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# Coordination-radical (co)polymerisation of vinyl monomers in the presence of organic compounds of Group III – V elements

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**Abstract.** The influence of catalytic amounts of organic compounds of Group III – V elements on the initiation stage and chain propagation in the (co)polymerisation of vinyl and certain other monomers is discussed. The question concerning the formation of complexes by the monomers and growth radicals with organoelement additives are examined. Examples of the practical application of the coordination-radical (co)polymerisation with participation of organic compounds of Group III – V elements, including peroxides, in the synthesis of high-molecular-mass substances, including the copolymers of vinyl monomers and olefins as well as alternating copolymers based on acrylates, are presented. The bibliography includes 105 references.

## I. Introduction

The use of modifying additives, which alter the reactivity of monomers and macroradicals as well as the kinetic parameters of the process, and of novel initiators, ensuring the effective generation of radicals under energetically favourable conditions and the regulation of chain propagation and termination, leads to promising ways of solving the problem of the synthesis of polymers with specified properties. The first procedure (using protic and aprotic acids as additives) has already led to the creation of a new aspect of polymer chemistry — the complex-radical polymerisation.[1-3] The effectiveness of the second procedure depends on the use, together with azo-compounds and peroxides, of radical initiators based on organoelement compounds (OEC), subdivided into oxygen-reduction systems based on organic derivatives of non-transition metals and oxidants (oxygen, peroxide) and Ziegler-Natta catalysts.[4-7] The latter are used predominantly for the synthesis of the (co)polymers of olefins and dienes and are used for the polymerisation of vinyl monomers to a limited extent.

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## II. Characteristics of radical formation in organoelement compound – peroxide systems

The oxidation – reduction systems based on OEC and oxygen as well as OEC and hydroperoxides have been investigated in fair detail.[4, 5, 7-9]

The study of the products of the reactions of OEC with organic and then organoelement peroxides was begun as early as the 1960s. Such studies have been performed by a number of schools of organic chemists, including the school directed by Academician G A Razuvaev (see, for example, Refs 10 and 11).

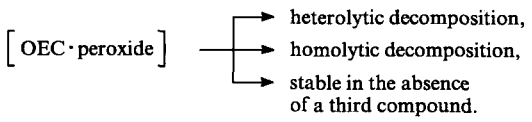
As a result of the vigorous application of physicochemical methods to the study of the above reactions, the use of kinetic approaches, and allowance for the influence of electron-donating and electron-accepting additives on the radical generation stage, a series of new data have appeared in recent years concerning the application of the systems in (co)polymerisation processes, which permitted certain generalisations.

It has now been reliably established that one of the initial stages in the interaction of organometallic compounds with peroxides is the formation of a complex of the donor – acceptor type:[12-14]

$$R_nM + R'OOR'' \rightleftharpoons \left[R_nM \cdot R'OOR''\right]. \qquad (1)$$

The majority of organoelement peroxides (OEP) of Group IV and V metals are fairly stable compounds, the thermal stability of which is likewise high and which undergo homolytic or heterolytic decomposition only at temperatures not below 80 – 100 °C.[5] As a result of the formation of the peroxide – OEC complex, the electron density in the peroxide molecule is redistributed, which leads to the loosening of the oxygen – oxygen bond and appreciably facilitates thereby its dissociation.

The OEC – peroxide complex can decompose both heterolytically with formation of ethers and homolytically with generation of radicals, or can dissociate reversibly into the initial components.



The complex formation constants in the OEC–peroxide system have been estimated in a series of studies[14–16] in relation to organoboron compounds (Table 1). Donor–acceptor complexes involving boron compounds have been investigated in greatest detail. The is because trialkylboranes are fairly convenient in practical use, are synthesised under industrial conditions, and are most promising as radical polymerisation coinitiators.

**Table 1.** The complex formation constants (litre $mol^{-1}$) in the OEC–peroxide system ($T$ = 293 K).

| OEC | $Bu^tOOBu^t$ | $(C_6H_5)_3SiOOBu^t$ | $(CH_3)_3SiOOBu^t$ |
|---|---|---|---|
| $Bu^n_2BC_6H_5$ | – | – | 0.33 |
| $Bu^i_3B$ | – | – | 0.64 |
| $Bu^n_3B$ | 0.37 | 0.46 | 1.16 |
| $Bu^n_2BOBu$ | – | – | 1.42 |
| $Bu^n_2BCl$ | – | – | 2.78 |

The stability of the OEC–peroxide complex as well as the mode of its decomposition are determined by the structure of the peroxide and the OEC as well as the nature of the metal atom. Thus, whereas the complexes of organoboron compounds with *tert*-butyl peroxide (TBP) and its organosilicon and organogermanium analogues (*tert*-butylperoxytrimethylsilicon, *tert*-butylperoxytriethylgermanium) are stable in the temperature range up to 300 K and decompose reversibly to the initial components, the complexes involving *tert*-butylperoxytriethyltin, *tert*-butylperoxytetraphenylantimony, and di-*tert*-butylperoxytriphenylantimony undergo spontaneous homolytic decomposition at room temperature with formation of alkyl and alkoxyl radicals.[16]

$$R_3B + Bu^tOOER'_n \longrightarrow \left[R_3B\cdot Bu^tOOER'_n\right] \longrightarrow \begin{cases} \longrightarrow R^\cdot + R_2BOBu^t + {}^\cdot OER'_n, \\ \longrightarrow R^\cdot + R_2BOER'_n + Bu^tO^\cdot; \end{cases} \quad (2)$$

E = Sn, Sb; $n$ = 3, 4.

The complexes of OEP with organic derivatives of aluminium, gallium, indium, and thallium undergo similar reactions. However, in this case there is both homolytic and heterolytic decomposition of the complexes.[17, 18]

$$\left[R_3Al\cdot R'OOR'\right] \begin{cases} \longrightarrow R_2AlOR' + R^\cdot + {}^\cdot OR', \\ \longrightarrow R_2AlOR' + ROR'. \end{cases} \quad (3)$$

It has been shown in relation to the ethyl, butyl, and isobutyl derivatives of these metals with the aid of EPR[17, 18] and by analysing the reaction products that the ratio of the components in the complex is 1 : 1.

The methyl derivatives of Group III elements react with acyl peroxides, affording 1 : 2 complexes. The complex decomposes homolytically and the oxygen-centred radicals do not emerge into the solution under these conditions.

$$(CH_3)_3E + (C_6H_5COO)_2 \longrightarrow \left[\begin{array}{l} E(CH_3)_3 \\ \vdots \\ O \\ \| \\ C_6H_5C-O-O-CC_6H_5 \\ \| \\ O \\ \vdots \\ E(CH_3)_3 \end{array}\right] \longrightarrow 2C_6H_5COOE(CH_3)_2 + 2CH_3^\cdot . \quad (4)$$

The existence of the homolytic and heterolytic pathways in the decomposition of the OEC–peroxide complex makes it possible to postulate a one-electron transfer between the components of the complex as one of the probable stages of the process.

$$R_nE + R'OOR' \rightleftharpoons \left[R_nE\cdot R'OOR'\right], \quad (5)$$

$$\left[R_nE\overset{e}{\cdots}R'OOR'\right] \longleftrightarrow \left[R_nE^{\cdot+}\cdots{}^{\cdot-}R'OOR'\right], \quad (6)$$

$$\left[R_nE^{\cdot+}\cdots{}^{\cdot-}R'OOR'\right] \longrightarrow \begin{bmatrix} R^\cdot & {}^+ER_{n-1} \\ R'O^\cdot & {}^-OR' \end{bmatrix} \longrightarrow \begin{cases} \longrightarrow ROR' + R'OER_{n-1} \\ \longrightarrow R^\cdot + R'O^\cdot + R'OER_{n-1}. \end{cases} \quad (7)$$

The hypothesis of the one-electron transfer in the reactions of the OEC of nontransition elements with peroxides has been put forward in a number of studies[4, 19, 20] and has been demonstrated unambiguously by the EPR method in relation to organic compounds of iron and chromium and the peroxides of Group IV elements.[21]

$$Cr(C_6H_5C_2H_5)_2 + R'OOR' \longrightarrow \longrightarrow \left[(C_6H_5C_2H_5)_2Cr^{\cdot+}\cdots{}^{\cdot-}R'OOR'\right]. \quad (8)$$

The complex formed decomposes via a radical mechanism and the alkoxyl radicals, obtained in the reaction, are not released into the surrounding volume but remain coordinated to the metal atom. This is followed by the abstraction of a hydrogen atom from the alkyl fragment of the OEC.

$$\left[(C_6H_5C_2H_5)_2Cr^{\cdot+}\cdots{}^{\cdot-}R'OOR'\right] \xrightarrow{-R'OH} \longrightarrow \left[C_2H_5C_6H_5CrC_6H_5\dot{C}HCH_3\right]^+O\bar{R}' \longrightarrow \longrightarrow Cr(OR')_4 + C_6H_5CH_2CH_3 + C_6H_5\dot{C}HCH_3. \quad (9)$$

Organometallic compounds of Group V also react with OEP via a radical mechanism but without the liberation of alkoxyl radicals into the surrounding volume.[22]

$$R_3Bi + Bu^tOOER'_3 \longrightarrow \left[R_3Bi\cdot(Bu^tO)OER'_3\right] \longrightarrow \longrightarrow 2R^\cdot + RBi(OBu^t)OER'_3. \quad (10)$$

Oxygen-containing radicals remain in the coordination sphere of the metal atom. For example, evidence for the existence of radicals in the coordination sphere of the bismuth atom has been obtained in an EPR study of the interaction of triphenylbismuth with alcohols and alkoxides.[23]

A free-radical mechanism has been proposed for the interaction of TBP and acyl peroxides with organomercury and organotin compounds. It is believed[24] that the donor–acceptor complexes of the above OEC with peroxides are convenient sources of free radicals and that the addition of organomercury and organotin compounds greatly increases the initiating capacity of the organic peroxides.

Radicals (alkyl and alkoxyl) are formed in the reactions of virtually all the alkyl derivatives of Group II, III, and V elements with peroxides. Despite this, it is organoboron and organoaluminium compounds[12, 25] as well as alkyl derivatives of bismuth,[22] tin, and mercury[24] that have found the greatest application as initiators.

Initiating systems based on organoboron compounds occupy a special position. They make it possible to polymerise vinyl chloride and acrylates with a conversion close to 100% over a wide temperature range and to obtain polymers with effective physicochemical properties. Compositions based on trialkylboranes and peroxides are capable of glueing together Teflon, polyethylene, and a number of other 'nongluable' thermoplastic materials without a preliminary treatment of the surface.[10, 11, 25]

As stated above,[14, 15, 18] the complexes of trialkylboranes with TBP and its organosilicon and organogermanium analogues are stable at room temperature and dissociate reversibly into the initial components. The complexes decompose into radicals in the presence of a third compound — an electron-accepting additive, for example the polar vinyl monomer.[6, 26]

$$\left[R_3B\cdot(CH_3)_3SiOOBu^t\right] + M \longrightarrow \begin{cases} \longrightarrow R-M^{\cdot} + (CH_3)_3SiO^{\cdot} + R_2BOBu^t, \\ \longrightarrow R-M^{\cdot} + Bu^tO^{\cdot} + R_2BOSi(CH_3)_3; \end{cases} \quad (11)$$

(M = monomer).

Thus the monomer is directly involved in the radical generation stage.

The structure of the ternary OEC–OEP–monomer complex has not been established experimentally. It has been demonstrated by IR[27] and $^1$H NMR[28] spectroscopy and by calorimetry[29] that the unsaturated compound may be coordinated both to the element in the peroxide and to the oxygen bridge.

$$R_nEOOR' + CH_2{=}CH{-}X \longrightarrow \begin{cases} \left[\begin{array}{c} CH_2{=}CH{-}X \\ \vdots \\ R_nEOOR' \end{array}\right], \\ \left[\begin{array}{c} CH_2{=}CH{-}X \\ \vdots \\ R_nE{-}O{-}OR' \end{array}\right]. \end{cases} \quad (12)$$

Like organoaluminium compounds,[30] trialkylborane can be bound to the monomer also via an unoccupied *p* orbital.

$$R_3B + CH_2{=}CH{-}X \rightleftharpoons \left[R_3B\cdots\begin{array}{c} CH_2 \\ \| \\ CH{-}X \end{array}\right]. \quad (13)$$

Ternary systems involving organoaluminium compounds have been investigated in detail by Milovskaya and coworkers.[12] According to Milovskaya,[12] an OEC–monomer complex is formed initially in the trialkylaluminium–peroxide–monomer complex and then reacts with the peroxide, affording radicals.

$$R_3Al + M \rightleftharpoons \left[R_3Al\cdot M\right], \quad (14)$$

$$\left[R_3Al\cdot M\right] + R'OOR' \rightleftharpoons \left[R_3Al\cdot M\cdot R'OOR'\right], \quad (15)$$

$$\left[R_3Al\cdot M\cdot R'OOR'\right] \longrightarrow R_2AlOR' + R^{\cdot} + R'OM^{\cdot}. \quad (16)$$

Aleksandrov and coworkers[31] put forward a general mechanism taking into account virtually all the principal coordination interactions in the three-component system:

$$MMA + A \rightleftharpoons \left[MMA\cdots A\right], \quad (17)$$

$$MMA + P \rightleftharpoons \left[MMA\cdots P\right], \quad (18)$$

$$P + A \rightleftharpoons \left[P\cdots A\right], \quad (19)$$

$$\left[MMA\cdots A\right] + P \rightleftharpoons \left[MMA\cdots A\cdots P\right], \quad (20)$$

$$MMA + \left[P\cdots A\right] \rightleftharpoons \left[MMA\cdots P\cdots A\right], \quad (21)$$

$$\left[P\cdots MMA\right] + A \rightleftharpoons \left[P\cdots MMA\cdots A\right], \quad (22)$$

where MMA = methyl methacrylate, P = peroxide, and A = Lewis acid.

The mechanism of the generation of radicals in such systems has not been established, but one can postulate that the monomer is capable of combining with the components of the complex [the organometallic compound (OMC) and the OEP]. Such interaction alters the reactivity of the monomers, which is characteristic of the so called complex-radical polymerisation.[3] The study of the characteristics of the (co)polymerisation of vinyl monomers and olefins has confirmed the above hypothesis.

## III. Accelerating influence of organoelement compounds on the homo- and copolymerisation of vinyl monomers

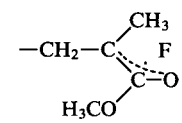
As stated above, organoelement initiating systems based on the OEC of Group III elements and OEP have a number of advantages compared with the traditional radical initiators,[10, 11, 25] in particular they are more effective than azo-compounds and percarbonates and make it possible to obtain a large amount of the polymer per unit time.[25, 32, 33]

The rapid chain propagation and certain features of the physicochemical properties suggest that the components of the organoelement initiator participate not only in the radical generation stage but also in the chain propagation and termination processes. As mentioned above, unsaturated compounds, including monomers, are capable of coordinating to the OEC of non-transition elements and OEP [Eqns (12) and (13)]. In these complexes, the monomers function as electron donors. On the one hand, such complex formation facilitates the decomposition of the peroxide into radicals and hence increases the rate of initiation[27] and, on the other, it promotes a redistribution of electron density to the π-bonds of the monomer and thereby alters its reactivity.

Complexes of vinyl monomers with Lewis acids (metal halides) have long been known and have been studied in detail by a number of investigators.[3] It has been established by IR[35–38] and NMR[39] spectroscopy that metal halides are coordinated to the carbonyl group of the monomer.[35] The constants for the complex formation reactions of organic compounds of Group III elements with MMA and acrylonitrile (AN) have been estimated in relation to organoaluminium compounds.[30]

Together with the formation of complexes with the monomers, organometallic compounds are capable of forming complexes with radicals,[40] including polymeric ones.[35]

It has been established by the EPR method that the components of the organoelement initiator trialkylborane(TAB)-di-*tert*-butylperoxytriphenylantimony (DPA), containing boron and antimony atoms with unoccupied *p* and *d* orbitals, are coordinated during the chain propagation process to the growing MMA macroradical.[41, 42]




F — fragment of the organoelement initiator

The formation of similar complexes of the macroradical with Group II and III metal halides as Lewis acids has been noted.[35]

Such interaction enhances the electron-accepting properties (electrophilicity) of the growing macroradical and increases its reactivity relative to the double bond of the monomer. This increases the propagation rate constant. Thus the rate of polymerisation of MMA in the presence of typical radical initiators — dicyclohexyl peroxydicarbonate (DCC) and azoisobutyronitrile (AIBN) — increases significantly after the introduction of triisobutylborane in amounts comparable to the initiator concentration.[43] Boron alkyls have no catalytic effects on the decomposition of the above initiators.

| | | | |
|---|---|---|---|
| Rate of polymerisation/ $10^4$ mol litre$^{-1}$ s$^{-1}$ | 0.74 | 1.08 | 1.48 |
| Triisobutylborane concentration (mol.%) | 0 | 0.2 | 0.4 |

The polymerisation of acrylonitrile in the presence of AIBN is also accelerated by trialkylboranes. The rate of the process increases synchronously with increase in the content of the OEC in the mixture. Similar data have been obtained in studies of the copolymerisation of MMA with styrene[44] and allyl chloride[45] in

the presence of organoelement initiators. Other OEC of Group III elements, in particular dibutylbutoxyborane and triethylaluminium, also have an accelerating effect on the polymerisation of MMA (Table 2). Being a stronger Lewis acid than trialkylboranes, dibutylbutoxyborane exhibits an increased coordinating capacity and has an appreciably greater influence on the rate of polymerisation.

**Table 2.** The influence of certain OEC of Group III elements and phenolic inhibitors (1 mol.%) on the rate of polymerisation of MMA ($10^3 v$/mol litre$^{-1}$ s$^{-1}$).

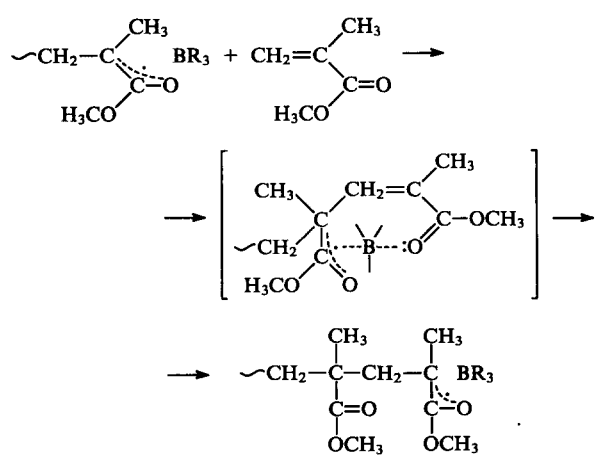
| OEC | Without inhibitor | Hydroquinone | Di(hydroxyphenyl)propane | Ionol | Benzoquinone |
|---|---|---|---|---|---|
| – | 0.08 | 0.01 | – | – | – |
| $Bu^i_3B$ | 0.22 | 0.40 | 0.24 | 0.17 | 0.04 |
| $Bu^i_2BOBu$ | 0.43 | – | 0.50 | 0.15 | 0.02 |
| $(C_2H_5)_3Al$ | 0.11 | 0.16 | 0.20 | 0.12 | 0.01 |

Note. In all cases, the initiator was AIBN (0.1 mol.%). $T$ = 313 K.

Certain metal halides have a similar activating effect on chain propagation in the polymerisation of acrylic monomers.[3] Thus, according to the data of Bamford et al.,[46] the propagation rate constant in the polymerisation of acrylonitrile in the presence of lithium chloride increases by a factor of two, while the termination rate constant remains unaltered. The accelerating effect is due to the formation of complexes between lithium ions and the acrylonitrile growth radical. It was shown subsequently in a series of studies[47–56] that the activating effect of the coordinatively unsaturated metal salts on the polymerisation of acrylic monomers is a common phenomenon, which has been discussed in detail in a monograph.[3]

In contrast to metal halides (Lewis acids), organometallic additives have a catalytic effect on chain propagation when they are introduced into the system in amounts comparable to the initiator concentration (0.01–0.1 mol.% relative to the monomers). This fact definitely shows that the formation of a complex between the OEC and the macroradical and not the monomer is responsible for the increase in the rate of (co)polymerisation in the presence of the Lewis acid indicator, particularly since the complex between the electron acceptor and the growth radical is somewhat more stable than the analogous complex with the monomer.[35]

Taking into account the foregoing, one may postulate that the same OEC molecule, functioning as a complex forming agent, can participate in several consecutive chain propagation stages, permanently retaining the growing macroradical in its coordination sphere. Chain propagation then occurs in a six-membered reaction complex, which includes the growing macroradical, the monomer, and the complex forming agent.



(23)

By retaining in its coordination sphere the growing macroradical, the atom of the element orients the monomer molecule and creates conditions for chain propagation which are most favourable from the energetic and steric standpoints.

A similar mechanism, except for the fact that it incorporates an eight-membered reaction complex, has been proposed by Kabanov[57] to explain the increase in the chain propagation rate constant in the polymerisation of MMA in the presence of metal halides and also by Semchikov and coworkers[58, 59] in studies of the copolymerisation of acrylic acid with vinyl acetate in the presence of germanium salts. However, the six-membered complex presented above, which includes a delocalised allylic macroradical, is thermodynamically most stable.[60]

The concept of the cyclic transition state has been frequently used in coordination chemistry to account for the characteristics of the chain propagation.[61] Precisely this analogy probably enabled Kabanov et al.[3] to introduce the term 'coordination-radical polymerisation' for polymer formation processes occurring in the presence of metal compounds as electron acceptors. However, the term 'complex-radical polymerisation' is used more frequently to describe the above reactions in both Russian and foreign literature. However, when organoelement compounds are used as chain propagation regulators the term 'coordination-radical polymerisation' appears more apt, since, firstly, it emphasises the interrelation and common features of the mechanisms in coordination and radical polymerisation with participation of OEC and, secondly, the coordination interaction between the monomer and the OEC and between the macroradical and the OEC is fairly weak, as stated above, and the formation of stable complexes should not be considered.

## IV. Specific effects of hydroquinone, benzoquinone, and other phenolic inhibitors on the (co)polymerisation of acrylates in the presence of organoelement compounds

Hydroquinone, ionol, and certain other phenols are familiar inhibitors of the radical polymerisation of vinyl monomers and are used traditionally as stabilisers. The effectiveness of the inhibition increases significantly in the presence of oxygen, which, according to Dolgoplosk and Tinyakova,[62] is associated with the oxidation of phenols to quinones, which exert a stronger retarding effect on chain propagation.

According to the most common point of view,[62, 63] the inhibiting effect of hydroquinone is based on the ready abstraction by the radical of the mobile hydrogen atom from the phenol molecule with formation of a phenoxyl radical.

$$R^{\cdot} + ArOH \longrightarrow RH + ArO^{\cdot} . \qquad (24)$$

As a consequence of its low reactivity relative to the multiple bond in the monomer, the phenoxyl radical cannot initiate the radical process (polymerisation).

As early as the 1960s, it was noted[64–67] that the addition of certain OEC of Group III elements makes it possible to carry out the polymerisation of MMA with a high conversion in the presence of benzoyl peroxide (BP) or AIBN despite the presence of comparable amounts of hydroquinone.

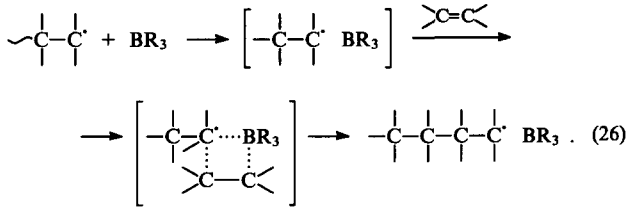
In the presence of OEC, the phenoxyl radicals probably enter into a $S_N2$ substitution reaction at a high rate.[68]

$$ArO^{\cdot} + R_3E \longrightarrow R^{\cdot} + ArOER_2 . \qquad (25)$$

The alkyl radicals formed in this reaction can again initiate the polymerisation. This means that organoboron compounds can function as chain transfer agents in the polymerisation of acrylates. The chain transfer rate constant in the polymerisation of MMA initiated by peroxides is $1.5 \times 10^{-2}$ for tri-n-butylborane and $1.0 \times 10^{-2}$ for triisobutylborane.[69]

A somewhat different point of view on the causes of the lack of the inhibiting effect of phenols in polymerisation in the

presence of organometallic compounds has been expressed by Arimoto,[65] who suggested that the OEC is coordinated to the growing macroradical via the unpaired electron of the latter.



(26)

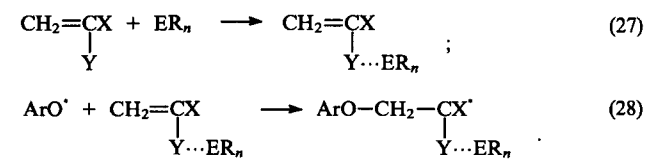
This results in the blocking of the reaction centre of the radical and its interaction with the phenol becomes impossible. It is essential to note that the experimental results obtained by Arimoto have been questioned.[64]

It has been shown in a number of studies published in the 1990s[43, 70–72] that hydroquinone and di(hydroxyphenyl)propane not only do not inhibit the radical polymerisation of acrylates but actually accelerate it (Table 3). Thus the rate of polymerisation of MMA and acrylonitrile increases significantly in the presence of the OEC of Group III elements and increases synchronously with increase in the content of the OEC and of the inhibitor. Such an unusual accelerating effect is associated with reactions involving chain transfer to the OEC [Eqn (25)]. However, the absence of the inhibiting effect in the polymerisation of MMA, acrylonitrile, and methyl acrylate in the presence of large amounts (an order of magnitude higher than the initiator concentration) of hydroquinone and di(hydroxyphenyl)propane as well as a significant weakening of the inhibiting effect when Lewis acids (metal halides) are introduced into the polymerising system cannot be accounted for solely by this factor.[73–75] Such nontraditional behaviour of phenols can be caused by the coordination-radical nature of the (co)polymerisation of acrylic monomers in the presence of organoelement initiators. In the presence of Lewis acids as electron acceptors, the macroradical and the monomer are coordinated (see above) to the components of the initiator. The formation of a complex between the OEC and the monomer activates the latter, as a result of which the initiation of the polymerisation by phenoxyl radicals becomes possible.

**Table 3.** The influence of hydroquinone, di(hydroxyphenyl)propane, and ionol on the rate of polymerisation of acrylic monomers.

| Monomer | Inhibitor concentration (%) | Rate of polymerisation ($10^3 v$/ mol litre$^{-1}$ s$^{-1}$) in the presence of different inhibitors | | |
|---|---|---|---|---|
| | | hydro-quinone | di(hydroxy-phenyl)propane | ionol |
| MMA | 0 | 1.20 | 1.20 | 1.20 |
| | 0.5 | 1.40 | 1.31 | 0.78 |
| | 1.0 | 1.67 | 1.40 | 0.63 |
| | 5.0 | – | 1.59 | 0.28 |
| AN | 0 | 4.50 | – | 4.50 |
| | 0.5 | 6.10 | – | 1.31 |
| | 1.0 | 7.70 | – | 0.51 |
| VA* | 0 | 9.10 | 9.10 | 9.10 |
| | 0.1 | 4.30 | – | – |
| | 0.5 | – | 2.50 | 0.17 |
| | 1.0 | 0.05 | 0.75 | 0.04 |
| | 5.0 | – | 0.38 | – |

Note. In all cases, the initiator was triisobutylborane–di-*tert*-butylperoxytriphenylantimony (the content of triisobutylborane was 0.4 mol.%). $T$ = 293 K.
*VA = vinyl acetate.



(27)



(28)

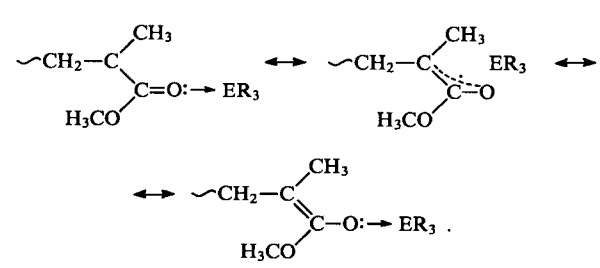
The hypothesis of the activation of the monomer by the complex-forming agent has been confirmed by the data of Bamford et al.,[53] who demonstrated a threefold increase (compared with the monomer) in the reactivity of the complex of MMA with zinc dichloride in the chain propagation stage. This permits the hypothesis that phenoxyl radicals can initiate the polymerisation of the monomer bound in a complex.

The occurrence of reaction (28) has been confirmed also by the detection of phenoxy-groups in poly(methyl methacrylate) by UV[70] and IR[72] spectroscopy. An indirect confirmation of the validity of the proposed approach to the consideration of the kinetic features of the polymerisation of acrylates in the presence of OEC and inhibitors is provided by the absence or weakening of the inhibiting effect in the polymerisation of MMA with added Group III metal halides. In this case, the occurrence of the $S_R2$ substitution reaction [Eqn (25)] is in principle impossible and an explanation of the observed effect can be found either in terms of Arimoto's mechanism [Eqn (26)] or in terms of the approach put forward above [Eqns (27) and (28)].

Reactions (25)–(28) lead to the observed increase in the rate of polymerisation of acrylates in the presence of OEC of Group III elements and phenols such as hydroquinone and di(hydroxyphenyl)propane. However, in the case of ionol—a sterically hindered phenol—some decrease in the rate of polymerisation of the monomers investigated has been observed.[70, 72] This is probably associated with the fact that, owing to steric factors, reactions (25) and (28) involving ionol proceed much less effectively than those involving hydroquinone and di(hydroxyphenyl)propane.

In contrast to acrylates, the polymerisation of vinyl acetate in the presence of OEC is effectively inhibited by phenols (Table 3) and, after the introduction of hydroquinone in amounts exceeding the concentration of trialkylborane, ceases completely.[71] The above inhibitors retard significantly also the polymerisation of vinyl chloride in the presence of organoelement initiators, but the process cannot be fully inhibited because of the low solubility of hydroquinone in vinyl chloride.

Trialkylborane is incapable of activating vinyl chloride and vinyl acetate owing to the characteristic features of their structure as electron-donating monomers.[76] As a consequence of the remoteness of the oxygen atom of the carbonyl group from the carbon–carbon double bond, in the coordination of the Lewis acid to vinyl acetate the activation of the π-bond of the latter is not quite so marked as in the case of acrylate and reaction (28) does not take place. Furthermore, whereas an appreciable delocalisation of the unpaired electron in the growing macroradical on coordination to the OEC (π-e conjugation[71]) is characteristic of acrylonitrile and (meth)acrylates, this is not possible in the poly(vinyl acetate) radical for steric reasons—as a consequence of a different disposition of the carboxy-group and the unpaired electron.[76]

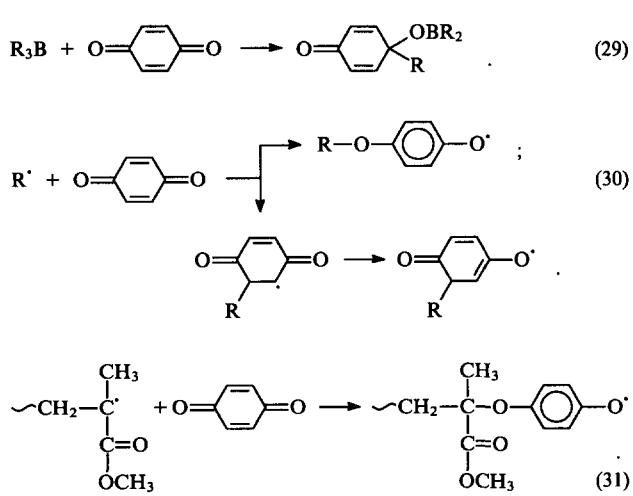


It is quite likely that, on transfer of electron density to the unoccupied orbitals of the trialkylborane as a result of coordination to the macroradical, the borane increases the electrophilicity of the coordinated poly(methyl methacrylate) radical or the polyacrylonitrile radical. This makes them inert to phenols [see Eqn (24)]. In this case, chain propagation takes place in a cyclic reaction complex incorporating the monomer, the growing macroradical, and the OEC, directly in the coordination sphere of the metal, which hinders the reaction of the macroradical with the mobile hydrogen atom of the phenol. Because of this, the polymerisation of MMA continues up to a high degree of conversion in the presence of a tenfold excess of the inhibitor relative to the OEC.[70]

Phenolic inhibitors exert a definite influence also on the molecular mass of the polymer:[70-72] thus the molecular mass of poly(methyl methacrylate) diminishes synchronously with increase in the content of the inhibitor in the monomer mixture. However, this change is insignificant compared with the analogous influence of the above inhibitors in the absence of OEC or when traditional chain transfer agents are introduced.

A significant role is attributed to oxygen in the mechanism of the inhibition of radical polymerisation by various phenols. According to Dolgoplosk, the influence of oxygen reduces to the oxidation of the phenol to the corresponding stable radicals or quinones. In the presence of organic compounds of boron and aluminium[64-67, 70] as well as benzoquinone (BQ), there is no induction period in the polymerisation of MMA. The inhibiting effect of benzoquinone in the presence of added trialkylborane depends on the molar ratio [TAB]:[BQ]. If the amount of benzoquinone is smaller than that of trialkylborane, the inhibiting effect hardly influences the polymerisation kinetics. The process proceeds up to a high degree of conversion and the molecular mass changes insignificantly.[72] Under similar conditions in the absence of trialkylborane, benzoquinone effectively inhibits the polymerisation of acrylates: the rate of polymerisation is initially close to zero and the limiting degree of conversion does not exceed 0.5%.[71, 72]

With increase in the concentration of benzoquinone, the rate of polymerisation diminishes. However, even in the presence of a twofold excess of benzoquinone relative to trialkylborane, it is significantly higher than in the absence of the latter. Analysis of the literature as well as data on the reactivities of organoboron compounds relative to benzoquinone indicates the effective involvement of trialkylborane and benzoquinone in the processes.[70-72, 77, 78]



(29)

(30)

(31)

The phenoxyl radicals formed by reactions (30) and (31) enter into the $S_R2$ substitution reaction with generation of alkyl radicals which are capable of again initiating the polymerisation [Eqn (25)]. The average chain length indicates that there are two chain transfers to the trialkylborane molecule.[66]

Organoaluminium compounds exert a no less effective influence on the polymerisation of acrylates in the presence of quinones.[67, 72] The rate of polymerisation increases with increase in the ratio [trialkylaluminium]:[BQ], reaches a maximum, and then falls again. Grotewold and Hirschler[67] explained this by the operation of two initiation mechanisms: the first is associated with the decomposition of the initiator into radicals and the second with the generation of radical centres as a result of the decomposition of the complex between triethylaluminium and the quinone. Analysis of the products of the reactions of organoaluminium compounds with quinones[79, 80] showed that the latter mechanism appears extremely controversial.

As in the case of trialkylboranes, a heterolytic reaction [Eqns (29)-(31)] and homolytic transfer of the reaction centre to the metal atom [Eqn (25)] probably take place in the given instance. Whereas the reaction involving trialkylborane can involve two alkyl groups, in the case of triethylaluminium only one such group is involved[67] (the chain transfer rate constant is 89 litre $mol^{-1}$ $s^{-1}$; we may note for comparison that the chain propagation rate constant is 576 mol $litre^{-1}$ $s^{-1}$).[81]

## V. The influence of organoelement additives on the composition of the copolymer and on the kinetics of the copolymerisation of vinyl monomers

Copolymerisation is at present the main method of synthesis of polymers with the required set of chemical and physical properties. This can be explained by the fact that in most cases it is difficult to regulate the properties of homopolymers while the need for such regulation in order to obtain polymers for different purposes does exist.[2, 3, 6]

Copolymerisation usually leads to the formation of statistical copolymers the composition and properties of which are determined both by the initial content of the monomers in the mixture and by the reactivity of the monomers and growth radicals. However, there exist monomer pairs in the copolymerisation of which a regular alternation of units in the monomer takes place. As a rule, a strict alternation of the monomer units is observed when one of the monomers is a distinct donor of electron density while the other is an electron acceptor. Since the number of monomers with pronounced electron-accepting properties is small (for example, maleic anhydride and its derivatives, sulfur dioxide), the number of monomer pairs forming alternating copolymers is likewise small.

For this reason, methods based on the introduction of special additives into the system, as a rule protic or aprotic acids, have been developed for the regulation of the composition of the copolymers.[2] As shown above, the acids are coordinated to the monomers or growth radicals, enhancing thereby their electron-accepting properties and permitting the synthesis of alternating copolymers.[1, 2] The main disadvantage of this procedure is the need for a large excess of the regulating additive (by 1-3 orders of magnitude) relative to the initiator. This leads to the contamination of the polymeric product and precludes the industrial application of this method for the regulation of the composition.

The use of initiators based on organometallic compounds of Group III elements and peroxides makes it possible to eliminate the above disadvantage because the regulating effect of these compounds on chain propagation is manifested, as stated above, when catalytic amounts of the initiator (0.1-1.0 mol.%) are used.

The effects of complex formation in radical copolymerisation in the presence of Lewis acids are determined to a large extent by the electronic structure of the monomer. The limiting systems are those in which only one of the monomers interacts with the complex-forming agent and also those in which both monomers interact with it. Both versions are analysed below.

It has been established unambiguously for the copolymerisation of acrylonitrile with a series of vinyl monomers[82, 83] that the organoelement initiator exerts a significant influence on the dependence of the composition of the copolymer on that of the monomer mixture.

Thus, in the case of the classical radical initiator—azoisobutyronitrile, the acrylonitrile–vinyl acetate (VA) copolymer is enriched in acrylonitrile as the more active monomer whatever the composition of the monomer mixture (the coefficients of the relative reactivities of the monomers are $r_{AN} = 4.05$ and $r_{VA} = 0.06$). When the trialkylborane–OEP organoelement initiator is used, the composition curve is S-shaped (Fig. 1). The section of the curve where the composition of the copolymer is virtually independent of that of the monomer mixture can be clearly seen, which suggests that there is a tendency towards the alternation of monomer units in the copolymer and indicates that the copolymerisation is of the complex-radical type. This is also indicated by the equalisation of the relative reactivities of the monomers [$r_{AN} = 0.35$ and $r_{VA} = 0.42$; for comparison, we may note that $r_1$ and $r_2$ calculated in accordance with the $Q-e$ scheme (the Alfrey–Price scheme)[6] are respectively 4.27 and 0.06] and by the deviation from linearity in the calculation of the copolymerisation constants by the Kelen–Tüdös method.

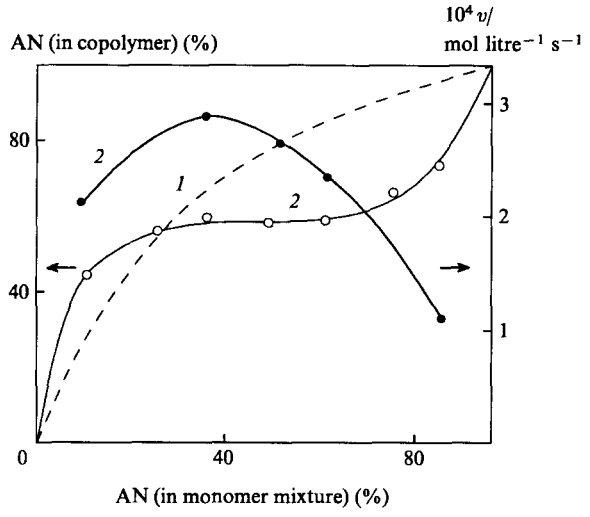



**Figure 1.** Dependence of the composition of the acrylonitrile–vinyl acetate copolymer and of the rate of copolymerisation on the composition of the monomer mixture. Initiator: (*1*) AIBN; (*2*) triisobutylborane–di-*tert*-butylperoxytriphenylantimony.

**Table 4.** Effective reactivities of the monomers.

| Monomer | | $r_1$ | $r_2$ | Initiator | Ref. | Monomer | | $r_1$ | $r_2$ | Initiator | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | | | | | 1 | 2 | | | | |
| AN | VA | 4.05 | 0.06 | AIBN | 63 | | VC | 15.0 | 0.02 | AIBN | 63 |
| | | 0.97 | 0.20 | TBB–TBP | 83 | | | 6.7 | 0.02 | TBB–TBPA | 42 |
| | | 0.90 | 0.04 | TBB–TBPT | 83 | | AA | 1.08 | 0.003 | TBB–TBPS | 42 |
| | | 0.85 | 0.05 | TBB–TBPG | 83 | VA | VDC | 0.03 | 3.60 | AIBN | 88 |
| | | 0.40 | 0.03 | TBB–TBPA | 83 | | | 0.12 | 0.20 | TBB–DPA | 88 |
| | | 0.35 | 0.42 | TBB–DPA | 82 | | VC | 0.23 | 1.68 | AIBN | 63 |
| | MMA | 0.15 | 1.20 | AIBN | 63 | | | 0.58 | 0.97 | TBB–DPA | 88 |
| | | 0.04 | 3.53 | TBB–TBP | 42 | | VPD | 0.20 | 3.02 | AIBN | 63 |
| | | 0.15 | 0.75 | TBB–TBPT | 83 | | | 0.32 | 0.19 | TBB–TBP | 33 |
| | | 0.26 | 0.67 | TBB–TBPG | 83 | | | 0.17 | 0.15 | TBB–TBPG | 33 |
| | | 0.10 | 0.64 | TBB–DPA | 83 | | | 0.30 | 0.28 | TBB–DPA | 33 |
| | VC | 2.8 | 0.04 | AIBN | 63 | VPD | ST | 0.05 | 5.20 | CPC | 63 |
| | | 0.86 | 0.05 | TBB–DPA | 99 | | | 0.05 | 0.96 | TBB–DPA | 33 |
| | | 0.74 | 0.05 | TBB–TBPT | 99 | | | 0.29 | 0.94 | TBB–TBPG | 33 |
| | AA | 0.35 | 1.15 | AIBN | 63 | | VDC | 0.40 | 0.35 | CPC | 63 |
| | | 0.33 | 0.08 | TBB–DPA | 42 | | | 0.26 | 2.16 | TBB–DPA | 33 |
| | VDC | 0.91 | 0.37 | AIBN | 63 | ST | AA | 0.15 | 0.25 | BP | 63 |
| | | 0.12 | 0.14 | TBB–DPA | 32 | | | 0.87 | 0.04 | TBB–TBPA | 41 |
| | MAA | 0.15 | 5.50 | AIBN | 63 | | MAA | 0.15 | 0.70 | BP | 63 |
| | | 0.15 | 0.43 | TBB–DPA | 83 | | | 0.27 | 0.03 | TBB–TBPA | 41 |
| | ST | 0.04 | 0.40 | AIBN | 63 | Ethylene | VA | 0.80 | 1.20 | TBB–DPA | 87 |
| | | 0.04 | 0.27 | TBB–DPA | 83 | | | 0.95 | 1.10 | TBB–TBPS | 87 |
| MMA | MAA | 0.58 | 1.40 | BP | 44 | | | 1.0 | 1.30 | AIBN | 63 |
| | | 0.95 | 0.99 | AIBN–TBB | 44 | | VC | 0.22 | 0.50 | TBB–DPA | 94 |
| | | 1.07 | 0.62 | AIBN–DPA | 44 | | | 0.24 | 3.60 | AIBN | 63 |
| | | 0.45 | 0.28 | TBB–DPA | 44 | | | 0.20 | 2.0 | Ziegler–Natta | 89 |
| | | 1.10 | 0.85 | AIBN–DBPS | 44 | Propene | VC | 0.28 | 0.39 | TBB–DPA | 94 |
| | ST | 0.46 | 0.52 | CPC | 63 | Hex-1-ene | VC | 0.05 | 0.65 | TBB–DPA | 94 |
| | | 0.37 | 0.57 | TBB–DPA | 86 | | | 0.06 | 0.88 | TBB–TBPA | 94 |
| | | 0.32 | 0.33 | CPC–DPA | 86 | | | 0.13 | 0.94 | TBB–TBPS | 94 |
| | VDC | 2.50 | 0.50 | AIBN | 63 | | AN | 0.10 | 4.60 | TBB–DPA | 94 |
| | | 1.04 | 0.06 | TBB–DPA | 32 | | | 0 | 12.2 | AIBN | 63 |

Note. The following abbreviations have been adopted: TBB = triisobutylborane, DPA = di-*tert*-butylperoxytriphenylantimony, TBPA = *tert*-butylperoxytetraphenylantimony, TBPS = *tert*-butylperoxytrimethylsilicon, TBPG = *tert*-butylperoxytriethylgermanium, TBPT = *tert*-butylperoxytriethyltin, VPD = *N*-vinylpyrrolidinone, VC = vinyl chloride, ST = styrene, VDC = vinylidene chloride, and CPC = dicyclohexylperoxy carbonate.

Such an appreciable influence of low concentrations of the initiator {[TAB] = $(2-8) \times 10^{-3}$ mol/mol of the monomer mixture, [OEP] = $10^{-3}$ mol/mol of the monomer mixture} is due to the coordination of the growing macroradical to the components of the initiating system. The trialkylborane, which has an unoccupied orbital in the boron atom, should then play the most active role. Its coordination to the growing acrylonitrile radical leads to a redistribution of electron density and enhances the electron-accepting properties of the polyacrylonitrile radical. The dependence of the rate of copolymerisation on the composition of the monomer mixture has a distinct maximum (Fig. 1). This suggests that the monomers form a reaction complex in the chain propagation stage.[1, 3]

Similar features have been observed also in the copolymerisation of acrylonitrile with acrylic and methacrylic acids and also with MMA.[83] Thus the composition curve for the acrylonitrile–vinyl acetate monomer pair contains a section where the composition of the copolymer is virtually independent of that of the monomer mixture. The relative reactivities (Table 4) in the case of an organoelement initiator differ appreciably from the values calculated in accordance with the $Q-e$ scheme and literature data.[63] The observed equalisation of the copolymerisation constants should lead to the synthesis of a polymer with a uniform composition.

Organoelement compounds exert a no less powerful influence on the dependence of the composition of the copolymer on that of the monomer mixture in the case of the methyl methacrylate–methacrylic acid pair as well.[41, 44] In the copolymerisation of the above monomers without the addition of organoelement compounds (with AIBN as the initiator, Table 4), the copolymer is enriched in methacrylic acid (MAA) whatever the composition of the monomer mixture. In the presence of the trialkylborane–OEP binary organoelement initiator, the composition curve is S-shaped and the relative reactivities of both monomers are significantly less than unity (Table 4). The product of the copolymerisation constants ($r_{MMA} \cdot r_{MAA}$) tends to zero, which indicates the alternation of the monomer units in the copolymer.[3]

The study of the separate influences of the components of the binary organoelement initiator on the chain propagation showed that the addition of 0.2 mol.% of triisobutylborane at a AIBN initiator concentration of 0.1% leads to an appreciable equalisation of the relative reactivities of the monomers. The introduction of an organoantimony peroxide together with AIBN also exerts a fairly strong influence on the reactivity of the monomers and growth radicals—the copolymer is enriched in MMA along all the sections of the composition curve. *tert*-Butylperoxytrimethylsilicon, which is used as a fairly effective coinitiator in relation to trialkylboranes, has a similar influence on the effective constants for the copolymerisation of MMA and methacrylic acid.[25, 32] Thus both components of the organoelement initiator (trialkylborane and OEP) have a regulating effect on the composition of the copolymer in the copolymerisation of acrylic monomers.

The rate of copolymerisation and the degree of conversion depend significantly on the nature of the heteroatom in the peroxide. Thus, in the copolymerisation of acrylonitrile with vinyl acetate, organoantimony and organotin peroxides are the most active as coinitiators in relation to trialkylborane (Table 5), while the composition with *tert*-butyl peroxide is least active: after 3 h, the degree of conversion does not exceed 5%. These data agree with the available information about the homopolymerisation of vinyl monomers in the presence of organoelement initiators[11, 25, 32, 33] and indicate a direct influence of the nature of the heteroatom in the peroxide on the rate of generation of radicals and on the chain propagation stage.

The last conclusion has been confirmed by a study of the dependence of the composition of the acrylonitrile–vinyl acetate copolymer on the composition of the monomer mixture when various OEP (Fig. 2) and *tert*-butyl peroxides are used. The form of the composition curves as well as the dependences

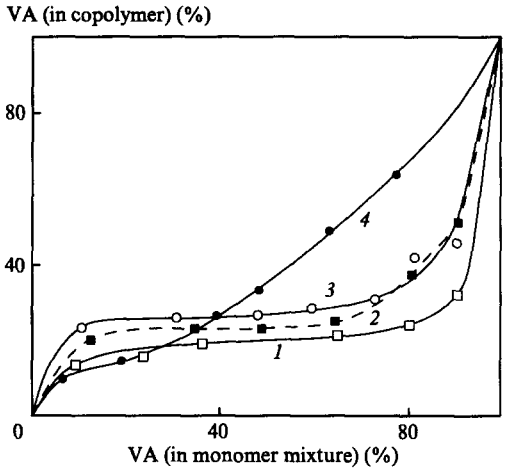



**Figure 2.** The influence of the nature of the heteroatom in the organoelement peroxide on the dependence of the composition of the vinyl acetate–acrylonitrile copolymer on the composition of the monomer mixture ($T$ = 293 K) in the presence of the triisobutylborane–peroxide initiator; peroxide: (*1*) *tert*-butylperoxytriethylgermanium; (*2*) *tert*-butylperoxytriethyltin; (*3*) *tert*-butylperoxytetraphenylantimony; (*4*) *tert*-butyl peroxide.

of the rate of copolymerisation on the composition of the monomer mixture differ significantly in the case of *tert*-butyl peroxide and its organoelement analogues. When germanium, tin, and antimony OEP are used, a section is observed on the composition curve where the composition of the copolymer is virtually independent of the composition of the monomer mixture. For the composition involving *tert*-butyl peroxide, the composition curve is also S-shaped, but there is no linear section.

Similar relations have been observed also in the case of the acrylonitrile–MMA monomer pair.[83] When organoelement peroxides are used, the reactivities of the monomers are equalised, whereas in the presence of *tert*-butyl peroxide as the coinitiator, the composition curve is close to the analogous curve for AIBN as the initiator.[63] When OEP are used for the copolymerisation of MMA with acrylonitrile, the copolymerisation constants of the monomer are similar and less than unity in all cases (Table 4), differing from the analogous constants for *tert*-butyl peroxide and AIBN.

Organosilicon peroxides exert a regulating effect on the copolymerisation of acrylates in the presence of sulfuryl chloride and phosphorus trichloride,[84, 85] but it is not quite so explicit as in the case of organic compounds of Group III elements, which can be accounted for by the difference between the electron-accepting properties of the modifying agents.

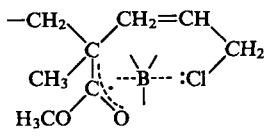
In the copolymerisation of two structurally related monomers, for example MMA–methacrylic acid, the differences between the coordination capacities of the heteroatoms in the peroxides do not exert a significant influence on the composition of the copolymer (Table 5),[41, 44] although on the whole a binary organoelement initiator exerts a regulating effect manifested by the equalisation of the relative reactivities of the monomer and by the S-shape of the composition curves. Similar features have

**Table 5.** Dependence of the rate of copolymerisation of acrylonitrile with vinyl acetate and methyl methacrylate in the presence of the triisobutylborane–peroxide binary initiator on the nature of the peroxide component ($T$ = 293 K).

| Comonomer (mol.%) | $10^4 v$ / mol litre$^{-1}$ s$^{-1}$ | | | |
|---|---|---|---|---|
| | TBP | TBPG | TBPT | DPA |
| VA, 49 | 0.05 | 0.86 | 1.40 | 2.02 |
| MMA, 45 | 0.05 | 0.76 | 0.81 | 2.32 |

been observed also for the acrylonitrile–MMA, acrylonitrile–methacrylic acid, and acrylonitrile–acrylic acid monomer pairs.[41, 83] In all these pairs, two electron-accepting monomers are copolymerised, each of them being capable of coordination interaction with the OEC via its functional groups.

In the copolymerisation of electron-donating and electron-accepting monomers, for example MMA–styrene,[86] MMA–allyl chloride,[45] acrylonitrile–styrene,[83] and acrylonitrile–vinyl acetate, the regulating effect of the organoelement initiators is most explicit. The initiator influences not only the dependence of the composition of the copolymer on that of the monomer mixture but also the dependence of the rate of copolymerisation on the initial contents of the monomers in the mixture. For the monomer pairs indicated, the dependence of the rate of copolymerisation on composition passes through a maximum in the vicinity of a nearly equimolar monomer ratio (Fig. 1). This yet again constitutes evidence in support of the complex-radical nature of the copolymerisation and also suggests that the monomers and macroradicals can form a complex in the chain propagation stage.[45]



$^1$H NMR study of the MMA–styrene copolymer obtained in the presence of dicyclohexyl peroxydicarbonate (DCC) and an organoelement initiator has shown that the microstructures of the specimens differ significantly.[86] A satisfactory agreement between the calculated and experimental fractions of the triads has been observed for the copolymer synthesised using DCC. For the specimens obtained in the presence of organoelement compounds, the discrepancy between the experimental and calculated data is significant (Table 6), which demonstrates the inapplicability of the Mayo–Lewis scheme under these conditions. The triad ratio calculated from the relative reactivities in conformity with the penultimate unit model showed that the Mertz–Alfrey–Goldfinger equation describes the copolymerisation process much better. However, it is seen from the data presented that the influence of the penultimate unit is not the only factor which alters the composition of the copolymer. These data indicate yet again that the complex formation reaction between the monomer and the initiator and also between the initiator and the macroradical makes an appreciable contribution to the change in the relative reactivities of the monomers.

**Table 6.** The triad ratios (1–3) in the $^1$H NMR spectra of the MMA–styrene copolymer (mole fraction of MMA in the copolymer 0.6)[86]

| Triad* | DCC | | $Bu^i_3B$–$Ph_4SbOOBu^t$ | | |
|---|---|---|---|---|---|
| | 1 | 2 | 1 | 2 | 3 |
| AAA | 0.42 | 0.38 | 0.13 | 0.24 | 0.17 |
| BAA | 0.37 | 0.33 | 0.62 | 0.33 | 0.43 |
| BAB | 0.21 | 0.29 | 0.25 | 0.43 | 0.50 |

Note. 1–experimental fraction; 2–fraction calculated for the terminal model; 3–fraction calculated for the penultimate model.
* In the triads, A = MMA and B = styrene.

Data concerning the dependence of the instantaneous and overall compositions of the MMA–styrene copolymer on the degree of conversion show that, in copolymerisation in the presence of DCC, the copolymer is enriched in MMA at high degrees of conversion. This indicates the nonuniformity of the product. Initiation by the tetraalkylborane–OEP system leads to the formation of a copolymer with a narrower distribution of the fractions with respect to composition.[86]

In the copolymerisation of acrylates with alkenes, the regulating effect of organoelement compounds is not quite so explicit as in the examples examined above. The rate of copolymerisation of acrylonitrile with hex-1-ene and cyclohexene, of MMA with ethylene, and of vinyl acetate with ethylene diminishes linearly with increase in the content of the olefin in the mixture.[87] Although the relative reactivities of the monomers do differ somewhat from those for the classical radical initiators the difference is less than for the copolymerisation of two vinyl monomers (Table 4). This is associated with the fact that olefins and especially the growth radicals associated with them show a smaller tendency towards complex formation than the monomers containing functional groups or atoms with lone electron pairs.

An organoelement initiator exerts a modifying influence also on both copolymerising monomers or electron donors, for example *N*-vinylpyrrolidinone (VPD)–vinyl acetate.[33, 88] For this pair, the composition of the copolymer is constant within a certain range of monomer compositions, which indicates the alternation of the monomer units in the copolymer. This is also indicated by the equalisation of the relative reactivities of the monomers (Table 4) and also by the deviation from the linear variation of the calculated parameters in the determination of the copolymerisation constants by the Kelen–Tüdös method. The dependence of the rate of copolymerisation on the composition of the monomer mixture passes through an extremum in the region of the equimolar composition of the monomer mixture (Fig. 3). One cannot rule out the possibility that the monomers form a 1 : 1 reaction complex during chain propagation.[1]

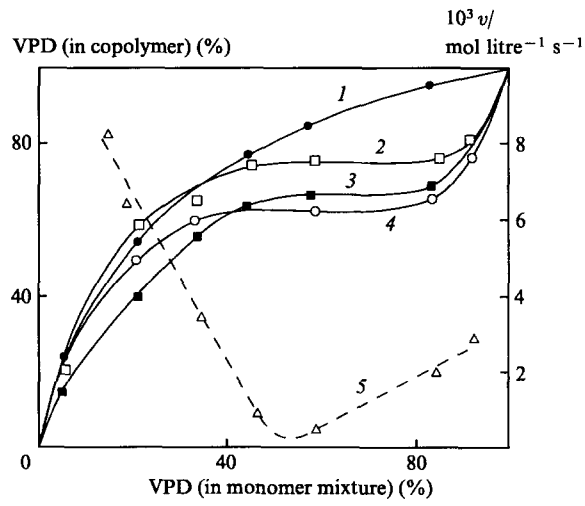



**Figure 3.** Composition curves (curves *1–4*) and the rates of copolymerisation (curve *5*) of *N*-vinylpyrrolidinone with vinyl acetate. Initiator: (*1*) AIBN; (*2*) triisobutylborane–*tert*-butyl peroxide; (*3*) and (*5*) triisobutylborane–di-*tert*-butylperoxytriphenylantimony; (*4*) triisobutylborane–*tert*-butylperoxytriethylgermanium.

The organoelement exerts a significant influence also on the copolymerisation of *N*-vinylpyrrolidinone with vinylidene chloride (*N*-vinylpyrrolidinone and vinylidene chloride are 'naturally alternating' comonomers).[33] The composition curve is S-shaped when DCC is used as the initiator. In the copolymerisation of the above pair of monomers in the presence of the trialkylborane–OEP initiator, a unilateral enrichment of the copolymer in vinylidene chloride is observed.

Thus catalytic amounts of organic compounds of Group III–V elements not only effectively initiate the low-temperature (co)polymerisation of vinyl monomers but also exhibit a regulating activity on the rate of (co)polymerisation and the composition of the copolymers.

## VI. Copolymerisation of vinyl chloride with ethylene and α-olefins in the presence of organometallic compound–peroxide initiating systems

Vinyl chloride and α-olefins are known to polymerise effectively at a low pressure via different mechanisms: vinyl chloride via a radical mechanism and ethylene and its homologues via a coordination mechanism in the presence of Ziegler–Natta catalysts.[6, 7] The copolymers of vinyl chloride with olefins cannot be synthesised with a high degree of conversion under technologically convenient conditions in the presence of the usual radical initiators:[89] the maximum degree of conversion is 17% in the presence of AIBN,[90] 24% in the presence of Ziegler–Natta catalysts,[91] and 30% in the presence of electron-donating additives.[92] The lack of effective initiators has held back the industrial production in our country of the above copolymers, which are extremely promising as plastics: they can be easily worked, have a larger elongation on rupture than poly(vinyl chloride), have an enhanced impact strength, etc. Furthermore, the introduction of even 5%–10% of ethylene into poly(vinyl chloride) appreciably lowers the cost of the monomer.

The coordination-radical initiators based on organic compounds of Group III elements and organic peroxides of Group IV elements occupy an intermediate position between the traditional radical initiators and Ziegler–Natta catalysts by virtue of their structural characteristics. They make it possible to copolymerise vinyl chloride with ethylene and α-olefins at a high rate and with a high conversion under energetically convenient conditions.[93, 94]

After 5 h, the limiting conversion for the vinyl chloride–ethylene copolymer in the presence of the trialkylborane–OEP organoelement initiator reaches 90%. With increase in the length of the alkyl group in the olefin, the rate of polymerisation and the conversion fall and in the case of oct-1-ene the yield of the copolymer does not exceed 20%. The additional introduction of the initiator into the system leads merely to a slight increase in the yield of the copolymer. The reason for the decrease in conversion is probably associated with chain termination due to the mobile hydrogen atoms in the olefin in the α-position relative to the double bond.

The structure of the peroxide and the composition of the monomer mixture exert direct influence on the process kinetics. It has been shown in relation to hex-1-ene that, with increase in the content of vinyl chloride in the monomer mixture from 6% to 89%, the limiting conversion rises from 3% to 49%, which agrees well with the reactivity of the copolymerising monomers. It has been found that the olefins themselves are incapable of homopolymerisation in the presence of the systems indicated.[25, 94] Organoantimony peroxides are more active as coinitiators than their organogermanium and organosilicon analogues, which is probably associated with the characteristic features of the radical formation in the OEC–peroxide systems[27] and also agrees with data on the homopolymerisation of vinyl chloride in the presence of organoelement initiators.[95]

When traditional radical initiators as well as Ziegler–Natta catalysts are used for the copolymerisation of vinyl chloride with olefins, the possibilities for the variation of the composition of the copolymer are extremely limited. The form of the composition curves and the relative reactivities of the monomers (Table 4) show that the copolymer is enriched in one of the monomers. This is associated with the significant difference between the reactivities of vinyl chloride and olefins. The use of trialkylborane–OEP systems leads to an appreciable equalisation of the copolymerisation constants. For a series of systems, the composition of the copolymer is almost independent of the composition of the monomer mixture and is nearly equimolecular over a wide range of [mixture] compositions.[87, 94]

Calculations of the relative reactivities of the monomers by the Kelen–Tüdös and Fineman–Rossi methods reveal a deviation of the calculated parameters from the linear relation. This indicates the system does not obey the classical Mayo–Lewis equation and can be explained within the framework of the coordination-radical copolymerisation mechanism: the boron atom in trialkylborane and the element in the peroxide may be coordinated both to the monomers and to the growing macroradicals, altering their reactivity and hence the relative reactivities of the monomers.

Analysis of the physicochemical properties of the copolymers of vinyl chloride with olefins showed that, when olefin units are introduced, the Fikentscher constant is reduced. This facilitates the processing of the polymeric product and improves its plasticity.[96]

When oxidation-reduction systems based on triethylborane and organic oxidants (oxygen, *tert*-butyl hydroperoxide) are used, the regulating activity is manifested to a lesser extent[92, 97, 98] than in the case of the trialkylborane–OEP binary initiator. It is quite evident that the heteroatom in the OEP also participates in the propagation stage by virtue of its unoccupied *d* orbitals. The possibility of the formation of complexes between the peroxides of Group IV elements and the monomers, including olefins, has been demonstrated in a series of studies.[9, 28, 29]

The regulating activity of the OEC–peroxide initiator is manifested not only in the presence of organoboron compounds but also in the presence of alkyl derivatives of aluminium and bismuth.[99]

The trialkylborane–OEP binary initiator also made it possible to achieve the single-stage synthesis of terpolymers containing vinyl chloride, vinyl acetate, and olefin units.[100] The above terpolymers can be used as elastomers, effective adhesives, and constructional materials, including materials for the medical industry. A series of such copolymers, obtained in recent years by foreign companies, can be processed without the introduction of plasticisers. They have been called third generation polymers with internal plasticisation.

As for the ethylene–divinyl chloride copolymers, the main complication in the synthesis of the above terpolymers consists in the fact that under mild conditions (room temperature, low pressure) olefins and vinyl monomers in the presence of traditional radical initiators copolymerise ineffectively and as a rule graft polymerisation is used for their synthesis.[101, 102] The trialkylborane–OEP binary initiator makes it possible to obtain the above polymers with conversions up to 70% over a period of 5–6 h within a wide range of compositions. It is of interest that, along the initial sections, the copolymer is enriched in ethylene although its relative reactivity constant is somewhat lower than for vinyl acetate and vinyl chloride. On the other hand, for the limiting conversion the copolymer contains more vinyl chloride. The above features demonstrate yet again that the components of the initiator are capable of coordinating to the growing macroradicals and monomers and of altering their reactivity. In ter- and tetra-polymerisation in the presence of complex forming agents, the overall proportions of the monomer-donor and monomer-acceptor units which have entered into the polymer are known to be similar.[103–105]

## VII. Conclusion

The set of data presented indicates the development of a promising aspect of the synthetic chemistry of polymers involving the application of catalytic amounts of organometallic compounds as modifying agents for the homo- and co-polymerisation of vinyl monomers and olefins. Small amounts of added organoelement compounds make it possible to influence the reactivity of the monomers and the macroradicals and to regulate thereby the kinetic process parameters in the initiation, chain propagation, and chain termination stages as well as the composition, structure, and properties of the (co)polymers.

The use of catalytic amounts of the modifying agent eliminates the problem of its removal from the final product and leads to the prospect of the industrial application of the above approach to the synthesis of (co)polymers with specified properties without the preliminary elimination of stabilisers.

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