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Characteristic features of radical polymerisation occurring under the influence of non-traditional initiators

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ABSTRACT. The kinetics of free radical polymerisation processes during which macromolecules grow stepwise are examined. A general approach suitable for the calculation of the molecular weight distribution of the products of the polymerisation initiated by various classes of non-traditional initiators is formulated. The effectiveness of this theoretical approach is illustrated in numerous examples of the solution of specific practical problems.

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I. Introduction

A common feature of a large proportion of radical polymerisation processes is a decrease in molecular weight with increase in the concentration of traditional initiators, which imposes fundamental limitations on the increase in the productivity of the corresponding processes. This is associated with the fact that the length of the material chain in the absence of transferring agents is equal either to the length of the kinetic chain or to twice its length respectively in cases where the termination reaction proceeds via a combination or disproportionation mechanism. An increase in the rate of polymerisation as a result of an increase in the rate of initiation in the processes considered therefore leads to a simultaneous decrease in the length of the kinetic chain and hence to a decrease in molecular weight.

This undesirable effect can be avoided by employing non-traditional radical polymerisation initiators whereupon the material chain consists of several elementary chains whose number increases continuously in the course of the process. An increase in the molecular weight of the polymer with conversion and a narrowing of its molecular weight distribution are then observed. These features are qualitatively different from those noted in the usual processes.

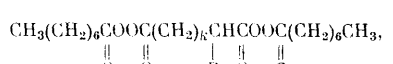
This review deals with questions concerning the quantitative description of such pseudolive radical polymerisation initiated by non-traditional compounds of two classes. The first includes polyfunctional initiators, for example, polyperoxides, containing more than one labile group in each molecule. The second contains so called "inferters" participating in chain transfer and termination reactions apart from initiation. A characteristic feature of both classes of these non-traditional initiators is that during polymerisation processes with their participation macromolecules capable of further reactivation and chain propagation are formed.

II. Polyfunctional initiators

1. Introduction

In conformity with their name, the molecules of polyfunctional initiators contain two or more functional groups capable of forming free radicals on decomposition. These groups are characterised by the chemical nature of the labile interatomic bond present in them, for example, the bond in the azo- and peroxy-groups. A fairly large number of chemically different types of polyfunctional initiators are now known. Information about the structure and method of synthesis of these compounds can be found in reviews.[1–6] Polyperoxides, in relation to which the general theoretical postulates will be illustrated below, have been most thoroughly investigated among them (to a large extent as a result of the fundamental research by Ivanchev and co-workers[7–16]).

The molecules of polyfunctional initiators can differ by the number of labile groups of various types. The simplest among initiators of this kind, such as, for example, diacyl diperoxide



(I)

contain two labile groups. For a sufficient length of the methylene bridge separating them, when the number k of the CH_2 units exceeds 6–8, both these groups decompose independently.[12,15] The entire discussion below will refer solely to polyinitiators with similar kinetically independent labile groups.

Generally speaking, the peroxy-groups in the diperoxide (I) have different thermal stabilities, since one of them contains an unsubstituted acyl group while the other has an α-substituted acyl group. The difference between the rate constants for the decomposition of these groups may be very appreciable depending on the nature of the substituent R. Thus Ivanchev and co-workers[9,10,12,15] determined the kinetic parameters of the thermolysis of a large number of different polyperoxides which they synthesised and also established the dependence of these parameters on the length k of the bridge, the nature of the substituent R, and the number of peroxy-groups in the molecules. Some data concerning the parameters, indicated above, of the decomposition of polyfunctional initiators have also been presented in communications by other investigators (see, for example, Refs. 17–20).

It has been established[12,18] that polyperoxides with independent peroxy-groups are most suitable for practical application. The rate of polymerisation initiated by such compounds will evidently be identical, under the conditions of the applicability of the Flory principle,[21] with the rate of polymerisation under the influence of traditional monofunctional initiators containing the same peroxy-groups and present at the same overall concentrations in both systems mentioned above.[22,23] The task of the quantitative theory of homopolymerisation with participation of polyfunctional initiators is therefore only the calculation of the molecular weight distribution (MWD) and of its statistical moments while for joint polymerisation it also includes the calculation of the composition distribution of the products formed.

2. The polymerisation mechanism

The main feature of the polymerisation in the presence of polyfunctional initiators consists in the formation, during the process, of macromolecules containing labile groups in the main chain (within it and/or at its ends). The mechanism of the formation of such macromolecules is illustrated schematically in Fig. 1 for the simplest case of the synthesis of monomers of the type of polystyrene under the influence of a diperoxide with the same peroxy-groups. The decomposition of any of the peroxy-groups results in the formation of a pair of free radicals each of which recombines, after the readdition in the course of its growth of a certain number of monomers, with one of the other similar macroradicals, generating macromolecules of the "dead" polymer. The latter contain only the elementary polymer chain and differ by the number of terminal peroxy-groups whose subsequent decomposition leads to the formation of a pair of polymeric radicals capable of further growth and recombination.

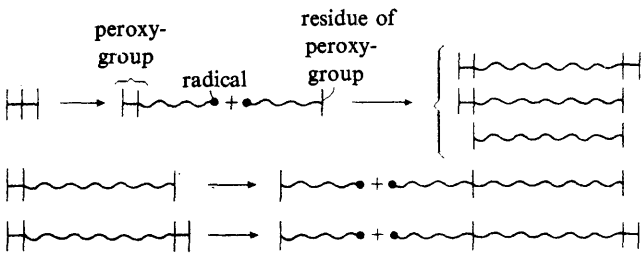


Figure 1. Schematic illustration of the formation of the polymer chain during polymerisation initiated by a symmetrical diperoxide.

The set of such parallel-consecutive reactions characterises the polymerisation-recombination mechanism of the formation of macromolecules in the presence of polyfunctional initiators discussed here.[1,23] Naturally, if the molecules of the initiators include more than two labile groups, then the molecules of the macroinitiator formed during polymerisation may contain these groups not only at the edge but also within the main chain. The structure of such macromolecules, formed during the consecutive decomposition of peroxy-groups and of the recombination of macroradicals, may be complex (Fig. 2). An arbitrary polymer chain may consist of any number m of elementary chains separated by peroxide clusters containing one, two, three, etc. peroxy-groups. The term "cluster" implies here a sequence of peroxy-groups bounded either by two elementary chains or by an elementary chain and the end of the macromolecule. In the former case, the cluster is referred to as closed and in the latter as semi-open.

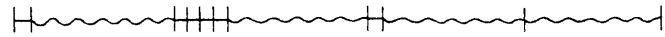


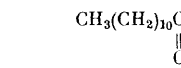
Figure 2. Schematic illustration of one of the polymer chains formed during the process presented in Fig. 1.

For polyinitiators with independent functional groups, the thermal stability of each of them should not depend on the cluster to which it belongs and on the site where it is located. The decomposition constant for any such peroxy-groups will then be identical with the constant characterising it in the molecule of the initial polyinitiator.

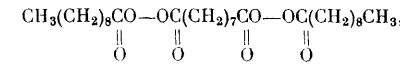
Examples of similar polyperoxides are well known.[1–3,5] The rate of polymerisation W initiated by such compounds should not evidently depend on their functionality for the same overall concentration C of peroxy-groups in the reaction system and is described by the usual formula

$$W = k_p M (I/k_t)^{1/2}, \text{ where } I = 2fk_dC, \quad (1)$$

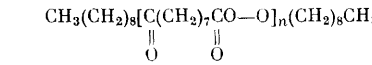
used in the traditional theory of radical polymerisation with participation of monofunctional initiators.[21] The following notation is used here and henceforth: I and f are the rate and efficiency of initiation, M is the concentration of the monomer, and k_d, k_p, and k_t are respectively the rate constants for the elementary reactions involving the decomposition of the peroxy-groups and chain propagation and termination. In conformity with the Flory principle, these constants do not change on passing from monofunctional to polyfunctional initiators, which has been confirmed in relation to the peroxides



(II)



(III)



(IV)

by the experimental data presented in Fig. 3.

In contrast to the kinetics, the traditional theory of radical polymerisation cannot be used for the calculation of the molecular weight characteristics of the polymer. Thus even the simplest formula of this theory[21]

$$P'_N = \frac{2}{1+\lambda}\nu, \text{ where } \nu = \frac{W}{I}, \ \lambda = \frac{k_{td}}{k_t}, \ k_t = k_{td} + k_{tc}, \quad (2)$$

which relates the number-average degree of polymerisation P_N of the macromolecules for the initial conversions to the length of the kinetic chains ν and also to the constants of elementary reactions

involving chain termination by the combination (k_{tc}) and the disproportionation (k_{td}) of the radicals, proves to be invalid. Contrary to Eqn. (2), the average molecular weight begins to increase from the very beginning of the polymerisation, provided that it is initiated by polyfunctional compounds.[1-3,5] This result follows naturally from the polymerisation-recombination mechanism of the formation of macromolecules (Fig. 1), because the formation in the polymer of one or two new elementary chains, depending on whether the kinetic chain is terminated by combination or disproportionation, corresponds to each effectively decomposed labile bond.

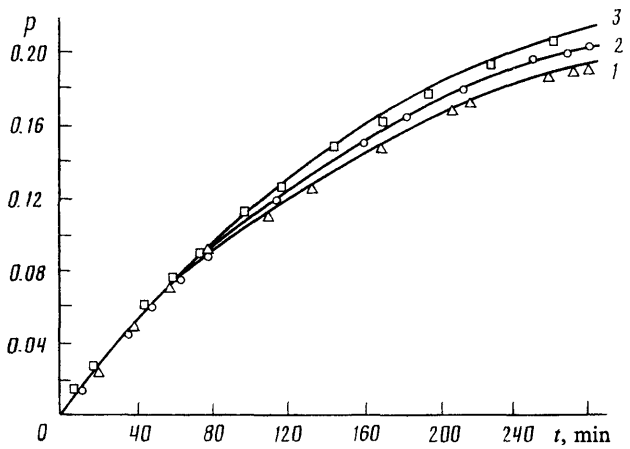


Figure 3. Kinetic curves for the polymerisation of styrene in bulk at T = 80 °C and at a peroxy-group concentration $C^0 = 2.5 \times 10^{-3}$ M for initiation by monoperoxides (curve *1*), diperoxides (curve *2*), and polyperoxides (curve *3*) containing 18 peroxy-groups.[23]

3. The superposition principle

For the calculation of the molecular weight distribution of the products of polymerisation initiated by polyperoxide, it is convenient to distinguish the macromolecules in terms of the number m of elementary chains included in them. The total number $l = l^{(1)} + l^{(2)} + ... + l^{(m)}$ of the monomer units in the given macromolecule will determine (neglecting the contribution of the peroxide clusters) its molecular weight. For the calculation of the numerical molecular weight distribution $f_N(l, t)$ of the polymer formed by time t, one can use the expression

$$f_N(l, t) = \sum_{m=1}^{\infty} P_m(t)\, W_m(l), \tag{3}$$

where $P_m(t)$ is the fraction of the macromolecules containing m elementary chains at time t and $W_m(l)$ is the conventional probability that the degree of polymerisation of such a macromolecule is l.

In conformity with the general ideas of the statistical chemistry of polymers, instead of the molecular weight distribution of the polymer one can use its generating function

$$G_N(s, t) = \sum_{l=1}^{\infty} f_N(l, t)\, s^l, \tag{4}$$

ich is fully equivalent to the molecular weight distribution but is more convenient in the calculation of its statistical moments.[24] These characteristics, which determine in particular, the number-average, weight-average, and z-average molecular weights of the polymer, can be calculated as the corresponding derivatives of the generating function $G_N(s)$ at the point $s = 1$. The molecular weight distribution itself can be found from Eqn. (4) by expanding $G_N(s)$ in a power series in terms of s.

For the calculation of the molecular weight distribution, it is necessary to find separately two generating functions:

$$U(x, t) = \sum_{m=1}^{\infty} P_m(t)\, x^m; \quad g(s) = \sum_{l=1}^{\infty} \varphi_l s^l. \tag{5}$$

the first of which corresponds to the distribution $P_m(t)$ of the macromolecules with respect to m elementary chains and the second corresponds to the distribution of these chains with respect to l monomer units in them. The generating function of the molecular weight distribution can then be obtained after substituting the function $g(s)$ in $U(x,t)$ instead of its argument x. One obtains as a result the important relation[23]

$$G_N(s, t) = U(g(s), t), \tag{6}$$

which represents the mathematical formulation of the principle of the superposition of the distributions φ_l and P_m.

The first of these evidently represents molecular weight distribution of the elementary chains, the length of each of which (in the given case $k_{td} = 0$) is made up of two lengths of kinetic chains. Their distribution with respect to length is described by the most probable Flory distribution whose generating function

$$g_k(s) = \frac{(1-a)s}{1-as}, \quad \text{where} \quad a = 1 - 1/\nu, \tag{7}$$

is determined by the unique parameter a, which depends solely on the average length ν of the kinetic chain [see Eqn. (2)]. Evidently the distribution φ_l of the elementary chains is identical with the molecular weight distribution of the products of polymerisation under the influence of a traditional monofunctional initiator and is described by the generating function $g(s) = g_k^2(s)$. Its substitution in Eqn. (6) yields a solution of the problem of the calculation of the molecular weight distribution of polymer chains subject to the condition that the generating function $U(x, t)$ of the distribution $P_m(t)$ is known.

However, the procedure indicated is valid only in the case where the kinetic parameter ν does not vary during polymerisation as a consequence of the variation of the monomer or initiator concentrations. On the other hand, if such variation does occur then, instead of the function $g(s)$, its average value

$$\langle g(s) \rangle = \int_0^t g(s, t')\, I(t')\, dt' \Big/ \int_0^t I(t')\, dt', \tag{8}$$

should be substituted in Eqn. (6). Here the angular brackets denote averaging with respect to time of the characteristic placed between them.

When traditional monofunctional initiators are used, whereupon each polymer chain consists of one elementary chain, Eqn. (8) evidently describes the molecular weight distribution of the polymerisation products over the entire range of conversions taking into account the consumption of the monomer and initiator during the process. Such consumption may induce a broadening of the

molecular weight distribution with respect to conversion, which is undesirable for practical purposes, and which is characterised by the quantitatively appreciable increase with conversion of the polydispersity coefficient $K' = P'_W/P'_N$ which is equal, by definition, to the ratio of the weight-average and number-average degrees of polymerisation. Eqns. (7) and (8) make it possible to obtain simple formulae for these statistical characteristics:

$$P'_N = 2\langle\nu\rangle, \quad K' = \frac{3\langle\nu^2\rangle}{2\langle\nu\rangle^2}. \tag{9}$$

The effect of the conversion-induced broadening of the MWD indicated can be appreciably diminished if the polymerisation is carried out in the presence of polyperoxides containing a sufficient number of functional groups. This fundamental conclusion follows directly from the general expressions

$$P_N = P'_N P''_N, \quad K = K'' + \frac{(K'-1)}{P''_N}, \tag{10}$$

which can be derived simply from the superposition principle (6) (formulated above) taking into account Eqn. (8). According to Eqn. (10), the molecular weight and the polydispersity coefficient of the polymer obtained depend on similar characteristics: both on the distribution with respect to the lengths of the elementary chains [Eqns. (9)] and on the distribution P_m of the macromolecules with respect to the number m of such chains. The average value $P''_N = \overline{m}$ of this random quantity, which is identical at the end of the polymerisation with the average number of the effectively decomposed labile bonds in the polyperoxide molecule, can be fairly large when the functionality of the polyperoxide is high. In the latter case, the transition from monofunctional to polyfunctional initiators should be accompanied by an appreciable (by the factor P''_N) increase in the average molecular weight and by the simultaneous narrowing of the molecular weight distribution. For sufficiently large values of P''_N, when it is possible to neglect the second term in Eqn. (10) for K compared with the first, the use of polyperoxides makes it possible to suppress completely the conversion factor for the non-uniformity of the molecular weight distribution. The latter can be determined in this case only by the polydispersity coefficient K'' of the distribution P_m, which, as will be seen from the discussion below, is usually not unduly great.

We shall now consider how the superposition principle can be extended to the polymerisation reactions of monomers of the type of methyl methacrylate in which the fraction of the radicals [λ in Eqn. (2)] losing their activity via the disproportionation mechanism is non-zero. As a result of the elementary kinetic chain termination step via this mechanism, the macromolecules lose their activity, being converted into macro-initiator molecules with formation of an additional elementary chain at the end of each of them. However, in contrast to chain termination via combination, its length is equal to the length of not two but only one kinetic chain. Consequently the following formula constitutes an extension of Eqn. (6):

$$G_N(s, t) = U(\langle g_k^2(s)\rangle, \langle g_k(s)\rangle; t), \tag{11}$$

where $U(x, y; t)$ is the generating function of the joint distribution of polymer chains with respect to m and i elementary chains formed respectively by the combination and disproportionation of the radicals. It is easy to obtain from Eqn. (11) a relation, analogous to Eqn. (10), containing the quantities

$$P'_N = \frac{2\langle\nu\rangle}{1+\lambda}; \qquad K' = \frac{(\lambda+1)(3-\lambda)}{2}\frac{\langle\nu^2\rangle}{\langle\nu\rangle^2}. \tag{12}$$

Naturally, with increase in λ, the efficiency of the formation of polyinitiators falls as a consequence of the decrease in the fraction of the combination steps leading to the strengthening of the polymer chains. In order to estimate this effect quantitatively, it is sufficient to find from Eqn. (11) the generating function $U(x, y; t)$.

4. Polyinitiators with labile groups of one type

According to the superposition principle described above, in order to calculate the molecular weight distribution in the case of chain termination via combination, it is sufficient to find the generating function $U(x, t)$ of the distribution $P_m(t)$ of macromolecules with respect to m elementary chains. In order to find $U(x, t)$, the corresponding system of kinetic equations was formulated[23] for this distribution and its exact solution was found. According to the latter, for any initial distribution α_j of polyperoxide molecules with respect to j peroxy-groups, the distribution P_m has the generating function

$$U(x,t) = \frac{(1-\rho)x}{1-\rho x}, \quad P_m = (1-\rho)\rho^{m-1}. \tag{13}$$

The form of the α_j distribution affects only the nature of the time variation of the single parameter ρ:

$$\rho(t) = 1 - \sum_j a_j[1-(1-\theta)^j]\Big/\theta\sum_j ja_j,$$
$$\text{where } \theta = f(1-e^{-\tau}), \quad \tau = k_d t. \tag{14}$$

In the case of function (13), the superposition principle (10) leads to a simple expression for the molecular weight distribution when account is taken of Eqn. (7):

$$f_N(l,t) = \frac{(1-\rho)}{2\sqrt{\rho}}(1-a)\{[a+(1-a)\sqrt{\rho}]^{l-1} -$$
$$-[a-(1-a)\sqrt{\rho}]^{l-1}\}. \tag{15}$$

It is evidently unimodal. The use of Eqns. (10) makes it possible to obtain from Eqn. (13) the formulae

$$P_N = P'_N(1-\rho)^{-1} \text{ and } K = (1-\rho)K' + 2\rho, \tag{16}$$

which are valid over the entire range of conversions when account is taken of Eqn. (9).

According to the first of these formulae, the molecular weight increases during the process from P'_N, obtained when the monoperoxide is used, to a maximum value P_N^{max} which depends on the distribution, α_j, of the peroxy-groups in the polyperoxide molecules and on the efficiency of the initiator f. In the case of polyinitiators with a fairly high functionality, the theory predicts a linear dependence of the molecular weight of the polymer on the conversion over a wide range of the latter. Under these conditions, the slope of the straight line is proportional to the functionality of the polyinitiator, in conformity with Eqns. (14) and (16). These theoretical predictions are satisfactorily confirmed by the experimental data presented in Fig. 4.

An extension of Eqn. (13), taking into account the possibility of chain termination via disproportionation, has been obtained[23] with the aid of the kinetic approach:

$$U(x,y;t) = \frac{V(x,y;t)}{V(1,1;t)}, \quad V(x,y;t) = \frac{(1+dy)^2}{1-b^2x} - 1,$$
$$\text{where } d = \lambda\rho(1-\rho)^{-1}, \quad b^2 = (1-\lambda)\rho. \tag{17}$$

In the case where the length of the kinetic chain ν is large and

constant, the superposition principle (11) makes it possible to find from Eqn. (17) the following expression for the molecular weight distribution of the polymer:

$$f_N(l, t) = \frac{1-b^2}{2b(d^2+b^2+2d)}\{(d+b)^2 e^{-l/(1-b)\nu} - (d-b)^2 e^{-l/(1+b)\nu}\}, \quad (18)$$

which, like the molecular weight distribution defined by Eqn. (15), is unimodal.

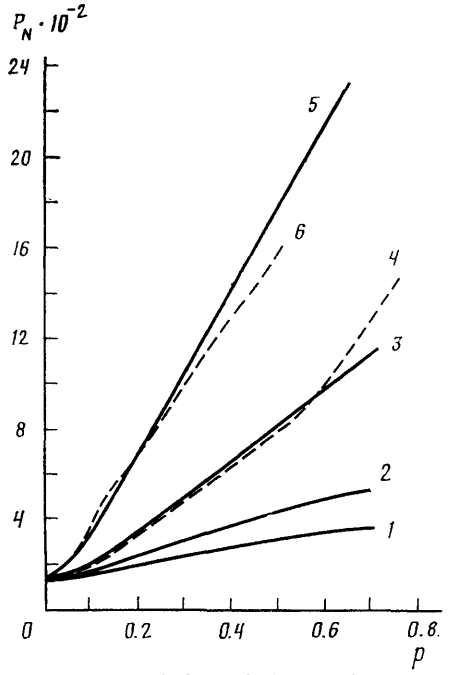


Figure 4. Variation of the number-average molecular weight of polystyrene with conversion in the polymerisation of styrene in bulk in the presence of oligoperoxides with different average numbers of groups; number of groups: *1*, 1; *2*, 2; *3*, and *4*, 4.6; *5*, and *6*, 10.7. Continuous lines—theoretical data; dashed lines—experimental data.[12]

The following formulae serve as extensions of Eqns. (16):

$$P_N = \frac{\lambda+1}{\lambda+1-\rho} P'_N,$$

$$K = \frac{\lambda+1-\rho}{\lambda+1} K' + \frac{(2-\lambda)^2\rho(\lambda+1-\rho)}{2(1-\rho+\lambda\rho)}. \quad (19)$$

They demonstrate to what extent the disproportionation reaction eliminates all the advantages of employing polyfunctional initiators. Indeed, regardless of the type of the latter and the kinetic polymerisation parameters, it is impossible, according to Eqns. (19), to increase the molecular weight of the polymer (compared with that which is obtained under the same conditions using the usual monoperoxide) by a factor greater than $(\lambda + 1)/\lambda$. For example, in the polymerisation of methyl methacrylate, where λ is close to 0.5, this factor is close to 3. In such systems, the transition from monoinitiators to polyinitiators is much less effective, as follows from the second Eqn. (19), for the restriction of the increase in the conversion-induced non-uniformity of the polymerisation products. The above factor is one of the fundamental disadvantages of the use of polyperoxides in practice.

5. Polyinitiators with labile groups of several types

The use of polyperoxides containing peroxy-groups with different thermal stabilities leads to extensive possibilities for the molecular design of polymers.[1-6] Under these conditions, questions concerning the dependence of their statistical characteristics on the functionality, composition, and structure of the initial initiating compounds arise. The answers to these questions are provided by the quantitative theory, developed by Ivanov et al.,[31] some of the main results of which are presented below.

The general formulae (3)–(10) for the calculation of the molecular weight and the molecular weight distribution remain valid also on passing to polyinitiators with several types of peroxy-groups. However, the forms of the distribution functions $P_m(p)$ of the macromolecules with respect to m elementary chains are naturally different. In order to find this distribution, it is very convenient to employ a statistical approach according to which any arbitrarily selected macromolecule in the reaction system can be regarded as the realisation of a random process involving conventional motion along the macromolecule.[21,24] It is found that such a random process, describing the products of the homopolymerisation initiated by arbitrary polyperoxides with independent groups, may be a Markov chain. This result is valid for any number r of types of labile groups regardless of the way in which they are distributed among the molecules of the initial polyperoxide. The nature of the distribution will influence only the statistical parameters of the Markov chain; the matrix $\mathbf{Q}$ (with the elements ν_{ij}) of the transitional probabilities and the vector $\vec{v}$ (with the components v_i) of the initial states. In the case considered, the following expression is an extension of Eqn. (13):

$$U(x, t) = \sum_{i=1}^{r}\sum_{j=1}^{r} v_1 x [(\mathbf{E} - \tilde{\mathbf{Q}}x)^{-1}]_{ij}\nu_{j0}, \quad (20)$$

where $\mathbf{E}$ is a unit matrix (with the elements δ_{ij}), $\tilde{\mathbf{Q}}$ the matrix of the transitions (with the elements ν_{ij}, $i \neq 0, j \neq 0$) between r non-return states, and ν_{j0} the probability of the transition from such a jth state to the zeroth state, which is absorbing.

All the parameters of the Markov chain in Eqn. (20) are expressed in terms of the kinetic structural parameters of the initial polyinitiator. The former include the decomposition constants k_{di} and the efficiences of the initiation f_i ($i = 1, ..., r$) by all types of peroxy-groups, while the latter include the fractions of the chemically individual polyperoxide molecules with a fixed set of numbers of groups of all types and the order in which they alternate.

The structure of the macromolecules in the given case is similar to that illustrated in Fig. 3 with the sole difference that the peroxide clusters can now consist of groups of different types. In the statistical approach, it is convenient to distinguish (to differentiate arbitrarily) the radicals, elementary chains, and clusters as a function of the mode of their formation. Thus, in the effective decomposition of an ith type labile group, a pair of macroradicals is formed to which the same type i is attributed. Each step involving the recombination of two such macroradicals of types i and j leads to the formation of the elementary chain (ij). The peroxide clusters can

be differentiated in accordance with the same principle in terms of their types as a function of the type of radicals which were formed at one time at the ends of the given cluster. Consequently the elementary chain (ij) is connected to the chain (kl) by a closed cluster of type (jk), while a semiopen cluster of type $(j0)$ or $(0j)$, containing the 0, 1...peroxy-groups, connects the elementary chain to the end or start of the macromolecule. The molecules of the initial polyperoxide are included among the open clusters.

The concentrations N_{ij} of the peroxide clusters of different types (ij) as well as the rates I_i of generation of macroradicals of types $i = 1, ..., r$, i.e.

$$I_i = 2f_i k_{di} C_i, \quad C_i = C_i^0 \exp(-k_{di}t), \quad I = \sum_{i=1}^{r} I_i , \tag{21}$$

are determined by the elements ρ_{ik} and ρ_{kj} of the matrices $\boldsymbol{\rho}$ and $\boldsymbol{\sigma}$:

$$\rho_{ik} = N_{ik} \Big/ \sum_{k=0}^{r} N_{ik} \; (i, k = 1, \ldots r), \quad \rho_{i0} = N_{i0} \Big/ \sum_{k=0}^{r} N_{ik}; \tag{22}$$

$$\sigma_{kj} = \int_0^t \frac{I_k I_j}{I} \, dt' \Big/ \int_0^t I_k dt', \quad \rho_{0k} = N_{0k} \Big/ \sum_{k=1}^{r} N_{0k}, \tag{23}$$

in terms of which all the parameters of the Markov chain in Eqn. (20) are expressed simply by means of the formulae

$$\nu_{ij} = \sum_{k=1}^{r} \rho_{ik}\sigma_{kj} \; (i, j = 1, \ldots r), \quad \nu_{i0} = \rho_{i0} \tag{24}$$

$$v_i = \sum_{k=1}^{r} \rho_{0k}\sigma_{ki} \; . \tag{25}$$

The overall concentration of the polymer molecules Π is equal to the difference between the initial I^0 and current $I(t)$ concentrations of the initiator molecules:

$$\Pi = I^0 - I(t) = I^0 \left[1 - \sum_{\vec{j}} \alpha(\vec{j}) \prod_{i=1}^{r} (1 - \theta_i)^{j_i} \right], \tag{26}$$

where $\alpha(\vec{j})$ is the fraction of the molecules of the initial polyperoxide having a functionality vector $\vec{j}$ with the components $\{j_1, ..., j_i, ..., j_r\}$ equal to the numbers of functional groups of each type. The quantities

$$\theta_i = f_i[1 - \exp(-k_{di}t)] \quad (i = 1 \ldots, r), \tag{27}$$

have the significance of the probability that an arbitrarily selected peroxy-group of the ith type decomposes effectivey at time t.

All the formulae in subsection 3 are valid in the general case considered. Thus the average number of elementary chains in the macromolecule

$$P_N'' = \sum_{i=1}^{r} \sum_{j=1}^{r} v_i [(\mathbf{E} - \tilde{\mathbf{Q}})^{-1}]_{ij} = \sum_{i=1}^{r} C_i^0 \theta_i / \Pi, \tag{28}$$

and hence, according to Eqn. (10), also the number-average molecular weight of the polymer are independent, for the given $\alpha(\vec{j})$ distribution, of the sequence of the peroxy-groups of different types in the polyinitiator molecules. However, the microstructure of the polyperoxide nevertheless exerts an influence on the form of the molecular weight distribution and the degree of its polydispersity K [Eqn. (10)], as follows from the formula

$$K'' = 1 + \sum_{i=1}^{r} \sum_{j=1}^{r} v_i [(\mathbf{E} - \tilde{\mathbf{Q}})^{-2} \tilde{\mathbf{Q}}]_{ij} \Big/ \left\{ \sum_{i=1}^{r} \sum_{j=1}^{r} v_i [(\mathbf{E} - \tilde{\mathbf{Q}})^{-1}]_{ij} \right\}^2 . \tag{29}$$

In the simplest and experimentally most thoroughly investigated case of initiators with two types of peroxy-groups, the general formula (20) reduces to the form

$$U(x, t) = \frac{x(b_1 + b_2 x)}{1 - d_1 x + d_2 x^2}, \tag{30}$$

where

$$b_1 = v_1\nu_{10} + v_2\nu_{20}, \quad b_2 = v_1(\nu_{12}\nu_{20} - \nu_{22}\nu_{10}) + v_2(\nu_{21}\nu_{10} - \nu_{11}\nu_{20})$$
$$d_1 = \nu_{11} + \nu_{22}, \quad d_2 = \nu_{11}\nu_{22} - \nu_{12}\nu_{21} . \tag{31}$$

When the conditions $b_2 < 0$ and $d_2 > 0$ hold, analysis of Eqn. (30) predicts the possibility of the appearance in the initial polymerisation stage of a bimodal molecular weight distribution, which may then become unimodal as the degree of conversion increases. This nature of the evolution of the molecular weight distribution was in fact observed in certain experiments[5,8,11,12] when the process was initiated by peroxide with two types of labile groups having different thermal stabilities. The polydispersity coefficient K can be easily calculated by Eqn. (10) because Eqn. (29) reduces to the simple form

$$K'' = \frac{4(1 - d_2) - (b_1 + d_1)(3 - d_1 - d_2)}{(2 - b_1 - d_1)^2} \tag{32}$$

when $r = 2$.

In order to find with the aid of the generating function (30) the molecular weight distribution or the polydispersity coefficients (10) and (32), it is necessary to find beforehand with the aid of Eqn. (31) the parameters of the Markov chain, which are fully defined, according to Eqns. (24) and (25), by the matrices $\boldsymbol{\rho}$ and $\boldsymbol{\sigma}$. Their elements can be calculated by Eqns. (22) and (23) provided that the concentrations N_{ik} of the different clusters (ik) are known. Several ways of finding the concentrations N_{ij} for different types of initial polyperoxides have been proposed.[31] The polyperoxides can be both individual chemical compounds and mixtures of molecules differing in the number of peroxy-groups of different types (composition) and their sequence (structure).

Examination of such mixtures is of practical importance because oligomeric initiators are usually synthesised by the polycondensation method.[1-6] As a consequence of the random character of its reactions, the products of this process naturally have a distribution with respect to composition and structure. The latter has been described in many cases[24] by a Markov chain whose non-return states are peroxy-groups of r types and the zeroth absorbing state corresponding to going outside the limits of the molecule. If the matrix of the transition probabilities between the non-return states of this Markov chain is denoted by $\tilde{\mathbf{Q}}^0$ and its initial vector is denoted by $\overleftarrow{v}^0$, when the matrix ρ can be written in the form

$$\boldsymbol{\rho} = [\mathbf{E} - \tilde{\mathbf{Q}}^0(\mathbf{E} - \mathbf{D})]^{-1} \tilde{\mathbf{Q}}^0 \mathbf{D}, \tag{33}$$

where **D** is a diagonal matrix with the elements $\theta_i\delta_{ij}$. Other parameters in Eqns. (22) and (23) are defined similarly:

$$\rho_{i0} = \sum_{j=1}^{r} \{[\mathbf{E} - \tilde{\mathbf{Q}}^0(\mathbf{E} - \mathbf{D})]^{-1}\}_{ij} v_{j0}^0, \tag{34}$$

$$\rho_{0i} = \frac{I^0}{\Pi} \sum_{j=1}^{r} v_j^0[\theta_j\delta_{ji} + (1-\theta_j)\rho_{ji}], \tag{35}$$

$$\Pi = I^0 - I(t) = I^0\left[1 - \sum_{i=1}^{r} v_i^0(1-\theta_i)\rho_{i0}\right]. \tag{36}$$

Together with Eqns. (10) and (28), Eqns. (34) and (36) provide an exhaustive solution of the problem of the calculation of the number-average molecular weights of the products of polymerisation initiated by polyperoxides with Markov statistics of the sequence of labile groups of different types in them.

The possibility of using a statistical approach to the calculation of the molecular weight distribution of the polyperoxide-initiated polymerisation products is associated with the independent decomposition of all their labile groups. This factor serves as yet another illustration of Flory's idea,[21] which is of general importance for the chemistry of polymers. In the spirit of this idea, the molecular weight distribution functions depend on time only in terms of probability parameters, which in the systems examined here are the elements σ_{kj} [see Eqn. (23)] of the matrix σ and the components θ_i see Eqn. (27) of the vector $\vec{\theta}$.

Rigorous kinetic examination shows that the formulae derived by the statistical method retain their form in systems where the temperature varies during polymerisation. However, the time variation of the probability parameters in these formulae is determined by expressions more general than in the case of an isothermal process. Such an expression, which is an extension of Eqn. (27), is

$$\theta_i(t) = \int_0^t f_i(t')\, k_{di}(t') \exp\left[-\int_0^{t'} k_{di}(t'')\, dt''\right] dt', \tag{37}$$

while in the calculation of the quantities σ_{kj} [see Eqn. (23)], one should take into account the time variation of the kinetic parameters f_i and k_{di} in the functions I_i [Eqn. (21)]. The above explanations make it possible to embrace by the theory described above the polymerisation processes occurring in practice with a programmed increase in temperature, which have a number of advantages compared with isothermal processes.[5]

6. Synthesis of block copolymers

Polymerisation processes with participation of polyinitiators having two types of groups with markedly different thermal stabilities are apparently of greatest practical interest. Such polyperoxides are characterised by decomposition constants $k_{d1} \gg k_{d2}$, which makes it possible to carry out the polymerisation in two stages. In the first stage, carried out at a specific temperature, virtually only the more labile peroxy-groups of the first type decompose with formation of polymer molecules containing peroxide clusters comprising the groups of the second type in the main chain, which are capable of further reactions. After raising the temperature in the polymerisation system, the process goes over to the second stage, during which the less labile groups of the second type are decomposed which is accompanied by the growth of the macroradicals formed and their subsequent recombination. If the monomer is replaced at the end of the first stage, then molecules containing blocks of different monomers are formed during the second stage. This method of synthesis of block-copolymers is extremely simple and promising.[13–15,25–30]

The change in the composition and structure of polyperoxide makes it possible to influence the architecture and statistical characteristics of the block-copolymers formed. In the simplest case, it is possible to select as the initiator an asymmetric diperoxide of the type of, for example, compound (I) with an appropriate substituent R ensuring a sufficient difference between the thermal stabilities of the two peroxy-groups. In particular, the use of a boron atom as R leads to a difference between the decomposition constants k_{d1} and k_{d2} for these groups differing by a factor greater than 20,[12] which guarantees the possibility of carrying out the two-stage synthesis of a block copolymer with participation of the initiator.

The formation during the synthesis of homopolymer molecules as side products in both stages is a disadvantage in this case. It can be eliminated in the first stage by going over from diperoxides to symmetrical triperoxides which contain two identical groups of the first type separated by a central, more stable group of the second type.[10,32] In order to reduce to a minimum the formation of the homopolymer also in the second stage of the process, it is necessary to carry it out in the presence of a polyperoxide with the highest possible functionality and it is desirable to have alternating groups of both types. The latter factor promotes an increase in the uniformity of the compositions of the copolymerisation product, because it ensures a regular alternation in the latter of macromolecular blocks each of which consists in the given instance of a single elementary chain.

In the general case of an arbitrary polyperoxide, selected by guesswork, the block of monomer ith type units in the molecule of the block-copolymer can consist of any number n of elementary chains of the corresponding monomer. The random quantity n has the distribution function $(1-\rho_{ii})\rho_{ii}^{n-1}$, so that the average number of elementary chains in one block is $(1-\rho_{ii})^{-1}$. The distribution of the blocks of the ith monomer with respect to lengths is described by Eqn. (7) and by Eqn. (15) for a constant length ν of the kinetic chain, but in the latter equation ρ must be replaced by ρ_{ii}.

The superposition principle, in a somewhat more general formulation, can also be used for the calculation of the distribution of the block-copolymer with respect to composition. In contrast to the homopolymer, the macromolecules of a binary block-copolymer are characterised by the composition vector $\vec{l}$ (instead of the degree of polymerisation l), whose components l_1 and l_2 are equal to the numbers of monomer units of the first and second type. The corresponding type of elementary homopolymer chain corresponds to each of these types, and the numbers m_1 and m_2 of such chains in the macromolecule can also be regarded as components of the vector $\vec{m}$. When such notation is used, the principal relations (3)–(6) of the superposition principle retain their significance if one goes over in them from the scalar variables l and m to the vector variables $\vec{l}$ and $\vec{m}$. As a result of this, it is sufficient to find a generating function $U(\vec{x}, t)$ of the distribution of polymer chains with respect to the vector $\vec{m}$ characterising them. The solution of the given problem leads to the following expression for this function $U(x_1, x_2)$:[31]

$$\frac{\rho_{01}\rho_{10}x_1 + \rho_{02}\rho_{20}x_2 + (\rho_{01}\rho_{12}\rho_{20} + \rho_{02}\rho_{21}\rho_{10} - \rho_{01}\rho_{22}\rho_{10} - \rho_{02}\rho_{11}\rho_{20})x_1x_2}{1 - \rho_{11}x_1 - \rho_{22}x_2 + (\rho_{11}\rho_{22} - \rho_{12}\rho_{21})x_1x_2}. \tag{38}$$

The subsequent substitution in this formula, instead of x_1 and x_2, of the generating functions $<g_1(s_1)>$ and $<g_2(s_2)>$ of the distributions with respect to the lengths of the elementary chains of each of the two types yields an expression for the generating function $G_N(\vec{s})$ for the required distribution $f_N(\vec{l}, t)$.

The average number $\bar{m}_1$ and $\bar{m}_2$ of the elementary chains of both types per polymer molecule can be calculated simply from Eqn. (38):

$$\frac{\bar{m}_1}{\Pi}=\frac{\rho_{12}+(\rho_{11}+\rho_{21})\rho_{10}}{\rho_{12}\rho_{20}+\rho_{21}\rho_{10}+\rho_{10}\rho_{20}},\quad \frac{\bar{m}_2}{\Pi}=\frac{\rho_{21}+(\rho_{22}+\rho_{12})\rho_{20}}{\rho_{12}\rho_{20}+\rho_{21}\rho_{10}+\rho_{10}\rho_{20}}. \quad (39)$$

They define the average composition of the block-copolymer:

$$\langle\zeta_i\rangle=\langle\nu_i\rangle\bar{m}_i/(\langle\nu_1\rangle\bar{m}_1+\langle\nu_2\rangle\bar{m}_2)\quad (i=1, 2). \quad (40)$$

where $2<\nu_1>$ is the average length of the elementary chain of the i-th type.

The quantities e_1 and e_2, equal to the fractions of the monomer units of each type forming part of the composition of the homopolymers formed during the synthesis as side products, are important process characteristics. Theory yields simple expressions for these quantities:

$$e_i=\Pi\rho_{0i}\rho_{i0}/C_i^0\theta_i(1-\rho_{ii})^2\quad (i=1, 2), \quad (41)$$

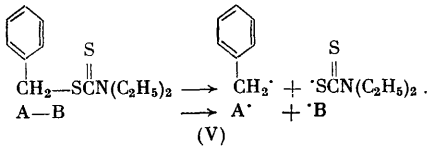
They are suitable for the estimation of the efficiency of the practical employment of various polyinitiators in the synthesis of block copolymers.

III. Iniferters

1. Introduction

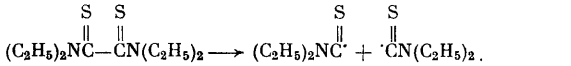
The term "iniferters", proposed first by Otsu and co-workers,[33] is a result of the combination of three words: *Ini*tiator–Trans*fer* agent–*Ter*minator. A characteristic feature of an iniferter is that it participates in all three reactions mentioned above: initiation, chain transfer, and chain termination. Certain features of the polymerisation of monomers such as styrene, methyl methacrylate, methyl acrylate, etc. in the presence of a whole series of such compounds have now been investigated. Among them, mention may be made of various phenylazomethanes, dithiocarbamates, disulphides, etc.[33–50] The studies by Japanese workers and especially those by Otsu and co-workers,[33,34,36,41–52] who discovered a series of characteristics of the polymerisation with participation of iniferters, are outstanding among these investigations. The extensive possibilities of the use of these compounds for the molecular design of polymers synthesised has also been demonstrated.[42,44,45,50–52]

A common feature of all iniferters, regardless of their structure, is the presence in their molecules of labile interatomic bonds capable of decomposing under the conditions of the synthesis with formation of a pair of primary radicals at least one of which is not converted into the polymeric radical although it does participate in chain termination reactions. *S*-Benzyl-*N*,*N*-diethyldithiocarbamate can be quoted as an example of an iniferter:



(V)

It has been used to initiate the photopolymerisation of styrene.[49,55–57] The decomposition of a molecule of this initiator affords two primary radicals, A (benzyl) and B (dithiocarbamyl), with appreciably different chemical reactivities. The primary active radical A is capable of further growth after the addition of the monomer to it, while the second primary radical B hardly reacts with the monomer under the conditions of the synthesis as a consequence of its unduly low reactivity. Apart from such asymmetric compounds, there exist also symmetrical iniferters of the type of tetraethylthiuram disulphide:



(VI)

On decomposition, they afford two identical inactive radicals B. Together with the recombination of radicals of this type with one another at a fairly low concentration, they can combine with the monomer and can thus initiate polymerisation. Depending on what is the main cause responsible for the decomposition of the labile bond, thermo- and photo-iniferters are distinguished. The ability of various chemical compounds to function as iniferters of each of these types has been discussed in a review by Australian workers.[59]

2. The mechanism and kinetics of polymerisation

During the process with participation of an iniferter, polymer chains containing a fairly labile bond at the end are formed. Subsequently each of these bonds can break down under the influence of heat or light with formation of a macroradical and a small radical B, incapable of initiating a new polymer chain. On the other hand, after the addition of a certain number of monomer species, the macroradical recombines with the stable radical B and is converted into a polymeric macroiniferter molecule. The latter decomposes again into a pair of radicals differing significantly in their reactivity, and so on. In conformity with this picture of stepwise polymerisation, each polymer chain exists in succession in two states: the live state (as a macroradical) and the dead state (as a macromolecule). Since the polymer chain lives for a very short time, compared with its inactive state, one can assume that it grows in separate steps. In each such step, the molecular weight increases exactly by one length of the elementary chain.

The characteristic features of the mechanism of radical polymerisation in the presence of iniferters can be understood by resorting to the general kinetic scheme for this process, which assumes the following form, for example, in the case of an asymmetric iniferter I of type (V):

$$\begin{aligned}
&(a)\ \mathrm{I}\xrightarrow{k_d'}\mathrm{A}+\mathrm{B}\ \text{chain initiation}\\
&\left.\begin{aligned}(b)\ &\mathrm{A}+\mathrm{M}\xrightarrow{k_{pA}'}\mathrm{R}(1)\\ (c)\ &\mathrm{R}(l)+\mathrm{M}\xrightarrow{k_p}\mathrm{R}(l+1)\end{aligned}\right\}\text{chain propagation}\\
&\left.\begin{aligned}(d)\ &\mathrm{R}(l)+\mathrm{R}(n)\xrightarrow{k_{tc}}\mathrm{P}(l+n)\\ (e)\ &\mathrm{R}(l)+\mathrm{R}(n)\xrightarrow{k_{td}}\mathrm{P}(l)+\mathrm{P}(n)\\ (f)\ &\mathrm{R}(l)+\mathrm{B}\xrightarrow{k_t'}\mathrm{P}(l)\mathrm{B}\\ (g)\ &\mathrm{B}+\mathrm{B}\xrightarrow{k_t''}\mathrm{BB}\end{aligned}\right\}\text{chain termination}\\
&\left.\begin{aligned}(h)\ &\mathrm{R}(l)+\mathrm{I}\xrightarrow{k_t}\mathrm{P}(l)\mathrm{B}+\mathrm{A}\\ (i)\ &\mathrm{R}(l)+P(n)\,\mathrm{B}\xrightarrow{k_{PB}}\mathrm{P}(l)\,\mathrm{B}+\mathrm{R}(n)\end{aligned}\right\}\text{chain transfer}\\
&(j)\ \mathrm{P}(l)\,\mathrm{B}\xrightarrow{k_d}\mathrm{R}(l)+\mathrm{B}\qquad\text{chain reinitiation}.
\end{aligned}\quad (42)$$

Apart from the usual reactions of traditional radical polymerisation, this scheme includes the reinitiation reaction (*j*), which constitutes the main feature of the process considered. A second important feature of the process is that the chain termination in it is effected solely by reaction (*f*) via the recombination of the polymeric and inactive primary radicals.

Indeed, rigorous analysis of the kinetic equations correpsonding to Scheme (42) has shown[55] that the chain termination reactions (*d*), (*e*), and (*g*) can be frequently neglected compared with reaction (*f*). The condition for such neglect is a sufficiently high value of the dimensionless parameter $\Phi = k_t'(k_t k_t'')^{-1/2}$, which depends solely on the elementary chain termination constants. This condition is always fulfilled, because the above constants for diffusion-controlled reactions are linked, in terms of order of magnitude, by the relations $k_t'' \sim k_t' \sim (10^2-10^3)k_t$.

The theoretical expressions for the rate of polymerisation under the influence of iniferters,[55] i.e.

$$W = k_p M\sqrt{I/k_t^e}, \text{ where } k_t^e = k_t\Phi, \qquad (43)$$

have the same form as for traditional polymerisation. The only difference is the replacement of the usual termination rate constant k_t by its effective value k_t^e. The ratio of the latter to the former is equal to Φ and therefore even for the same rate of initiation I the use of iniferters retards the rate of polymerisation by more than an order of magnitude compared with the usual initiators.

The systems in which the rate constant k_d for the breakdown of the terminal labile bond in the molecule is independent of its length and is identical with the constant k_d' for the decomposition of the iniferter are simplest. For ideal systems, where the familiar Flory principle[21] holds for all the elementary reactions, the reduced rate of polymerisation

$$W/M = k_p\sqrt{k_d C^0/k_t^e}, \quad I = k_d C^0 \qquad (44)$$

is constant and proportional to the square root of the initial iniferter concentration C_I^0.

Together with ideal systems, where this condition holds,[41,47] a considerable number of monomer + iniferter pairs have been observed experimentally for which the rate of polymerisation varies from the very beginning of the process.[41,42,44] A typical form of the kinetic curve for such non-ideal systems is illustrated in Fig. 5. It shows that in the initial stage of the conversion, the rate of its change diminishes, starting from an initial value W_0, gradually attaining a stationary value W_S.

In order to account for this form of the kinetic curve, the hypothesis of the possible breakdown of the Flory principle in the polymerisation initiation reactions with participation of certain iniferters was put forward and justified experimentally.[55] For this purpose, the rate of decomposition of the terminal labile groups within narrow fractions of macroiniferters of different molecular weight, obtained in the course of the photopolymerisation of styrene in the presence of compound (V), was measured by the spin trapping method.[55–57] The results of this experiment, presented in Fig. 6, demonstrate a fairly sharp decrease in the reinitiation rate constant k_d with increase in the number of units l of the oligoiniferters up to a certain limiting value k_d for values of l exceeding ~100 units. After the attainment during the polymerisation process of P_N close to 100, the rate of polymerisation actually attains a constant value, in full agreement with Eqn. (43). The latter predicts also a proportionality between the initial (W_0) and stationary (W_S) rates of polymerisation and the square root of the concentration of iniferters. This conclusion was confirmed experimentally[55–57] in relation to the photopolymerisation of styrene in the presence of the iniferter (V) over a wide range of concentrations of the latter. Furthermore, it was found that the observed experimental ratio W_0/W_S is virtually constant in this range and equal to approximately three. This in fact agrees with the theoretical predictions, if one takes into account the dependence of the rate constants k_d for the decomposition of macroiniferters on their length illustrated in Fig. 6.

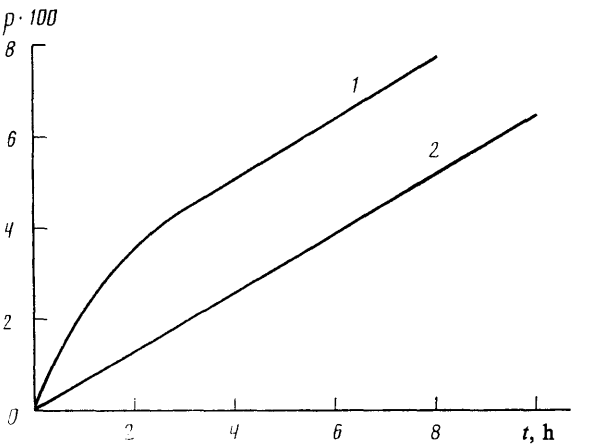


Figure 5. Kinetic curves for the photopolymerisation of styrene in solution in benzene in the presence of the iniferter (II) (curve *1*) and the macroiniferter (curve *2*) containing about 170 styrene units.[55–57]

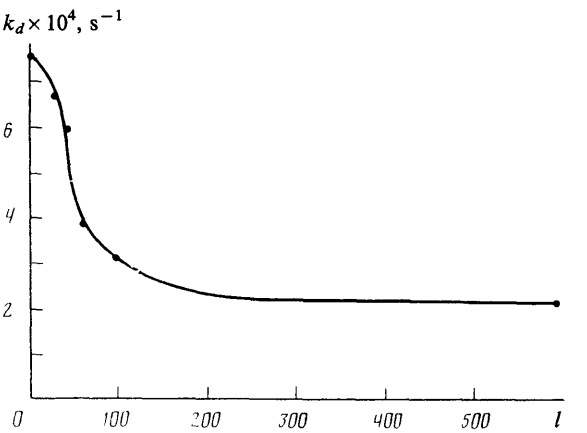


Figure 6. Dependence of the rate constant for the decomposition of the labile bond in the macroiniferter (oligostyrene with a terminal thiocarbamate group) molecule on the degree of polymerisation of the latter.[55–57]

Since this dependence in the given system is important only for macroiniferters whose length is less than 100 units, in the case of the initiation and polymerisation by higher-molecular-weight homologues

one may expect a constant rate of polymerisation W from the very beginning of the process. Furthermore, this value of W should agree with the stationary rate of polymerisation W_S carried out under the same conditions in the presence of the low-molecular-weight iniferter (V). Indeed, the experimental kinetic curve *2* in Fig. 5 fully confirms these theoretical conclusions.

The very fact that there is virtualy no chain termination via the interaction of polymeric radicals with one another during polymerisation in the presence of the iniferter leads to interesting conclusions concerning the kinetics of certain extremely important industrial processes. These include the polymerisation of vinyl monomers in bulk, which is of great interest in the manufacture of plastics and especially organic glasses. During such processes, a sharp increase in the rate of polymerisation is usually observed in the region of moderate conversions, which can exceed by several tens its initial value. This phenomenon, referred to as the "gel effect", is extremely undesirable in the planning of industrial manufacturing processes, because it induces overheating in the reaction system and the impairment of the operating parameters of the polymer.

The cause of the "gel effect" is the appreciable decrease in the rate constants k_t for reaction (*d*) and (*e*) in Scheme (42) associated with the significant retardation of the mutual diffusion of the macroradicals when the solution becomes concentrated as a result of the conversion of the monomer into the polymer. Since in the course of polymerisation with participation of an iniferter these chain termination reactions do not play a significant role, there is every reason to expect the absence of the "gel effect" in such processes. This theoretical conclusion was convincingly confirmed[58] in the bulk polymerisation of styrene and methylmethacrylate in the presence of *N,N,N',N'*-tetraethylthiuram disulphide as the iniferter.

In conclusion of this section, it is natural to formulate the quantitative conditions for the applicability of the iniferter mechanism of radical polymerisation decribed above. Here it is most important to answer the question whether or not a specific initiator will manifest the properties of an iniferter. This depends both on the occurrence of the reinitiation reaction and on the choice of the reaction pathway for the less reactive of the two primary radicals formed on decomposition of the initiator molecule.

This primary radical B has two possibilities of reacting—either with the monomer M or with the polymeric radical R. The predominance of one of these reactions depends on the relation between their probabilities $\mathscr{P}_a = k_{pB}M$ and $\mathscr{P}_t = k'_o R$. Evidently, if the activation reaction of the primary radical B predominates, the traditional radical polymerisation occurs. Otherwise, when $\mathscr{P}_a \ll \mathscr{P}_t$, whereupon the chain termination reaction becomes dominant for B, iniferter polymerisation takes place. The range of rates of polymerisation corresponding to this is wider the greater the ratio $k'_{pA}k'_{pB}$ of the rate constants for the addition of the monomer to the active (A) and inactive (B) primary radicals. Only for a sufficiently large difference between the reactivities can the following inequalities hold:

$$1 \ll \frac{W}{W^*} \ll \frac{k'_{pA}}{k'_{pB}}, \text{ where } W^* \frac{k'_{pB}k_p}{k'_t}M^2. \qquad (45)$$

When these inequalities are valid, the iniferter polymerisation mechanism operates. The first inequality implies that the rate of polymerisation must be fairly high compared with the characteristic value W^* so that the primary radicals B do not have enough time to initiate the polymer chains. On the other hand, according to the second inequality, the rate W should be significantly smaller than the quantity $(k'_{pA}/k'_{pB})W^*$ to rule out the chain termination by the primary radicals A which leads to the formation of polymer molecules incapable of reinitiation.

3. The molecular weight distribution and its characteristics

In the iniferter mechanism of polymerisation, the macromolecules consist of several elementary chains. This makes it possible to employ the superposition principle formulated in Section II.3 for the calculation of the molecular weight of the polymer in ideal systems. The generating function

$$U(x, t) = [e^{(x-1)\tau} - e^{-\tau}]/[1 - e^{-\tau}], \text{where } \tau = k_d t, \qquad (46)$$

found neglecting the chain transfer reactions, leads to the simple expressions

$$P_N = \frac{\tau\langle\nu\rangle}{1 - \exp(-\tau)}, \quad K = \frac{[1 - \exp(-\tau)]}{\tau}\left[\tau + 2\frac{\langle\nu^2\rangle}{\langle\nu\rangle^2}\right] \qquad (47)$$

for the number-average degree of polymerisation and the polydispersity coefficient. An increase in the number of elementary chains in the macromolecule naturally promotes an increase in their molecular weight and a narrowing of the molecular weight distribution, which can be seen from Eqns. (47). However, the opposite effects are induced by a decrease in the course of the polymerisation of the length $\nu = \nu^0 M/M^0$ of the kinetic chain from its initial value $\nu = \nu^0$ to $\nu = 0$ when the monomer concentration changes from M^0 to 0. When account is taken of this effect, Eqns. (47) assume the following form:

$$P_N = \frac{\nu^0(1 - e^{-\beta\tau})}{\beta(1 - e^{-\tau})}, \quad \beta = \frac{C^0}{M^0}\nu^0, \quad \nu^0 = \frac{k_p M^0}{(k_t \Phi k_d C^0)^{1/2}}; \qquad (48)$$

$$K = (1 - e^{-\tau})[\beta \operatorname{cth}(\beta\tau/2) + 1]. \qquad (49)$$

The quantity P_N increases with time from $P_N^0 = \nu^0$ to $P_N^* = \nu^0\beta^{-1}$, where the parameter β^{-1}, having the significance of the average number $\bar{m}$ of elementary chains in the macromolecule of the final polymer, can be fairly large in the iniferter polymerisation mechanism. In this case, the limiting value $K = 1 + \beta$ of the polydispersity coefficient [Eqn. (49)] corresponding to $\tau \to \infty$ differs little from unity, which indicates a fairly high degree of uniformity of the molecular weight distribution of the final polymerisation product. Eqns. (48) and (49) predict a monotonic time variation of the quantities P_N and K. As regards the molecular weight distribution function, an explicit expression can be quoted for it in two important cases. One of them refers to the region of initial conversions:

$$f_N(l, t) = (\tau/\nu^0)\exp[-\tau(z/\tau - 1)^2]\psi(z),$$
$$\psi(z) = \exp(-2z)I_1(2z)/z, \quad z = (l\tau/\nu^0)^{1/2}, \qquad (50)$$

where I_1 is a modified first-order Bessel function of the first kind. The other describes the final polymerisation products:

$$f_N(l, \infty) = [\nu^0\Gamma(1/\beta)]^{-1}(l/\nu^0)^{1/(\beta-1)}\exp(-l/\nu^0), \qquad (51)$$

where Γ is the Euler gamma-function.

The inclusion in the consideration of reactions (*h*) and (*i*) of Scheme (42), which take into account the chain transfer to the iniferter, leads to only non-fundamental modifications of Eqns. (46)–(49). They all retain their form as functions of τ when the average length ν of the kinetic chain is replaced in them by the average length $\nu[1 + k_1 C^0(k_t \Phi k_d C^0)^{-1/2}]^{-1}$ of the elementary chain.

In the more general model of ideal polymerisation, the labile bonds in the initial iniferter and in the polymer molecules differ kinetically. For a large difference $k'_d \gg k_d$ between the rate constants k'_d and k_d for their decomposition reactions, the polymerisation will actually occur in two stages. In the first comparatively short stage, all the molecules of the initial iniferter decompose and macromolecules, each of which consists of exactly one elementary chain, are formed. During the second, longer stage, these macroiniferter molecules initiate further polymerisation. Here it is significant that the molecular weight distribution of the products formed is initially broadened and then narrowed. Such non-monotonic variation of the polydispersity coefficients k is possible in systems where the rate constant k_d for the breakdown of the labile bond diminishes fairly sharply as a function of the length of the macroiniferter molecule containing it. This theoretical conclusion follows from the solution of the system of kinetic equations quoted[55] for an arbitrary $k_d(l)$ relation. The experimental $K(t)$ curves obtained for the polymerisation of styrene in the presence of the iniferter (V)[56] pass in certain cases through a maximum, confirming the theoretical conclusions.

One of the most characteristic features of polymerisation with participation of iniferters is the linear increase with the degree of conversion p of the number-average molecular weight of the products formed.[38,41–43,48,53–57] This relation $P_N = (M^0/I^0)p$ follows directly from the iniferter polymerisation mechanism itself in the range of conversions $p \gg p^* = k_p(I^0/k_t\Phi k'_d)^{1/2}$, where there is virtually no initial initiator in the reaction system. Since each initiator molecule initiated the polymer chain on decomposition, the concentration of such chains corresponding to $p \gg p^*$ is identical with I^0.[42,44–45,53–57] For fairly low conversions, comparable to p^*, the expression $P_N = (M^0/I^0)p$ is naturally invalid because in this range of conversions the number of polymer chains increases with conversion. A correct extrapolation of the variation of P_N to the point $p = 0$ yields $P_N = \nu^0 = k_pM(k_t\Phi k'_dC^0)^{-1/2}$, which reflects the fact that the macromolecules formed at the very beginning of polymerisation consist of only one elementary chain.

In conclusion of Section III, one may say that at present there is sufficient experimental justification of the main features of the iniferter polymerisation mechanism. Naturally, in individual specific processes there is a possibility of side reactions which are not represented in Scheme (42) and which must be taken into account in kinetic calculations for the polymerisation and the molecular weight distribution of its products. Allowance for these side reactions involves the specific features of a particular monomer–iniferter pair, each of which can differ in its non-fundamental characteristics. On the other hand, the most characteristic general features typical for the iniferter polymerisation mechanism are reflected by its simplest kinetic Scheme (42).

IV. Conclusion

Radical polymerisations in the presence of polyfunctional initiators and iniferters have a whole series of common features despite the fundamental differences between the mechanisms of the formation of polymer chains. We shall now list the main features of this kind which distinguish these processes from the usual polymerisation with participation of traditional initiators.

The most important feature is the continuous growth of the molecular weight of the polymer with conversion, which is described by a linear law for a fairly large average number of elementary chains in the macromolecule. Under these conditions, the initial initiator disappears in the very early stages of the process, after which the number of polymer chains remains unchanged and only their length increases.

The second common feature of the processes is that the mechanism of the formation of macromolecules during polymerisation promotes a decrease in the conversion-induced broadening of the molecular weight distribution associated with the exhaustion of the concentrations of the monomer and initiator during the process. For the same reason, one should expect an appreciable increase in the non-uniformity, as regards composition, of the products of joint polymerisation obtained at advanced conversions.

The third common feature of the two processes is the formation during them of macroinitiator molecules, which are capable, after liberation, of promoting further growth of the molecular weight under appropriate conditions on coming into fresh contact with the monomer. This property makes it possible to employ both types of non-traditional initiators for the synthesis of block-copolymers. Polyperoxides make it possible under these conditions to obtain macromolecules with a fairly large number of blocks, while iniferters are used to obtain diblock copolymers.

The principal disadvantages of polyfunctional initiators are the ineffectiveness of their use in the polymerisation of monomers of the type of methyl methacrylate, where the fraction of radicals destroyed via the disproportionation mechanism is fairly large. The polymerisation initiated by iniferters is free from this disadvantage. The use of iniferters makes it possible, in addition, to eliminate almost completely the undesirable "gel-effect", manifested in the bulk polymerisation reactions of certain monomers. Polyperoxides do not allow this.

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