Russian Chemical Reviews **70** (5) 425 – 447 (2001) © 2001 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2001v070n05ABEH000635

Problems of control of the reactivity of macroradicals and the growth of polymer chains

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Abstract. Data on the influence of stable radicals, iniferters, organoelement compounds and other active additives on the reactivity of macroradicals and the elementary steps of the (co)polymerisation of acrylic and some other monomers are generalised. New approaches to the control of the lifetime of the polymer chain and of the chain propagation stage are analysed. The problems of synthesis of compositionally homogeneous homo- and copolymers by radical polymerisation are considered. The bibliography includes 247 references.

I. Introduction

Polymerisation involving radical species has long been and still remains the key method for the synthesis of polymers. Obvious advantages of radical polymerisation are the methodical and technical simplicity of its implementation and good reproducibility of the results. A significant drawback of the method which somewhat delays its practical use is the difficulty of controlling the kinetics of polymerisation and compositional homogeneneity of the products, caused by the fact that the reactivity of free radicals participating in the polymerisation barely depends on the medium composition or other conditions.[1–4]

In this connection, development of effective methods for controlling the growth and the lifetime of a polymer chain is a topical task. This problem could be solved if it were possible to change the reactivity of the chain-propagating radicals in the required manner.

In recent years, several new approaches for controlling the growth of a polymer chain under the conditions of radical polymerisation have been proposed. These approaches include reversible inhibition by stable radicals, the use of iniferters as controlling initiators of a new type and the use of catalytic amounts of stable radicals or coordinatively unsaturated organoelement compounds (OEC) as reactive additives, *etc*. These methods have been used to develop effective methods for the synthesis of compositionally uniform polymeric materials with a specified set of properties. This review is devoted to the analysis of these methods.

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Received 13 November 2000
Uspekhi Khimii **70** (5) 486 – 510 (2001); translated by Z P Bobkova

II. Coordination interactions of organic compounds of Group II and III elements with macroradicals and their influence on chain propagation

The search for the ways of target-directed change in the reactivity of monomers and chain-propagating radicals directly during polymerisation is one of the most important aspects in the studies on the methods of synthesis of polymeric materials of a particular structure with specified properties.

In the 1970 – 1980s, the vigorous studies concerning the use of protic and aprotic Lewis acids (halides of Group II and III elements and some transition metals) for controlling the reactivity of vinyl and, especially, acrylic monomers carried out in a number of leading scientific schools of the world gave rise to a new line of research in the synthetic chemistry of polymers, namely, coordinated radical polymerisation.[5–7]

It was found that Lewis acids, which are strong electron acceptors, can substantially influence the electron density distribution over the monomer π-bond and functional group and are thus able to change the kinetic parameters of homo- and copolymerisation and the relative activities of monomers. On the basis of this approach, original methods for the synthesis of alternating and compositionally homogeneous copolymers, physiologically active high-molecular-mass compounds, graft and block copolymers, and a number of promising composite materials have been developed.

The main drawback of this method for modification of polymeric materials is that the controlling additive is introduced, as a rule, in a substantial excess with respect to the initiator (1% – 5% relative to the monomer). This leads to contamination of the resulting polymer. The cost of its purification is high; therefore, this method for the control of the composition and structure of polymers does not have prospects in industry.

The use of OEC as initiators has laid the foundations of a new stage in the development of the synthetic chemistry of polymers.

The Ziegler – Natta catalysts proposed for the synthesis of homo- and copolymers of alkenes and dienes are of limited utility for (co)polymerisation of vinyl monomers, especially acrylates,

because these monomers are highly reactive towards the components of these organometallic catalysts.[8]

Conversely, initiating systems based on alkyl derivatives of non-transition elements and oxidants including organic and organoelement peroxides (OEP) not only initiate efficiently radical homo- and copolymerisation of a broad range of monomers but also control the composition of copolymers and the kinetics of processes; they also change noticeably the properties of polymers. Based on the analysis of the characteristic features of polymerisation kinetics and unusual properties of macromolecules synthesised in the presence of organoelement initiators, it was initially suggested and later convincingly proved that the features mentioned above are related to the coordination interaction of the OEC with the growing radical. This interaction promotes an increase in the electron-withdrawing properties (electrophilicity) of the macroradical.[9–11]

1. The effect of coordinatively unsaturated organoelement compounds on the polymerisation kinetics of vinyl monomers and on the molecular-mass characteristics of polymers

Among organoelement initiators of the redox type, it is necessary first of all to distinguish compositions based on alkyl derivatives of boron and aluminium, which possess a number of advantages over the conventional radical initiators.[11–20] In particular, boron and aluminium alkyl derivatives in combination with organic and organoelement peroxides permit one to carry out polymerisation of vinyl monomers, which occurs at a high initial rate over a broad temperature range,† from 0 to 50 °C,[13–15] and copolymerisation of vinyl monomers with alkenes and allylic monomers.[23–25] Polymers and copolymers prepared in the presence of these organoelement initiators have unusual properties such as stability against thermal treatment and unusual molecular-mass characteristics; copolymers possess a number of unique mechanical properties.[13–29]

In view of the fact that the rates of chain propagation during the synthesis are high and based on the studies of some physicochemical properties of the prepared polymers, it has been suggested [14,27–29] that components of an organoelement initiator not only participate in the stage of generation of chain-propagating radicals but also influence the chain propagation and termination stages.

It is known that unsaturated compounds including monomers are able to be coordinated to OEP.[30–32] In these compounds, monomers act as electron density donors. On the one hand, complex formation increases the rate of peroxide decomposition and, hence, increases the initiation rate, while, on the other hand, it favours redistribution of electron density on the monomer π-bond and thus changes the reactivity of the monomer including that with respect to radicals. Similar complexes of vinyl monomers with Lewis acids (metal halides) have long been known and studied in detail.[5] It was shown reliably by IR [33–36] and NMR [37] spectroscopy that metal halides are coordinated to the carbonyl group of the monomer. The constants of complex formation of organic compounds of Group III elements with methyl methacrylate (MMA) and acrylonitrile (AN) were estimated taking organoaluminium compounds as examples.[38]

If the concentration of the OEC used as the initiator amounts to 0.01 mol.% – 0.05 mol.%, the formation of OEC complexes with radicals,[39–41] including polymeric radicals, appears more likely.[28,33] Upon the OEC – radical coordination interaction, the electron-withdrawing properties of the growing macroradical are enhanced and its reactivity with respect to the multiple bonds in monomers increases. This interaction results in a higher rate constant for chain propagation. In addition, due to steric factors and the enhanced electrophilicity of the species, the rate constant for chain termination decreases.

† For vinyl chloride (VC), this range is −60 to 50 °C.[15,19,21,22]

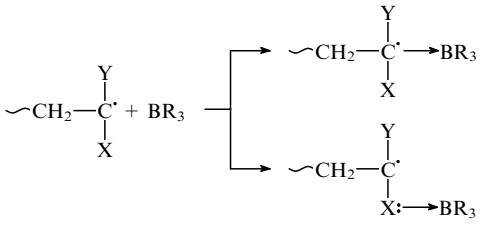
In a series of studies,[17–19,40,41] it was demonstrated that the addition of catalytic amounts of OEC derived from Group II and III elements in a polymerising mixture which contains peroxide and azo initiators entails an increase in the rate of polymerisation of (meth)acrylic and some vinyl monomers and markedly influences the properties of the resulting polymers (Table 1).

Table 1. Influence of triisobutylborane (TIBB) on the rate of polymerisation (V) of vinyl monomers and the molecular mass (MM) of polymers (T = 313 K).

Monomer	Initiator (0.1 mol.%)	TIBB (mol.%)	$10^4 V$ /mol litre^{-1} s^{-1}	10^{-3} MM
VA	AIBN	0.0	0.3	737
		0.2	1.7	614
		0.3	6.0	503
BA	DCHPD	0.0	0.3	2680
		0.2	19.9	610
		0.4		440
		0.6		380
		0.8		200
AN	AIBN	0.0	21.0	–
		0.5	159.2	–
		1.0	295.1	–
		1.5	237.3	–
MMA	DCHPD	0.0	0.7	610
		0.2	1.1	586
		0.4	1.5	560
			1.8	
AA (in THF)	DCHPD	0.0	0.09	9.4
		0.015	0.22	–
		0.045	0.56	–
		0.060	1.12	7.7
St	DCHPD	0.0	3.4	1800
		0.2	3.6	1780
		0.3	3.7	1660

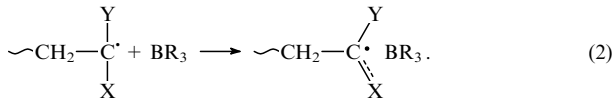
Note. The following designations are used: VA is vinyl acetate, AIBN is azobisisobutyronitrile; BA is butyl acrylate, DCHPD is dicyclohexyl peroxydicarbonate, AA is acrylamide, St is styrene.

Thus the rate of polymerisation of AN and butyl acrylate (BA) increases by almost two orders of magnitude upon introduction of trialkylborane in the system. Meanwhile, although organoboron compounds are capable of initiating homolytic decomposition of hydroperoxides,[42,43] they do not exert catalytic action on the decomposition of acyl peroxides [in particular, benzoyl peroxide (BP)[44] or dicyclohexyl peroxydicarbonate (DCHPD)],[18] or other compounds,[45] used in the studies cited as initiators. The researchers concluded that the accelerating influence of trialkylboranes on the polymerisation of polar vinyl monomers can be due exclusively to the coordination interaction of the growing macroradicals with the boron atom in the OEC. This interaction occurs either directly at the reaction centre (with participation of the unpaired electron), or at the functional group



(1)

(where X is a functional group, Y is the hydrogen atom or a methyl group), or simultaneously at both sites with delocalisation of the unpaired electron

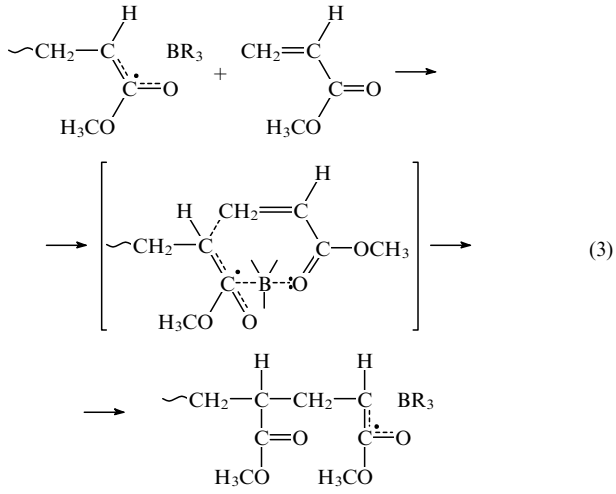


(2)

On the basis of studies of copolymerisation of MMA with electron-donating monomers involving binary trialkylborane–OEP initiators,[11,14] it was suggested that the Lewis acid might be involved in the coordination interaction with the poly(methyl methacrylate) (PMMA) radical; this hypotheisis was proved by EPR spectroscopy[28,46] and confirmed by quantum-chemical calculations.[47] In addition, it was shown by quantum-chemical calculations[48] that in the case of radicals containing a C=O group in the α-position to the reaction centre, the reaction centre is delocalised over three atoms.

Unlike metal halides (Lewis acids), organometallic additives introduced in the system in amounts comparable with the initiator concentration (0.1 mol.% – 0.5 mol.% with respect to the monomer), influence appreciably the growth of the polymer chain. This fact indicates unambiguously that an increase in the polymerisation rate in the presence of these compounds is due to complex formation of the OEC exactly with the macroradical rather than with the monomer.

It has been suggested[49] that one OEC molecule can participate consecutively in several chain propagation steps, while retaining the growing macroradical in its coordination sphere. In this case, chain propagation occurs in a cyclic reaction complex which incorporates the growing macroradical, the monomer, and the complex-forming agent.



(3)

A similar mechanism involving an eight-membered reaction complex has been proposed by Kabanov[50] to interpret the increase in the propagation rate constant in the polymerisation of MMA in the presence of metal halides and by Smirnova and coworkers,[51,52] who studied copolymerisation of acrylic acid with VA (vinyl acetate) in the presence of germanium salts. In our opinion, the above-presented reaction complex [see Eqn (3)], which includes the allylic delocalised macroradical is thermodynamically and geometrically more stable.

It was found[53] that the addition of trialkylborane accelerates processes with monomers containing a polar substituent. In the case of styrene, organoelement additives have little influence on the polymerisation. Apparently, this is due to the fact that the St macroradical contains no functional groups capable of being coordinated to trialkylborane; therefore, the additive almost does not change the electrophilicity of the growing macroradical. The coordination directly to the reaction centre, namely, to the carbon atom carrying the unpaired electron is relatively unlikely. Moreover, this interaction can create steric hindrance to chain propagation. It is not by chance that the St polymerisation rate is lower in the presence of some organic compounds of Group III elements than without any complex-forming additives.[49]

The features of electronic and spatial structures of the growing macroradical play a crucial role in the chain propagation stage of coordinated radical polymerisation. On the one hand, coordination of an OEC molecule to a macroradical increases the electrophilicity of the latter and thus enhances its reactivity with respect to the monomer π-bond. It is evident that this effect is more pronounced in the case of polymerisation of sterically nonhindered monomers such as BA, AN and VA. On the other hand, upon the coordination interaction of the radical with OEC, the size of the reaction centre increases and additional steric hindrance to the chain propagation can arise. In the case of bulky radicals, for example, those of PPMA or polystyrene (PS), steric factors are, naturally, more significant in the chain propagation step than in the case of the BA or VA macroradicals. This is why the activating effect of Group III element alkyl derivatives is manifested most clearly in the polymerisation of esters and other functional derivatives of acrylic acid (amides, nitriles). The effect involved in the polymerisation of methacrylates, for example, MMA and butyl methacrylate (BMA) is much less pronounced.

The structure of OEC also influences the reactivity of the chain-propagating radicals and, hence, the kinetic parameters of polymerisation of acrylic monomers. For example, replacement of the alkyl radical in the trialkylborane molecule by a halogen atom [dibutylboron bromide (DBBB)] deteriorates the coordination capacity of boron due to the partial blocking of its vacant *p* orbital ($p_\pi - p_\pi$ conjugation). As a consequence, DBBB is less active as a controller of acrylate polymerisation than TIBB (triisobutylborane).[49]

Similar regularities can be observed in the case of phenyl derivatives of boron. Triphenylborane and dibutylphenylborane[53] were found to accelerate polymerisation of acrylic monomers to a smaller extent than TIBB.

This can be due both to the steric restrictions involved in the coordination of triphenylborane to the growing polymer radical and to the conjugation of one phenyl group of the substituent with the vacant *p* orbital of boron. Consequently, as in the case of DBBB, the electron-withdrawing capacity of the central atom in the OEC decreases. These results do not contradict the published data on the relationship of the reactivities of alkyl and phenyl derivatives of boron.[54]

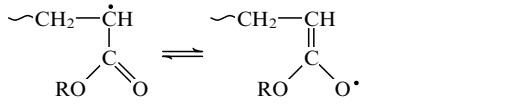
The alkyl derivatives of boron analogues — aluminium, gallium and indium — also increase somewhat the rate of polymerisation of acrylic monomers and VA;[49] however, as in the case of DBBB, their influence on the chain propagation stage is less pronounced than that of TIBB. The difference between the effects of organoboron compounds, on the one hand, and organoaluminium, -gallium and -indium compounds, on the other hand, is, apparently, due to different coordination capacities of the central atoms in the OEC and, as a consequence, their dissimilar influence on the reactivity of the macroradical. A similar consideration can be used to interpret the lower efficiency, compared to that of trialkylboranes,[53] of zinc and cadmium alkyl derivatives as controllers of the polymer chain growth in the polymerisation of acrylic monomers.

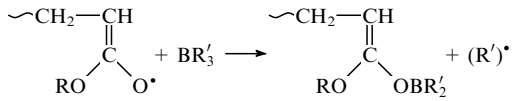
Thus, alkyl derivatives of boron exert a greater influence on chain propagation in the radical polymerisation of vinyl monomers than other coordinatively unsaturated OEC derived from Group II and III elements.[54]

The participation of OEC in the elementary steps of polymerisation (chain propagation, transfer, termination) opens broad opportunities for controlling the MM of the resulting polymers. The introduction in the polymerisate of boron alkyl derivatives in amounts commensurable with the concentration of the initiator decreases substantially the MM. The calculated constants for the chain transfer to TIBB are 1×10^{-2} for MMA and 2.2×10^{-2} for VA.[53] The addition of TIBB also influences markedly the MM of poly(butyl acrylate) when polymerisation is carried out in an ethyl acetate solution.[49] The molecular mass of the polymer decreases with an increase in the OEC concentration; upon the introduction of 0.8 mol % of trialkylborane, it decreases by more than an order

of magnitude. The calculated constant for chain transfer to the organoboron compound is 7.4×10^{-2}; this is somewhat higher than the constant for chain transfer to TIBB during MMA polymerisation and appreciably higher than the chain transfer constant to BA (0.3×10^{-4}).[55]

The high constants of chain transfer to trialkylboranes can be due to two processes involving the macroradical and the OEC. One process is free-radical substitution of the growing polymer radical for the alkyl radical in OEC

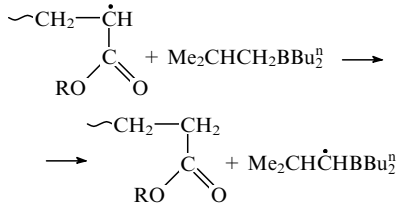

(4)


(5)

R, R′ is alkyl (isobutyl, ethyl, n-butyl).

Using EPR spectroscopy and quantum-chemical calculations, it has been shown [48] that (meth)acrylate macroradicals are prone to exist in a state typical of alkyl radicals, *i.e.*, the reaction centre is delocalised to give both carbon- and oxygen-centred radicals [Eqn (4)]. However, the rate constant for the replacement of alkyl radicals in trialkylborane by oxygen-centred radicals [Eqn (5)] is rather high, $\sim 10^5$ litre mol^{-1} s^{-1}.[56]

The second process which is also favourable for the control of the polymer MM is the abstraction of a hydrogen atom from the α-methylene unit of an alkyl group in OEC by the growing macroradical.

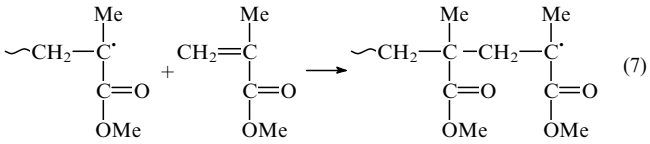

(6)

The occurrence of this reaction was proved unambiguously by EPR using the spin trap technique in a study of the influence of small additives of methyl acrylate (MA) and other acrylic monomers on the polymerisation of MMA with organoelement initiators.[57] The rate constant for this reaction in the case of triethylborane is $\sim 10^4$ litre mol^{-1} s^{-1}.[56]

In the polymerisation of styrene (St), the MM of the product barely changes, which is consistent with the results of kinetic measurements and indicates that OEC does not interact with the growing macroradical of PS.[49, 53]

The influence of added OEC on the molecular-mass distribution (MMD) of polymers has been studied by gel permeation chromatography (GPC).[58] In the presence of AIBN as the initiator, a unimodal MMD curve is observed; however, when TIBB is added to the system, the curve becomes clearly bimodal. As a consequence, the polydispersity of samples increases somewhat. Evidently, in the presence of TIBB, the growth of the polymer chain occurs in parallel by two mechanisms, namely, coordinated radical and radical mechanisms.

On the one hand, OEC is coordinated to the growing macroradical, thus increasing its electrophilicity and, hence, its reactivity with respect to the monomer. As noted above, chain propagation takes place in a cyclic reaction complex [see, for example, Eqn (2)]. This interaction changes the chain propagation and termination rate constants and decreases the MM of the polymer. On the other hand, growth of the polymer chain occurs simultaneously by the classical radical mechanism


(7)

A bimodal MMD curve is also observed when polymerisation of MMA is carried out with a binary initiator, TIBB–di-*tert*-butylperoxytriphenylantimony (DPA), which is an efficient low-temperature initiator controlling polymerisation of vinyl monomers.[13, 15, 19, 22, 32, 44]

The conclusions drawn confirm indirectly the results of studies of the MMD of PS samples synthesised in the presence of various OEC derived from Group II and III elements.[52] The introduction of these compounds barely influences both the general pattern of the MMD curve and the degree of polydispersity of samples. It has been noted above that OEC do not react with the growing polystyrene radical due to electronic and steric factors.[49, 58] Therefore, in the polymerisation of St, chain propagation follows only the traditional radical mechanism without participation of the complex-forming agent.

Thus, the data outlined above indicate that organic compounds of Group III elements provide effective control of the molecular-mass characteristics of polyacrylates. This way of controlling polymerisation of acrylic monomers opens up new opportunities for the synthesis of polymers with novel physicochemical and practical properties. A certain drawback of the proposed method is the higher polydispersity of the resulting polymers, caused by the fact that polymerisation in the presence of organoelement additives follows two parallel mechanisms.

2. Specific influence of phenolic inhibitors on homo- and copolymerisation of vinyl monomers in the presence of organic compounds of Group III elements

Hydroquinone, ionol, diphenylolpropane and some other phenols are known inhibitors of radical polymerisation; they are traditionally used as stabilisers for the storage of vinyl monomers. The inhibiting efficiency substantially increases in the presence of oxygen; this may be due to oxidation of phenols to quinones, which retard chain propagation more appreciably.[59]

According to the most popular viewpoint,[59, 60] the inhibitory influence of hydroquinone is due to the easy abstraction of the active hydrogen atom from the phenol molecule giving rise to a phenoxyl radical.

$$R^{\bullet} + ArOH \longrightarrow R-H + ArO^{\bullet}. \qquad (8)$$

The phenoxyl radical, which exhibits a low reactivity towards the monomer multiple bond, is unable to initiate a radical process (polymerisation).

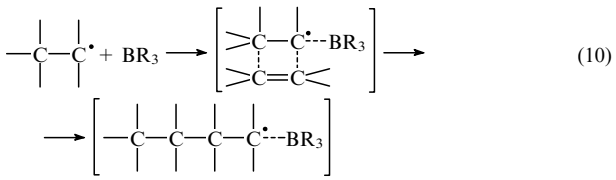
Back in the 1960s, it was found [61–64] that the addition of some OEC derived from Group III elements makes it possible to carry out polymerisation of MMA in the presence of BP or AIBN to a high degree of conversion, despite the presence of comparable amounts of hydroquinone. Apparently,[56] in the presence of OEC, the phenoxyl radicals undergo a fast S_R2 substitution reaction.

$$ArO^{\bullet} + MR_3 \longrightarrow R^{\bullet} + ArOMR_2 \qquad (9)$$

M is a Group II or III metal.

The alkyl radicals formed in this reaction can subsequently initiate polymerisation. It is in these processes that organoboron compounds can act as chain transfer agents in the polymerisation of acrylates. As noted above, the rate constants for the chain transfer in peroxide-initiated polymerisation of MMA are equal to 0.015 for tri-n-butylborane and 0.01 for TIBB.[20]

A somewhat different interpretation of the absence of inhibitory influence of phenols on polymerisation in the presence of OEC was proposed by Arimoto,[62] who suggested that trialkylborane is coordinated to the growing macroradical through the unpaired electron of the latter.

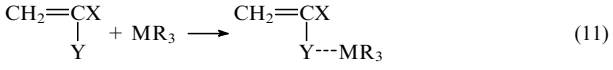


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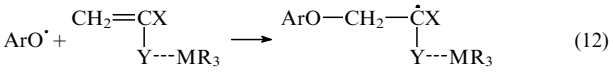
As a consequence, the reaction centre of the radical becomes blocked and the interaction with phenol is made impossible. It should be noted that Grotewold *et al.*[61] cast doubt on the experimental results obtained by Arimoto.

In some studies published in the 1990s,[16–18, 65] it was shown that diphenylolpropane and hydroquinone are not merely inactive as inhibitors of radical polymerisation of acrylates in the presence of trialkylboranes but, conversely, accelerate it. Indeed, the rates of MMA and AN polymerisation markedly increase in the presence of organic compounds of Group III elements, the effect becoming more pronounced with an increase in the contents of OEC and the above-mentioned diphenols. Similar data have also been obtained for reactions carried out in the presence of alkylalkoxy boron derivatives.[44]

This unusual accelerating effect can be due to some extent to the occurrence of chain transfer to the OEC [Eqn (9)]. However, this fact alone cannot account for the absence of the inhibiting effect in the polymerisation of MMA, AN, and MA in the presence of substantial concentrations of hydroquinone and diphenylolpropane (an order of magnitude higher than the initiator concentration) or for the absence of inhibiting effect after the introduction of Lewis acids in the system which undergoes polymerisation.[66–68] The unusual behaviour of phenols can be explained in terms of the coordinated radical mechanism of (co)polymerisation of acrylic monomers on organoelement initiators. In the presence of electron acceptors such as Lewis acids, the macroradical and the monomer are coordinated to components of the initiator. The complex formation of OEC with the monomer activates the monomer;[58] this enables initiation of the polymerisation by phenoxyl radicals.



(11)



(12)

M is a Group III metal.

The coordinated macroradical, unlike the non-coordinated one, exhibits enhanced electrophilicity with respect to the monomer π-bond, which results in a higher propagation rate constant.[5, 11, 18]

The occurrence of reaction (12) is also confirmed by the fact that IR- and UV-spectroscopic studies show the presence of phenoxy groups in the MMA polymer. This view on the kinetics of polymerisation of acrylates in the presence of OEC and inhibitors is indirectly supported by the absence or attenuation of the inhibiting effect in MMA polymerisation in the presence of Group III metal halides.[66–68] In this case, S_R2 reactions [Eqn (9)] are impossible in principle; therefore, the effect observed can be interpreted in terms of either the Arimoto scheme, or reactions (11) and (12), or the cyclic mechanism of chain propagation [see Eqn (3)].[7, 20, 49] The same trialkylborane molecule can be involved in several consecutive chain propagation events, while retaining the growing macroradical in the coordination sphere of the boron atom and 'receiving' (coordinating) new monomer molecules. Chain propagation in the cyclic reaction complex hampers the interaction of the growing macroradical with the inhibitor.

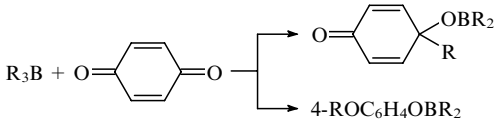
It is the processes considered above that account for the increase in the rate of MMA, AN and MA polymerisation in the presence of organic compounds of Group III elements and phenols such as hydroquinone and diphenylolpropane. However, in the case of ionol, which is a sterically hindered phenol, polymerisation rate somewhat decreases.[7, 16] This appears to be due to the fact that reactions (9) and (12) are much less efficient for ionol than for hydroquinone or diphenylolpropane.

In view of the foregoing, it can be assumed that the vacant orbitals of TIBB accept electron density through coordination to the macroradical. This increases the electrophilicity of the coordinated poly(methyl methacrylate) radicals; therefore, they become relatively 'inert' with respect to the abstraction of a hydrogen atom from phenol. In addition, chain propagation takes place in the cyclic reaction complex, which also hampers the reaction of the macroradical with the active hydrogen atom of the phenol hydroxy group. As a consequence, polymerisation of MMA proceeds up to a high degree of conversion in the presence of a 10-fold excess of the inhibitor with respect to OEC.

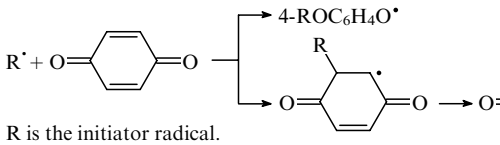
Phenolic inhibitors have also a certain influence on the polymer MM.[7, 16, 49, 65] In particular, the molecular mass of PMMA decreases upon the introduction of phenols. However, this influence is not so pronounced (as could be expected) as that observed in the absence of OEC or in the presence of conventional chain transfer agents.

Oxygen plays an important role in the mechanism of inhibition of radical polymerisation by various phenols. According to one view,[59] the influence of oxygen reduces to the oxidation of phenol to the corresponding stable radical or quinone. In the presence of organic compounds of boron or aluminium or of benzoquinone, polymerisation of MMA proceeds without an induction effect.[40, 61–64] The inhibitory effect of benzoquinone after the addition of TIBB depends on the [TIBB] : [benzoquinone] molar ratio. If the amount of benzoquinone is smaller than that of TIBB, the inhibitory action has virtually no effect on the polymerisation kinetics. The process occurs up to a high degree of conversion and the molecular mass of PMMA changes insignificantly. In the absence of OEC, benzoquinone efficiently inhibits polymerisation of acrylates: the rate of polymerisation in the initial stages is close to zero, the limiting degree of conversion is less than 0.5%.[49, 58]

As the benzoquinone concentration increases, the rate of polymerisation decreases. However, even with a twofold excess of benzoquinone with respect to alkylborane, it is markedly higher than that in the absence of OEC. Analysis of the publications cited and data on the reactivity of organoboron compounds and quinones point to efficient consumption of trialkylborane and quinone.[69–74]

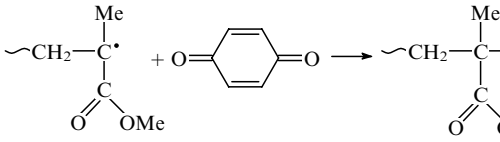


(13)



(14)

R is the initiator radical.



(15)

Reaction (14) and the regularities of inhibition of alternating copolymerisation by quinones have been studied comprehensively by EPR spectroscopy by Golubev,[70] who used the reactions of benzoquinone, naphthoquinone, and fluoranil with organic radicals of different electrophilicity as examples to demonstrate that the abnormally slight influence of quinoid-type radical inhibitors on the alternating copolymerisation is related to substantial polar effects involved in this reaction. In accordance with this concept, the increase in the electrophilicity of macroradicals upon the coordination to OEC should substantially influence the reactivity

of the macroradical with respect to the quinone [chain termination, Eqns (13)–(15)].

It is beyond doubt that in the presence of OEC in a polymerising system, the factor of polarity would play a vital part in the attenuation of the inhibiting effect of quinones. In particular, the phenoxyl radicals generated in processes (13)–(15) enter into S_R2 substitution to give alkyl radicals able to initiate polymerisation once again [see Eqn (9)]. Judging from the average chain length, two chain transfers to the trialkylborane molecule take place.[63]

The influence of organoaluminium compounds on the polymerisation of acrylates in the presence of benzoquinone is equally efficient.[58] The rate of polymerisation increases with an increase in the [triethylaluminium]:[benzoquinone] ratio, passes through a maximum, and then decreases. This was attributed[64] to the occurrence of two mechanisms of initiation; one of them is related to the decomposition of the initiator into radicals and the other, to the generation of radical centres upon decomposition of the triethylaluminium complex with quinone. In view of the analysis of products of the reaction of organoaluminum compounds with quinones, the latter mechanism seems quite debatable.

Apparently, in this case, as for trialkylborane, both the heterolytic reaction [Eqns (13)–(15)] and the homolytic transfer of the reaction centre to the metal atom in OEC [see Eqn (9)] take place. In addition, whereas in the case of TIBB, the reaction can involve two alkyl groups, in the case of triethylaluminium, only one group is involved[64] (the rate constant for chain transfer is equal to 89 litre $mol^{-1} s^{-1}$; for comparison, the rate constant for chain propagation is 576 mol $litre^{-1} s^{-1}$.[75]).

Organoelement compounds formed by Group III elements and the inhibitors chosen accelerate not only homo- but also copolymerisation of MMA with a number of vinyl monomers, including St, VA, and methacrylic acid (MAA).[7] Similar features have also been found for the MAA–VA pair of monomers. It was shown in relation to the copolymerisation of these monomers in the presence of hydroquinone and OEC that the inhibitor participates in the chain propagation and termination stages and influences the dependence of the copolymer composition on the composition of the monomer mixture.[17] For MAA contents in the monomer mixture ranging from 20 mol.% to 80 mol %, the addition of hydroquinone virtually does not change the composition of the MAA–VA copolymer, which does not depend on the composition of the monomer mixture. In the Kelen–Tudoc calculation of the copolymerisation constants, the intermediate calculated parameters (η and ψ) are found to deviate from the linear dependence; this is evidence supporting the coordinated radical mechanism of copolymerisation.

3. The coordinated radical copolymerisation of vinyl and some other monomers in the presence of organoelement initiators

At present, copolymerisation is an important method for the preparation of polymers with a specified set of chemical and physical properties because it is difficult in most cases to control the properties of homopolymers. Meanwhile the need to control these properties is a topical task in preparing materials for various purposes.[4,76]

Copolymerisation normally affords random copolymers, the composition and properties of which are determined by the composition of the monomer mixture and the reactivity of monomers and chain-propagating radicals. However, there exist monomer pairs copolymerisation of which gives polymers with regular alternation of the units. As a rule, strict alternation of monomer units is observed if one monomer is a clear-cut donor of electron density, and the other one is an acceptor. Since the number of monomers with clearly defined electron-withdrawing properties is small [maleic anhydride and its derivatives, sulfur(IV) dioxide], the number of monomer pairs that can form alternating copolymers is also few.

The main method for controlling the composition of copolymers is introduction of special additives, usually, protic and aprotic acids, into the system. The latter are coordinated to the monomers or to the chain-propagating radicals and thus enhance their electron-withdrawing properties and provide the possibility of preparing alternating copolymers.[5,77,78] The main drawback of this method of modification of polymer materials is that the controlling additive is introduced in a large excess with respect to the initiator (1–3 orders of magnitude), which results in contamination of the polymer formed. The cost of polymer purification is high; therefore, the use of this method to control the polymer composition on an industrial scale is non-expedient.

The use of organoelement initiators based on Group III element organic compound and peroxides eliminates this drawback because the controlling influence of these additives on chain propagation manifests itself, as noted above, when catalytic amounts of the initiator are used (0.01 mol %–1.00 mol %).

The complex formation effects in the radical copolymerisation in the presence of Lewis acids are largely determined by the electronic structure of the monomer.[6,79] In the possible limiting cases, either one monomer or both monomers react with the complex-forming agent. Both situations are analysed below.

It has been shown in relation to a number of monomer pairs that an organoelement initiator influences directly the variation of the copolymer composition and the copolymerisation rate *vs.* the composition of the monomer mixture. The controlling influence of OEC is most pronounced in the copolymerisation of (meth)acrylates with electron-donating monomers.[7,58] For instance, in the copolymerisation of MMA with allyl chloride (AC) with a classical radical initiator AIBN, the copolymer is enriched in the more active monomer, MMA, in each section of the composition curve (the relative activities of the monomers are $r_{MMA} = 3.05$; $r_{AC} = 0.05$).[23,77] The rate of copolymerisation decreases with an increase in the content of AC in the monomer mixture. When a binary initiator, TIBB–DPA, is used,[80] the composition curve is S-shaped. A section in which the copolymer composition does not depend on the composition of the monomer mixture can be clearly seen in the curve; in this case, the trend for the alternation of monomer units is close to its limiting value.

The relative activities of both monomers become much less different and smaller than unity (Table 2); the product $r_1 r_2 \rightarrow 0$, pointing to a coordinated radical mechanism of (co)polymerisation.[5,6] This is also indicated by the deviation from linearity of the calculated parameters in the determination of the copolymerisation constants by the Kelen–Tudoc method.

Organoelement initiators, even present in low concentrations (0.01 mol %–0.10 mol %), have a noticeable controlling influence on the composition and structure of the MMA–AC copolymer. This is due to the coordination of the growing macroradical to the components of the initial system. Studies of the separate effects of the initiator components on the dependence of the copolymer composition on the composition of the monomer mixture indicate that TIBB, which contains a boron atom with a vacant *p* orbital, plays the most active role in the complex formation with the macroradical.[80] Its coordination to the growing poly(methyl methacrylate) radical induces electron density redistribution in the radical, increases the radical electrophilicity, and enhances its reactivity towards the π-bond of the electron-donating monomer AC.

The variation of the rate of copolymerisation of AC with MMA as a function of the initial composition of the monomer mixture has a clear-cut maximum at a monomer ratio close to the equimolar ratio. This is evidence in favour of the coordinated radical mechanism of copolymerisation and also provides grounds for believing that the monomers and macroradicals form a cyclic reaction complex in the chain propagation stage.

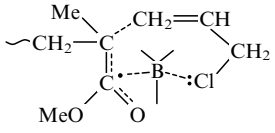


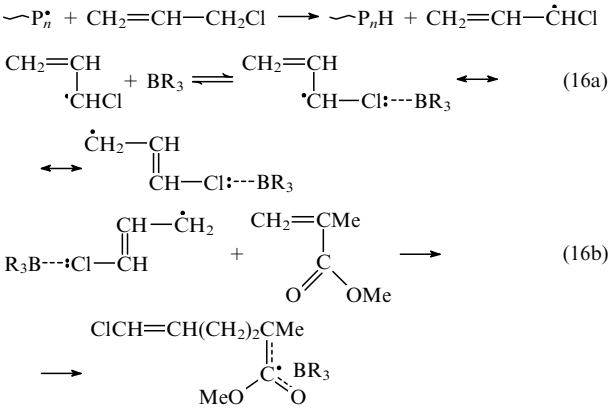
Table 2. Effective values for the relative activity of monomers.

Monomers		r_1	r_2	Initiator	Monomers		r_1	r_2	Initiator
1	2				1	2			
AN	VA	4.05	0.06	AIBN	MMA	VDC	2.50	0.50	AIBN
		0.97	0.20	TIBB – TBP			1.04	0.06	TIBB – DPA
		0.90	0.04	TIBB – TBPT	MMA	VC	15.0	0.02	AIBN
		0.85	0.05	TIBB – TBPG			6.7	0.02	TIBB – TBPA
		0.40	0.03	TIBB – TBPA	MMA	AA	1.03	0.03	TIBB – TBPS
		0.35	0.42	TIBB – DPA	VA	VDC	0.03	3.60	AIBN
AN	AC	3.05	0.05	AIBN			0.12	0.20	TIBB – DPA
		3.78	0.15	TIBB – DPA	VA	VC	0.23	1.68	AIBN
AN	MMA	0.15	1.35	PB			0.58	0.97	TIBB – DPA
		0.15	1.10	TIBB – oxygen	VA	VPD	0.20	3.02	AIBN
		0.04	1.53	TIBB – TPB			0.32	0.19	TIBB – TBP
		0.15	0.75	TIBB – TBPT			0.17	0.15	TIBB – TBPG
		0.26	0.67	TIBB – TBPG			0.30	0.28	TIBB – DPA
		0.10	0.64	TIBB – DPA	VPD	St	0.05	5.20	DCHPD
AN	VC	2.80	0.04	AIBN			0.05	0.96	TIBB – DPA
		2.20	0.05	TIBB – oxygen			0.29	0.94	TIBB – TBPG
		0.86	0.05	TIBB – DPA	St	AA	0.15	0.25	BP
		0.74	0.05	TIBB – TBPA			0.87	0.04	TIBB – TBPA
AN	VDC	0.91	0.37	AIBN	St	MAA	0.15	0.70	BP
		0.12	0.14	TIBB – DPA			0.27	0.03	TIBB – TBPA
AN	MAA	0.15	5.50	AIBN	Ethylene	VA	1.00	1.30	AIBN
		0.15	0.43	TIBB – DPA			0.80	1.20	TIBB – DPA
AN	St	0.04	0.40	AIBN			0.95	1.10	TIBB – TBPS
		0.19	0.45	TBPS	Ethylene	VC	0.24	3.60	AIBN
		0.14	0.26	TBPT			0.22	0.50	TIBB – DPA
		0.04	0.27	TIBB – DPA			0.20	2.0	Ziegler – Natta
MMA	MAA	0.58	1.40	BP	MMA	St	0.32	0.33	DCHPD – DPA
		0.95	0.99	AIBN – TIBB			0.50	0.60	TIBB – oxygen
		1.07	0.62	AIBN – DPA					
		1.10	0.85	AIBN – TBPS	Propene	VC	0.28	0.39	TIBB – DPA
		0.45	0.28	TIBB – DPA	Hex-1-ene	VC	0.05	0.65	TIBB – DPA
MMA	AC	48.10	0.03	AIBN			0.06	0.88	TIBB – TBPA
		0.57	0.03	TIBB – DPA			0.13	0.94	TIBB – TBPS
MMA	St	0.46	0.52	DCHPD	Hex-1-ene	AN	0.0	12.2	AIBN
		0.37	0.57	TIBB – DPA			0.10	4.60	TIBB – DPA

Note. The following designations are used: VDC is vinylidene chloride, AA is acrylic acid, VPD is vinylpyrrolidone, TBP is *tert*-butyl peroxide; TBPT is *tert*-butylperoxytriethyltin; TBPG is *tert*-butylperoxytriethylgermane; TBPS is *tert*-butylperoxytriphenylantimony; TBPS is *tert*-butylperoxytrimethylsilane.

The cyclic mechanism of propagation prevents the destructive chain transfer to the allylic monomer; this accounts for the high degree of conversion in the copolymerisation of AC with acrylates.

The presence of fragments with double bonds in the MMA – AC copolymer ($\sim$4% – 5%) can be explained by assuming that allyl-type radicals formed upon abstraction of a hydrogen atom from AC can again initiate polymerisation in the presence of OEC by the following scheme:



(16a)

(16b)

Coordination of OEC to an allyl type radical increases the radical electrophilicity and reactivity with respect to the π-bond of the monomer. The coordinated allylic radical, unlike a non-coordinated one, is able to re-initiate polymerisation [Eqn (16b)].

The possibility of initiating polymerisation by an allylic macroradical in the presence of Lewis acids (metal halides) was also mentioned in other publications. [5, 81, 82]

The NMR spectra of MMA – AC copolymers and syndiotactic PMMA coincide,[80] which confirms the radical mechanism of the copolymerisation of MMA with AC.

A thermomechanical study of MMA – AC copolymers showed [80] a sharp decrease in the glass transition temperature and a decrease in the ultimate strength and in the modulus of elasticity of copolymers with respect to the corresponding characteristics of the MMA homopolymer prepared both with the DPA – TIBB initiating system [83] and with a classical radical initiator.[84] Hence, the presence of AC (10 mol % – 15 mol %) in the copolymer has a substantial influence on its properties.

The decrease in the glass transition temperature of the MMA – AC copolymer noted above extends the temperature range of the highly elastic state of the copolymer and thus increases its frost resistance, which is significant for practical purposes.

Copolymerisation of AC with the electron-donating VA monomer in the presence of organoelement initiators proceeds to a lower degree of conversion (less than 10% over a period of 7 days)[85,86] than copolymerisation of AC with acrylates. This copolymer was also found to contain fragments with double bonds, which can serve as evidence for initiation of the polymerisation by allyl-type radicals in the presence of OEC [see Eqns (16a,b)].

In the copolymerisation of AN and AC, the formation of a cyclic reaction complex is impossible for steric reasons;[87] therefore, the influence of an organoelement initiator on the dependences of the copolymer composition and copolymerisation rate on the composition of the monomer mixture is less pronounced.[80] In all sections of the composition curve, the copolymer is enriched in AN, which is more reactive ($r_1 > 1$, $r_2 < 1$), although the relative activities of the monomers found in AIBN- and OEP-initiated reactions differ somewhat from each other.

Conversely, copolymerisation of MMA with an electron-donating monomer (St) is subject to regularities[27,88] similar to those observed in the copolymerisation of the MMA–AC pair, namely, the variation of copolymerisation rate as a function of the initial composition of the monomer mixture passes through an extremum (this may also imply the formation of a reaction complex in the chain propagation stage) and the relative activities of both monomers are much smaller than unity.

According to NMR study of the MMA–St copolymers synthesised using DCHPD and organoelement initiators, the microstructures of the specimens obtained are markedly different.[88] The copolymer synthesised in the presence of DCHPD shows a good agreement of the calculated content of triads with that found experimentally. However, in the case of the copolymer prepared in the presence of an organoelement initiator, the discrepancy between the experimental and theoretical values is substantial, indicating that the Mayo–Lewis scheme is inapplicable under these conditions. The ratio of triads calculated from the relative activities in accordance with the pre-terminal unit model showed that the Mertz–Alfrey–Goldfinger equation describes the polymerisation process much more adequately. It can be seen from the data presented that the effect of the pre-terminal unit is not the only factor able to change the copolymer composition. This indicates once again that complex formation between the monomer and the initiator and especially, between the initiator and the macroradical contributes significantly to the change in the monomer relative activities.

Analysis of the dependences of the instantaneous and gross compositions of MMA–St copolymers on the degree of conversion shows that the product of copolymerisation in the presence of DCHPD is enriched in MMA at high degrees of conversion. Initiation by the TIBB–OEP system gives rise to a copolymer with a narrower composition distribution of fractions.[88]

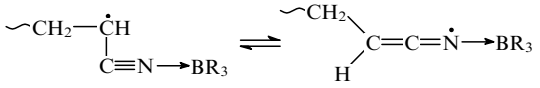
Hirai *et al.*,[89,90] who studied the controlling influence of boron compounds on the composition of the MMA–St copolymer, demonstrated that photoinitiation in the presence of 1 mol % of boron trichloride or ethylboron dichloride gives rise to an alternating St–MMA copolymer. On the basis of kinetic measurements and study of the microtacticity of copolymers, it was concluded that copolymerisation involves the ternary complex 'MMA–St–organoboron compound'. It was noted that diethylboron chloride and triethylborane have a weaker effect on the composition of the MMA–St copolymer than trialkylboranes. In the presence of boron trifluoride, homopolymerisation of styrene takes place.

It has been proposed[91] to use a mixture of alkylboron halides for the synthesis of alternating copolymers of acrylates with alkenes over a broad temperature range (−150 to 100 °C) and at a relatively low pressure (< 100 atm). The degree of conversion reaches 70% over 5–6 h. However, the controlling effect of the organoelement additive shows itself only when the amount of the additive is comparable with the monomer concentration. In this case, the influence of OEC on the copolymer composition is likely to be due to the coordination interaction of the OEC with the monomer rather than with the macroradical.

Blends based on organoelement derivatives of Group II elements in combination with Group IV element halides influence the composition of copolymers in a similar way.[92]

An efficient controlling influence of the binary initiator trialkylborane–OEP can be traced in the copolymerisation of AN with VA.[14,93,94] In the case of the classical radical initiator AIBN, the AN–VA copolymer is enriched in AN, which is the more reactive monomer ($r_{AN} = 4.05$, $r_{VA} = 0.06$) at any composition of the monomer mixture. When the organoelement initiator TIBB–OEP is employed, the composition curve is S-shaped. A section in which the copolymer composition barely depends on the composition of the monomer mixture can be clearly distinguished on the curve; this suggests the trend for alternation of the monomer units in the copolymer and points to the coordinated radical mechanism of copolymerisation. The same is indicated by equalisation of the relative activities of the monomers: $r_{AN} = 0.35$; $r_{VA} = 0.42$ (for comparison, r_1 and r_2 found in terms of the $Q-e$ scheme are 4.27 and 0.06, respectively) and by the deviation from linear dependence of the calculated parameters in the Kelen–Tudoc determination of the copolymerisation constants.

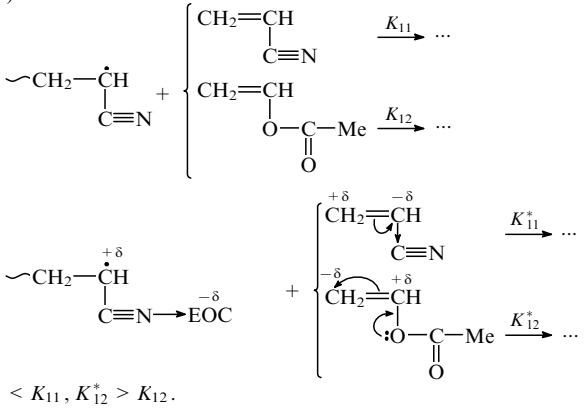
In our opinion, the very pronounced influence of low concentrations of the initiator (0.1 mol %–1.0 mol %) is due to the coordination interaction of the growing macroradical with the components of the initiating system. Important roles should be played by both trialkylborane, which has a vacant orbital at the boron atom, and the organoelement peroxide. This interaction results in electron density redistribution and contributes to the stabilisation of the species



The decrease in the relative activity of AN, found as the ratio of the rate constant for the reaction of the radical with the like monomer (K_{11}) to the rate constant for its reaction with the foreign monomer (K_{12})

$$r_{AN} = \frac{K_{11}}{K_{12}},$$

in the presence of OEC can be related to either a decrease in K_{11}, or an increase K_{12}, or a simultaneous change of both rate constants in the above-indicated directions. These changes can be brought about by an increase in the electron-withdrawing properties of the polyacrylonitrile radical coordinated to the OEC. It is evident that an increase in the electrophilicity decreases the reactivity of the macroradical towards the π-bond of AN (the monomer with a strong electron-withdrawing group) and increases the reactivity towards VA (the electron-donating monomer).



$K^*_{11} < K_{11}$, $K^*_{12} > K_{12}$.

These changes result in a substantial decrease in the relative activity of acrylonitrile ($r^*_{AN} < r_{AN}$).

The rate constant for the addition to VA of the poly(vinyl acetate) radical coordinated to the OEC increases, while that for the addition to AN decreases. As a consequence, the relative activities of the monomers which undergo copolymerisation (AN and VA) become nearly equal and smaller than unity (see Table 2), which generates the trend for alternation of the monomer units. The relative activity of AN changes more sharply than the copolymerisation constant of VA; this indicates that complex formation of OEC with the polyacrylonitrile radical is the governing factor in this system.

The dependence of the rate of copolymerisation of AN with VA in the presence of organoelement initiator on the composition of the monomer mixture has a clear-cut maximum, as in the case of the MMA – AC monomer pair.[14] This points to a coordinated radical character of the process. Similar features have been found for the copolymerisation of AN with MAA, acrylic acid and MMA.[7] As for the AN – VA pair of monomers, the composition curve has a section in which the copolymer composition virtually does not depend on the composition of the monomer mixture. It can be seen from the data of Table 2 that the relative activities of the monomers in the presence of organelement initiators differ markedly from the values calculated using the $Q-e$ scheme or published data. The observed levelling of the relative activities of monomers entails the compositional uniformity of the resulting polymer.

The influence of the components of organelement initiators on the dependence of the copolymer composition on the composition of the monomer mixture in the case of MMA – MAA monomer pair is equally significant.[95] When copolymerisation of these monomers is carried out without OEC additives (AIBN initiation, see Table 2), the copolymer is enriched in the more active monomer, MAA, at any composition of the monomer mixture. In the case of a binary organoelement initiator, TIBB – DPA, the composition curve follows an S-shaped pattern, and the relative activities of both monomers are substantially smaller than unity. The product of the copolymerisation constants tends to zero, pointing to the alternation of monomer units in the copolymer.

Studies of the separate influence of components of the binary organoelement initiator on the chain propagation[27] demonstrated that the addition of 0.2 mol % of TIBB (the concentration of the AIBN initiator is 0.1 mol %) results in substantial levelling of the relative activities of the monomers (see Table 2). The addition of an organosilicon peroxide to AIBN also influences appreciably the reactivities of the monomers and the chain-propagating radicals — the copolymer is enriched in MMA in each section of the curve. The effective values of the relative activities of MMA and MAA are also subject to the controlling influence of DPA, which is an efficient co-initiator for trialkylboranes.[13–15] Thus, both components of the organoelement initiator (alkylborane and OEP) have a controlling influence on the copolymerisation of acrylic monomers.

Copolymerisation of MMA with an electron-donating monomer (St) is influenced by components of an organoelement initiator in a different way.[88] For the polymerisation of these monomers initiated by organoelement initiators, the composition curve is also S-shaped. The relative activities of both monomers are smaller than unity, their numerical values being slightly dependent on the initiator. However, for the MMA – St monomer pair with the use of organoelement initiators, the dependence of the copolymerisation rate on the composition of the monomer mixture has a clear-cut maximum at a nearly equimolar monomer ratio, which is indicative of a coordinated radical copolymerisation mechanism and of the participation of the initiator components in the propagation stage.

The different effects of OEC as weak Lewis acids on the copolymerisation of MMA with MAA and with St are due to the fact that in the former case, the two monomers (MMA and MAA) are similar in structure and electron-withdrawing properties and thus both can react with the complex-forming agent, whereas in the latter case (MMA and St), only one monomer, namely, MMA, reacts with the Lewis acid.

These conclusions are in good agreement with the results of kinetic studies of the copolymerisation of AN with VA and with (meth)acrylates.[7,93–95]

The effect of the heteroatom of the organoelement peroxide on the copolymer composition and the copolymerisation rate was also found for the AN – St pair of monomers at 343 – 353 K,[96] although it is less pronounced than in the case of a binary organoelement initiator.

A quantitative estimate of the change in the reactivity (including electrophilicity) of macroradicals and monomers induced by coordination to the components of an organoelement initiator is provided by the $Q-e$ parameters of the Alfrey – Price equation.[97,98] These parameters are known to have a clear physical meaning and to correlate with the energy of localisation, the order and the π-electron density of the monomer double bond. Comparative analysis of the published Q and e values for various vinyl monomers and the values of these parameters calculated using the relative activities of monomers for the case of organoelement initiators shows that the introduction of organoelement additives changes these values appreciably. Indeed, judging by the Q and e parameters, in the presence of the binary TIBB – OEP initiator, *N*-vinylpyrrolidone acts as an electron density acceptor ($e = 0.94$) rather than an electron density donor ($e = -1.0$), as usual.[97]

Similar regularities have been observed for other vinyl monomers (Table 3): the parameter e, which characterises the electronic structure of the monomer, substantially increases.

Table 3. The parameters Q and e for several vinyl monomers.

Monomer	Q	e	Monomer	Q	e
St	1.0	0.8	MA	0.74	0.40
	1.0	0.8		0.76	0.45
AN	0.60	1.20	VC	0.04	0.20
	0.90	1.33		0.94	0.97
VPD	0.20	−1.00	VDC	0.22	0.36
	1.31 [a]	1.89 [a]		0.29	1.07
AA	1.15	0.77		0.33	0.94
	0.34	1.03		0.50 [d]	0.34 [d]
MAA	1.50	0.68		0.50 [e]	1.50 [e]
	0.86	1.39	VA	0.03	−0.22
	0.74 [b]	0.40 [b]		0.85	−0.06
	1.15 [c]	0.53 [c]			

Note. The values obtained in the absence of initiators are given above the stroke; those in the presence of the organoelement initiator TIBB – DPA are below the stroke.

Additives: [a] tin tetrachloride, [b] dimethylformamide, [c] Lewis base, [d] TBPG – TIBB, [e] acetic acid.

An increase in the numerical value of e in (meth)acrylates attests to an increase in the energy of conjugation and a decrease in the electrophilicity of the double bond. This means an increase in the reactivity of the monomer π-bond towards elctrophilic radicals.

It has been found within the empirical Alfrey – Price scheme that an increase in the parameter e, which is related to the polarity of the monomer double bond, entails an increase in the rate constant for propagation and, hence, in the rate of homo- and copolymerisation.[97,98] As noted above, this is actually observed in the study of the kinetics of homo- and copolymerisation of (meth)acrylates in the presence of catalytic amounts of organoelement compounds.

The efficient controlling influence of organoelement initiators based on trialkylboranes and Group IV – V element peroxides is also manifested in those cases where both monomers involved in copolymerisation are electron donors but contain functional

groups able to be coordinated to Lewis acids. These monomers can be represented, for example, by VPD and VA.[99] The results of studies of the kinetic dependences for the composition and structure of copolymers point unambiguously to a coordinated radical mechanism of copolymerisation. The monomers form a reaction complex with the components of the initiator during the chain propagation stage: the dependence of the copolymerisation rate on the composition of the monomer mixture has an extremum in the region of equimolar amounts of monomers in the initial mixture.

An organoelement initiator has a substantial influence on the copolymerisation of VPD with VDC, which are 'naturally alternating' comonomers.[99,100] The composition curve is S-shaped when DCHPD is used as an initiator. When copolymerisation of this pair is carried out with a binary initiator, TIBB–OEP, the resulting copolymer is enriched in VDC.

Organosilicon peroxides have a controlling influence on the copolymerisation of acrylates in the presence of sulfuryl chloride and phosphorus trichloride;[101,102] however, for the monomer pairs considered in the studies cited, this influence is less pronounced than that in the case of Group III element OEC; this is undoubtedly due to the difference between the electron-withdrawing properties of the modifiers.

Thus, catalytic amounts of coordinatively unsaturated OEC not only effectively initiate low-temperature polymerisation of vinyl monomers but also have a controlling effect on the kinetic parameters of copolymerisation of a broad range of monomers and the composition of copolymers.

The compositional uniformities of macromolecules for one– and two-centre copolymerisation are substantially different.[103] Therefore, important information on the chain propagation mechanism can be gained by performing copolymerisation of a broad range of monomers.

It was found in relation to copolymerisation of MMA with MAA that the integral curves for the distribution over composition for MMA–MAA copolymers synthesised in the presence of a conventional organic (DCHPD)[104] and organoelement (TIBB–DPA)[105] initiators are different. The curve for DCHPD is unimodal,[104] while that obtained with organoelement initiators is bimodal.[105]

When acrylates are made to copolymerise with alkenes, the controlling effect of OEC is not so pronounced as in the copolymerisation of vinyl monomers with each other. The rates of copolymerisation of AN with cyclohexene and hex-1-ene, MMA with ethylene, and VA with ethylene [106] decrease linearly with an increase in the alkene content in the monomer mixture. The degree of conversion does not exceed 30%. The relative activities still differ somewhat from those found for classical radical initiators but this difference is less significant than in the case of copolymerisation of two vinyl monomers.[7] Apparently, this is due to the fact that alkenes and, especially, chain-propagating radicals derived from them, are less prone to form complexes than monomers containing functional groups or atoms with lone electron pairs.

In should be noted that low-pressure radical copolymerisation of ethylene and α-olefins with polar vinyl monomers is quite a topical problem in polymer chemistry. This is especially true for the synthesis of VC copolymers with α-olefins.

Vinyl chloride and α-olefins are known to undergo efficient polymerisation at low pressure according to different mechanisms, namely, polymerisation of VC follows a radical mechanism, while ethylene and its homologues polymerise by a coordination mechanism in the presence of Ziegler–Natta catalysts.[107,108] It is impossible to synthesise VC–olefin copolymers with a high degree of conversion under technologically beneficial conditions in the presence of conventional initiators. The highest degree of conversion on the Ziegler–Natta catalysts does not exceed 24% (in the presence of electron-donor additives, 30%),[109] that in the presence of AIBN is 17%.[110]

It should be noted that physicochemical properties of VC copolymers with ethylene or α-olefins, *e.g.*, good processability, great elongation at rupture, enhanced specific impact strength, *etc.*, make them promising as plastics. In addition, the introduction of even 5%–10% of ethylene units in poly(vinyl chloride) markedly decreases the cost of manufacture of the polymer. The absence of efficient initiators holds up large-scale production of these copolymers.

As shown above, the coordination-radical initiators based on OEC with Group III elements and OEP with Group IV elements, due to the specific features of their structure, occupy an intermediate position between the traditional radical initiators and Ziegler–Natta catalysts. With these initiators, copolymerisation of VC with ethylene and with α-olefins can be carried out at high rates and high degrees of conversion with minimum energy expenditure.[106,111,112]

The degree of conversion in the homopolymerisation of alkenes initiated by these compounds does not exceed 3%–5%, which may be due to the specific features of radical formation in the TIBB–OEP systems.[57,113] However, copolymerisation of ethylene and other alkenes with vinyl monomers can be performed in the presence of the TIBB–OEP systems over a broad range of compositions and with high yields.

Using the vinyl acetate–ethylene and AN–hex-1-ene monomer pairs as examples, the activation energies for copolymerisation on the TIBB–*tert*-butylperoxytetraphenylantimony binary initiator were estimated to be 25.8 and 36.4 kJ mol^{-1}, respectively.[29,106] These values are much lower than the activation energies found for the use of diazo compounds and acyl peroxides as initiators and are close to the data for homopolymerisation of vinyl monomers with organoelement initiators.

The rate of copolymerisation of alkenes with vinyl monomers and the degree of conversion depend substantially on the composition of the monomer mixture and the number of carbon atoms in the alkene molecule. Thus in the case of the VC–ethylene pair, the yield of the copolymer reaches 90% over a period of 5–6 h.[112]

As the alkyl chain length in the alkene increases, the rate of polymerisation and the degree of conversion decrease; in the case of oct-1-ene, the yield of the copolymer does not exceed 20%. Additional introduction of an initiator results in only a slight increase in the yield. The reason for the decrease in the degree of conversion on passing from ethylene to α-olefins is probably related to the chain termination involving the active hydrogen atoms in the α-position relative to the alkene double bond.

In the case where traditional radical initiators or Ziegler–Natta catalysts are used in the VC copolymerisation with alkenes, the possibility of varying the copolymer composition is quite limited. The course of the composition curves and the relative activities of the monomers indicate that the copolymer is enriched in one monomer at any composition of the initial mixture. This is due to the considerable difference between the reactivities of VC and alkenes. The use of the trialkylborane–OEP systems results in substantial equalisation of the copolymerisation constants. Thus the composition curve for VC copolymerisation with ethylene or other alkenes follows an S-shaped pattern; for alkene contents in the monomer mixture ranging from 30 mol.% to 70 mol.%, the copolymer composition is virtually constant and does not depend on the composition of the mixture.[112]

The introduction of alkene units in vinyl polymers influences the physicochemical properties of the product in a definite manner. In particular, in the case of the ethylene–VA pair of monomers, the intrinsic viscosity of the copolymer increases with an increase in the alkene fraction. Conversely, the intrinsic viscosity (and MM) of the ethylene–VC copolymer decreases with an increase in the ethylene mole fraction. We calculated the Fickentcher constant (K_F), characterising the MM of poly(vinyl chloride) for a number of VC–alkene copolymer specimens.[114] The constant proved to be much lower (K_F = 40–70) than in the case of poly(vinyl chloride) synthesised with these initiators.[22] A decrease in the Fickentcher constant is known to facilitate

processing and to enhance the plasticity of the polymeric product.[14] It is worthy of note that an increase in the concentration of the initiator for an invariant ratio of the monomers in the mixture decreases the viscosity of the copolymers and slightly (by 5% – 6%) increases the degree of conversion.[106]

Thus, the use of coordinatively unsaturated OEC able to change the reactivity of macroradicals in a desired manner is an efficient technique for controlling the growth of the polymer chain under conditions of radical polymerisation. One more way of controlling the lifetime of a polymer chain aimed at synthesising compositionally uniform polymers is the use of stable radicals.

III. Growth of the polymer chain in the presence of stable radicals and iniferters

In recent years, a new concept of controlled processes called 'pseudo-living'-chain ‡ (or 'living'-chain) radical polymerisation has been vigorously developing. This polymerisation is of considerable interest as a simple and reliable method for the synthesis of polymers with a definite structure and specified properties.

The essence of the 'pseudo-living' polymerisation is as follows.[76, 117 – 120] The polymerisate contains catalytic amounts of active additives of a specific type (for example, stable radicals or their sources, complex ions of variable-valence metals, and other chain propagation controllers), able to undergo a reversible reaction with chain-propagating active radicals ($R^{\bullet}$) to give a labile adduct [R–X], which decomposes under certain conditions to recover the same chain-propagating macroradical.

$$R^{\bullet} + {}^{\bullet}X \rightleftharpoons RX. \qquad (17)$$

An important feature of 'pseudo-living' radical processes is alternation of the periods of chain propagation, termination and re-initiation. An obvious advantage of this approach is that the polymer chain grows step-by-step, *i.e.*, it becomes possible to control the lifetime of the growing radical. This brings about the following specific features of both the polymerisation kinetics and the properties of the resulting polymer:

— the number of polymer chains and active centres remains constant at any degree of conversion;

— starting from a low degree of conversion, the polymer MM continuously increases, the number-average MM value (M_n) increasing linearly with the degree of conversion;

— a narrow polydispersity (M_w/M_n, where M_w is the weight-average MM) of the polymer is observed at any degree of conversion;

— the isolated products of polymerisation can also act as macroinitiators; the addition of a new portion of the monomer results in further polymerisation and an increase in the polymer MM;

— when two or more monomers are added successively, block copolymers are formed.

Although the 'pseudo-living' radical polymerisation is a relatively new line in the research dealing with controlled radical processes, quite a few organic and organoelement compounds which permit radical polymerisation to be carried out in the 'living' regime have been proposed to date. Currently, more than a hundred publications devoted to this topic appear annually, and this flow does not decrease.§

‡ The process has been called 'pseudo-living' radical polymerisation because it has some features peculiar to the ionic 'living' polymerisation in which no chain termination takes place and chain propagation is continued until the monomer is exhausted.[115, 116]

§ Suffice it to say that in the section 'Radical Polymerisation' of the World Congress 'IUPAC MACRO-2000,' the problems of 'pseudo-living' polymerisation were the most vigorously discussed topic: of 36 oral reports and 51 posters, 17 reports and 20 posters were related to 'pseudo-living' polymerisation; and 18 posters were presented at the separate poster session on 'pseudo-living' polymerisation.[121]

Depending on the active additives (chain propagation controllers) used, the processes carried out in the 'living'-chain regime can be classified into the following types:

— polymerisation involving stable carbon-centred radicals and nitroxides, first of all, 2,2,4,4-tetramethyl-1-piperidinoxyl (TEMPO) and its analogues;

— polymerisation in the presence of spin traps and other potential sources of stable radicals;

— polymerisation using iniferters, controlling initiators of a new type;

— polymerisation in the presence of OEC, mainly, transition metal halides (atom transfer radical polymerisation — ATRP).

1. 'Pseudo-living'-chain polymerisation with participation of carbon-centred radicals and nitroxides

Examples of using stable radicals for controlling the kinetic parameters of radical polymerisation are well known and have been described fairly comprehensively not only in original publications but in relevant monographs.[76] Stable radicals, for example, galvinoxyl, phenoxyl and nitroxide spin adducts are active acceptors of free radicals, including polymeric radicals, over a broad temperature range. In recent years, in relation to the development of the reversible inhibition concept,[122 – 124] the interest in these compounds, especially nitroxides, has substantially increased as they can be used to control the chain propagation.

An important feature of some nitroxides is reversible interaction with a number of growing polymeric radicals at temperatures above 100 °C. This opens up some prospects for controlling the growth and, mainly, the lifetime of the polymeric chain. Over a fairly short period, the studies on the influence of nitroxides [76, 118 – 120, 125 – 136] and alkoxyamines [76, 118 – 120, 137 – 139] have occupied a prominent place in the research on 'pseudo-living' polymerisation.

The compounds used most often to control the lifetime of the growing chain include TEMPO [125 – 133] and its substituted analogues such as 4-methoxy-2,2,6,6-tetramethyl-1-piperidinoxyl,[137] 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinoxyl,[135] *etc.* These nitroxides are used both as such (in the case of thermally initiated polymerisation) and in combination with traditional radical initiators (BP, AIBN, *etc.*).[125 – 136, 140] 'Pseudo-living' polymerisation in the presence of nitroxides based on TEMPO is normally carried out at temperatures of 95 – 130 °C; it is most typical of St and its derivatives (4-bromostyrene,[137] 3- and 4-chloromethylstyrenes,[140] *etc.*), as well as some acrylic monomers.[127, 135] However, it should be noted that in the case of acrylates, nitroxide spin adducts are much less efficient. In all probability, this is due to the fact that the bond (C – O – N) formed according to reaction (17) between the growing macroradical and the nitroxide is stronger, and hence, less labile in the case of polyacrylate radicals than in the case of styrene. Thus, dissociation of this bond requires more energy and, correspondingly, a higher temperature. However, raising the temperature of the synthesis can result in irreversible transformation of the terminal fragment into hydroxylamine.[120, 141] This may account for the fact that in the case of acrylates and other vinyl monomers, 'pseudo-living' mechanism could not be induced by increasing polymerisation temperature to 150 °C.[130, 135, 142, 143] Nevertheless, poly(butyl acrylate) with M_n = 10 500 – 27 000 and M_w/M_n = 1.53 has been prepared in the presence of 2,2,6,6-tetramethyl-4-hydroxy-1-piperidinoxyl at 150 °C.[135] Copolymerisation of St with BA in the presence of TEMPO using an azeotropic monomer mixture (St : BA = 7 : 3) at 120 °C also proceeds by a 'pseudo-living' mechanism.[144]

Kuchanov [124] has studied the effect of nitroxides on block polymerisation of St carried out at 120 °C, with different initial concentrations of TEMPO and without initiators.[124] In the presence of an initiator, polymerisation follows a 'pseudo-living' mechanism,[129, 144, 145] as indicated by the absence of a gel effect and low polydispersity coefficients of the resulting polymer as well

as by the increase in MM following an increase in the degree of conversion. 'Pseudo-living' copolymerisation of St with BA was carried out under similar conditions.[144]

In the presence of TEMPO, block copolymers of St with MMA and with butyl methacrylate have been synthesised.[128,146] It was shown that PS macromolecules are capable of re-initiating polymerisation. Yoshida and Sugita[147] combined cationic and radical polymerisation to prepare a biterminal polymer, poly-(styrene-β-tetrahydrofuran), with two terminal TEMPO radicals, which subsequently undergoes copolymerisation with St to give triblock copolymer.

A detailed and thoroughly justified description of the kinetic features of the 'living'-chain polymerisation in the presence of nitroxides has been reported.[120]

In addition to nitroxides, stable radicals of other classes have also found use in 'pseudo-living' radical polymerisation processes. In particular, the influence of the triphenylmethyl (trityl) radical, formed upon homolytic decomposition of hexaphenylethane (HPE)

$$Ph_3C-CPh_3 \longrightarrow 2\,Ph_3C^{\bullet}, \quad (18)$$

on the polymerisation of acrylic monomers has been studied. It was shown[148,149] in relation to the AIBN-initiated polymerisation of MMA at 80 °C that in the presence of excess HPE ([HPE] : [AIBN] > 5), the process switches to the 'pseudo-living' regime, which is characterised by successive increase in the polymer MM and suppression of the gel effect at high degrees of conversion. However, unlike nitroxides (TEMPO and its analogues), which do not react with the monomer double bond, the triphenylmethyl radical can itself initiate polymerisation.[148,150] Therefore, radical polymerisation of MMA in the presence of HPE has a number of specific features.

It was shown[148,150] that polymerisation of MMA at 80 °C with the addition of HPE and in the absence of AIBN proceeds very slowly (polymerisation time up to a high degree of conversion at [HPE] = 0.1 mol % is ~50 h; for the same AIBN concentration, it is 2–3 h) and exhibits features of a 'pseudo-living' process. In particular, gel effect is scarcely observed, the MM of the polymer linearly increases with an increase in the degree of conversion, and the polydispersity decreases with an increase in the degree of conversion of the monomer. The researchers cited[150] convincingly demonstrated that in this case, polymerisation of MMA follows a two-stage 'pseudo-living' mechanism.

The first stage is due to fast consumption of the trityl radicals in chain initiation and termination. At this stage, a reactive PMMA oligomer containing trityl groups at both ends of the chain is formed and rapidly accumulated

$$Ph_3C^{\bullet} + MMA \longrightarrow Ph_3C-MMA^{\bullet}, \quad (19)$$

$$Ph_3C-MMA^{\bullet} + {}^{\bullet}CPh_3 \longrightarrow Ph_3C-MMA-CPh_3\,. \quad (20)$$

The terminal bond in this oligomer remains labile. The PMMA oligomer re-initiates polymerisation at the second stage of the process, giving rise to a polymeric product in the system. During polymerisation at the second stage, the average MM continuously increases due to the formation of the polymer with a higher molecular mass and gradual consumption of the oligomer.

By analysis of the molecular-mass characteristics of the synthesised PMMA, interesting features of this process were identified.[148,150] The products formed at the first stage show a bimodal MMD. The position of the low-molecular-mass mode corresponding to oligomers virtually does not change during the process; however, its area gradually decreases. The high-molecular-mass mode shifts to higher MM with an increase in the degree of conversion, and its area increases. At high degrees of conversion, the oligomer mode virtually disappears, and the chromatogram becomes unimodal. Similar changes in the MMD of the final product — PMMA — were also observed when MMA polymerisation was carried out in the presence of specially synthesised and isolated oligomer.

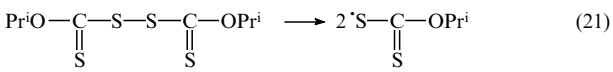
Taking into account the experimental data considered above on the polymerisation of MMA in the presence of HPE, the following mechanism of the AIBN-initiated formation of PMMA was proposed.[148,150] Hexaphenylethane dissociates at 80 °C to afford trityl radicals, which initiate polymerisation; the rate constant for this reaction is 1×10^{-3} litre mol^{-1} s^{-1} (the rate of initiation at [HPE] = 5.0×10^{-3} mol litre^{-1} is 5×10^{-5} mol litre^{-1} s^{-1}). In parallel with this process, initiation at a rate of 5×10^{-8} mol litre^{-1} s^{-1} due to the thermal decomposition of AIBN takes place. It is clear that initiation caused by decomposition of AIBN at the beginning of the process can be neglected. The resulting oligomers re-initiate polymerisation; the parallel polymerisation due to initiation by AIBN also continues. The ratio of the rates of these processes is determined by the ratio of the initial concentrations of HPE and AIBN (the rate constants of these reactions are close[1]). If excess HPE is used (for example, [HPE] : [AIBN] > 50), the mechanism of this process is close to the 'pseudo-living' polymerisation mechanism.

In the opinion of the researchers cited,[148–150] HPE can be regarded as an iniferter because in the absence of a reactive competing agent, initiator (in this case, AIBN), the relatively inert trityl radical has time to attack the monomer and participates in the step of initiation of polymerisation; however, the rate of polymerisation with HPE is much lower than the rate of the AIBN-initiated process.

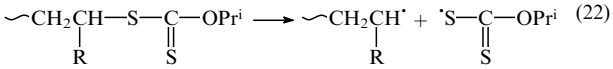
The diphenylmethyl and (trimethylsilyloxy)diphenylmethyl radicals, formed upon decomposition of tetraphenylethane[117,151–154] and bis(trimethylsilyloxy)tetraphenylethane,[117,155] respectively, behave similarly to the trityl radical in the 'pseudo-living' thermal polymerisation. In the first stage consisting of initiation and termination of the growing chains, the radicals formed upon thermal decomposition are rapidly consumed, and the reactive oligomeric product is accumulated. This product re-initiates polymerisation in the second stage of the process, which gives rise to the polymeric product. The polymers formed in the first stage are characterised by a bimodal MMD. The position of the low-molecular-mass mode, corresponding to oligomers, barely changes during the process; however, its area gradually decreases.

Study of copolymerisation of vinyl monomers in the presence of stable carbon-centred radicals is of obvious interest. The first data on the mechanism of copolymerisation involving carbon-centred radicals were obtained back in 1985.[156,157]

The use of *O*,*O*′-diisopropyl xanthogen sulfide (DXS) as a controlling additive made it possible to perform 'pseudo-living' copolymerisation of St with MA at 120–140 °C.[158,159] A specific feature of this process is a substantial decrease in the copolymerisation rate. Apparently, this is due to the fact that the rate of re-initiation in this system is lower than the rate of initiation;[159] this is obviously due to the difference between the energies of the S–S bond in the dissociating DXS and the C–S bond in the terminal group of the copolymer



(21)



(22)

It can be seen from Eqn (22) that under these conditions, the stable S-centred radical formed acts as both an initiator and a chain propagation controller, similarly to carbon-centred radicals such as the trityl[148–150] or diphenylmethyl radical.[151–155] The copolymers considered are gradient polymers the properties of which differ from the properties of random polymers.[159]

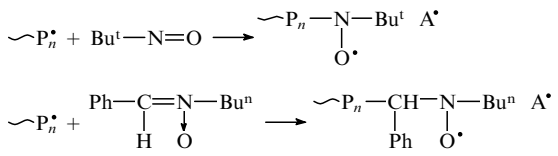
2. Controlled radical polymerisation in the presence of spin traps and other sources of stable radicals

As noted above, a substantial drawback of the control of chain propagation by stable radicals is that the use of these species allows one to perform 'pseudo-living' radical polymerisation only at relatively high temperatures, above 100 °C. It is clear that development of effective methods for conducting polymerisation in the 'living'-chain regime at lower temperatures, normal for radical polymerisation of vinyl monomers under industrial conditions (50–80 °C), is a topical problem of synthetic polymer chemistry.

In this respect, the use of peroxides and azo compounds (typical radical initiators) in combination with active additives able to generate stable radicals, chain propagation controllers, directly in the polymerisation system (*in situ*) appears to be promising for performing controlled polymerisation. Nitroso compounds, nitrones, and other acceptors of free radicals used as spin traps in the studies of homolytic processes in organic and polymer chemistry can be used for this purpose.[160] For example, the use of *C*-phenyl-*N*-*tert*-butylnitrone (PBN) and 2-methyl-2-nitrosopropane (MNP) as effective controllers of the lifetime of a polymer chain for a number of vinyl monomers of various structures has been proposed.[161–169] These compounds exert an effective controlling influence on the polymerisation of various monomers in the temperature range of 50–80 °C.

On the basis of analysis of experimental data on the reactivity of nitrones and nitroso compounds, the following scheme of chain propagation in the presence of these additives was proposed.[161–163]

At the first stage, MNP (or PBN) react with the growing macroradical ($\sim P_n^{\bullet}$) to give a stable nitroxide.



(23)

The nitroxide spin adduct $A^{\bullet}$ further reacts with the chain-propagating radical $\sim P_n^{\bullet}$ to give a labile bond

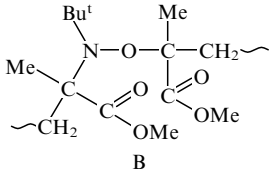
$$\sim P_n^{\bullet} + {}^{\bullet}A \rightleftharpoons [\sim P_n\text{---}A]. \quad (24)$$

The reversible reaction (24) results in alternation of the 'sleeping' and 'living' periods of the polymeric radical: the monomer (M) molecules add successively to the macroradical; thus, the polymer chain grows.

$$[\sim P_n\text{---}A] + M \longrightarrow [\sim P_{n+1}\text{---}A]. \quad (25)$$

The lability (relative instability) of the resulting $[\sim P_{n+1}\text{---}A]$ bond under conditions of polymerisation of vinyl monomers (50–80 °C) is due to both high stability of the nitroxide spin adduct ($A^{\bullet}$) and specific features of the structure of the polymeric radical ($\sim P_n^{\bullet}$). In particular, the energy of the R^1-O bond in the R^1-O-N bridge of the $R^1-O-N(R^3)R^2$ type nitroxide adducts formed according to Eqn (23) depends appreciably on the nature of radicals surrounding the N–O group, especially on their spatial structure. Thus in the case of TEMPO, a known controller of chain propagation, or the methyl radical, the bond energy is ~30 kcal mol^{-1}. Apparently, this is why TEMPO and its analogues are able to control efficiently the radical polymerisation of St and some acrylic monomers only at relatively high temperatures (100–130 °C). For a more bulky ethyl radical, the energy of this bond is ~25 kcal mol^{-1}, and in the case of sterically hindered *tert*-butyl or polyacrylate radicals, it is even lower (~20 kcal mol^{-1}).

When vinyl monomers are made to polymerise in the presence of PBN (or MNP), the nitrogen atom in the $R^1-O-N(R^3)R^2$ nitroxide adduct is linked to even more bulky and sterically hindered radicals. For example, in the case of MMA and MNP, it is linked to a *tert*-butyl radical (from MNP) and two polyacrylate radicals, having a high-molecular-mass 'tail'.



B

The strength of this bond is much lower than that in the case of TEMPO; naturally, it will dissociate rather easily at lower temperatures to give the initial radicals.

Moreover, since the nitroxide adduct B is formed initially upon the interaction of two bulky radicals directly during the synthesis of the polymer at a temperature of 50–80 °C, it cannot be ruled out that the chemical bond between the chain-propagating radical ($\sim P_n^{\bullet}$) and the nitroxide spin adduct ($A^{\bullet}$) is a vibrationally excited molecule (an analogue of a radical pair in the $[\sim P_n\text{---}A]$ solid matrix) even at the instant of formation.

To date, 'pseudo-living' polymerisation in the presence of PBN has been accomplished for a number of vinyl monomers, namely, MMA,[161–164, 166–168] butyl methacrylate, BA, St, and VC.[165–167] The main process parameters and the properties of polymers prepared in the presence of PBN are listed in Table 4. Some common features of the mechanism of the 'pseudo-living' radical polymerisation in the presence of PBN can be distinguished.

In particular, the introduction of a controlling additive results in an appreciable decrease, down to complete suppression, of the gel effect and allows conduction of the polymerisation to high degrees of conversion (80%–90%). It is very important for practical purposes that the time of polymerisation increases insignificantly (with respect to that for the process without an additive), as a rule, not more than twofold (see Table 4). The duration of polymerisation of St and MMA by the 'pseudo-living'

Table 4. Some kinetic parameters for the polymerisation of vinyl monomers in the presence of PBN and molecular-mass characteristics of polymers (initiator AIBN, 0.1 mol.%).

Monomer	[PBN] (mol.%)	T /°C	$10^4 V$ /mol litre^{-1} s^{-1}	Time /h	Degree of monomer conversion (%)	$10^6 M_\eta$	M_w/M_n	Ref.
MMA	–	50	1.2	8	91	4.3	>2.0	161, 162
	0.80	50	0.8	17	75	1.2	1.7	
BA	–	65	2.1	2	98	–	>2.0	169
	0.02	65	0.1 [a]	7	65	0.7 [b]	1.7	
BMA	–	50	1.1	12	99	10.7	–	169
	0.2	50	0.8 [a]	24	78	6.5	–	
VC	–	50	9.1	3	92	70 [c]	2.5	165
	0.01	50	0.6	5	89	66 [c]	1.7	

[a] The rates are given for [PBN] = 0.1 mol.%. [b] The M_n value. [c] The Fickentcher constants are given.

radical mechanism is known to increase severalfold in the presence of TEMPO,[125–136] triphenylmethyl radicals[148–150] or other radicals. The PBN concentration at which the gel effect is suppressed depends on the structures of the monomer and, especially, the growing macroradical; in any case, this concentration is commensurable with the content of the initiator (0.01 mol.%–0.80 mol.%).[161, 162, 164, 169]

The number-average and viscosity-average (M_η) molecular masses of the polymer prepared in the presence of PBN follow a linear dependence on the degree of conversion, which is typical of polymerisation by the 'pseudo-living' mechanism. The shift of the low-molecular-mass shoulder and the whole mode to higher molecular masses with an increase in the degree of conversion of the monomer can be clearly seen in the MMD curves.[161, 162, 169]

An important feature of the proposed controller is the fact that stable radicals able to control chain propagation are formed directly during polymerisation as a result of interaction of the macroradicals with an additive introduced to the system, which effectively controls the synthesis of macromolecules even at 50–80 °C.

A shortcoming of this method for controlling the growth of a polymer chain is that the MMD of the resulting polymer is broader than, for example, in the case of ATRP.[76, 119, 120] In our opinion, this is due to the inhomogeneity of high-molecular-mass nitroxides formed by reaction (23) as chain propagation controllers.

It should be noted that the structures of the macroradical and the monomer have a substantial influence on the polymerisation kinetics and the polymer MM under the conditions of reversible inhibition in the presence of PBN. Thus comparison of acrylic monomers, namely, MMA, butyl methacrylate and BA, shows that the process involving BA occurs at higher temperature (> 65 °C) and at much lower concentrations of the active additive and has a longer induction period than the processes with MMA or butyl methacrylate.[166–169]

The differences in the regularities of polymerisation of MMA and butyl methacrylate, on the one hand, and BA, on the other hand, are undoubtedly due to specific features of the structure of growing macroradicals and the reactivity of the macroradicals towards nitroxide spin adducts. Thus, from a thermodynamic standpoint, sterically hindered PMMA and poly(butyl methacrylate) macroradicals (tertiary radicals) form a weaker and, hence, a more labile bond with the nitroxide used as a chain propagation controller [reaction (23)]. In the case of polymerisation of BA, the bond between the nitroxide spin adduct and the growing macroradical of poly(butyl acrylate) (secondary radical) is stronger and more stable against dissociation. As a consequence, in the case of polymerisation of BA, the 'living'-chain mechanism can be accomplished at a higher temperature. In addition, the rate constant for the acceptance of secondary and tertiary radicals by a spin trap (PBN) are known to differ by almost an order of magnitude. In our opinion, this can account for the long induction period in BA polymerisation and for the possibility of using lower concentrations of nitrone as a controller of the chain propagation than those required in the polymerisation of MMA and butyl methacrylate.[166–169]

The foregoing is confirmed by the data on the polymerisation of VC[165, 166, 168] and St[166, 168] in the presence of PBN: the growing polymer radicals derived from these monomers are secondary radicals; hence, as in the case of BA, the controlled process takes place at a lower PBN concentration.

It was shown in relation to the polymerisation of MMA that the use of MNP as a controlling additive entails effects similar to those observed with PBN; in the latter case, the control of the polymer chain propagation requires lower concentrations of the additive (0.005 mol.% – 0.01 mol.%). Apparently, this is due to higher constants for the acceptance of macroradicals by nitroso compounds than by nitrones.[163, 166–169]

3. Iniferters as controlling initiators of polymerisation of a new type

Yet another elegant method for performing controlled radical polymerisation proposed in recent years is based on the use of a special class of initiators called iniferters.¶ These compounds decompose rather readily to give free radicals ($A^\bullet$) and ($B^\bullet$)

$$A-B \rightleftharpoons A^\bullet + B^\bullet. \quad (26)$$

One radical is reactive ($A^\bullet$), it can react with the monomer and thus initiate the chain propagation. The second radical ($B^\bullet$) is reactive only with respect to the growing macroradical and can react with it according to the reversible inhibition pattern

$$A^\bullet + M \longrightarrow A-M^\bullet, \quad (27)$$

$$A-M^\bullet + {}^\bullet B \rightleftharpoons A-M-B. \quad (28)$$

Chain termination *via* recombination of the growing macroradical with the primary radical of the iniferter [reaction (28)] occurs much faster than chain termination *via* recombination or disproportionation of the growing radicals. In addition, iniferter participates in chain transfer reactions.

In terms of their chemical nature, the iniferters known to date can be conventionally divided into three groups.

In the iniferters of the first group, homolytic decomposition of both the initial and the resulting macromolecular initiator involves a labile bond of the same chemical nature. Examples of these iniferters are alkoxyamines[76, 118–120, 137–142] and alkylthiocarbamates.[170–174]

In the case of second-group iniferters, the steps of decomposition of the initial and macromolecular initiators involve bonds of different chemical natures. This group of iniferters includes, for example, phenylazotriphenylmethane[117, 148, 175, 176] and some thio iniferters.[117]

Binary redox systems based on organic and organoelement compounds and the corresponding oxidants (sterically hindered quinones, oxytriazenes, *etc*.) can be classified as the third type of iniferters.[177–182]

Alkoxyamines, which are used most often as iniferters, are compounds of the $R-M_n-X$ type, where R is the radical formed upon decomposition of a conventional initiator of radical polymerisation (BP, AIBN, DCHPD[135, 183–189]), M is the monomer (most often, St), X is a nitroxide (as a rule, TEMPO or its analogue).

It has been noted above that the parameters of polymerisation in the presence of TEMPO are close to the parameters of 'living' ionic processes; this is due to the high re-initiation constant by reaction (17). In this connection, vigorous studies into the use of alkoxyamines as iniferters are being carried out.

Numerous publications have been devoted to the synthesis of new alkoxyamines[189–195] and their application in the polymerisation processes. The results of these studies can be used to select the compounds $R-M_n-X$ the half-life of which is shorter than the period of complete polymerisation transformation by factors of tens or even hundreds;[120] this, in turn, can increase the efficiency of a nitroxide as a 'pseudo-living' polymerisation agent. An important indication of a 'living' process is polydispersity. If ordinary quadratic termination does not take place, the polydispersity of the polymer should be equal to unity. Polystyrene samples with polydispersity values close to unity have been obtained with a number of alkoxyamines.[120]

The results of kinetic studies of the mechanism of 'living' radical polymerisation of St in the presence of alkoxyamines and of analytical calculation studies were considered in detail in a review.[120] Polymerisation in the presence of alkoxyamines occurs by the following scheme:

¶ The term iniferter is composed of the names of elementary steps of radical polymerisation: ini (initiation), fer (transfer), ter (termination).[117, 124]

$$\begin{aligned} &R-R \longrightarrow 2\,R^{\bullet}\ \text{(initiation)},\\ &R-X \longrightarrow R^{\bullet} + X^{\bullet},\\ &R^{\bullet} + X^{\bullet} \longrightarrow R-X,\\ &R^{\bullet} + M \longrightarrow R-M^{\bullet},\\ &R^{\bullet} + R^{\bullet} \longrightarrow R-R. \end{aligned} \qquad (29)$$

The process kinetics has the following specific features: the rate of polymerisation is proportional to the monomer concentration and does not depend on the alkoxyamine concentration; the polymer MM increases linearly with an increase in the degree of polymerisation (this regularity holds, at least, up to $M_n = 20\,000 - 30\,000$); the polydispersity of the polymer normally first decreases with an increase in the degree of conversion and then increases; the polydispersity coefficient fluctuates depending on the process conditions but, as a rule, it remains less than 1.3; the concentration of the stable nitroxide (EPR detection) is equal to 0.1% – 1.0% relative to the initial concentration of the alkoxyamine throughout the whole process.[196]

Computer analysis of the kinetic data and the molecular-mass characteristics[197–199] made it possible to establish correlations between reaction parameters (temperature, concentration of the reactants) and the properties of 'living' polymerisation agents [the rate constants for the forward and back reactions (28)]. These results can be used to choose the optimum conditions for performing polymerisation of St with a particular iniferter.

However, it should be noted that, similarly to the polymerisation in the presence of TEMPO (and, evidently, for the same reasons), these compounds can be used at temperatures above 100 °C and only for polymerisation of St and its analogues[137,140,198,200,201] and copolymerisation or preparation of block copolymers of St with other monomers, most commonly, acrylates.[202–204]

Dissociation of alkoxyamines at high temperatures (above 135 °C) has been studied in detail in relation to 1-methylbenzyloxy-2,2,6,6-tetramethyl-1-piperidine[205] and its derivatives resulting from decomposition of BP in St.[141] The process follows two pathways, one to give a reactive hydrocarbon radical and a stable nitroxide (it is this reaction that is responsible for the 'living' polymerisation mechanism) and the other, giving rise to an unsaturated hydrocarbon and hydroxylamine (hydride transfer).

Alkoxyamines based on TEMPO have been used[206–209] to synthesise densely cross-linked glassy polymers by 'pseudo-living' radical three-dimensional polymerisation; copolymerisation of St with MA was taken as an example. Due to the 'pseudo-living' polymerisation mechanism, the point at which a continuous network was formed was shifted appreciably towards higher degrees of conversion (> 17% – 35%) compared to that observed for conventional three-dimensional radical polymerisation.

Block copolymerisation of St and its analogues with acrylates has proved to be a more efficient method for the extension of the scope of application of alkoxyamines. Block copolymers based on PS or on St copolymers with acrylates with high St contents prepared in the presence of alkoxyamines have been considered in detail in reviews[120,210] and monographs.[76,119]

The use of derivatives of thiocarbamates as photoiniferters has been studied extensively.[124,170–174] Unlike the iniferters which decompose at high temperatures, thiocarbamates tend to decompose on exposure to UV radiation at much lower temperatures than alkoxyamines. The polymerisation of St in the presence of these reagents has all the main features of 'pseudo-living' polymerisation.[173,174]

An EPR study of the photo decomposition of *S*-benzyl *N*,*N*-diethyldithiocabamate and PS containing a terminal dithiocarbamate group induced by UV radiation ($\lambda = 365$ nm, 25 °C) has shown[120,211] that decomposition follows the same mechanism with rupture of the C–S bond to give reactive benzyl (or polystyrene) and stable *N*,*N*-diethyldithiyl radicals.

$$\mathrm{BnSC(S)NEt_2} \xrightarrow{h\nu} \mathrm{Bn^{\bullet}} + {}^{\bullet}\mathrm{SC(S)NEt_2} \qquad (30)$$

$$\sim\!\mathrm{CH_2CH(Ph)SC(S)NEt_2} \longrightarrow \sim\!\mathrm{CH_2CH^{\bullet}(Ph)} + {}^{\bullet}\mathrm{SC(S)NEt_2} \qquad (31)$$

By assuming that decomposition of these compounds occurs by the same mechanism, one can explain the fact that the regularities of polymerisation in the presence of low- and high-molecular-mass iniferters — *S*-benzyl *N*,*N*-diethyldithiocabamate and the PS containing a terminal dithiocabamate group — prove to be qualitatively the same.

Research into the photo and thermal decomposition of thio iniferters showed[212–215] that decomposition of symmetric molecules involves either the S–S bond

$$\mathrm{RSSR} \xrightarrow{h\nu} 2\,\mathrm{RS^{\bullet}} \qquad (32)$$

R = Ph, $\mathrm{C(S)NAlk_2}$,

or both the S–S and C–S bonds

$$\begin{aligned} &\mathrm{RSSR} \xrightarrow{h\nu} 2\,\mathrm{RS^{\bullet}},\\ &\mathrm{RSSR} \xrightarrow{h\nu} \mathrm{R^{\bullet}} + {}^{\bullet}\mathrm{SSR} \end{aligned} \qquad (33)$$

R = C(O)Ph.

In the case of nonsymmetric dithiocarbamates and dithiocarbonates $\mathrm{R(CH_2)_nSC(S)NAlk_2}$ and $\mathrm{R(CH_2)_nSC(S)OAlk}$ (R = Ph, R′CO), the formation of dithiyl (stable) radicals needed to induce 'pseudo-living' polymerisation takes place only for the compounds $\mathrm{BnSC(S)NAlk_2}$, BnSC(S)OAlk and AlkCOO.$\mathrm{CH_2SC(S)NAlk_2}$.[216–218]

Other compounds that can be attributed to the class of iniferters in question include HPE,[148–150] tetraphenylethane[117,151–154] and bis(trimethylsilyloxy)tetraphenylethane,[117,155] which do decompose under polymerisation conditions to yield symmetric inert radicals but only in the case where they are added without an initiator. In the absence of an active competing agent, initiator, the low-reactivity radical has time to attack the monomer and participates in the initiation of polymerisation. However, the rate of polymerisation in the presence of HPE or related tetraphenylethane or bis(trimethylsilyloxy)tetraphenylethane is much lower than that of the process initiated by AIBN or an organic peroxide.

Another type of iniferters includes phenyl azotriphenylmethane (PAT); the use of this compound as the initiator of 'pseudo-living' polymerisation of MMA was first described by Otsu and Matsumoto.[117]

The thermal decomposition of PAT occurs at a high rate with rupture of the C–N bond; it is accompanied by evolution of nitrogen and gives rise to phenyl and triphenylmethyl radicals according to the following scheme

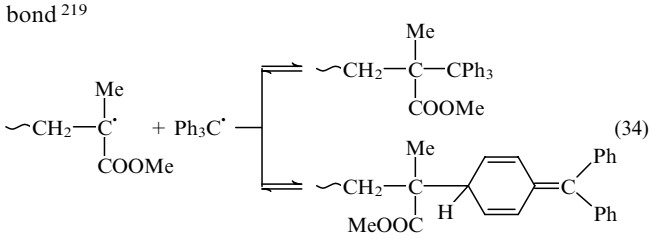
$$\mathrm{Ph-N=N-CPh_3} \longrightarrow \mathrm{Ph^{\bullet}} + \mathrm{N_2} + {}^{\bullet}\mathrm{CPh_3}.$$

The reactive phenyl radicals initiate polymerisation, while the relatively stable triphenylmethyl radicals participate only in the chain termination by macroradicals to give a terminal bond. As has already been noted, the terminal bonds are fairly labile thermally and their homolytic cleavage results in re-initiation of polymerisation. It was found that up to a degree of conversion of ~2%, the polymerisation rate of MMA[148,175] and MA[176] increases (as in the presence of HPE); subsequently, in the transient region up to degrees of conversion of 5% – 15%, the rate markedly decreases; finally, gradual self-acceleration of the reaction starts. The dependence of the MM on the degree of conversion for polymer samples is linear up to 50% degree of conversion.

The MMD follows a specific pattern of variation during polymerisation, namely, the products formed at degrees of con-

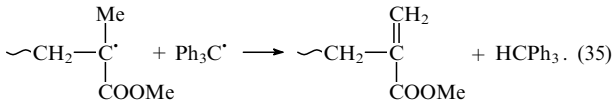
version ranging from 1% to 7% exhibit a unimodal MMD and are oligomeric products. As the degree of conversion increases, the MMD curves become bimodal: a second mode arises, which shifts to higher MM as polymerisation advances, and its area continuously increases. The position of the oligomeric mode does not change; however, its area gradually decreases. When the degree of conversion is high (nearly limiting), the oligomeric mode completely disappears, and the MMD of the resulting PMMA and poly(methyl acrylate) becomes again unimodal. A similar pattern of variation of the MMD is observed for 'pseudo-living' polymerisation of MMA involving trityl radicals.[148–150] Evidently, the mechanism of formation of PMMA in the presence of PAT is underlain by the same processes as in the initiation by AIBN with HPE [148–150] (see the previous Section).

An interesting feature of MMA polymerisation in the presence of PAT has been identified.[148,175] Starting with some degree of conversion (40%–50%), the MMD mode stops moving to higher molecular masses, *i.e.*, the contribution of the 'pseudo-living' polymerisation to the formation of the polymer markedly decreases. In the opinion of the researchers cited, this may be due to the fact that the trityl radical is capable of initiating polymerisation of the acrylate, giving rise to a conventional 'dead' polymer, this process being more active at high degrees of conversion. In addition, accumulation of the 'dead' polymer in the system can be due to side reactions, resulting in deactivation of the labile bond in the macroiniferter, namely, isomerisation of the triphenylmethyl radical followed by its addition to the macroradical, which occurs in parallel with the formation of the labile bond [219]



(34)

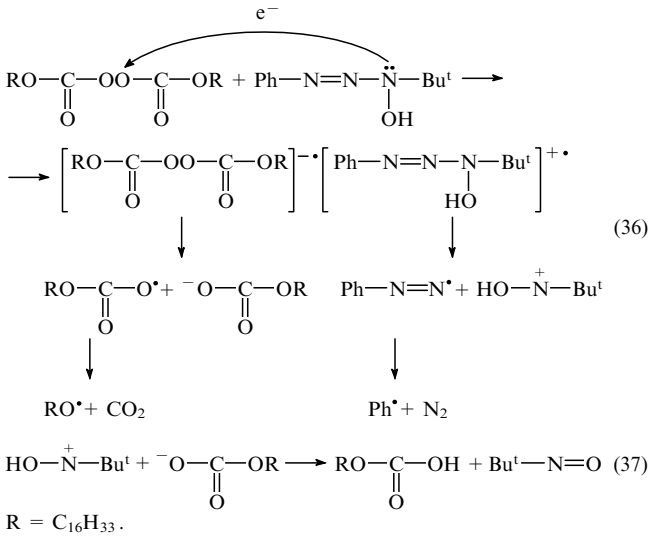
and disproportionation of these radicals [219]



(35)

As noted above, decomposition of the symmetric molecules of thio iniferters involves either the S–S bond or both the S–S and C–S bonds [see reactions (32) and (33)]. The former route yields symmetric S-centred radicals, which can initiate polymerisation without AIBN or peroxide. We have already discussed data on the use of DXS as a controlling additive in the copolymerisation of vinyl monomers.[158,159] The stable S-centred radical arising according to reactions (32) and (33) under the indicated conditions acts as both an initiator and a chain propagation controller and can be attributed to the class of iniferters under consideration because the labile bond in the terminal group of the copolymer is the C–S bond.

Original binary initiators and chain propagation controllers based on oxytriazenes and oxidants (metal oxides, organic and inorganic peroxides and hydroperoxides) have been proposed.[179–182] It was found by EPR spectroscopy that, owing to the simultaneous generation of reactive phenyl radicals (chain propagation initiators) and nitroso compounds, which can react with chain-propagating radicals to give nitroxides (which control the chain propagation), these systems are able, on the one hand, to initiate radical polymerisation, and, on the other hand, to act as process controllers.



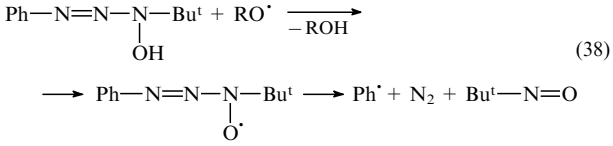
(36)

(37)

$R = C_{16}H_{33}$.

The possibility of realisation of a similar single-electron transfer mechanism in the reaction of acyl peroxides with substituted amines has been demonstrated previously.[220]

In addition, it cannot be ruled out that secondary reactions take place between triazene and the alkoxide radicals derived from the peroxide, which results in triazene decomposition.



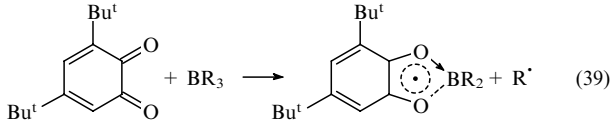
(38)

The presence of nitroxides in the polymerisate was detected by EPR using the spin trap technique [a triplet with the splitting constant at nitrogen $a_N = 15.6$ Oe corresponding to the adduct of the nitroso compound with the poly(methyl methacrylate) radical].

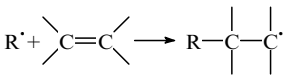
Polymerisation of MMA in the presence of oxytriazene, like that in the presence of MNP,[163,166–168] proceeds under relatively mild temperature conditions (50–60 °C) and exhibits features peculiar to 'pseudo-living' polymerisation, namely, the absence of gel effect in the polymerisation up to high degrees of conversion, linear increase in the MM following an increase in the degree of conversion, relatively low polydispersity, *etc.*[179–182] Thus, these systems can be regarded as a sort of binary iniferter.

Yet another example of unusual initiators and controllers of polymer chain propagation is provided by compositions based on sterically hindered quinones and OEC. Thus it has been found [177,178] that 3,5-di-*tert*-butylquinone, used traditionally as the inhibitor of radical processes, when combined with trialkylborane, is able not only to initiate effectively radical polymerisation of various monomers but also to control the propagation of the polymeric chain according to the 'pseudo-living' mechanism. It was found by EPR spectroscopy and by kinetic measurements that the rate of MMA polymerisation is comparable in this case with the rate of polymerisation of acrylic monomers in the presence of traditional radical initiators, AIBN and acyl peroxides, and in some cases, even exceeds it.

Analysis of the data obtained shows that several processes occur in the system. One process is the reaction of quinone, for example, with TIBB, which gives rise to radicals carrying the polymerisation.

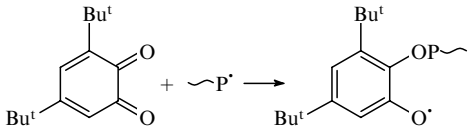


(39)

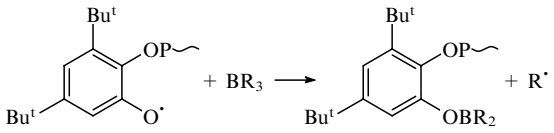


(40)

The occurrence of reaction (39) has also been assumed in other studies [221, 222] (this assumption was made taking account of the results of EPR investigations of the reaction of quinones with alkyl derivatives of Group III elements, in particular, gallium). In addition, the chain-propagating radicals can react with quinones to give oxygen-centred radicals of the phenoxyl type, which react with TIBB to generate new alkyl radicals,[223] able to initiate polymerisation.



(41)



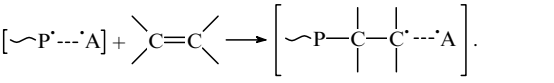
(42)

P is the chain-propagating (polymeric) radical.

The dependence of MM of poly(methyl methacrylate) synthesised in the presence of the 3,5-di-*tert*-butylquinone – TIBB system on the degree of conversion is linear over a broad range of MM values, from 17 000 to 200 000. As the degree of conversion increases, the polymer MMD mode moves continuously to higher molecular masses. This type of dependence of the polymer MM on the degree of conversion is characteristic of 'pseudo-living' chain propagation, including that in the presence of iniferters. It can be seen from Eqn (39) that the reaction of the components of the 3,5-di-*tert*-butylquinone – TIBB binary initiator furnishes the reactive alkyl radical R$^{\bullet}$, capable of initiating polymerisation, and a stable radical (A$^{\bullet}$), which can be coordinated to the chain-propagating radical to afford a labile bond.

$$\sim P^{\bullet} + {}^{\bullet}A \rightleftharpoons [\sim P^{\bullet}\text{---}{}^{\bullet}A]. \quad (43)$$

The polymer chain grows according to a stepwise pattern as a result of consecutive steps of cleavage of the terminal labile bond [$\sim$P---A] and consecutive addition of some number of monomer units to give a new labile bond according to the scheme



(44)

Thus, quinones combined with OEC act as a sort of low-temperature binary iniferters. In this case, the reactive radical (R$^{\bullet}$) which initiates polymerisation and the stable radical (A$^{\bullet}$) which controls the chain propagation are generated directly in the reaction system upon the reaction of the components of a binary initiator with each other [see Eqns (39) – (43)].

Similar regularities are also characteristic of some other quinones and OEC derived from Group III — V elements.[224]

Original initiators-chain propagation controllers based on sterically hindered trialkylboranes and oxidants have been proposed by Chung *et al.*[225] These investigators were the first to use stable boron-containing radicals produced upon oxidation of 1-octyl-9-borabicyclononane to control the chain propagation in the polymerisation of MMA. The use of this additive brings about the features typical of 'pseudo-living' radical polymerisation. It is of fundamental importance that, unlike most known systems, with this system the process occurs at room temperature which allows one to eliminate the undesirable thermal constituent of the process, which markedly deteriorates the MMD of the polymer.

4. Radical polymerisation in the 'living' chain regime in the presence of organoelement compounds

The use of OEC as chain propagation controllers in the 'pseudo-living' radical polymerisation of vinyl monomers opens up prospects for modelling 'pseudo-living' processes using individual features of the metal or non-metal atom in OEC.

Processes in which organic compounds of transition metal halides are used to control the growth of a polymer chain have been studied to date.[76, 119, 226 – 228]

It is known [229] that transition metal halides with the formula $X^n - Y_m - L_x$ (X is a transition metal, n is the valence of the metal, Y is chloride or bromide, L is an organic ligand, most often, a Lewis base) containing metal in a lower oxidation state react with alkyl halides (RX) at $\sim$100 °C to give the alkyl radicals R$^{\bullet}$ capable of initiating polymerisation. Simultaneously, oxidation of the transition metal takes place according to the reversible Kharasch reaction.[229]

$$R - X + X^n - Y_m - L_x \rightleftharpoons R^{\bullet} + X^{n+1} - Y_m - L_x, \quad (45)$$

$$R^{\bullet} + xM \longrightarrow R - M_x^{\bullet}, \quad (46)$$

M is monomer.

When this reaction was induced in the medium of a vinyl monomer, stepwise growth of the polymer chain was observed, *i.e.*, a 'pseudo-living' chain process took place.

Currently, a broad range of OEC (copper, iron, palladium and other compounds) are used as controlling additives; the organic ligands most often contained in these systems are 2,2′-bipyridine,[230, 231] 4,4′-di(non-5-yl)-2,2′-bipyridine,[232 – 236] triphenylphosphine,[226 – 228, 237] *etc*. The alkyl halides normally used for this purpose include alkyl(or aryl) bromides and dialkyl(or diaryl)- alkylaryl bromides.[226, 230, 232, 233, 235, 236]

For a series of vinyl monomers, namely, St,[226, 228, 232 – 235] MA,[233, 234] MMA,[226, 232, 234, 237 – 239] AN [230] and so on, the ATRP process has been accomplished [see redox reaction (45)]. The rate of this process is rather high; therefore, all the polymer chains are initiated almost simultaneously; this allows the manufacture of polymers with a polydispersity close to unity (1.05 – 1.30).[227, 228, 230, 232 – 239] Unlike the controlling additives on the basis of stable radicals considered above, the ATRP agents are not incorporated in the polymer chain and, hence, they can be regarded as analogues of catalysts.

In addition to transition metal compounds (for example, as in ATRP), other OEC are also employed to induce 'pseudo-living' radical polymerisation. As early as in the 1970s, Academician G A Razuvaev and co-workers [240, 241] synthesised block copolymers of MMA with AN using radical initiation by organo-mercury and -tin compounds. It was established by emission spectroscopy that PMMA contained mercury in the terminal groups, and subsequently these macromolecules can act as peculiar macroinitiators. The molecular mass of the secondary polymer is twice as high as the MM of the initial one, which confirms indirectly the possibility of a 'pseudo-living' chain mechanism.

IV. Characteristic features of homo- and co-polymerisation of vinyl monomers in the presence of organoelement compounds derived from Group V elements

The coordinatively unsaturated OEC containing Group II and, especially, Group III elements participate directly in the chain propagation step. The addition of compounds derived from Group IV and V elements also influences the elementary steps in polymerisation. These compounds have vacant *d* orbitals, which stipulates their electron density acceptor properties.

Tin and germanium tetrachlorides can influence significantly co-polymerisation of MAA esters with MMA.[51, 52] The introduction of 1 mol.% of these compounds to a polymerisate gives rise to alternating copolymers. Conversely, the addition of tetrabutyltin

barely influences either polymerisation rate or the MM of polymers. Apparently, this is due to the fact that vacant *d* orbitals of the tin atom are removed from the nucleus and, therefore, the electron-acceptor capacity of these orbitals is too low to activate the chain-propagating radical. Electron-donating alkyl radicals do not promote the coordinating capacity of OEC either. Data on the copolymerisation of MMA with MAA in the presence of tetrabutyltin additives confirm the conclusion that the activities of monomers and growing macroradicals virtually do not change.

Meanwhile, the controlling effect of Group IV element halides on the copolymerisation of acrylates, described by Smirnova and coworkers,[51, 52] can be explained by the fact that inorganic Lewis acids are more prone to form intermolecular complexes than organic compounds of the same elements.

A specific position is occupied by OEC containing Group V elements because they contain both a lone electron pair in the *p* orbital suitable for a nucleophilic attack and vacant *d* orbitals, which can give rise to electron-withdrawing properties.

It has been shown [242, 243] that the addition of alkyl derivatives of bismuth and antimony influences directly the kinetic parameters of polymerisation of vinyl monomers. Thus the rate of BA and VA polymerisation increases by more than an order of magnitude in the presence of catalytic amounts of triisobutylbismuth. The addition of triethylantimony markedly accelerates not only bulk polymerisation of acrylates but also solution polymerisation in ethyl acetate, which is a polar solvent and can be regarded as a hydrogenated analogue of MMA in terms of its electronic structure; like the monomer, it contains an ester group able to be coordinated to electron density acceptors. Organic compounds of bismuth and antimony, like those of Group III elements, do not exert any substantial catalytic effect on the decomposition of an initiator such as AIBN either in inert hydrocarbons or in the presence of vinyl monomers.[53]

Thus, the data presented above indicate unambiguously that acceleration of polymerisation of acrylic monomers in the presence of OEC containing Group V elements is due to the direct participation of these additives in the chain propagation stage.

It should be noted that catalytic amounts of OEC accelerate chain propagation in the polymerisation of VA and BA much more efficiently than in the polymerisation of MMA, which is in good agreement with the results of investigations into the influence of Group III element compounds on the polymerisation of acrylates.

The phenyl derivatives of Group V elements stable against oxidation by atmospheric oxygen also activate somewhat the process of MMA polymerisation. The accelerating effect of these derivatives decreases in the series $Ph_3Bi > Ph_3Sb > Ph_3As$, which is in line with the variation of nucleophilic properties of these compounds.

It is clear that the influence of organic derivatives of Group V elements on the polymerisation of acrylic monomers is directly related to the presence of the lone electron pair in the *p* orbital. This conclusion is supported by the fact that introduction of pentaphenylantimony in the polymerisate barely changes the polymerisation rate and the polymer MM.[242, 243]

Apparently, during its growth, a macroradical reacts with the metal atom in the OEC to give a four-coordinate radical complex

$$\sim P^{\bullet} + \ddot{E}R_3 \longrightarrow [\sim P^{\bullet}\text{---}\dot{E}R_3], \qquad (47)$$

where $\sim P^{\bullet}$ is the growing macroradical; E is a Group V element (antimony, bismuth); R = Et, Ph, Bu^i.

It is known [56] that, owing to the lone electron pair in the *p* orbital and free *d* orbitals, Group V elements are capable of expanding their electron shells. It has been shown by EPR [56] that compounds of trivalent Group V elements can react with free oxygen- and carbon-centred radicals; as this takes place, the coordination number increases to four and the corresponding intermediates are formed [reaction (47)].

The $[\sim P\text{---}ER_3]$ bond thus formed between the growing macroradical and a Group V element is labile and can be cleaved either yielding the initial compounds (OEC and the chain-propagating radical, which can continue polymerisation) or with the 'ejection' of a radical from the organoelement compound (S_R2 substitution).

$$\left[\sim P^{\bullet}\text{---}\dot{E}R_3\right] \longrightarrow \sim P^{\bullet} + \ddot{E}R_3 \quad \sim P\ddot{E}R_2 + R^{\bullet} \qquad (48)$$

Thus, one of the variants for the participation of OEC in the chain transfer stage and in the control of MM is realised.

It cannot be ruled out that in the presence of coordinatively unsaturated OEC, chain propagation takes place *via* insertion of the monomer at the labile $[\sim P^{\bullet}\text{---}\dot{E}R_3]$ bond to give a new coordinated macroradical.

$$\left[\sim P^{\bullet}\text{---}\dot{E}R_3\right] + CH_2{=}CH(X) \longrightarrow \left[\sim P^{\bullet}\text{----}\dot{E}R_3 \;\; CH_2{=}CH(X)\right] \longrightarrow \left[\sim P{-}CH_2{-}\dot{C}H(X)\text{---}\dot{E}R_3\right] \qquad (49)$$

Thus, OEC is coordinated to the growing macroradical and thus participates directly in chain propagation and prevents bimolecular chain termination upon recombination of growing macroradicals. This type of process can be considered as a variant of 'pseudo-living' polymerisation.

It has been noted above that an increase in the rate of complex-radical polymerisation in the presence of metal halides can be explained by assuming the cyclic mechanism of chain propagation.[5] Similarly to OEC containing Group III elements, the alkyl derivatives of antimony and bismuth have a more pronounced influence on the chain propagation in the polymerisation of VA and BA than in the polymerisation of MMA.[242, 243] Since the distributions of electron density in the molecules of alkyl acrylates and methacrylates (for example, in MMA and BA) differ insignificantly,[79] it can be suggested that steric factors make the crucial contribution to the change in the kinetic parameters of polymerisation (in particular, the rate constants for chain propagation). The absence of substituents at the central carbon atom in the butyl acrylate radical makes the reaction centre more readily accessible for the coordination to OEC and subsequent chain propagation than in the case of MMA (tertiary radical).

The mechanism of chain propagation proposed above is also supported by the absence of inhibitory effect upon joint introduction of hydroquinone and triethylantimony in the polymerisate.[53] The organoelement additive enters into the coordination interaction with the growing macroradical and thus 'blocks' the reaction centre and prevents its interaction with the inhibitor. Consequently, the rate of polymerisation and the MM of polymers virtually do not change in the presence of hydroquinone and triethylantimony.

The character of influence of benzoquinone (a more effective inhibitor of radical polymerisation) on the kinetics of the processes studied is determined by the quinone concentration in the monomer mixture.[53] When the ratio [benzoquinone] : [triethylantimony] < 1, the rate of polymerisation virtually does not change. Conversely, with an excess of the quinone, polymerisation is retarded.

This pattern of variation indicates, apparently, that at least two independent processes take place. One process is fast reaction of triethylantimony with benzoquinone in which quinone is reduced to hydroquinone.[244, 245] As noted above, hydroquinone influences only slightly the kinetics of polymerisation of acrylic monomers in the presence of organic compounds of Group V elements. In addition, when [benzoquinone] : [triethylantimony] > 1, the excess benzoquinone reacts with the growing macroradical to give stable phenoxyl radicals; as a consequence, polymerisation also slows down. The substantial decrease in the molecular mass of PMMA upon introduction of the quinone

confirms the assumption that it participates in the chain termination step.[243]

Organoelement compounds containing Group V elements not only influence the rate of polymerisation of vinyl monomers but also control the MM of polymers, the effect being more pronounced than that induced by the addition of trialkylboranes.[53]

The addition of triethylantimony in amounts comparable with the concentration of the initiator markedly decreases the MM of poly(butyl acrylate) both for bulk polymerisation and for solution polymerisation in ethyl acetate.[243] The molecular mass of the polymer decreases with an increase in the OEC concentration: on introduction of 0.8 mol.% of triethylantimony, it decreases by more than an order of magnitude. The rate constant for the chain transfer to triethylantimony amounts to 0.118, which markedly exceeds the corresponding value for the chain transfer to the monomer (0.003).

The rate constants for the chain transfer to triisobutylbismuth in the polymerisation of MMA and VA calculated from experimental data are equal to 0.011 and 0.71, respectively.[242, 243] The values for the chain transfer to antimony and bismuth alkyl derivatives considerably exceed the corresponding parameters for TIBB (1×10^{-2} and 2.2×10^{-2} for MMA and VA, respectively).[20, 53] The very high rate constants for chain transfer in the polymerisation of BA and VA can be due to the occurrence of two processes involving the macroradical and OEC. One process, namely, free-radical substitution of the growing polymeric radical for the alkyl radical in organo-antimony and -bismuth compounds, occurs by a scheme similar to that presented above for trialkylboranes [see reactions (4) and (5)]. The rate constant for the substitution of oxygen-centred radicals for the alkyl radicals in triethylantimony is $\sim 10^5$ litre mol^{-1} s^{-1} (see Refs 246 and 247).

The second process, which also contributes to the control of the polymer MM, is abstraction of a hydrogen atom from the alkyl group of the OEC by the growing macroradical [similarly to Eqn (6)]. The occurrence of this reaction was proved unambiguously by EPR using the spin trap technique in a study of the influence of minor additives of methyl acrylate and other acrylic monomers on the control of the PMMA molecular mass during polymerisation involving organoelement initiators.[113]

It was found that, like trialkylboranes, organic compounds of antimony and bismuth also influence the composition of copolymers. Thus in the case of the MMA – MAA pair of monomers, the addition of triethylantimony in amounts commensurable with the concentration of the initiator induces transition from the copolymer enriched in one component ($r_{MAA} = 1.40$, $r_{MMA} = 0.08$) to strict alternation of units in the copolymer.[243] The appearance of alternation of units can be explained by an increase in the rate of cross propagation as a result of the formation of a cyclic reaction complex involving the monomer, the growing macroradical and the OEC. It is noteworthy that, as in the case of TIBB, the flat section in the composition curve corresponds to an MAA content in the copolymer, equal to 0.66 mol.%. This indicates that MAA is involved in the chain propagation step as a dimer.[243] Triethylantimony also influences somewhat the regularities of copolymerisation of MAA with the electron-donor St monomer:[53] the introduction of triethylantimony substantially increases the rate of copolymerisation; however, neither the composition of the copolymers, nor the relative activities of the monomers change noticeably.

The difference from the copolymerisation of the MAA – MMA pair of monomers is caused by the different in kind structures of MMA (electron density acceptor) and St (electron density donor), and the corresponding macroradicals.

Thus, OEC containing Group V elements participate directly in the elementary steps of polymerisation of vinyl monomers and control efficiently polymerisation kinetics and the MM and composition of copolymers prepared both in the bulk and in solution.

V. Conclusion

The effective methods for controlling the reactivity of macroradicals developed to date permit the preparation of homo- and copolymers uniform in composition and molecular mass. The control is attained *via* active influence on the elementary processes of polymerisation including the chain propagation step. The introduction of very small amounts of active additives makes it possible to achieve substantial and, what is more important, targeted change in the reactivity of the macroradicals and to control systematically the polymer chain propagation. It is of prime importance that some OEC, spin traps, iniferters and other controllers of chain propagation considered above are active when present in amounts comparable with the concentration of the initiator. Hence, in the future, they could be used in the industrial synthesis of polymers.

The analysis of published data given above demonstrates, in our opinion, considerable achievements in the development of controlled radical polymerisation — a new and promising line of research in the synthetic chemistry of polymers.

The review was supported by the Russian Foundation for Basic Research (Project No. 99-03-33346).

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