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# Polyfunctional components in radical polymerisation and in the preparation of polymer compositions

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ABSTRACT. The possibilities in the use of polyfunctional components in polymerisation systems are surveyed and analysed in the present review. The kinetics and mechanisms of the chemical reactions of polyfunctional monomers, initiators, emulsifying agents, and modified reactive fillers in radical polymerisation are examined. The kinetics and mechanism of polymerisation in systems with polyfunctional emulsifying agents or modified fillers are considered from the standpoint of considering them as locally organised systems with a regulated distribution of components.

A classification of polyfunctional components based on the available data is proposed.

The bibliography includes 90 references.

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## I. Introduction

The development of optimum procedures for the preparation of various polymers or polymer systems by radical polymerisation has been achieved over several decades on the basis of the theory of radical reactivity and the advances in technology. As a result, the view has been established in practice that the optimum components for the preparation of polymers ensuring the necessary molecular structure and properties of the product and a satisfactory reproducibility of the process are monofunctional components—monomers, initiators, regulators, emulsifying agents, etc. Indeed, in recipes for polymerisation systems using monofunctional components, the highest selectivity of the polymerisation process is achieved and possible side reactions, associated with polyfunctionality and introducing disturbances and defects into the structure of the macromolecules formed, are eliminated. These factors account for the fact that in the course of a long period efforts in the research into radical polymerisation processes and in the development of procedures for polymerisation systems were directed to the study of the reactivity of functional groups and the possibility of regulating it for monofunctional compounds—monomers, initiators, emulsifying agents, etc. By the beginning of the 1960's, the construction of an elegant theory of radical polymerisation, which has since become classical, ensuring the development of a technology for many large-scale processes involving the synthesis of polymers and polymer systems, was completed. This was the reason for the temporary loss of interest by investigators in radical polymerisation processes.

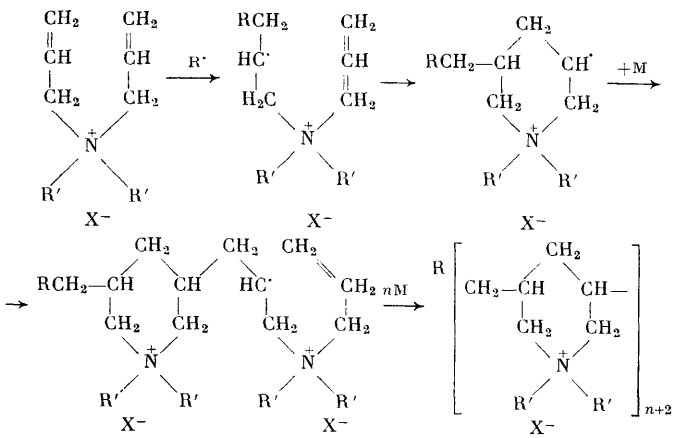
However, for some time there has been a renewed growth of interest in radical polymerisation processes. On the one hand, this has been reflected in the new scientific field of complex-radical polymerisation,[1–3] which suggested ways of controlling the elementary reactions in radical polymerisation via the formation of complexes by monomer molecules and the radicals. On the other hand, investigators have become interested in polymerisation systems involving the use of components (monomers, initiators, and emulsifying agents) of the polyfunctional type, capable of reacting via different functional groups.[4–7] Such polymerisation systems make it possible to reduce the number of components in procedures for polymerisation systems, for example, by combining the functions of the monomer and initiator in one molecule, to simplify the technology of the process, and to obtain reactive polymer systems with new chemical structures, capable, without special additives, of further chemical or structural changes. Such polymers can be used to obtain block-copolymers or graft polymers[4,5,7] in processes involving the liquid-phase formation of polymer articles,[8,9] for the creation of rubbers capable of self-induced structure formation,[10] etc.

Yet another important consideration has been developed very recently. Using polyfunctional components in polymerisation systems, it is possible to achieve under appropriate conditions a consecutive series of reactions via the appropriate functional groups and the formation of a pre-specified structure of the polymer matrix produced. This approach makes it possible to devise specific rules for the preparation of linear, comb or three-dimensional macromolecules with a particular branching density, reactive oligomers or polymers, and hence block-copolymers based on them. Thus, it is possible to devise procedures for regulating the structure of the macromolecular systems formed in the polymerisation process and to some extent also procedures for macromolecular design.

Numerous results of studies of the kinetics and mechanism of the polymerisation of systems with polyfunctional components have accumulated during the last 15 years. A survey of such data has become not only realistic but also desirable. In the present review, we attempt to consider the main advances in the use of polyfunctional components in polymerisation systems. Naturally, whilst endeavouring to achieve an objective analysis, the author is not always able to avoid a subjective view on the problem, which is reflected also in the treatment and selection of data. Nevertheless, the author hopes that the review will be of interest to a wide range of specialists in the field of the synthesis of polymers.

## II. Polyfunctional monomers

Polyfunctional monomers include those whose molecules contain, apart form the polymerisable double bond, also another functional group (or other functional groups). Monomers with conjugated double bonds (butadiene, isoprene, etc.) can also be classified as polyfunctional monomers (PFM). Bearing in mind that information about such monomers is widely available in the literature on rubbers,[11] we shall not discuss the characteristic features of their reactions. As regards polyfunctional monomers with non-conjugated double bonds, the results of systematic studies on the intramolecular and intermolecular mechanisms of chain propagation in the polymerisation of non-conjugated dienes have been included in numerous other reviews and monographs[12,13] and were subsequently revised in a more recent publication.[14]



The cyclisation process in the polymerisation of various conjugated dienes can also proceed vigorously with formation of six-membered[13] and five-membered[14] rings or may not occur at all. The characteristic features of the polymerisation of alkene-alkyne polyfunctional monomers are determined by their structure. The polymerisation process usually involves a double bond with formation of reactive macromolecules with multiple bonds in the side chain which subsequently readily form a structured system.

In the last two decades, there has been a wide-scale growth of interest in monomers with peroxy-groups, which arose as a result of the studies by Yurzhenko and his school.[10,15–25] Monomers involving a combination of peroxy-groups of different structure in their molecules have been synthesised. This made it possible to regulate within certain limits the reactivity of the multiple bond and of the initiating peroxy-group.

In the first studies, the polymerisation of peroxides of the polyfunctional monomer type was achieved by simply heating them or by initiating the process by their own peroxy-groups. The polymerisation proceeded up to a conversion of 20–50%, after which the reaction mixture decomposed with formation of gaseous products without the formation of the polymer.

In copolymerisation with other monomers, a decrease in the rate of polymerisation and in the molecular weight of the copolymer formed with increase in the concentration of the peroxide monomer was observed, which made it possible to put forward the hypothesis of weak inhibiting effects of the peroxide monomer in the polymerisation process as a result of the degradative chain transfer to the peroxide monomer with formation of a less reactive radical.[17,18]

In self-initiation without the addition of another initiator, the polymerisation process is complicated by structure formation in the polymer, which precludes a reliable determination of the molecular weight and of the structure of the polymer formed. Because of this, the subsequent study of the polymerisation of peroxide monomers was carried out using another lower-temperature initiator and temperatures permitting the maximum retention of the peroxy-groups of the polyfunctional monomer in the unreacted state. The conditions for the preparation of virtually unbranched soluble copolymers of styrene with unsaturated esters of α-hydroxydialkyl peroxide containing peroxy-groups in the side chain were thus established.[19] Comb graft polymers can be readily obtained from such polymers.[20]

New procedures for the preparation of impact-resistant polystyrene plastics, (including ABS-plastics),[5,22,23] synthetic rubbers capable of sulphur-free vulcanisation, benzene- and oil-resistant cured rubbers, reactive oligomers, reactive latexes, and other polymer systems of practical importance have been proposed on the basis of polyfunctional monomer peroxides.[5,10,15,24,25]

The data presented above demonstrate the possibility of using polyfunctional monomers for the synthesis of branched and cross-linked polymers and copolymers and for the preparation of microheterogeneous polymer systems with a controllable microheterogeneity.

## III. Polyfunctional initiators of radical polymerisation

Polymer systems based on polyfunctional components have been developed most vigorously in the last two decades using polyfunctional initiators.[4–7] Compounds (Table 1) whose molecules contain two or more groups capable of generating free radicals initiating the polymerisation process, or containing, apart from the initiating group, other functional groups capable of subsequent chemical reaction can be classified as polyfunctional initiators (PFI). Peroxides and azo-compounds of different structure have come to be most widely used as polymerisation initiators. Peroxides and azo-compounds with functional group substituents, for example, di-, oligo- and polyperoxides,[4,5,7,9] di- and poly-azo-compounds,[4,5,7,9] azoperoxides,[5,7,9] as well as peroxides or azo-compounds containing other reactive functional groups (hydroxy-, carboxy-, etc.,[4,7,9]) have been most widely used as polyfunctional initiators. Polyfunctional initiators of the last type do not differ, as regards the mechanism of their initiating action in polymerisation, from monofunctional initiating systems and are normally used in the preparation of reactive oligomers and polymers with functional end groups. They have been examined in detail in other reviews.[7,9]

Polyfunctional initiators of the type of di- and poly-peroxides have been studied systematically by Ivanchev and co-workers[4–6,9,26–30,36–39] and Tsvetkov and co-workers.[31–34]

In the study of the initiating capacity of diperoxides with structurally identical peroxy-groups separated by aliphatic bridges, it has been shown that the kinetics of the thermal decomposition of peroxy-groups can be characterised by a single set of parameters.[4,26] As shown in Fig. 1, the rate constants for the decomposition of diperoxides based on aliphatic dibasic acids depend on the length of the methylene bridge $n$ between the peroxy-groups, the rate constant increasing with increase in $n$ from 1 to 6 and subsequently remaining unchanged for $n \geqslant 6$.

**Table 1. Polyfunctional components of polymerisation of systems.**

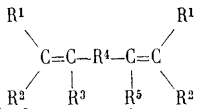
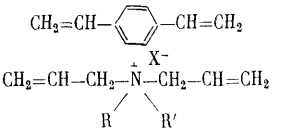
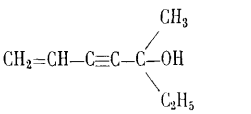
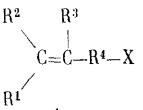
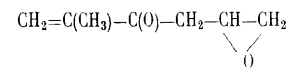
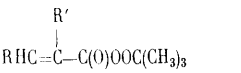
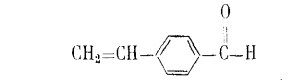
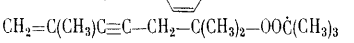
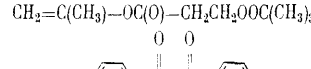
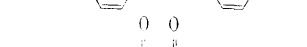
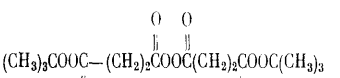
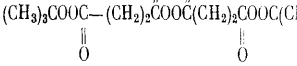
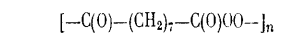
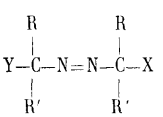
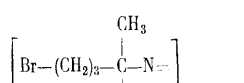
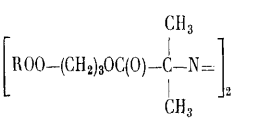
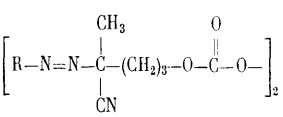
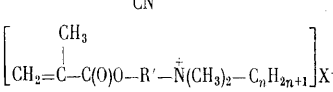
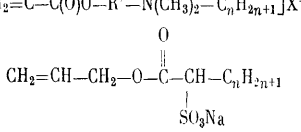
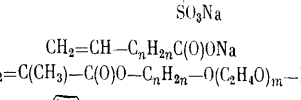
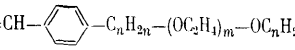
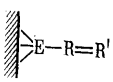
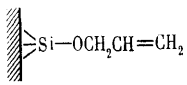
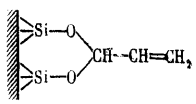
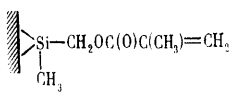
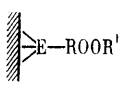
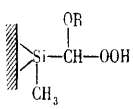
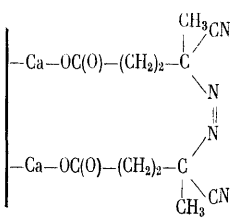
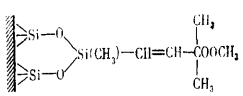
| Class of compound | Chemical formula | Examples of compounds |
|---|---|---|
| Non-conjugated dienes |  $R^1$, $R^2$, $R^3$, $R^5$ = Alk or H; $R^4$ = Alk; X = halogen |  |
| Alkene – alkyne systems | $CH_2=CR-C\equiv C-CRR^1R^2$ |  |
| Monomers containing other reactive groups |  $R^1R^2R^3$ = Alk or H; $R^4$ = Alk or Ar; X = functional group |     |
| Peroxides | $X'ROO-RX$ X, X' = functional groups |      |
| Azo-compounds |  R = Alk; R' = Alk or CN |   |
| EM-monomers | |          |

**Table 1** (contd.).

| Class of compound | Chemical formula | Examples of compounds |
|---|---|---|
| EM-initiators | | $R(OCH_2CH_2)_nOC(O)-CH_2CH_2-C(O)OC(CH_3)_3$<br>$R(OCH_2CH_2)_nOC(O)-CH=CH-CH_2$<br>$CH_2$ C C–$R^2$<br>$R^1-C=O$ O O OOH<br>$ROO-(CH_2CH_2O)_n-H$<br>$RC(O)OOC(O)CH_2CH_2C(O)(OCH_2CH_2)_nOC(O)-CH_2CH_2C(O)OOC(O)R$<br>$CH_3(CH_2)_6-C(OOH)-CH=CH-(CH_2)_7C(O)ONa$ |
| Filler-monomers |  | <br><br> |
| Filler-initiators |  | <br><br> |

The rate of polymerisation initiated by diperoxides varies in parallel with their $k_{decomp}$. A model has been proposed recently[35] which describes the rates of formation of various growing radicals and molecules in the polymerisation of styrene initiated by diperoxide initiators. The unimodal nature of the molecular weight distribution of the polymers formed, the slight increase in the molecular weight of the polymer with increase in the degree of conversion, and the inadequate fraction of polymers formed with terminal peroxide fragments lead to the conclusion that diperoxides with identical structures of peroxy-groups differ little as regards the mechanism of the initiating action from monoperoxides and are relatively ineffective in processes involving the formation of reactive polymers with peroxy-groups.[4,26]

It has been shown[31–34] that in the case of diacyl oligo- or polyperoxides the decomposition of peroxy-groups takes place statistically at rates which depend on the length of the bridge between the peroxy-groups and involve the insertion of polyperoxide fragments, and not individual peroxy-groups, into the macromolecule produced.

The degree of retention of the undecomposed peroxy-groups depends on the decomposition time and the process temperature. Systems of this type used as initiators make it possible to obtain reactive polymers and block-copolymers, but work with them entails a series of experimental difficulties because of the dangerous properties of polyperoxides.

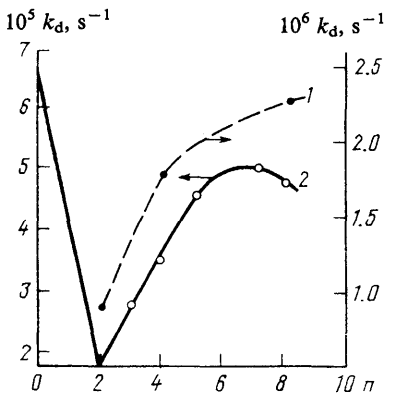



**Figure 1. Dependence of the decomposition rate constant $k_d$ on the length of the methylene bridge $n$ between the peroxy-groups of peresters (1) and diacyl peroxides (2) based on unsubstituted aliphatic acids.**

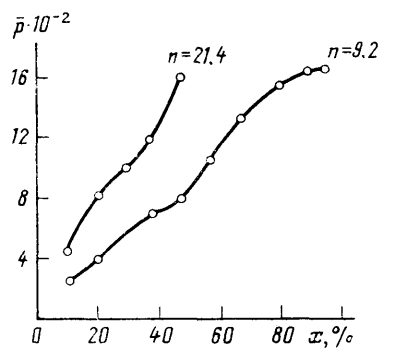



**Figure 2. Dependence of the average degree of polymerisation $\bar{p}$ of polystyrene on the degree of conversion $x$ for different "functionalities" of the initiator $[OOC(CH_2)_5COOCHBr(CH_2)_4C(O)-]_n$ (initiator concentration 0.025 M, temperature 80 °C).**

In order to eliminate these difficulties, bifunctional[4,27,36] and oligomeric[4,28,30,38] peroxides with peroxy-groups having different thermal stabilities, trifunctional peroxides having the bis-structure,[4,29,37] and azoperoxides[7,9,39–41] have been synthesised and investigated in polymerisation processes. It was shown that, depending on the polymerisation process temperature, new polyfunctional initiators make it possible to obtain polymers containing peroxy-groups in the polymer macrochain, or as end groups (bifunctional and trifunctional systems), or within the macrochain (polyfunctional systems). The rate of polymerisation is determined by the kinetic parameters of the decomposition of the peroxy-groups, whereas the molecular weight of the polymer formed depends on the degree of conversion and increases with polymerisation time. As shown in Fig. 2, the average degree of polymerisation of the polystyrene formed also depends on the "functionality" of the initiator and increases appreciably with the degree of conversion. Differential molecular weight distribution curves likewise vary sharply with the degree of conversion (Fig. 3) and the molecular weight distribution remains fairly narrow at advanced stages of the reaction.

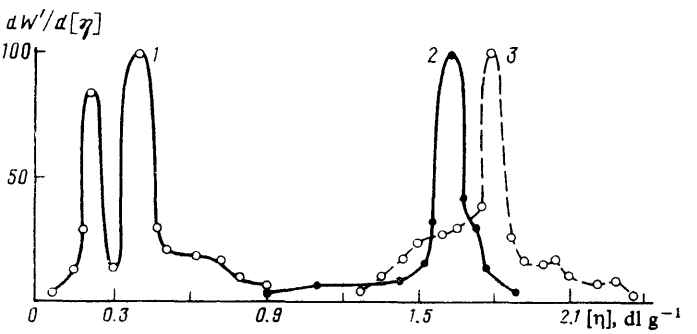



**Figure 3. Differential molecular weight distribution curves for polystyrene obtained in polymerisation initiated by the oligoperoxide $[C(O)(CH_2)_7C(O)OOC(O)CHBr(CH_2)_8C(O)OO]_{18}$. Initiator concentration 0.0125 M; degree of conversion 6% (curve *1*) and 100% (curves *2* and *3*); polymerisation temperature 60 °C (curves *1* and *3*) and 60 and 80 °C under two-stage polymerisation conditions (curve *2*).**

All these data enabled us to put forward a new polymerisation-polyrecombination mechanism of the formation of macromolecules[4] for radical polymerisation initiated by monofunctional initiators. This mechanism reduces to the following elementary reactions:

(1) initiation:

$$PFI \xrightarrow{k_{decomp}} 2R^{\cdot}; \quad R^{\cdot} + M \xrightarrow{k} RM^{\cdot};$$

(2) chain propagation:

$$RM^{\cdot} \xrightarrow[k_p]{nM} RM^{\cdot}_{n+1};$$

(3) chain termination:

$$RM^{\cdot}_{n+1} + RM^{\cdot}_{m} \begin{cases} \xrightarrow{\text{recombination}} \Pi_a \\ \xrightarrow{\text{disproportionation}} \Pi_{1a} + \Pi_{2a} \end{cases};$$

(4) repeated initiation by the initiating groups which have entered the macromolecule (reinitiation):

$$\Pi_a \xrightarrow{k_{decomp}} 2R_p^{\cdot} \xrightarrow{M} R_pM^{\cdot};$$

chain propagation:

$$R_pM^{\cdot} \xrightarrow[k_p]{nM} R_pM_{n+1}^{\cdot} \quad ;$$

chain termination:

$$R_pM_{n+1}^{\cdot} + R_pM_m^{\cdot} \xrightarrow{k_t} \Pi'_a(\Pi'_{1a} + \Pi'_{2a}),$$

$$\Pi'_a \xrightarrow{k_{decomp}} 2R_{p_2}^{\cdot}, \text{ etc.}$$

In the general case, all the elementary reactions should naturally be taken into account in the above scheme including reactions involving chain transfer to the monomer, the polymer, etc., but the reinitiation reactions or reactions involving the repeated formation of initiating radicals of the macromolecules formed, which depend on the functionality of the polyfunctional intiator employed, are decisive and fundamental.

The proposed mechanism of the formation of macromolecules makes it possible to explain the observed kinetics of the initiated polymerisation and the nature of the variation of the molecular weight and the molecular weight distribution of the polymer formed. It is of interest to note that, in the initiation of polymerisation by polyfunctional initiators, the inverse relationship, which follows from the main equation of radical polymerisation, between the rate of polymerisation and the molecular weight of the polymer formed as a function of the increasing initiator concentration may not hold because of the specific features of the mechanism of the formation of macromolecules.

Thus in industrial practice, the optimum process conditions and rate of initiation, ensuring the necessary molecular weight and the appropriate operating properties of the polymer, are selected in the preparation of the principal assortment of polymers. These requirements significantly restrict the possibilities of increasing the productivity of the reactor by increasing the rate of polymerisation as a result of increasing the concentration of the initiator. For polyfunctional initiators, this limitation is manifested to a much lesser extent because if the polyrecombination-polymerisation mechanism of the formation of macromolecules and the significant increase of the molecular weight with increasing degree of conversion. For polyfunctional initiators, it is possible to carry out a polymerisation with formation of a conditioned polymer having a narrow molecular weight distribution even at variable process temperatures.[4,5]

We are now able to predict the average molecular weight and the molecular weight distribution of the polymers formed when polymerisation is initiated by a polyfunctional initiator. Thus equations for the variation of the molecular weight and hence of the molecular weight distribution as a function of the degree of conversion of styrene were derived[42] in a study of the polymerisation of styrene initiated by various polyfunctional initiators. The calculation was performed on the assumption that the peroxy-groups decompose independently of one another, that the decomposition rate constant does not vary, that the radicals are formed effectively in the decomposition reaction, and that the rate of initiation is proportional to the overall concentration of peroxy-groups regardless of the nature of their distribution. The structure of the macromolecules formed during polymerisation constitutes a number of interconnected monomer units separated by peroxide clusters (Fig. 4).

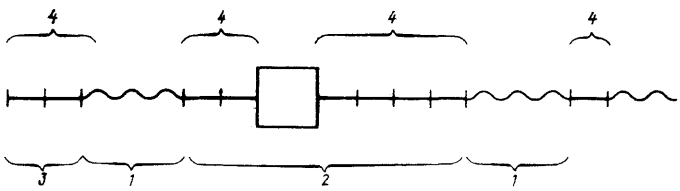



**Figure 4.** Schematic illustration of the structure of the macromolecules of the polymers formed in polymerisation initiated by a polyfunctional peroxide: *1*, elementary polymer chain; *2*, and *3*, closed and semi-open clusters; *4*, peroxide blocks.

Assuming that the contribution of the peroxide clusters to the molecular weight may be neglected because of their small size compared with the sequences of monomer units, the molecular weight distribution can be regarded as a superposition of the distributions of random quantities. As a result, we obtain the following equation for the dependence of the number-average molecular weights on the process time:

$$\frac{\overline{M}_n}{\overline{M}_n'} = \frac{\lambda + 1}{\lambda + 1 - \rho}; \quad \rho = \frac{1 - \sum_{j=1}^{\infty} \alpha_j (1 + \theta)^j}{\theta \sum_{j=1}^{\infty} j\alpha_j}, \qquad (1)$$

where $\overline{M}_n'$ is the number-average molecular weight of the polymer obtained using a simple monofunctional initiator under the same conditions and at the same concentration of $-O-O-$ groups, $\lambda$ the probability of termination as a result of disproportionation, $\alpha_j$ the fraction of initiator molecules containing $j$ peroxy-groups, and $\theta$ the fraction of the effectively decomposed $-O-O-$ groups: $\theta = f(1-e)^{-k_{decomp}t}$ ($f$ is the initiation efficiency).

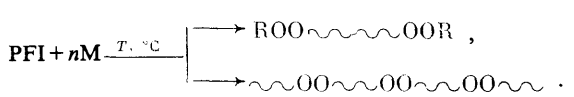
Putting Eqns. (1) in the form

$$\overline{M}_{n\infty} = \overline{M}_n \frac{\lambda + 1}{\lambda + 1 - \rho_\infty}; \quad \rho_\infty = \frac{\left[1 - \sum \alpha_j (1 - f)^j\right]}{\theta f \sum j\alpha_j}, \qquad (2)$$

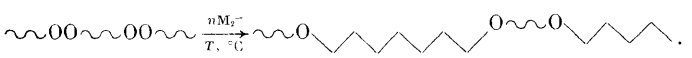
we find that the molecular weight increases continuously from $\overline{M}_n'$ to a limiting value $\overline{M}_{n\infty}$, which depends on the functionality of the peroxide and the initiation efficiency. The experimental confirmation of the validity of the proposed equations is demonstrated in Fig. 5. Somewhat later we carried out a similar calculation by solving differential material balance equations.[43]

The incorporation of the initiating groups into the composition of macromolecules in polymerisation initiated by polyfunctional initiators gives rise to effective possibilities for the preparation of block-copolymers. The essential feature of the mechanism of the formation of block-copolymers reduces to a two-stage process.

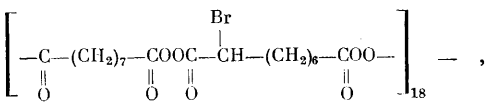
The first stage is the polymerisation of the first monomer using a monofunctional initiator under conditions ensuring the formation of polymer molecules with initiating groups incorporated into the macrochains, for example:



The second stage reduces to the polymerisation of the second monomer $M_2$ initiated by the "active" polymer (macroinitiator) obtained in the first stage.



styrene (polymerisation in block at 60 °C) using a polyfunctional initiator—oligoazelaoyldiperoxy-α-bromoazelaoyl peroxide having the general structure



a study was made of the kinetics of the decomposition of peroxy-groups by the method of inhibitors regulating simultaneously the variation of the average degree of polymerisation in the course of the decomposition of peroxy-groups. As shown in Figs. 6 and 7, the decomposition of the peroxy-groups in the macroinitiator produced is a first-order reaction; there is a simultaneous decrease in the degree of polymerisation of the macroinitiator, which confirms the intermolecular statistical distribution of the initiating groups in the macroinitiator.

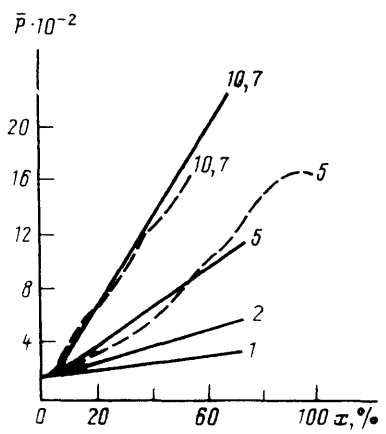



**Figure 5.** Dependence of the average degree of polymerisation of styrene $\bar{p}$ initiated by the oligoperoxide $[C(O)(CH_2)_7.C(O)OOC(O)CHBr(CH_2)_6C(O)OO-]_n$ for different values of $n$ on the degree of conversion $x$ at 80 °C and an initiator concentration of 0.025 M; continuous lines—calculated theoretically; dashed lines—determined experimentally. The numerals opposite the curves correspond to the numbers of peroxy-groups ($n$) in the peroxide.

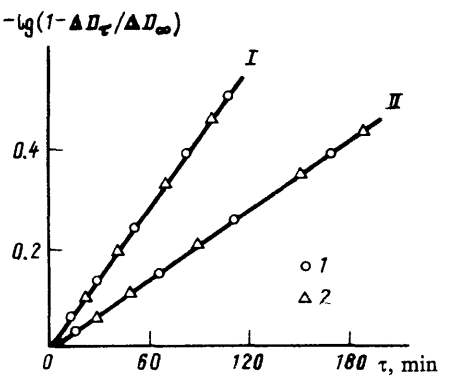



**Figure 6.** Semilogarithmic plots of the decomposition curves for the peroxy-groups in "active" polystyrene obtained in the presence of the oligoperoxide $[C(O)(CH_2)_7C(O)OOC(O)CHBr(CH_2)_6.C(O)OO-]_{18}$ at 80 °C (I) and 75 °C (II); $\Delta D\tau$—the change in the optical density of the inhibitor (iodine) solution during the decomposition of the initiator during a period τ; $\Delta D_\infty$—ditto for the complete decomposition of the initiator.

The dependence of the functionality of the polyfunctional initiator on the number of peroxy-groups in the macroinitiator is fairly simple.[4,5] For bifunctional initiators, there is a possibility of obtaining macromolecules which have on average one peroxy-group, while trifunctional initiators can give rise to macromolecules with two and more initiating groups. Accordingly, the second stage of the block-copolymerisation can give rise to block-copolymers of different structure—from diblock polymers of the type A–B (bifunctional initiators) to multiblock polymers of the type A–B–A–B.

The incorporation of initiating groups into the molecular chain of the macroinitiator formed when a polyfunctional initiator is used has been demonstrated experimentally.[44] For the synthesised and reprecipitated macroinitiator, obtained in the polymerisation of

Naturally, both the distribution of macromolecules with respect to molecular weight and the distribution with respect to the number of initiating functional groups are statistical. The block-copolymer is therefore non-uniform as regards the alternation of blocks.

The structure of the polyfunctional initiator, i.e. the presence in the structure of identical initiating functional groups or such groups differing in reactivity or thermal stability, is important in the synthesis of "active" polymers in the first stage. When polyfunctional initiators with initiating groups having identical structures are used, additional complications arise in the formation of macroinitiators, namely the necessity to restrict the process in time (and hence as regards the degree of conversion) in order to retain at least some of the initiating groups in the macroinitiator.

Polyfunctional initiators with initiating groups having different thermal stabilities, especially when these groups alternate in the molecule, are more convenient for the synthesis of the macroinitiator. The choice of temperature conditions in conformity with the thermal decomposition constant for the more reactive initiating group makes it possible to achieve the first stage of the polymerisation up to high degrees of conversion and to obtain a macroinitiator which is comparatively uniform as regard composition and molecular weight.

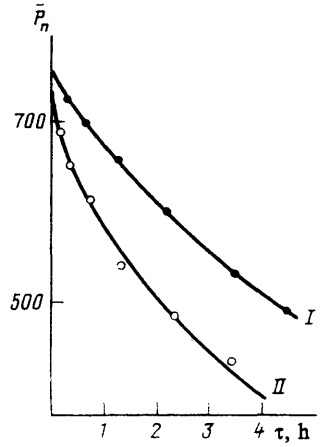



**Figure 7. Variation of the degree of polymerisation of "active" (containing peroxy-groups in the macrochain) polystyrene in the thermal decomposition of peroxy-groups in solution in chlorobenzene in the presence of iodine at 70 °C (I) and 80 °C (II).**

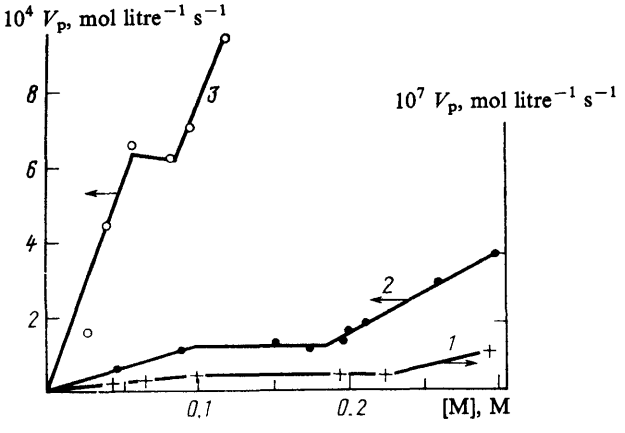



**Figure 8. Dependence of the initial rate of polymerisation of polyfunctional emulsifier salts of methacryloylethylammonium (curves *2* and *3*) and allyl ammonium (curve *2*) at 70 °C on the monomer concentration in water:**

(*1*) $[CH_2{=}CH{-}CH_2\overset{+}{N}(CH_3)_2CH_2COOC_{12}H_{25}]Br^-$;
(*2*) $[CH_2{=}C(CH_3){-}COOC_2H_4\overset{+}{N}(CH_3)_2CH_2COOC_{12}H_{25}]Br^-$;
(*3*) $[CH_2{=}C(CH_3){-}COOC_2H_4\overset{+}{N}(CH_3)_2CH_2COOC_{16}H_{25}]Br^-$.

The block-copolymers formed using a polyfunctional initiator are non-uniform both in molecular weight (molecular inhomogeneity) and in composition (composition inhomogeneity).

The synthesis of block-copolymers using polyfunctional initiators has been described in greater detail in a number of communications,[44–52] while other reports[49–52] give a more detailed account of polyfunctional azo-initiators or azoperoxides.

A calculation of the composition and microstructure of the block-copolymers formed using a polyfunctional initiator with two types of initiating groups differing in thermal stability, taking into account the molecular weight distribution of the macroinitiator formed in the first polymerisation stage, has been proposed.[46] The adequacy of the relations obtained has been tested experimentally.

The above brief analysis shows that the use of polyfunctional initiators of polymerisation makes it possible to improve significantly the possibilities available to us in the synthesis of polymers as a result of the increase in the amount of polymers recovered from a unit volume of the reactor and the preparation of reactive oligomers, polymers, and block-copolymers of different composition based on them.

## IV. Polyfunctional surfactants

Investigators have recently clearly manifested their interest in two types of polyfunctional surfactants—surface-active monomers (SAM), which are compounds exhibiting the properties of surfactants and simultaneously retaining their capacity for polymerisation or copolymerisation, and surface-active initiators (emulsifier-initiators) (SAI), which combine the properties of a surfactant with ability to generate free radicals in a certain temperature range (Table 1).

Surface-active monomers have been known for a comparatively long time.[53] In the first studies devoted to such monomers, attention was concentrated on the study of their copolymerising capacity without a profound analysis of the kinetic behaviour of these compounds in polymerisation systems. During the last two decades, there has been a growth of interest in their investigation and they have become the subject of a review.[54]

The characteristics of the molecular structure of surface-active monomers and their ability to form associated species (micelles, lamellae, etc.) make it possible to predict their influence on the polymerisation (or copolymerisation ) process. For a well founded explanation of the behaviour of such monomers in polymerisation systems, the polymerisation kinetics were therefore compared with the colloidal-chemical characteristics of solutions of surface-active monomers and the polymers formed from them.

Different dependences of the initial rate of polymerisation on the concentration of the surface-active monomer in water were observed for vinylpyridinium salts differing in the length of the aliphatic chain. For short-chain surface-active monomers, a linear growth of the rate of polymerisation with increase in the monomer concentration is observed, whereas in the case of long-chain surface-active monomers a break is observed at a certain concentration with a change in the slope of the straight line in the direction of an increase in the rate.[54] The increase in the rate of polymerisation is accompanied by the increase in the ratio of the propagation rate constant to the square root of the chain termination rate constant and by an increase in the rate of initiation.[55]

In the study of aqueous dispersions of surface-active monomer salts of methacryloylethylammonium and allylammonium, an even more complex dependence of the initial rate of polymerisation on the surface-active monomer concentration was observed. As shown in Fig. 8, in the region corresponding to the existence of micellar formations there are three sections on the curve relating the rate of polymerisation to the monomer concentration.[56] The first, initial section is characterised by a linear growth of the rate, the second by a constant rate, and the third by a renewed growth of the rate of polymerisation. The three linear sections in the variation of the rate of polymerisation were attributed by the authors to structural changes in the monomer formations within certain concentration ranges (spherical micelles, anisotropic micelles, multilayer lamellae).

In drawing a general conclusion concerning the outcome of the studies in this field,[53–58] one may note the following principal features. The polymerisation of surface-active monomers in aqueous micellar dispersions exhibits a series of differences from homogeneous polymerisation in solution, associated primarily with structure formation processes involving the molecules of the surface-active monomer and influencing the polymerisation kinetics and the microstructure of the polymer formed.

The nature of the kinetics of the polymerisation of surface-active monomers may vary as a function of the variation of the constants for the elementary reactions or of the reaction order with respect to the monomer and the initiator. The copolymerisation of surface-active monomers with other monomers takes place in those cases where the reactivity of the surface-active monomer is close to or greater than the reactivity of the comonomer.

Surface-active monomers can be used to prepare latexes not containing the free emulsifier in the aqueous phase, especially stable monodisperse latexes, ion-exchange resins, polymeric carriers for medicinal and biological preparations, etc. Surface-active monomers used to obtain thin molecular polymer layers are of special interest.

The effects observed in polymerisation systems of another type, comprising surface-active initiators — compounds in which surface-active properties and initiating capacity are combined — are extremely interesting. The location of the initiating centres in the region of adsorption layers or of the interface in heterogeneous polymerisation systems leads to extremely interesting kinetic effects associated with the change in the rates of elementary polymerisation reactions, in the first place initiation and chain termination reactions. We demonstrated experimentally the change in the rate of decomposition of a peroxide initiator located in the surface region of latex particles.[60]

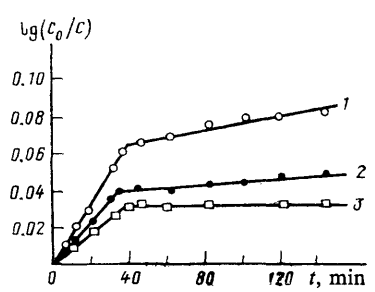



**Figure 9.** Semilogarithmic forms of the kinetic curves for the decomposition of the peroxy-groups of the polymeric initiator in the n-butyl acrylate — permonomer copolymer latex at 333 K. Diameter of the latex particles (nm): *1*, 50; *2*, 96; *3*, 160.

Fig. 9 presents the logarithmic forms of the curves for the decomposition of peroxy-groups located in the surface region of polymer-monomer species as a result of a special procedure for the metered introduction of the peroxide monomer in seeded emulsion copolymerisation in the system butyl acrylate — methacrylic ester of t-butyl α-hydroxyethyl peroxide.[59–61] Fig. 9 shows that the rate of decomposition of the peroxy-groups in the surface region is appreciably higher than in the bulk of the particle. A decrease in the rate constant leads to an alteration of the ratio of the peroxy-groups in the surface region of the particles. If kinetic relations are plotted taking into account the initial concentration of the peroxide, corresponding to its amount in the surface region of latex particles, then all the curves have the same slope regardless of the dispersity of the particles.

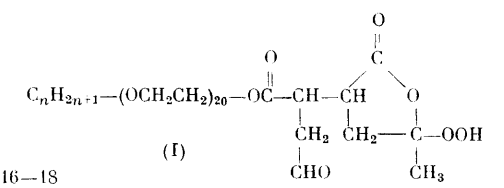
In the case of surface-active initiators, the region corresponding to the formation of free radicals is located either in the micelles or in the surface layers of latex particles depending on the characteristics of the structure of the surface-active initiator. This factor makes it possible to follow the influence of adsorption layers on the reactivity of the peroxy-groups and to investigate the characteristic features of the initiation reaction. The data presented in Table 2 make it possible to demonstrate the influence of the characteristics of the absorption layer on the rate constant for the decomposition of the surface-active initiator $k_{decomp}$.

**Table 2. Parameters of the thermal decomposition of surface-active peroxides (SAI) in aqueous solutions.**

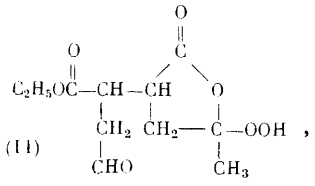
| SAI* | T, K | pH | $10^5 k_{decomp}$, $s^{-1}$ | E, kJ mol$^{-1}$ |
|---|---|---|---|---|
| (I) | 333 | 5 | 1.3 | 59.5 |
| (I) | 363 | 5 | 7.0 | |
| (I) with added Alkamon OS-2 | 333 | 7 | 3.3 | 63.5 |
| | 363 | 7 | 23.5 | |
| (I) with added E-30 | 333 | 7 | 3.3 | – |
| (I) with added SDS | 333 | 7 | 4.5 | – |
| (II) | 363 | 5 | 3.9 | – |
| (II) with added Alkamon OS-2 | 363 | 7 | 9.0 | – |
| (III) with added Alkamon OS-2 | 363 | 5 | 0.9 | – |

*Alkamon OS-2 = $[C_{16-18}H_{32-37}(OCH_2CH_2)_2CH_2\underset{\displaystyle CH_3}{\underset{|}{N}}(C_2H_5)_2]^+ . C_6H_5SO_3^-$; E-30 = $C_{15}H_{31}SO_3Na$; SDS = sodium dodecyl sulphate.

Evidently $k_{decomp}$ for micelle-forming surface-active initiators (I), having the same structure of the peroxy-group, i.e.

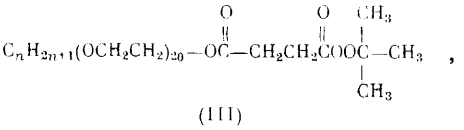


is initially higher than for the non-micelle-forming surface-active initiators (II):



(II)

It is of interest to note that, for the perester analogue (III), i.e.



(III)

$n = 16-18$

$k_{decomp}$ does not differ from the values for the usual peresters in hydrocarbon media. This is due to the fact that a special structure of the micelles, in which the hydrophobic fragment with the peroxy-group is drawn into the hydrocarbon nucleus of the micelle, is characteristic of compound (III).

The data presented emphasise the significant role not only of the structure but also of the location of the peroxy-group in the hydrophilic region of the micelle on the decomposition rate constants $k_{decomp}$.

The efficiencies of the initiation of emulsion polmerisation using surface-active initiators proved to be low (0.10–0.03).[60,61] This is probably due to the difficulties arising in the interaction of the primary radicals, fixed in the adsorption layer, with the monomer in the hydrocarbon nucleus of the micelle. The high rate of destruction of the primary radicals owing to their local concentration can be abolished with decrease in the concentration of the surface-active initiator. The observed increase in the initiation efficiency on reduction of the concentration of the surface-active initiator is associated with this factor.

The change in the initiation efficiency with decrease in the concentration of the surface-active initiator in the adsorption layer makes it possible to explain the change in the emulsion polymerisation reaction order with respeect to the initiator and the emulsifier. These phenomena are caused by the change in the average number of radicals in the polymer-monomer particles.

Experiments carried out[61] in order to investigate the influence of the surface-active initiator on the chain propagation reaction lead to the conclusion that the chain propagation reaction parameters in emulsion polymerisation are independent of the characteristics of the adsorption layer and the type of initiating group. Calculation showed that in this case the chain termination rate constants decrease sharply (by 2–4 orders of magnitude) compared with those for homogeneous systems and depend on the type of polymerisation system, the volume of the polymer-monomer particles, and the fixation of the growing radicals in the surface region. This is associated with the increase to some extent of the translational and possibly the conformational entropy of the macroradicals (depending on the structure of the surface-active initiator). These data permit the conclusion that in such systems the initiation reaction influences the chain termination steps and hence the chain termination constant. Hence the possibility arises of regulating with the aid of the surface-active initiators the chain termination reaction in emulsion polymerisation and of obtaining thereby ultra-high-molecular-weight polymers (with molecular weights up to $10^7$ and above).

Polyfunctional initiators can be used successfully in polymerisation systems in the preparation of ultra-high-molecular-weight polymers, highly stable polymer dispersions, polymer dispersions with a narrow size distribution of particles, etc.[59,60]

Although the history of the research into polyfunctional surfactants has so far been short, the possibilities in their use to obtain stable latexes with a specified particle size, for the creation of microheterogeneous polymer systems with a controllable size of the region of microheterogeneity, or for the creation of polymeric molecular layers are unique. It is difficult to overestimate their importance. They will undoubtedly develop in the near future.

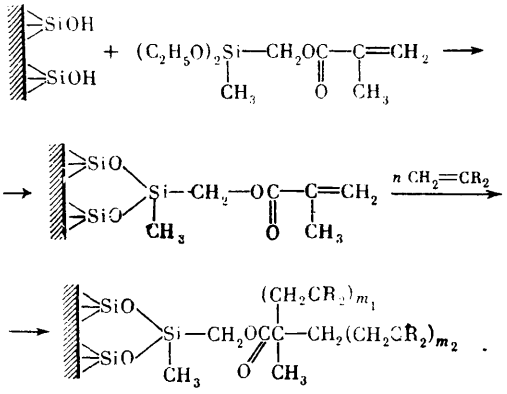
## V. Polyfunctional active fillers

Filled polymer compositions have been finding in recent years increasingly wider applications in a wide variety of fields in engineering and the National Economy. The introduction of various solid disperse or fibrous fillers into the polymer matrix makes it possible not only to economise on the polymer (which is important in the case of scarce polymers) but also to improve greatly the physicomechanical and operating properties of the polymer compositions obtained.[62–67]

One of the main factors determining the strengthening effect of fillers in polymer compositions is the polymer–filler interfacial interaction, which depends on the nature of the polymer and of the filler surface.[64–67] The partial or complete binding of the polymer matrix to the surface of inorganic fillers makes it possible to vary widely the physicomechanical, rheological, thermal, electrical, and other properties of filled polymer compositions. As shown comparatively recently,[65–67] the occurrence of such interaction may be predicted beforehand in the preparation of filled polymer compositions by the method of polymerisation filling. The physical significance of polymerisation filling reduces to carrying out the polymerisation (or copolymerisation) in a heterogeneous system containing a filler subjected to the preliminary surface modification by the chemical binding of compounds capable of interacting with the polymerisable monomer or the growing macroradicals. Such fillers, which are capable of reacting via their surface functional groups with the polymerising monomer, can be classified as polyfunctional fillers. Table 1 presents examples of polyfunctional filler-initiators and polyfunctional filler-comonomers, which, in conformity with the structure of the compounds grafted to the surface, can either initiate polymerisation or can function as comonomers. The characteristics of the behaviour of polyfunctional fillers in polymerisation reactions are described in detail in a recently published review.[65,67] Here we shall deal only with the most important features.

The fixation of groups capable of polymerising on the surface of the filler makes it possible to obtain a polymer grafted to the surface as a result of the copolymerisation reaction. The fixation of such compounds on the surface can be achieved via the formation of strong chemical bonds, for example, by the interaction of the hydroxy-groups of aerosil or silica gel with functional carboxy- and halo-groups. Thus the possibility of achieving the copolymerisation of unsaturated ethers or acetals (obtained by the reaction of silanol groups on the silica gel surface with allyl alcohol or acrolein)

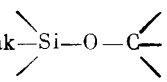
with butadiene has been described.[68] Alkoxy- or chloro-silanes, deposited on the surfaces, subjected to a preliminary treatment with an inorganic acid, of silica gel, aerosils, quartz, glass, etc. are widely used for the preparation of polyfunctional fillers.[69,71] The modification and grafting scheme is as follows [in relation to diethoxy(methacryloyloxymethyl)methylsilane]:

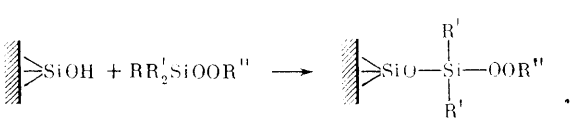


The density and hence the concentration of the monomeric groups bound to the surface can be regulated by varying the specific surface of the disperse filler and the conditions of the treatment of the surface.[67] The usual initiators are as a rule employed to initiate the polymerisation. During the polymerisation, a polymer not grafted to the surface is inevitably formed together with the grafted copolymer. The ratio of the grafted and non-grafted polymers depends on the degree of reaction, the content and surface area of the modified filler, and also the initiation procedure.[65,67]

It is possible to combine the stages involving the modification of the filler surface with the stage involving the copolymerisation and formation of the grafted copolymer.[73] The order in which the reactions between the modifier-copolymer and the filler surface and the copolymerisation reaction take place depends on the relative reactivities of the copolymerising groups and on the reactivity of the functional group which reacts with the surface silanol groups. However, when the modification and polymerisation stages are combined, it is not possible to avoid the excess consumption of the polyfunctional monomer, which is as a rule more scarce.

Another aspect of the chemical modification of the filler surface is the fixation on it of compouds with initating groups. For example, Dekking[74] achieved for the first time the synthesis of a monomer grafted to kaolin (or bentonite) via the emulsion polymerisation of vinyl monomers initiated by 2,2′-azobisisobutyramidine hydrochloride bound to the filler surface. Initiating systems for the surface-initiated polymerisation of vinyl monomers have been described. One of such systems consists of particles of calcium carbonate modified with 4-azobis-4-cyanopentanoic acid.[75–77]

Peroxidised fillers based on silicon-containing peroxides and not containing the hydrolytically weak  bonds are of great interest:[67,78]



where R = Cl, OR′, or $NH_2$ and R′ and R″ = alkyl. A convenient method for obtaining surface-peroxidised mineral fillers from modified vinyl-containing fillers by ozonisation has been proposed.[79,80] It must be emphasised that the use of peroxidised fillers with groups fixed to their surfaces makes it possible under certain conditions to synthesise monomers grafted to the filler surface without an admixture of non-grafted polymers. It has been shown[81] that, when an oxidation-reduction initiating system grafted to the surface of the hydroperoxide–iron stearate–benzoin system is used, it is possible to achieve the initiation of polymerisation exclusively on radicals grafted to the filler surface.

The kinetics of polymerisation with participation of polyfunctional fillers are associated, firstly, with the microheterogeneous nature of the polymerisation system and, secondly, with certain consequences of the fixed position of the monomeric or initiating group on the polyfunctional filler. The fixation of these groups on a solid surface leads to the restriction of the mobility of the comonomer groups or the primary initiating radicals and simultaneously to the concentration-dependent location of these groups on the surface. The set of these factors (taking into account the influence of the surface on the reactivity) leads to either the acceleration or retardation of the decomposition of the initiating group.[67] A common feature is the decrease of the initiating efficiency when polyfunctional filler-initiators are employed[67,75,78] and the dependence of the efficiency of the initiation of graft polymerisation on the concentration of the monomer in the surface region.

The fixation of the comonomers on the surface of silicon-containing fillers leads to a significant decrease in its reactivity relative to free radicals. The decrease depends on the structure of the monomer and on the nature of the surface.[82,83] An increase in the lifetime and a decrease in the probability of interaction with one another are characteristic of growing radicals fixed on the surface.[67] It has been noted that in this case the gel effect is manifested at earlier reaction stages than in the usual systems.[67,84] The increase in the molecular weight of the polymers formed as a result of the decrease in $k_0$ has been demonstrated.[76,81,82]

The prospects for the employment of polyfunctional fillers in the preparation of new polymeric composite materials are associated with the possibility of achieving high degrees of filling without disturbing the uniformity of the structure of the composition and with retention of high strength parameters.[85] An increased rigidity and thermal stability are characteristic of such systems. They are also distinguished from other systems in terms of their thermomechanical and rheological behaviour.[85,86]

The possibility of using polymers grafted to a disperse inorganic phase as sorbents for chromatography has been demonstrated recently.[87,88]

The polyfunctional components used to obtain polymer compositions were not touched upon to any extent in the preceding sections. The extensive possibilities for the use of polyfunctional fillers in the preparation of filled polymer compositions were examined in fair detail in previous publications. The prospects for the use of such fillers in polyolefin compositions capable of being cross-linked have also been examined in fair detail.[89,90]

In the general case, one should note that reactive oligomers and polymers readily obtained with the aid of polyfunctional components of polymerisation systems are exceptionally convenient for the formation of polymer compositions of a wide variety of types.

By varying the ratio of the components in the recipe, it is possible to vary within wide limits the structure and microheterogeneity of such compositions and hence their operating characteristics.

## VI. Classification of polyfunctional components of polymerisation systems

The above analysis of studies concerning the possibility of using polyfunctional components in polymerisation systems makes it possible to undertake a new attempt at a classification of such components.

From the standpoint of polyfunctionality, the components of polymerisation systems can be most conveniently classified as a function of the nature and number of the reactive functional groups in the molecule taking into account the main purpose of the component. Accordingly, we can distinguish (1) polyfunctional monomers (PFM), (2) polyfunctional initiators (PFI), (3) polyfunctional surfactants or polyfunctional emulsifiers (PFE), (4) polyfunctional fillers (PFF), and (5) polyfunctional modifiers, etc.

The principal purpose of the components is determined by the nature of the reactive group which reacts under the given conditions (monomeric, initiating, etc.) and determines the course of the main reaction in the given process. Depending on the reaction conditions (temperature, medium, additives) the interaction in the polyfunctional component can proceed via different functional groups. Thus, depending on the polymerisation conditions, there is a possibility of the transformation of the functional groups of the polyfunctional component, for example, from a monomer to an initiator, and conversely. Naturally, the proposed classification may be expanded and transformed as new data are accumulated.

In conclusion of the consideration of polyfunctional components of polymerisation systems, we must emphasise the exceptionally dynamic nature of the development of this field of polymer chemistry. The approaches to the preparation of reactive polymers and the introduction of functional groups into the polymer matrix for a wide variety of purposes have been vigorously discussed at conferences in recent years. The data presented in this review will help to some extent to arrange systematically the available approaches in this field.

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