree of branching can be expressed in terms of the parameter $\beta = k_{transfer}[P]/ak_g[M]$, where $k_{transfer}$ is the constant for transfer to the polymer, [P] the polymer concentration, $1/a$ the average number of monomeric units in the growing chain (main or lateral), k_g the rate constant for chain growth, and $[M]$ the concentration of monomer. The weight fraction of polymer with X monomeric units in the chain (including all degrees of branching) is given by the expression

$$W(X)dX = \frac{(1-\beta)(aX)\,d(aX)}{[1+\beta aX]^{(1+1/\beta)}}. \qquad (16)$$

The form of this distribution function for different values of β is shown in Fig. 13.

Cross-linking of macromolecules. When the MWD is already established (for example at high degrees of conversion) in polymerisation, this process leads to characteristic changes in the MWD, which reduce to the form[6]

$$q_n(M) = \sum_{k=0}^{\infty} p_k \frac{\alpha^{k+1}}{\Gamma(k+1)} M^k e^{-\alpha M}, \qquad (17)$$

where $\alpha = 1/\overline{M}_n$, p_k represents "weighting" coefficients, and k is the number of side-chains per macromolecule. When $p_k = 1$, this distribution is equivalent to (13)‡. The coefficients p_k take account of the distribution of doublets, triplets, etc., *i.e.* the increase in the width of the MWD due to cross-linking of existing macromolecules. Under certain conditions this distribution may prove to be equivalent to Beasley's distribution[2]. In the case of polydienes, where branching during polymerisation takes place as a result of chain transfer to the polymer, account is already taken of this process in the differential form of the MWD [Eqn. (16)]. In the polynomial of type (17) for this case ($p_k = 1$) the numerical fractions of doublets, triplets, etc. (more accurately, species with $1, 2, \ldots k$ side-chains) decrease successively [thanks to the factor $\alpha^{k+1}/\Gamma(k+1)$] and although the number-average molecular weights of the fractions are in simple ratios of the type $1:2:\ldots:k$, the distribution as a whole remains unimodal (see Fig. 14). When secondary reactions of the type under consideration take place (*i.e.* cross-linking of formed molecules with an established MWD), the number of fractions of doublets, triplets, etc. may be of the same order of magnitude (allowance is made for this by the coefficients p_k) as the number of linear (not cross-linked) macromolecules, the major fraction of which was formed at lower degrees of conversion. In this case the distribution maximum may be displaced towards higher values of M, but the *separation* of the maxima, of the type represented in Fig. 15, may be obtained only if each "k-th" fraction (17) corresponds to *its own* value of $\alpha = \alpha_k$. When α is constant, the polynomial (17) may have only one maximum, as can be seen by taking $e^{-\alpha M}$ outside the summation sign. The sum is now a monotonically increasing function of M, and multiplication of the latter by the monotonically decreasing $e^{-\alpha M}$ should give a bell-shaped curve so long as all the p_k are real and ≥ 0 ("Dodge's rule" of higher algebra).

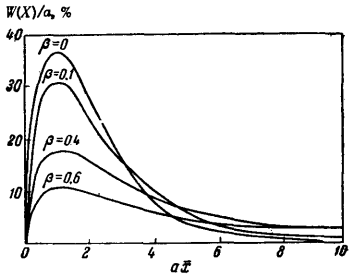


Fig. 13. Form of the Beasley weight distribution function for different degrees of branching produced as a result of chain transfer to the polymer[2].

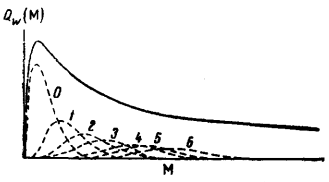


Fig. 14. Weight distribution function for a branched polymer[86]. The broken lines represent the partial distributions for fractions with different numbers of side chains per macromolecule (indicated by the numerals).

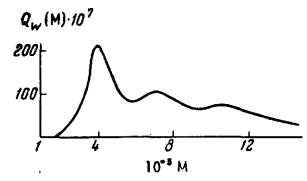


Fig. 15. Weight distribution function for poly(butyl phenyl methacrylate) obtained with stepwise increase in temperature[3].

‡ With allowance for the fact that (16) describes a numerical distribution function with respect to molecular weights and (13) a weight distribution function with respect to degrees of polymerisation[86].

The situation is different if the values of α_k differ; in this case even simple linear combinations of Schulz functions *of the same order of magnitude* may be given a multimodal curve. A large number of values of α may result from the succession or coexistence of *several* polymerisation mechanisms.

Under the conditions of a microheterogeneous medium at high values of ψ, polymerisation at different rates in different phases should initiate a multimodal distribution. In the case under discussion the cause of the multimodal character was most probably the two sudden increases in temperature.

Unlike the distributions $q_n(M)$, the corresponding distributions of $[\eta]$§ or of sedimentation coefficients *may* be resolved into separate maxima even when α = const. This can be seen from the following fundamental theorem of statistics:

$$q_n(M)\,dM = q_n(X)\,dX, \qquad (18)$$

where X is any single-single-valued function of M.

Assuming that $[\eta] = KM^{\beta}$ and substituting this in $q_n([\eta])$, corresponding to the distribution (17), we see that now the sum contains *variable* exponents of the form $\alpha + \beta_k$, since β depends on the degree of branching.

Thus, for example, analysis in the ultracentrifuge is more reliable than direct determination of $q_n(M)$, for in the first case we obtain the distribution of the sedimentation coefficients with respect to weight, which are sensitive to branching. It should again be emphasised that simply multimodal MWD may be produced in a number of cases without any secondary cross-linking reaction. This is the case with the superposition of several independent polymerisation mechanisms, each characterised by its own set of rate constants. Usually the presence of several maxima is due to a large number of polymerisation loci, *i.e.* the multimodal character should result from the heterogeneity of the polymerisation process.

b. Study of Secondary Reactions in Model Systems

The advantage of the MWD method is its general character and the fact that it can be used directly to study the products obtained in polymerisation. The fact that we are studying secondary reactions, which in ordinary polymerisation processes are "masked" by the main processes, however, means that this method is not always convenient. A more convenient method for studying secondary reactions is that involving model systems, in which these reactions take place in a more or less pure form.

The degradation of polymer chains in solutions at moderate temperatures (~ 100°) under the influence of small quantities of initiators causing degradation has been examined above. Particularly valuable results are obtained when the study of degradation gives not only one of the average molecular weights (or viscosity) before and after the reaction, but also the MWD (see above).

Inter-chain exchange may be detected directly by heating a solution of two fractions (differing considerably in molecular weight) of the same polymer in the presence of an agent causing degradation (or without it, if we are dealing with polycondensation products with active ends), with determination of the MWD before and after the reaction.

§ $[\eta]$ is the intrinsic viscosity.

Particularly interesting results may be obtained if one of the fractions is labelled with radioactive atoms. As a result of inter-chain exchange, a fraction of macromolecules with intermediate molecular weight should appear in the mixture, with a corresponding decrease in the proportions of macromolecules with extreme molecular weight values. A modification of this method involves analogous manipulations with a mixed solution of two different polymers. In this case inter-chain exchange and recombination by the centres (cross-linkages) give "hybrid" polymers of the block and graft type, the yield of which in these systems characterises the probability of inter-chain reactions. Although in principle this method may be quantitative data, detailed study of the reation product is difficult, since it contains both homopolymers (usually in the polydisperse state after the reaction, even if fractions were taken initially) and the hybrid polymer, which is polydisperse with respect to both composition and molecular weight.

For a quantitative study of inter-chain exchange, the most convenient method is by polymerisation of inactive monomer in the presence of "monodisperse" radioactive polymer of the same type, to a 100% degree of conversion, followed by fractionation and analysis of the distribution of radioactivity in the fractions. (The radioactive tracer technique can also be used in the experiment with two fractions, of the type considered above.)

Kinetic-chain transfer to an intermediate link of the polymer may be studied either by preparing graft polymers by polymerisation in the presence of an existing polymer of a different type or by establishing the deviation from the normal values (for linear polymers of this type) of the constants in the Mark–Kuhn–Hauwink relationship[87].

Henrici's method is particularly convenient for this purpose (see above).

The MWD method is the most reliable for establishing cross-linking of molecules. For this purpose, however, it is also possible to use the method of "hybrid polymer" preparation, used in the study of inter-chain exchange. It is also possible to use fractionation of the reaction product from a model system (or polymerisation boiler) with subsequent determination of the deviations from the relationship of type (13) for the corresponding linear polymer.

In the study of secondary reations during diene polymerisation, in addition to the MWD method and the methods used to study "branched" vinyl polymerisation, it is possible to use infrared analysis (to record the disappearance of double bonds) and also sol–gel analysis.

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Institute of Macromolecular Compounds,
Academy of Sciences of the USSR,
Leningrad

CHEMISTRY OF SOME INORGANIC NITROGEN FLUORIDES

A. V. Pankratov

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I. INTRODUCTION

In recent years there has been an increasing number of studies outside the Soviet Union of a new class of compounds characterised by the presence of the NF or NF_2 group. In the USA interest in compounds containing the NF_2 group is due to their use in rocket fuels[1]. The published studies relate mainly to the simplest gaseous nitrogen fluorides, most of which are reagents for the preparation of compounds containing the NF_2 group. These fluorides include tetrafluorohydrazine, the two difluorodiazine isomers, difluoramine, chlorodifluoramine, and fluorine azide.

This review is concerned with the chemistry of these nitrogen fluorides. The chapter on the structure of the nitrogen trifluoride molecule does not embrace all the literature data, but is given solely to provide a more correct understanding of the properties of the nitrogen fluorides.

II. STRUCTURE OF THE NITROGEN TRIFLUORIDE MOLECULE

The geometry of the nitrogen trifluoride molecule has been studied by electron diffraction[2,3] and by microwave spectroscopy[4]; the molecular dimensions have also been obtained from infrared spectroscopy and dipole moment measurements.

The nitrogen trifluoride molecule is an equilateral triangular pyramid in which the apex angle is 102°, N–F distance 1.37 Å, and F... F distance 2.14 Å.

The experimental N–F distance is in good agreement with the interatomic distance calculated from the Schomaker–Stevenson formula[5]:

$$r_{A-B} = r_A + r_B - 0.09(X_A - X_B),$$

where r_A and r_B are the covalent radii of atoms A and B, and X_A and X_B are the corresponding electronegativities. Here $r_F = 0.72$ Å, $r_N = 0.74$ Å, and $X_F - X_N = 0.95$,[6] and hence $r_{A-B} = 1.38$ Å. The above formula takes the ionic nature of the bond into account, and the agreement between the experimental and calculated distances demonstrates that the N–F bond is partially ionic.

The mean energy of the N–F bond, calculated from the heat of formation of NF_3 ($\Delta H = -29.7 \pm 1.8$ kcal mole^{-1} [7]), is 66.3 kcal mole^{-1}. The dissociation energy of the first bond D_{N-F} is determined[8–10] from the thermochemical equation

$$\Delta H_{NF_3} = \Delta H_{NF_2} + \Delta H_F - D_{N-F},$$

where $\Delta H_{NF_2} = 9.8 \pm 2.1$ kcal mole^{-1} (see Section III) and $\Delta H_F = 18.9 \pm 0.5$ kcal mole^{-1};[11] hence $D_{N-F} = 58.4 \pm 4.4$ kcal mole^{-1}. Assuming that the dissociation energies of the other two N–F bonds are the same, these will be 70.5 ± 1.6 kcal mole^{-1}.

Thus, unlike ammonia and many other inorganic substances[12], the energy of dissociation of the first bond in the NF_3 molecule is less than that of succeeding bonds.

Reese and Dibeler[13] recorded the mass spectrum of nitrogen trifluoride, determined the appearance potential of the ions NF_2^+ and NF^+, and calculated the ionisation potentials of the radicals NF_2 and NF. The appearance potential $A \geqslant I + D_{bond}$, where I is the ionisation potential and D_{bond} is the bond energy. The ionisation potentials, calculated from Reese and Dibeler's data using the above values for the N–F bond energies in nitrogen trifluoride and the experimental results of Herron and Dibeler[10], are $I_{NF_2} = 11.9 \pm 0.2$ eV and $I_{NF} = 12.4 \pm 0.3$ eV.

Ramaswamy determined the dielectric constant of NF_3 at -80°, -33°, 25°, and 95°, and calculated the dipole moment to be $\mu = 0.21$ D.[14,15] This low value is surprising (*cf.* the dipole moment of ammonia, which is 1.46 D). Almost all those who have studied the structure of the nitrogen trifluoride molecule have attempted some explanation of this low value, but despite the attempts made[16,17], there is no satisfactory quantitative explanation. The qualitative explanation[2,4,18–20] is that the moment due to the N–F bonds is counteracted by a moment, which must be of opposite sign, produced by the free electrons of N and F because of *sp* hybridisation.

The infrared spectrum of nitrogen trifluoride[21–23] contains four main frequencies: 907 cm^{-1}, $\nu_3(E)$, the doubly degenerate stretching frequency; 1031 cm^{-1}, $\nu_1(A_1)$, the fully symmetrical stretching frequency; 642 cm^{-1}, $\nu_2(A_1)$, the fully symmetrical deformation frequency; and 497 cm^{-1}, $\nu_4(E)$, the doubly degenerate deformation frequency.

The light absorption of nitrogen trifluoride commences at a wavelength < 1800 Å.[24] There are no absorption lines