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From phenol-type inhibitors to agents of the controlled synthesis of macromolecules

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Abstract. Data on the effect of a wide diversity of phenol-type inhibitors including their organoelement derivatives on the radical polymerization of vinyl monomers are analyzed. The prospects of using classical inhibitors and their derivatives in the controlled synthesis of macromolecules under radical initiation and metal-complex catalysis conditions are assessed. The bibliography includes 208 references.

I. Introduction

Polymers pertain to the most important class of modern structural materials. The wide spectrum of applications of polymer materials determined considerable differentiation of the requirements imposed, particularly, on their structure, molecular weight and physicochemical characteristics. Since their discovery and up to now, the radical polymerization has been the major method of synthesis of high-molecular compounds on the industrial scale. Polymers synthesized under the radical initiation conditions account for more than a half of world polymer production. The main advantages of radical polymerization are its simplicity, high rate, good reproducibility and the wide spectrum of monomers capable of polymerization in the presence of radical species. At the same time, the radical polymerization has several serious drawbacks associated first of all with the high reactivity of free radicals responsible for the initiation, chain propagation and termination. As a rule, this leads to autoacceleration of this process, the spontaneous uncontrolled growth of the polymer molecular weight (MW), the broadening of its molecular weight distribution (MWD) and in total has a negative effect on the properties of polymers, which in turn places certain limitations on their application and makes difficult further processing.

To minimize the adverse consequences of autoacceleration and improve the physicochemical characteristics of commercial homo- and copolymers, the approaches associated with the targeted impact on the elementary stages of the process (changing the temperature, varying the nature of initiator, using the method of weak inhibition, adding various regulators, *etc.*) were traditionally used.[1–4] Among the mentioned methods, special role belongs to regulation of kinetic parameters of polymerization by adding modifying agents capable of targeted change of the reactivity of both the monomer molecules and the propagating radical, which is the key factor of the control over elementary stages.[5–7]

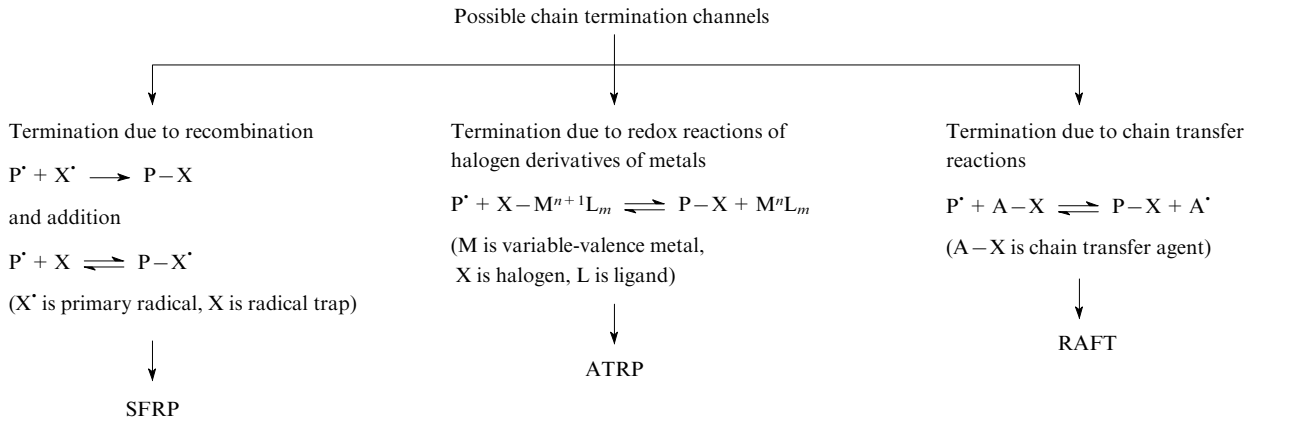
In the past decade, one of the most rational solutions of this problem was associated with the actively developed concept of the controlled/living radical polymerization (CRP).[8–29] It is noteworthy that three main directions of CRP formed to date [polymerization involving stable radicals, referred to as Stable Free-Radical Polymerization (SFRP); polymerization involving the transfer of an atom, namely, Atom Transfer Radical Polymerization (ATRP); polymerization with reversible chain transfer, *i.e.*, Reversible Addition Fragmentation Transfer (RAFT)] were actually stimulated by fundamental studies in the field of inhibition and chain transfer reactions in the polymerization of various vinyl monomers (Scheme 1).

Thus, back in 1955, Ferington and Tobolsky [30] proposed to use tetramethylthiuram disulfide as the regulator of radical polymerization of styrene (ST) and methyl methacrylate (MMA). However, insofar as the mentioned additive was characterized by the high transfer constants, this publication was forgotten up to the fundamental works by Otsu *et al.*,[31,32] who studied in detail several compounds capable of efficient regulation of polymerization and were the first to introduce the concept of 'iniferter'.

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Scheme 1



The use of nitroxides as the best studied regulators of radical polymerization dates back to the pioneering studies of the mechanism of radical initiation and the concomitant development of efficient traps of carbon-centred radicals. In the foreign literature, priority was often given to the works by Solomon, Rizzardo and Moad [33,34] dating back to the early 1980s, who have shown that at relatively low temperatures (40–60 °C), nitroxyl radicals such as 2,2,6,6-tetramethyl-1-piperidineoxyl (TEMPO) can react with radicals formed from a monomer and thus substantially affect the kinetics of polymerization and molecular-weight characteristics of polymers. However, it should be mentioned that in Russia these studies were started much earlier. Thus, as early as in 1966, Buchachenko and co-workers [35] proposed to use different nitrogen-oxide mono- and biradicals as the inhibitors of radical polymerization. Rafikov and Stepukhovich [36–40] also studied the inhibiting effect of nitoxide radicals of different structure on the radical polymerization of ST and (meth)acrylate monomers in the temperature range of 60–80 °C. These interactions produced alkoxyamine derivatives which were sufficiently stable at the mentioned temperatures and were not involved in further reactions.

The important breakthrough in the development of the theory of inhibition of radical polymerization was the assumption that chain propagation radicals can reversibly interact with the inhibitors of polymerization or inhibition products under certain conditions.[41,42] These very studies laid the basis for the formation of a new concept, the controlled synthesis of macromolecules under conditions of radical inhibition. Thus polystyrene (PS) synthesized [41] in the presence of TEMPO at 130 °C had a sufficiently low polydispersity index ($M_w/M_n \approx 1.2$), *i.e.*, much lower than the theoretical limit for radical processes (for ordinary radical polymerization, $M_w/M_n \geqslant 1.5$; however, under radical polymerization conditions, the real polydispersity indices always exceed 2.0).

Later, to carry out radical polymerization in the controlled mode, it was proposed [43–45] to use complexes of transition metals, namely, copper, ruthenium and nickel. This manifested the beginning of a new direction of synthetic chemistry of polymers, namely, the atom-transfer radical polymerization. The ATRP processes were found to be directly related to the redox reactions initiated by transition metals and also to the inhibition processes in the presence of transition metal compounds.[46,47] However, the main criterion of successful polymerization by the living mechanism is the possibility of a reversible redox processes in the system.

A relatively new field of controlled polymer synthesis is the polymerization with reversible chain transfer, particularly, by the mechanism of addition–fragmentation. Processes of this type were discovered only by the end of the past century.[48–50] For this process, the main reaction that determined the living polymerization was assumed to be the repeated chain transfer which involved aryl disulfides and their analogues.

It should be noted that in recent years, the number of reagents that make possible the CRP of different monomers substantially increased. Several reviews and original studies [8–29] were devoted to the analysis of specific features of polymerization involving carbon-centred and nitroxyl stable radicals, transition metal complexes and also thioesters, dithiocarbamates and their analogues. On the whole, the obvious quest for sufficiently simple but efficient systems capable of sustaining the synthesis of polymeric products with definite structure and properties under conditions resembling most closely the industrial conditions is observed.

This review considers the specific features of the synthesis of polymers in the presence of the best studied and most widely used inhibitors of polymerization, namely, phenols and quinones and also of their derivatives in the light of the latest achievements in the field of controlled synthesis of macromolecules. A comparative analysis is carried out for the methods of polymer synthesis in the presence of phenol- and quinone-based systems; their use as the common inhibitors in the synthesis of high-molecular compounds and also in initiation of radical polymerization is discussed. The possibility of the most interesting and promising directions of controlled polymerization in the presence of tested systems is analyzed, particularly, the synthesis of polymers with the desired structure, molecular-weight characteristics and properties. It is shown that modifying the structure of quinones themselves and their co-adjuvants (organoelement compounds, metal complexes, amines, *etc.*) and also of their certain metal-complex derivatives is the factor that makes possible the controlled polymerization processes.

II. Phenol-type inhibitors and systems based on them in the radical polymerization of vinyl monomers

Sterically hindered phenols and polyphenols are very reactive compounds due to the presence of a mobile hydrogen atom in the hydroxyl group. They serve as antioxidants in biological systems and are used in different fields of chemical industry.[51–54] Thus certain natural polyphenols were used in curing cancer, cardiovascular and other diseases.[53,54] Moreover, these compounds find wide application as stabilizers of destruction in the polyolefin processing and durable thermal ageing and the storage of unsaturated compounds and also as the inhibitors of radical polymerization in organic and aqueous media.

Thus Foord[55] was the first to assess the effect of compounds of different classes (polyphenols, quinones and aromatic nitro compounds) on the bulk autopolymerization of ST in the temperature range of 60–120°C in the absence of oxygen. Based on the criteria such as an increase or decrease in the polymerization rate, the appearance of an induction period in the presence of adjuvants, the following classification of regulators of radical polymerization was proposed: accelerators; compounds that have no effect on the polymerization; decelerators and inhibitors. According to this classification, polyphenols, *i.e.*, hydroquinone, pyrocatechol, pyrogallol, were assigned to the class of decelerators, *i.e.*, compounds that somewhat decrease the polymerization rate but do not completely inhibit the process. Under these conditions, phenols and their derivatives have no pronounced effect on the ST polymerization process. Analogous data on the slight deceleration of the MMA thermal polymerization in the presence of hydroquinone, 4-*tert*-butylpyrocatechol, or pyrogallol at 131 °C in the absence of oxygen were also obtained.[56]

Breitenbach *et al.*[57] were the first to show that in the absence of oxygen, hydroquinone failed to inhibit the thermal polymerization of ST. The hydroquinone efficiency as an inhibitor in the presence of oxygen was associated with its oxidation to quinone. However, no experimental evidence of this assumption was offered in the above study.

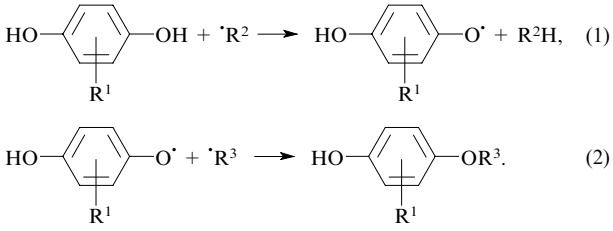
The effect of hydroquinone, 4-*tert*-butylpyrocatechol and 4-aminonaphthol on the thermal polymerization of ST, 3,4-dichlorostyrene and 2-vinyl-5-ethylpyridine at 100 °C was studied.[58] For polymerization carried out in the presence of oxygen, it was shown that the chosen regents served as inhibiters under the given conditions. The more so that as compared with the other inhibitors (picric acid, trinitrobenzene, quinone derivatives) also tested in the mentioned study, these compounds were less efficient.

In his study of ST polymerization initiated by benzoyl peroxide in the absence of oxygen, Cohen[59,60] has shown that hydroquinone and its substituted analogues including ethers have different effects on the polymerization rate and the polymer MW. Particularly, hydroquinone derivatives with alkyl and acyl groups substituted for the hydroxyl hydrogen atom had no noticeable effect on the polymerization and the polystyrene MW. Hydroquinone itself and its derivatives containing one or two free hydroxyl groups had a more pronounced effect on the kinetic parameters of polymerization. According to Cohen, this inverse dependence of the activity of hydroquinone and its derivatives observed in the presence of benzoyl peroxide, in contrast to polymerization in the absence of oxygen, was caused by the slow oxidation of tested compounds with peroxide or peroxide decomposition fragments to afford quinhydrone or quinones. In his later study[61] of different phenols, polyphenols and their derivatives (in total, eight compounds were tested), he has shown that in the MMA polymerization initiated by benzoyl peroxide, the mentioned compounds served as strong inhibitors.

A detailed study of the reaction products of hydroquinone with benzoyl peroxide and several other peroxides in different solvents was accomplished.[62,63] Its authors isolated and identified *p*-benzoquinone, the corresponding acids of the aromatic series, the products of their decarboxylation, 2,5-dibenzoyl derivatives of *p*-benzoquinone and several other compounds. The relative amounts of products were largely determined by the molar ratio of reagents and the nature of solvent. The wide diversity of isolated products pointed to the realization of several reaction mechanisms. Presumably, the synthesis of certain compounds in the presence of solvents may be explained by the heterolytic mechanism.

Dolgoplosk and Tinyakova[64,65] carried out complex studies of the effect of different polyphenols and their derivatives (hydroquinone, *tert*-butylhydroquinone, pyrocatechol, mono- and dimethyl ethers of hydroquinone) on the processes of radical oxidation and polymerization of ST, MMA, vinyl acetate (VA), chloroprene and isoprene both in the absence and in the presence of oxygen in the temperature range of 50–100 °C. It was found that polyphenols and hydroquinone monomethyl ether had an insignificant effect on the ST autopolymerization rate at 100 °C; moreover, the disubstituted hydroquinone analogue, namely, its dimethyl ether, had no effect on the polymerization kinetics. It was also shown that for the ST polymerization with radical initiation, hydroquinone had no effect on the polymerization rate in the absence of oxygen irrespective of the nature of initiator.

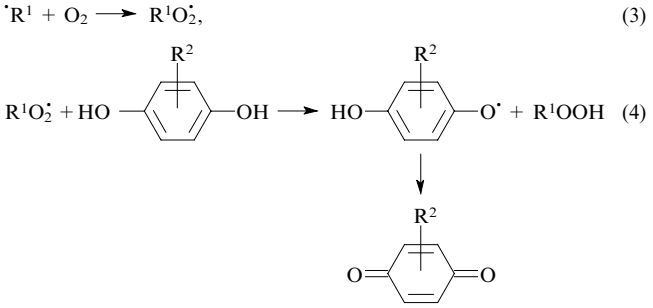
In contrast to other authors,[59,60] Dolgoplosk and Tinyakova[64,65] failed to observe any hydroquinone interaction with benzoyl peroxide at temperatures below 80 °C that could result in inhibition of polymerization. A similar effect of hydroquinone was observed for the polymerization of chloroprene, isoprene and MMA initiated by 2,2′-azobis(isobutyronitrile) (AIBN). However, under the latter conditions, the VA and acetyl acetate polymerization considerably slowed down in the presence of hydroquinone and *tert*-butylhydroquinone. This decrease in the polymerization rate was accompanied by a decrease in the MW, which was especially pronounced for polyvinyl acetate (PVA). This suggests that the reaction of chain transfer (reaction 1) proceeds at a low rate and is followed by quick termination as the result of radical recombination [reaction (2)].



Thus, in the absence of oxygen, polyphenols are more efficient as the inhibitors of polymerization of VA and allyl acetate, which form the most active radicals of chain

propagation with the high reactivity with respect to the hydrogen atom of the phenol hydroxyl group [reaction (1)]. The less active radicals formed in polymerization of ST, isoprene, chloroprene and MMA virtually fail to react with polyphenols. In this case, the effect of polyphenols as the polymerization inhibitors is insignificant.

In the presence of air oxygen, the polymerization involving polyphenols acquired the radically new character.[64, 65] Irrespective of the nature of initiator and monomer, hydroquinone and *tert*-butylhydroquinone cause a long induction period. Several direct experiments have shown that polyphenols in the presence of oxygen were oxidized to quinones and quinoid type compounds. Such an effect of oxygen on the polymerization process in the presence of polyphenols was explained by the formation of phenoxyl radicals in sequential reactions (3) and (4) and also by the possible involvement of oxidation products of the phenol-type.



Analogous data on the effect of polyphenols of different structure on the MMA polymerization in the presence and in the absence of oxygen were presented.[66, 67]

Canadian scientists studied the effect of several phenols [1-naphthol, 4-methoxyphenol, 2,6-diisopropylphenol, pyrocatechol, *tert*-butylpyrocatechol, pyrogallol, 2,6-di-*tert*-butyl-4-methylphenol (DBMP), *etc*.] on the rate and the degree of polymerization of MMA,[68] ST[69] and VA.[70] The phenomena of deceleration and the decrease of the polymer MW were shown to depend on the structure of phenols and the ability of active radicals to eliminate the hydrogen atom from the phenol hydroxyl group (the so-called chain transfer reaction; chain transfer constants were estimated for all phenols tested).

In the later study by Japanese scientists,[71] the processes of radical polymerization of MMA, ST and VA in the presence of an acrylate containing a sterically hindered phenol group were considered. It was shown that in the MMA and VA polymerization, this compound acted as the decelerator and the inhibitor, respectively. However, for ST, in the presence of a phenol-containing acrylate, copolymerization occurred, *i.e*., the latter served as the monomer.

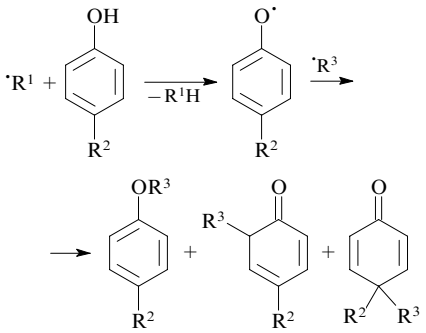
It should be noted that to date, the interest in such compounds is still very high. Thus Japanese scientists[72] revealed the inhibiting effect of certain bisphenol derivatives (2,2′-biphenol, 4,4′-biphenol, bisphenol A, diethylstilbestrol) in the MMA polymerization initiated by AIBN and benzoyl peroxide. It was shown that stoichiometric coefficients of the capture of free radicals by these phenols were ~2.0, with the exception of 2,2′-biphenol for which this value was 0.82. The mechanism and deviations in the action of listed bisphenol derivatives as the free radical scavengers and the inhibitors of MMA polymerization was explained by invoking the quantum chemical methods.[73] In other publications, the MMA polymerization initiated by AIBN and benzoyl peroxide at 70 °C in the presence of DBMP and its oxidation products[74] and also of epicatechol, resveratrole and n-propyl gallate[75] was used as a system modelling the biological antioxidants. The polymerization process was carried out at low oxygen concentrations imitating the anaerobic conditions. It was shown that the inhibiting action of DMBP and polyphenols was manifested most clearly for benzoyl peroxide used as the initiator.

It was shown that in the presence of oxygen, phenols are capable of inhibiting the photopolymerization of MMA[76] and other acrylates[77] and also the processes of photo-cross-linking of a film prepared from epoxy acrylates and monofunctional monomers (isobornyl acrylate and *N*-vinylpyrrolidone).[78] The role of phenol derivatives (phenol, vanillin, 2,6-dimethoxyphenol and eugenol) in the process of photopolymerization of trimethylolpropane triacrylate was studied by differential scanning calorimetry in the absence of air oxygen.[79] As the initiators, 2,2-dimethoxy-2-phenylacetophenone and the benzophenone–*N*-methyldiethanolamine system were used. In the latter case, the polymerization that involved phenols and proceeded in the absence of oxygen was observed to slow down. Presumably, this effect was due to the interaction of phenols with benzoquinone in the triplet state. The polymerization kinetic data were correlated with the oxidation potentials of phenols. Later, French scientists discovered the possibility of using photoinitiating systems involving phenol derivatives in carrying out polymerization on the surface of wood under industrial conditions.[80]

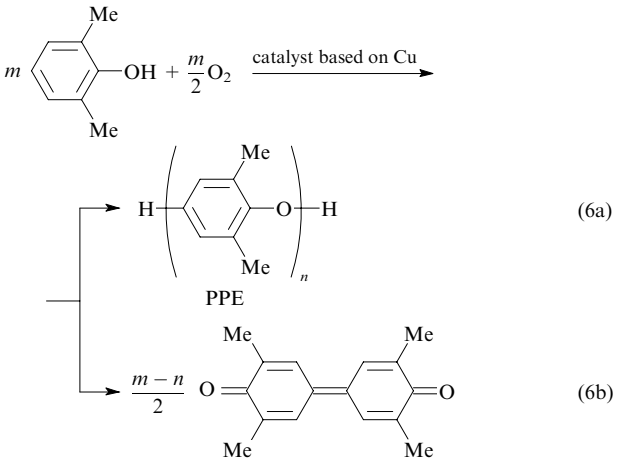
The effect of certain *para*-substituted phenols as the chain transfer agents on the photopolymerization of acrylamide and 1-vinyl-2-pyrrolidone in aqueous solutions was reported.[81] The ability of phenols for chain transfer was shown to depend on their donor–acceptor properties and increase with the introduction of electron-donating substituents into the phenol structure.

Thus, the analysis of published data suggests that the radical polymerization involving phenols is a complex multistage process. Taking into account the reactions of phenoxyl radicals that occur in organic media, the following pathways can be proposed for the formation of the final products in the medium of a monomer containing semiquinoid type radicals: addition with the formation of C–O and C–C bonds (in the *ortho*- and *para*-positions of original phenols) (C–O and C–C addition); formation of charge transfer complexes; oxidation followed by stages of initiation, chain propagation and termination involving the oxidation products.

Recombination of two phenoxyl radicals to form the O–O peroxide bond was ruled out because this bond was unstable under polymerization conditions.[82] For semiqui-



noid radicals, the processes of C—O- and C—C-addition could involve either the alkyl chain propagation radicals [to form ethers and quinoid-type derivatives, reaction (5)] or with another phenoxyl radical in the presence of catalysts [reactions (6)]. These reactions underlie oxidative polymerization of phenols [reaction (6a)].



PPE is polyphenylene ether.

Hay *et al.*[83] discovered the homogeneous oxidative polymerization of 2,6-disubstituted phenols catalyzed by Cu^{I} salts in the presence of amines. Polyphenylene ether formed under the action of this catalytic system by the multiple C—O-addition of phenol fragments [reaction (6a)]. Polyphenylene ether exhibits excellent mechanical properties and chemical stability even at elevated temperatures. The side product, diphenoquinone was formed as the result of the addition of two phenol molecules [reaction (6b)]. The latter was an unwanted product because it coloured the polymer material and led to its decomposition in the further high-temperature treatment. Further studies in the field of oxidative polymerization of phenols were concentrated on elucidation of the role of the copper-containing catalyst in the polymerization mechanism. Initially, the first stage was assumed to produce an intermediate (mononuclear Cu–phenol complex), which later generated the phenoxyl radicals and the latter formed the polymer.[83] In later studies, the formation of binuclear intermediates Cu–phenol was assumed. The decomposition of the latter produced phenoxonium cations as the active intermediate species.[84–87]

Japanese authors[88,89] put forward an original concept of controlled radical polymerization of 2,6-unsubstituted phenols. As compared with phenols substituted in both *ortho*-positions, it proved difficult to synthesize a linear unsubstituted polyphenol by using standard oxidizing systems. In the mentioned studies, the suppression of addition reactions to positions 2 and 6 was achieved due to the use of copper complexes with sterically hindered ligands.

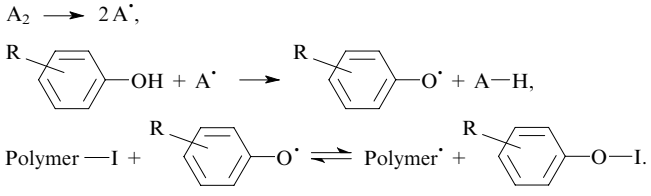
It deserves mention that the question on the mechanism of phenol oxidative polymerization remains so far open.[90–92] However, this problem and its detailed analysis are beyond the scope of this review.

The studies associated with the use of phenols in the controlled synthesis of macromolecules by the atom transfer mechanism are the closest to the subject of the present review.[93–95] Thus in one of these studies,[93] phenol and its derivatives in the presence of small amounts of oxygen were used as the reducing agents in the ATRP processes. The proposed method is based on the catalytic systems of oxidative polymerization in which Cu^{II} is reduced to Cu^{I} in the presence of phenols. The use of such systems in the ATRP process allows the catalyst to be brought into its active state. Thus, the controlled polymerization of MM, ST and methyl acrylate (MA) were carried out to afford materials with narrow MWD (the polydispersion coefficient was 1.1–1.5) in the temperature range of 80–100 °C. It was shown that phenols with electron-donating groups sufficiently increased the polymerization rate (sodium phenoxide proved to be the most efficient).

Somewhat later, such regularities were revealed by other scientists.[94,95] For the living radical polymerization with one-electron transfer, it was found[96] that in the ATRP mode, under the action of different solvents (water, alcohols, DMSO, *etc.*), Cu^{I} complexes were capable of spontaneous disproportionation to Cu^{0} and Cu^{II} at room temperature, which accelerated the controlled synthesis. Thus the effect of 4-methoxyphenol on the rate of Cu^{0}-catalyzed MA polymerization was studied.[94] It was shown that the presence of phenol insignificantly increased the process rate and gave rise to a short induction period. The authors of another study[95] used a large number of phenol derivatives in order to increase the MA polymerization rate in toluene at room temperature. Synthesized polymers had low polydispesity indices (1.05–1.25). The phenol structure was shown to substantially affect the polymerization mechanism. Thus the introduction of more serious steric hindrances in the *ortho*-position had the inverse effect on the polymerization rate. The use of sterically hindered phenols in this reaction gave rise to a considerable induction period.

A unique example of the use of phenols in a CRP process was described in the recently published study by Japanese scientists.[97] They were the first to use compositions based on conventional initiators, alkyl iodides and various phenol derivatives as the catalysts of reversible chain transfer catalyzed living radical polymerization (RTCP) (Scheme 2). The RTCP process is based on the interaction of initiator radicals (A$^{\bullet}$) with an oxygen-containing compound to afford *in situ* the phenoxyl radicals that later can activate either alkyl iodides or the polymer chain with a iodide atom at the end (Polymer–I).

Scheme 2



The main requirements to radicals acting as the activators are as follows: relative stability, easy formation, and the inertness with respect to polymerization initiation processes which is combined with the activity in reactions with alkyl iodides and iodine-containing polymers. Phenoxyl radicals, which are stable and as a rule incapable of initiating the radical polymerization, seem to be very promising RTCP activators. A wide series of non-toxic stable oxygen-containing compounds including well-known mono- and multiatomic phenols and their derivatives, antioxidants for foodstuffs and plastics (DBMP and 2,6-di-*tert*-

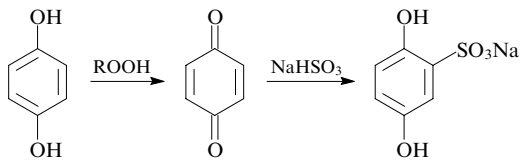
butyl-4-methoxyphenol) and also natural compounds (flavonoids, uric acid and vitamin C) were tested.[97]

The authors[97] demonstrated that in principle, polymerization can be carried out in the presence of proposed catalytic systems for a wide diversity of monomers including ST, MMA, benzyl, glycidyl, 2-hydroxyethylate and poly(ethylene glycol) methacrylates. These processes occurred at high rates up to deep degrees of conversion (~80%) in short times (from 10 min to 7 h depending on the nature of monomer) in the temperature interval of 80–100 °C. The polydispersity indices of polymers were 1.16–1.35 for PS, 1.23–1.41 for PMMA, 1.18–1.40 for methacrylate derivatives. Thus, in contrast to the well-known CRP processes carried out by the SFRP and ATRP mechanisms, the systems based on phenol derivatives, which were proposed by Japanese scientists, were distinguished by the ability of polymer materials to be relatively easily functionalized *via* random and block copolymerization with different monomers. Thus synthesized random and block copolymers had a narrow MWD (M_w/M_n = 1.25–1.33). Besides their importance for practice, the data of this study are very important for theory. Thus, a lot of phenols were studied and for the case of ST polymerization the effect of both spatial and electronic factors on the stability of formed activators (phenoxyl radicals) and the PS molecular-weight characteristics was considered.[97] It was shown that the polydispersity index decreases with an increase in the steric hindrances in the *ortho*-positions of phenols with respect to the hydroxyl group. This was associated with the quick formation of phenoxyl radicals and their sufficiently high activating ability. However, with a sufficient increase in the volume of substituents in these positions (for example, with the introduction of Bu^t groups), which can stabilize the phenoxyl radicals, the polydispersity index was observed to somewhat increase, which was attributed to the low activating ability of sterically hindered radicals (see Scheme 2). In the similar manner, the polydispersity index increased with the introduction of phenoxyl radicals due to the action of the electronic factor (resonance).

It deserves mention that the systems proposed in studies discussed above[93–95,97] make it possible to carry out controlled radical polymerization at high rate without preliminary cleaning of monomers from phenols added as the stabilizers during the storage.

As follows from the analysis of the literature, the multicomponent systems based on phenols proved to be most efficient in combination with active co-components.

In his studies, Dolgoplosk[64,65] has proposed multicomponent initiating compositions based on hydroquinone, peroxide and reducing agents (ammonia, amines, sodium sulfites and hydrosulfite). To a certain extent, the proposed systems were reversible, leading to the formation of hydroquinone derivatives.



With participation of these systems, the emulsion polymerization at 5 °C proceeded at a very high rate. The hydroperoxide–hydroquinone–sodium sulfite system was successfully used at the synthetic rubber plants in polymerization of butadiene and styrene mixtures (synthesis of SKS-30A rubber).

However, the alkyl derivatives of hydroquinone, particularly, diisobutylhydroquinone are weakly active in combination with hydroperoxide and sodium sulfite. This is due to the redox potentials of polyphenols and corresponding quinones. Diisobutylhydroquinone is oxidized much faster than hydroquinone but the resulting quinone is poorly reduced by sulfites. Thus, the reversibility of the system is violated and the polymerization is inhibited by the oxidation products of diphenol.[64,65]

Indian scientists[98] carried out a detailed study of the mechanism of charge transfer polymerization of styrene and alkyl methacrylates (MMA, ethyl and butyl methacrylate) in the presence of the hydroquinone–amine–CCl_4 system. It was found that with the use of such ternary systems, the polymerization affords higher yields as compared with the polymerization of these monomers in the presence of only hydroquinone. Presumably, the increase in the yield of polymers is associated with the formation of charge-transfer complexes that decompose to form not only radical species but also radical cations.

As early as in the 1960s, several authors[99,100] noted that a binary composition of hydroquinone with a certain organoelement compound (OEC) containing a group 13 element allowed the MMA polymerization to be carried out in the presence of either benzoyl peroxide or AIBN with high degrees of conversion. Particularly, detailed studies were carried out for systems based on triisobutylboron and a phenol-type inhibitor.[101–103] It was shown that the introduction of diphenylolpropane and hydroquinone not only failed to inhibit the radical polymerization of acrylates in the presence of trialkylboranes but, in contrast, accelerated it.[101–103] Thus, the polymerization rate of MMA and acrylonitrile (AN) substantially increased in the presence of Bu^i_3B and synchronously increased with the increase in contents of OEC and inhibitor. Analogous data were obtained in the presence of alkylalkoxyl derivatives of boron.[104] For polymerization of tested monomers in the presence of a sterically hindered phenol (ionol) and an OEC, the process was observed to slow down a little.[102,103]

Phenol-type inhibitors have a certain influence on the polymer MW too.[101–103] Particularly, the MW of polymethyl methacrylate (PMMA) decreased with the introduction of polyphenol but this effect was insignificant as compared with the similar effect of conventional chain transfer agents.

In contrast to acrylates, the polymerization of VA and vinyl chloride in the presence of OEC of group 13 elements was efficiently inhibited by hydroquinone. The introduction of the latter in amounts exceeding the trialkylborane concentration resulted in the complete cessation of the VA polymerization.[101]

Organoelement compounds of group 13 elements and the chosen inhibitors accelerated not only homo- but also copolymerization of methacrylic acid (MAA) with VA.[102] The this process, it was shown that the introduction of hydroquinone together with an OEC allowed the composition of copolymers to be regulated, particularly, for MAA

concentrations in the range of 20% – 80%, the copolymer composition remained unchanged.

Similar features, *i.e.*, the absence of the hydroquinone inhibiting effect at the polymerization of MA and ST were also observed in the presence of Lewis acids, namely, halides and certain metals.[105]

In the above studies,[101–103] the increase in the polymerization rate of acrylates in the presence of phenols and OEC was explained by several possible factors, first of all, by the reaction of S_R2-substitution between the formed phenoxyl radicals and the alkyl radicals from the OEC to afford new reaction sites.[106]

$$ArO^{\bullet} + ER_3 \longrightarrow R^{\bullet} + ArOER_2, \qquad (7)$$

E is element of group 13.

Second, the unusual effect of phenols was found explained in terms of radical polymerization. Formed phenoxyl radicals did not possess sufficient reactivity with respect the monomer multiple bond. In the presence of OEC or Lewis acids as the electron acceptors, the mentioned compounds were coordinated with macroradicals and acrylic monomers, which led to activation of the latter.[107] As the result, the initiation of polymerization by phenoxyl radicals became possible.

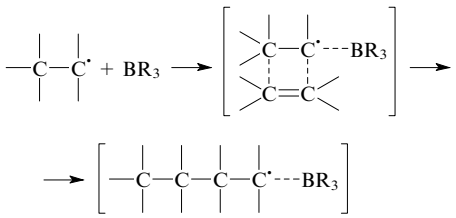
$$\begin{aligned} &CH_2{=}\underset{\displaystyle Y}{\underset{|}{C}}X + ER_3 \longrightarrow CH_2{=}\underset{\displaystyle Y{-}{-}{-}ER_3}{\underset{|}{C}}X \\ &ArO^{\bullet} + CH_2{=}\underset{\displaystyle Y{-}{-}{-}ER_3}{\underset{|}{C}}X \longrightarrow ArO{-}CH_2{-}\underset{\displaystyle Y{-}{-}{-}ER_3}{\underset{|}{\dot{C}}}X \end{aligned} \qquad (8)$$

The reaction (8) was also confirmed by IR and UV spectroscopic investigations, which revealed phenoxyl groups within the MMA polymer composition.[102, 103]

Moreover, the coordinated macroradical exhibits the enhanced electrophilicity with respect to the monomer π-bond as compared with noncoordinates radicals, which favours the increase in the propagation rate constant.[5] The chain propagation can occur within a cyclic reaction complex formed by the monomer, the propagating macroradical and the OEC, located directly in the metal coordination sphere.[5, 7, 107] This can also suppress the macroradical reaction with the mobile hydrogen atom of the phenol hydroxy group and thus prevent the inhibition. For the VA and vinyl chloride polymerization, neither original monomers nor the propagating radicals were activated by organoelement compounds and the polymerization of these monomers was thus inhibited.

The inhibiting effect of ionol in the presence of an OEC was probably associated with steric factors. For ionol as a sterically hindered phenol, reactions (7) and (8) proceed much more slowly as compared with hydroquinone and diphenylpropane.

A somewhat different point of view on the factors determining the inhibiting effect of phenols in the polymerization in the presence of OEC was voiced by Arimoto,[99] who proposed to consider the coordination of trialkylborane with the propagating macroradicals as the key factor in such processes. As the result, the radical reaction site is blocked and the reaction with phenol becomes impossible.



In contrast to the aforementioned phenol-based multicomponent systems that increase the polymerization rate of vinyl monomers, the highly efficient compositions based on the sterically hindered phenol of *tert*-butylpyrocatechol (BC) were proposed.[108] These compositions proved to be capable of inhibiting the ST thermal polymerization on the industrial scale. The following two-component systems were considered: BC – 3,5-di-*tert*-butyl-4-hydroxybenzyl(*N*,*N*-dimethyl)amine, BC – ionol, BC – 2,2′-methylenebis(6-*tert*-butyl-4-mehylphenol) (Agidol-2). The proposed systems were shown to surpass the already known inhibitors, *i.e.*, *p*-quinones, in the solubility in aromatic fractions and to compare well with systems based on *p*-quinone dioxime used in Russia and also with the new foreign inhibiting compositions in their efficiency.

Concluding this section, mention should be made of the important aspects such as the complexity and the multistage nature of the observed processes. Particularly, the limited possibilities of the CRP process do follow from the fact that the *in situ* synthesized phenoxyl (semiquinolate) radicals are involved in several competitive reactions mentioned above.

It is important that the occurrence of reaction (1) largely depends on the redox potential of phenol derivatives, the O–H bond energy and the reactivity of the radical species involved in this reaction. Thus, the introduction of electron-donating substituents into the phenol structure decreases the redox potentials and the O–H bond dissociation energies, which leads to the increase in the inhibiting ability of these phenols. Several studies published in recent years[109–113] comprehensively considered the thermodynamic and kinetic parameters of processes involving phenols and also the reactivity of semiquinolate radicals and its relationship with the phenol structure and the aforementioned parameters.

III. The inhibiting effect of quinones and their derivatives on the radical polymerization

The first publications that mentioned the effect of quinones on the radical processes date back to the beginning of the 20th century. These reports were of the practical rather than scientific interest. Quinones and their certain derivatives (together with aromatic nitro compounds) attracted attention of scientists as the substances capable of decelerating or completely suppressing the polymerization of vinyl monomers during their storage. The main criterion determining the efficiency of a quinone in the polymerization process was the appearance of an induction period upon its addition into the polymerization system.

The later studies elucidated qualitative and quantitative characteristics of polymers obtained in the presence of quinones and determined certain kinetic characteristics of hypothesized processes.[59, 60, 114]

Despite the numerous studies of polymerization of vinyl monomers in the presence of various quinones carried out

before the 1960s, their authors failed to draw reliable conclusions on the mechanism of their effect. One of the reasons was that the inhibition by quinones was mainly studied for the thermally initiated ST polymerization. By the end of these studies, it was generally agreed that the initiation reaction is bimolecular, *i.e.*, that the thermal polymerization of ST involves the formation of a biradical.[115] However, later, Mayo [116, 117] assumed that this reaction is trimilecular and proceeds through the primary formation of the Diels–Alder adduct from two ST molecules, followed by the homolysis to afford radicals upon the interaction with the third ST molecule. It should be noted that so far there is no agreement on the thermal initiation of ST polymerization, although the Mayo mechanism [118] is the most widely accepted and established. Moreover, unfortunately, the early studies showed no exact kinetic characteristics that would allow the comprehensive judgements on the efficiency of inhibitors (for instance, the stoichiometric coefficient of inhibition, the rate constant of radical scavenging by the inhibitor, *etc.*) to be drawn.

In line with this, attention should be focused on studies devoted to the inhibition of reagent-initiated polymerization. Thus, Cohen [59, 60] studied the polymerization of ST initiated by benzoyl peroxide in the presence of *p*-benzoquinone at temperatures of 64 and 74 °C. It was found that under these conditions, *p*-benzoquinone inhibited the ST polymerization; the reaction products of active radicals with quinones were phenoxyl derivatives, ethers and other hydroquinone derivatives.

Dolgoplosk and Tinyakova [64, 65] studied the effect of the nature of initiator on the kinetics of styrene polymerization with the inhibition by *p*-benzoquinone. It was shown that irrespective of the nature of initiator, in all the cases, quinone gave rise to the induction period the length of which depended inversely on the rate of formation of primary active sites. Under model conditions, the studies of the composition of reaction products of *p*-benzoquinone and AIBN free radicals have revealed the formation of both hydroquinone monoester and diester.

The considerable effect of the nature of quinones on the rate of MMA [119] and MA [120] polymerization initiated by AIBN at 44 °C was noted. *p*-Benzoquinone was shown to preferentially serve as a weak inhibitor of acrylate polymerization. Moreover, *p*-benzoquinone, 2,6-dichlorobenzoquinone and 2,5-dichlorobenzoquinone had virtually the same effect on the polymerization rate of both monomers; the reactivity of these quinones decreased insignificantly when going from methacrylate to acrylate. On the other hand, chloranil inhibited in the different fashion the polymerization of MA and spatially hindered MMA. Particularly, chloranil was shown to be 80% copolymerized with MMA. Such a dramatic difference in the behaviour of these two monomers was attributed to steric factors of the radical sites and the high electron-withdrawing properties of the quinoid ring in the presence of substituents.[120]

Aimed at studying the mechanism of slowing down and inhibition with quinones, Bevington *et al.* considered the MMA [121] and ST [122] polymerization and also their copolymerization [123] in the presence of the ^{14}C-labelled AIBN and *p*-benzoquinone. Using this approach, the ratio of different routes of radical transformations at the MMA polymerization was determined.[121] It was shown that nearly 86% of phenoxyl radicals formed in the system reacted with macroradicals; in the vast majority of cases, the propagation of two radicals was terminated on a single quinone molecule. Only 14% of phenoxyl radicals were capable of reacting with the monomer.

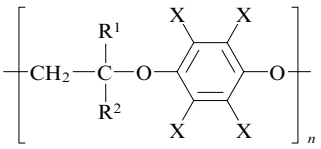
It was found [121] that upon the photochemical and thermal impacts on the MMA–quinone–initiator system, the polymerization occurred without induction period; moreover, both the yield and the MW of resulting PMMA decreased with the increase in quinone concentration. In this case, quinone removed both the cyanoisopropyl radicals and the propagating radicals from the reaction through the formation of diether 1,4-$(RO)_2C_6H_4$, where R is either initiating or polymeric radicals.

For ST, the yield of the polymer product depended on the composition of the initial reactant mixture.[122] For thermal initiation and low *p*-benzoquinone concentrations, the induction period appeared due to the deactivation of two initiating radicals by a single quinone molecule. The increase in the *p*-benzoquinone concentration had almost no effect on the ST polymerization rate, which pointed to the high reactivity of formed phenoxyl radicals with respect to monomer molecules. In fact, the product represented a copolymer of ST with *p*-benzoquinone. Later, such processes of reaction chain 'regeneration' in the presence of inhibitors (*i.e.*, the possible addition of the monomer to the radical formed in the interaction of the polymer radical with the inhibitor molecule) were taken into account in the kinetic scheme of polymerization.[124]

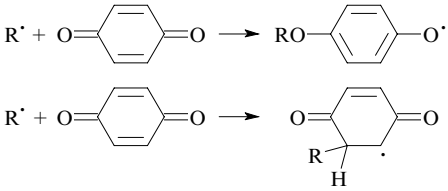
Later, in the studies by Tüdös,[125–130] for a wide range of quinones (*p*-benzoquinone, *o*-xyloquinone, *p*-xyloquinone, toluquinone, methoxyquinone, monochloro-*p*-benzoquinone, trimethyl-*p*-benzoquinone, *m*- and *p*-dichlorobenzoquinones, trichlorobenzoquinone, chroranil, bromanil, iodanil), it was shown that depending on the quinone concentration and structure, not only inhibition processes but also those of quinone copolymerization with the monomer could occur. For instance, it was shown [125] that in low concentrations, *p*-benzoquinone acted as the inhibitor of ST autopolymerization at 90–135 °C. The increase in the quinone concentration and in the temperature led to the synthesis of a ST copolymer with *p*-benzoquinone rather than to the inhibition of polymerization. The activation energies for reactions of inhibition (4.3 kcal mol^{-1}) and copolymerization (9.4 kcal mol^{-1}) were determined. For halogen-substituted quinones, it was shown [128, 129] that in the case of styrene, the charge transfer complexes were formed, which increased the probability of copolymerization of quinones with styrene. Furthermore, in the mentioned studies by Tüdös,[126–130] the relationship was found between the reactivity of quinones in scavenging of active radicals and the redox potentials of quinones and also the size of substituents.

A comprehensive study of copolymerization of vinyl monomers with various *p*-quinones (benzoquinones, chloro and methyl substituted analogues) was carried out.[131–133] As the co-monomers, a wide spectrum of compounds were chosen, namely, styrene and its substituted analogues, acrylonitrile, ethyl acrylate, vinylidene chloride, isobutylvinyl ether, 2-vinylpyridine, butadiene, *etc.* Among the series of tested quinones, tetrachloroanthraquinone was found to be the most active in copolymerization processes.

It was shown that the reactions of quinones with monomers occur according to the 1,4-addition mechanism and the copolymerization product can be generally represented as follows:



As a whole, it can be stated that the mechanism of quinone interaction with different radicals (not only initiating but also polymeric) relies on the possibility of adding radicals to both the oxygen atom and the carbon atom of the quinone molecule.



For a long time, there was no agreement as to the nature of quinone reaction centres. Some scientists assumed that radicals attacked the oxygen atom of the carbonyl group,[134,135] while the others considered addition to be more probable on the C=C bond of the quinoid ring. Thus the reaction products of quinones with initiating radicals in different solvents were considered in a cycle of studies.[136–141] The reaction of benzoyl peroxide with *p*-benzoquinone was shown to afford preferentially phenyl and benzoyloxy derivatives of *p*-benzoquinone. Moreover, no mono- and diethers of hydroquinone were detected.

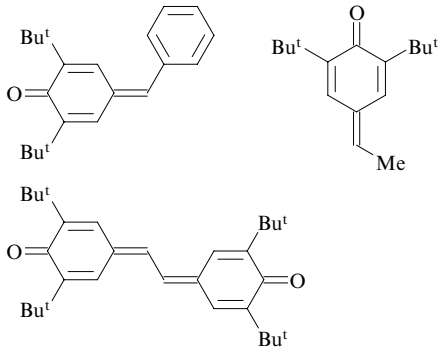
The development of physicochemical analytical methods allowed the mentioned problems to be solved. Tüdös *et al.*[142–145] carried out an EPR study of the reactions of 2,6-dialkyl-*p*-benzoquinones with different radicals and have shown that the cyanoisopropyl and polystyrene radicals could add to the carbonyl carbon atom while the radicals formed upon the decomposition of benzoyl peroxide could add to the C=C bond of the quinoid ring.[142]

Golubev *et al.*[146–148] used the spin trap method to elucidate that the addition of initiating radicals to quinones proceeds *via* parallel routes, *i.e.*, to both the C=O bond and the C=C bond. The ratio of directions of the radical attack depended on the structure of the quinone and the generated radical. Thus it was found[146] that the addition of cyanoisopropyl radicals to quinones (toluquinone, benzoquinone, naphthoquinone and fluoranil) preferentially occurred on the C=O bond, the *p*-methylbenzyl radical added equally frequently on the C=O bond and the C=C bonds, while the *tert*-butyl radical preferentially reacted with the C=C bond of quinones.

It was found[149] that the energy of reactions of radicals with *p*- and *o*-benzoquinones, and also with sterically hindered 3,5- (3,5-BQ) and 3,6-di-*tert*-butyl-*o*-benzoquinones (3,6-BQ) also depended on the quinone structure and the position of bulky substituents. According to quantum chemical calculations, for the interaction of a propagating polymer radical with 3,5-BQ and 3,6-BQ, due to the effect of bulky *tert*-butyl groups, the addition of the macroradical to the C=O bond was more preferential as compared with unsubstituted quinones. The rate constants for the scavenging were found to be 290 litre mol^{-1} s^{-1} for 3,6-BQ and 6340 litre mol^{-1} s^{-1} for 3,5-BQ.

A detailed study[149] of the effect of 3,5-BQ and 3,6-BQ on the molecular weight characteristics of the synthesized PMMA should be mentioned. It was shown that the AIBN-initiated polymerization of MMA at 70 °C in the presence of 3,6-BQ proceeded without any gel effect up to deep degrees of conversion in contrast to 3,5-BQ that inhibited the MMA polymerization and allowed the limiting degree of conversion no higher than 30%. The molecular weight of PMMA synthesized with participation of 3,6-BQ linearly increased with conversion but its MWD remained sufficiently broad at deep conversions ($M_w/M_n = 2.5$). However, no hypothetical mechanism was offered to explain the observed phenomena.

Wasserman and co-workers[150,151] carried out an EPR study of the structure of stable radicals formed either in the inert solvent medium or by the ST autopolymerization in the presence of the following quinonemethides (compounds belonging to the class of unsaturated cyclic ketones).



The concentration and the ratio of phenoxyl radicals formed in the presence of quinonemethides were found to depend on several factors. First, on the quinonemethide structure, because the structure of generated radicals is directly related to the possible side processes involving these derivatives (reactions of disproportionation, scavenging of the newly formed active radical by disproportionation products, the reversible interaction of phenoxyl radicals with active sites). Second, they depend on the experimental conditions and also on the time factor.

The involvement of studied compounds in CRP reactions was hypothesized.[150,151] Presumably, the efficiency of these compounds should depend on the fulfilment of the following 'necessary' requirements to the mentioned agents: the stability during the experiment, the effective and equilibrium concentrations of stable radicals formed in the course of polymerization, the absence of side reactions, *etc*. However, no sufficient evidence that would confirm the efficiency of such systems as the CRP agents was presented.

On the whole, it can be suggested that the mechanism of quinone interaction with different radicals (not only initiating and polymeric) was studied by many Russian and foreign scientists throughout the 20th century so that it is impossible to embrace the whole material within the frames of the present review. It should be noted that the behaviour of quinones as the chain propagation controllers and their efficiency in regulating the polymerization processes have not been adequately studied so far. The low efficiency of this approach is due to the wide diversity of quinone-involving side effects. It is also important that the reaction routes depend on several factors, including the quinone structure, their redox potentials, the nature of active sites. Thus systematic studies of the reactivity of quinones as the

alkyl radical scavengers were carried out.[109] The analysis of parameters of addition reactions and the kinetic calculations were carried out based on the parabolic model by taking into account the geometrical parameters of the transition state and the effect of polarity in addition reactions.

It should be noted that due to their trend for reversible redox processes, the quinone-based polymers find wide use in different fields of science and technology as the reducing agents, oxidants, enterio- and hemosorbents.[152–154] Moreover, due to their individual properties, quinones can interact with different organic compounds (phenols, amines) and metals. These directions open up wide prospects for further studies including those in the field of polymerization and macromolecular design aimed at the synthesis of functional polymers.

IV. Binary systems based on quinones in the synthesis of polymers

The radical polymerization in the presence of quinone-based binary systems is undeniably one of the most interesting application fields of the latter. The effect of such systems on the polymerization kinetics and the molecular weight characteristics of polymers and also their efficiency are determined not only by the quinone structure but also by the nature of the second component. Moreover, the possibility of formation of phenoxyl (or semiquinolate) derivatives in the quinone reactions with different organic and organoelement compounds plays the key role in such type of processes.

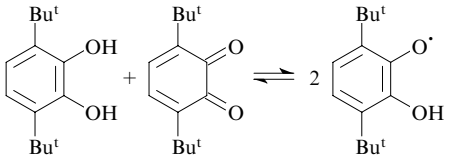
Quinone-based binary systems can act not only as inhibitors but also as initiators and the controllers of radical polymerization.

1. Inhibiting activity of binary systems based on spatially impeded quinones in the polymerization of vinyl monomers

According to several studies discussed in the previous sections, the phenoxyl-type radicals formed in reactions of quinones, phenols and active radicals are the main intermediates that determine the further direction of the polymerization process. Combination of quinones with polyphenols and also quinones with amines allowed the inhibiting efficiency of these compositions to be enhanced as compared with individual components.

Thus Mazaletskaya *et al.*[155,156] has shown that 3,6-di-*tert*-butylpyrocatechol (3,6-PC) and 3,6-di-*tert*-butyl-*o*-benzoquinone (3,6-BQ) exhibited the synergistic effect in inhibition of MMA polymerization. The initial reaction rate and the length of the induction period remained unchanged so far as the product of concentrations [3,6-PC]·[3,6-BQ] remained constant, which suggests that the mentioned compounds interacted in the course of the process. The individual components of the mixture did not affect the process, particularly, neither pyrocatechol, nor benzoquinone were observed to affect the rate of MMA polymerization catalyzed by AIBN at 60 °C.

The strengthening of the effect of 3,6-PC in its mixture with 3,6-BQ, was associated with the presence of phenoxyl-type radicals highly active in inhibition of polymerization, which were detected by EPR method.[156]



3,6-Di-*tert*-butyl-2-hydroxyphenoxyl radical

In was shown that one consumed quinone accounted for the loss of two radicals, in agreement with the proposed mechanism. The rate constant for the reaction of 3,6-di-*tert*-butyl-2-hydroxyphenoxyl radical with the propagating PMMA radicals was calculated to be 1.9×10^7 litre mol^{-1} s^{-1}.

The similar inhibiting compositions containing quinone dioxime and a mixture of sterically hindered phenols (4-*tert*-butylpyrocatechol – Agidol-2) find wide application as the inhibitors of thermal polymerization of ST in the course of its distillation.[157]

The inhibiting ability of quinones can be increased not only due to the action of the quinone – polyphenol redox system but also due to the use of the quinone – amine binary system. Thus the binary systems *N*,*N*-dimethylaniline – chloranil and triethylamine – chloranil were proposed[158–160] as the inhibiting compositions for the MMA radical polymerization. The inhibition mechanism was assumed to include the electron transfer from the propagating radical to the quinone molecule to form a charge-transfer molecular complex containing a polymeric cation and a semiquinolate anion. The further process depended on the stability of this complex. The Et_3N – chloranil mixture was shown to completely inhibit the process, whereas $PhNMe_2$ – chloranil was found to merely slow down the latter. The similar features were observed for the ST polymerization in the presence of the latter system[159] and also for the polymerization of acrylonitrile and vinyl acetate involving both systems mentioned.[160]

In contrast to the authors of studies[158–160] who assumed that amine is not consumed in this reaction, Mazletskaya *et al.*[161] has shown for the AIBN-initiated MMA polymerization in the presence of *p*-benzoquinone (Q) and amines (R_2NH) of different structure, that amines behaved in the same manner as the inhibitors of oxidation, *i.e.*, were consumed with elimination of the mobile hydrogen atom from the amino group. The analysis of different kinetic schemes has revealed that the activation of amines and their involvement in the reaction with propagating PMMA radicals can proceed in the following two directions: as the result of formation of species active in inhibition and involved in the donor – acceptor complex amine – quinone or as the radicals-inhibitors $R_2N^{\bullet}$ and $QH^{\bullet}$ that appear due to the transfer of an H atom from amine to quinone.

$$R_2NH + Q \rightleftharpoons [R_2NH^{+\bullet}, Q^{-\bullet}] \xrightarrow{2P_n^{\bullet}} \text{products},$$

$$R_2NH + Q \rightleftharpoons R_2N^{\bullet} + QH^{\bullet} \xrightarrow{2P_n^{\bullet}} \text{products}.$$

It was assumed that none of directions can be preferred and also that the parallel inhibition of the MMA polymer-

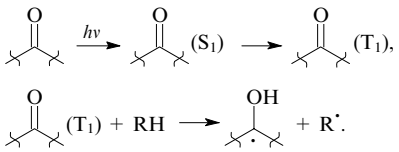
ization (simultaneously by both directions) in the presence of quinones and amines cannot be excluded without additional studies. By the example of primary (α-naphthylamine), secondary (diphenylamine) and ternary (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) amines, it was shown that the inhibition occurred only in the presence of binary systems containing an amine with the mobile hydrogen atom. In this case, the reaction could involve not only the mobile hydrogen atom of the amino groups of primary and secondary amines but also the hydrogen atom at the α-carbon atom of ternary amines.

2. Quinone-based composition systems as the photoinitiators of radical polymerization of vinyl monomers

The method of photoinitiated radical polymerization was actively used in the synthesis of a wide spectrum of high-molecular compounds. This involved the use of different compositions containing *o*- and *p*-quinones with fused aromatic systems, their alkyl- and halogen-substituted analogues, camphorquinone, *etc*. as the photosensitiers of polymerization (for example, see Refs 162 and 163). The range of monomers was also very diverse and included esters of acrylic acids, styrenes, acrylamides. Photopolymerization in the presence of quinones makes it possible to synthesize not only homopolymers but also copolymers containing the units of dienes and their halogen derivatives.[162, 163]

The presence of the donors of H atoms (solvents or other co-initiators) in the polymerization system allowed the time of the process to be considerably reduced. The polymer yield and MW depend not only on the quinone concentration but also on the [quinone] : [co-initiator] ratio. With the increase in the initiator concentration and the dilution of the system, the rate of the process increased and the MW of the product lowered down.

Studying quinone reactions with different compounds under UV radiation[164–166] allowed the most advantageous conditions for the polymer synthesis to be determined and the mechanisms of observed phenomena to be explained. It was shown that the quinone efficiency in initiation of polymerization and the polymerization rate were determined by the electron-acceptor properties of a given quinone in its photoexcited state, because the formation of the initiating radical occurs due to the abstraction of a hydrogen atom from a monomer or a solvent molecule by the quinone in its excited triplet state.

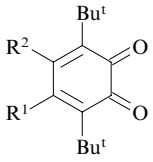


The activity of anthraquinone, 2-*tert*-butylanthraquinone and other quinones in the photopolymerization of different monomers in THF was analyzed.[167] The anthraquinone–THF system was shown to be a highly efficient photoinitiating composition for the free-radical polymerization of MMA, MA, ST, AN, but not of VA and vinylcarbazole. Systems based on the tested quinones can be graded in activity as follows: phenanthraquinone > naphthoquinone > anthraquinone > acenaphthenequinone > 2-methylnaphthaquinone > *p*-benzoquinone > chloranil.

Further studies[168] have revealed that for the photoinitiated polymerization by condensed aromatic systems, the solvent polarity was the key factor that determined the yield of the polymer. For the MMA polymerization at 30 °C in the presence of anthraquinone and its derivatives (2-methyl-, 2-*tert*-butyl-, 2-chloro- and 2-aminoanthraquinones) in cyclohexane, it was shown that the addition of isoproanol allowed the rate of the process to be sharply increased. The similar effect of Pr^iOH was observed for *p*-quinones, naphthoquinone and 2-methylnaphthoquinone.

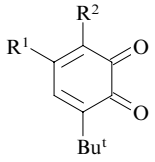
For the PMMA synthesis involving phenanthraquinone under the photoinitition conditions, it was found that the addition of onium salts including Ar_3S^+, Ar_2I^+ and ArN_2^+ cations favoured the increase in the polymerization rate.[169] The interaction of quinone with salts afforded a phenyl radical, which can initiate the polymerization, and also the semiquinolate adduct of phenathraquinone.

In a series of studies by Abakumov and co-workers,[170–172] it was shown that in the presence of tertiary amines, the systems based on *o*-benzoquinone derivatives allowed the polymerization of monomers of the methacryl series (particularly, oligoester acrylates) to be also initiated by visible light. A series of symmetrical and asymmertrical *tert*-butyl-substituted quinones **1**, **2** and their acyclic analogue **3** were examined.



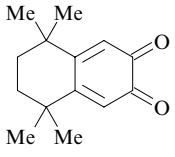
1

R^1 = H: R^2 = Pr^i, Pr^n, Ph, H, Cl, F, NO_2, CN; R^1 = R^2 = F.



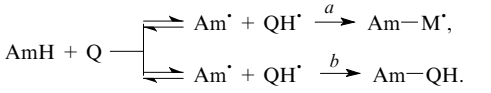
2

R^1 = Bu^t, R^2 = H; R^1 = H: R^2 = Me, Pr^i.



3

Systematic studies of the effect of the nature of *o*-benzoqiuonones[172] have shown that the efficiency of photoinitiation of the polymerization of oligoester acrylates with the quinone–tertiary amine (Q–AmH) system was determined by the energy and structural parameters of *o*-benzoquinone. The electron-withdrawing ability of *o*-benzoquinones and the electron-donating properties of the amine were shown to determine the rate of photoreduction of *o*-benzoquinone and thus affect the total efficiency of the formation of transient radical products. The molecular structure of *o*-benzoquinone predetermines the ratio of the two directions of photoreduction.

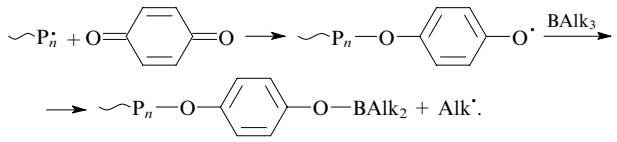


Pathway *a* represents the generation of free radicals capable of initiating polymerization into the reaction medium. Pathway *b* is the recombination of radicals in the solvent (monomer) 'cage' to form compounds inactive in the initiation of polymerization. The yield of initiating radicals depends on the steric factors due to the substituents in positions 3 and 6 of the quinoid ring of *o*-benzoquinone and is the maximum for symmetrical *o*-benzoquinones.

3. The effect of quinoid-type inhibitors on the polymerization of vinyl monomers in the presence of organoelement compounds

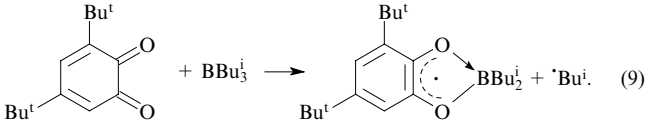
Interesting features were revealed in the polymerization of vinyl monomers in the presence of quinones upon the introduction of an OEC into the system. Particularly, the presence of an organoelement compound led to the weakening of the inhibiting effect and, in some cases, even the initiation of the polymerization process.

The effect of *p*-benzoquinone on the MMA polymerization in the presence of organoboron compounds was studied.[99–102] Polymerization was observed to slow down. The inhibiting effect of benzoquinone depended on the molar ratio [OEC] : [benzoquinone] as follows: for the ratio > 1, the inhibiting activity of quinone had virtually no effect on the polymerization kinetics. The reaction proceeded up to deep degrees of conversion. In the process, trialkylborane acted as the chain transfer agent and was consumed in this process according to the following equation:



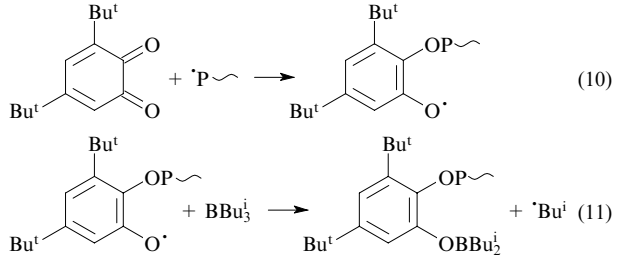
Organoaluminium compounds exhibited equally efficient activity in the acrylate polymerization in the presence of benzoquinone.[102,173] The polymerization rate increased with the increase in the [$AlEt_3$] : [benzoquinone] ratio, passed through the maximum and then decreased again.[173]

It was found[174,175] that sterically hindered quinones in the presence of organic compounds of the groups 13 and 15 elements (boron, aluminium, antimony) were capable of efficient initiation of the radical polymerization of acryl monomers at sufficiently high temperatures. For the system 3,5-di-*tert*-butyl-*o*-benzoquinone – BBu^i_3, it was shown[174,175] that the initiation of MMA polymerization at a moderate temperature (~ 40 °C) could occur as follows:



(9)

The dependence of the polymerization rate on the quinone concentration had an extremum, which suggests that several processes simultaneously occurred in the system. These are, on the one hand, the reaction of quinone with trialkylboron to afford primary free radicals initiating the polymerization [reaction (9)] and, on the other hand, the interaction of chain propagation radicals with quinones to form oxygen-containing radicals of the phenoxyl type which, in turn, react with BBu^i_3 to generate new alkyl radicals [reactions (10) and (11)].

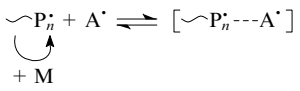


(10)

(11)

The decrease in the polymerization rate with the increase in the quinone concentration was explained by its active involvement in the chain termination reactions.

The molecular weight of PMMA synthesized in the presence of the aforementioned system increased directly with the degree of conversion in the wide range of the latter, which is typical of the 'pseudoliving' mechanism. Presumably, in this case, the radical-initiator of polymerization and the stable radical that controls the polymer chain propagation were formed immediately in the reaction system as the result of interaction between the components of the binary initiator [reaction (9)] and the polymerization proceeded by the following mechanism:



M is monomer.

The undeniable advantage of the quinone – OEC binary system in the polymerization of acryl monomers is the high polymerization rate and the moderate temperature conditions of this process. The main drawback is the MWD very wide for the controlled synthesis processes, which was associated with the involvement of quinone molecules in stages of chain termination and transfer.[175]

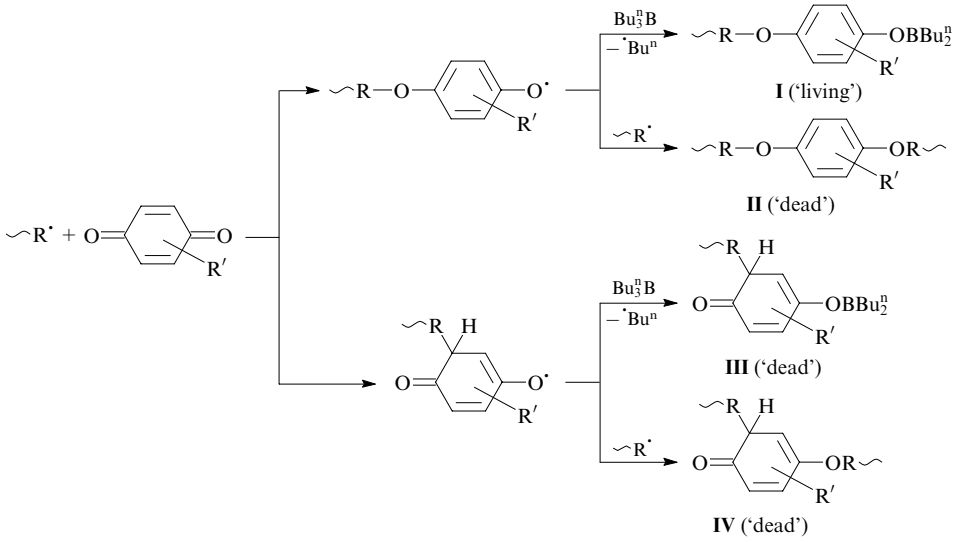
In their studies, Dodonov *et al.*[176–181] considered the specific features of MMA polymerization initiated by dicyclohexyl peroxydicarbonate (CPC) in the presence of binary systems based on tri-n-butylboron and the following various quinones: *p*-benzoquinone, chloranil, 2,5-di-*tert*-butyl-*p*-benzoquinone[176,177] and also duroquinone, naphthoquinone and anthraquinone.[178,179] It was shown that for the MMA polymerization catalyzed by CPC at 30 °C in the presence of even relatively high *p*-quinone concentrations, the introduction of alkylboranes eliminates the inhibiting effect of the latter (analogous effects were also observed earlier[101,102]).

The primary polymerization rate substantially depends on the molar ratio [BBu^n_3] : [*p*-quinone] and also on the quinone structure. Thus, the dependence of the initial polymerization rate on the quinone concentration passed through the maximum at the ratio [BBu^n_3] : [*p*-benzoquinone] = 1.6 : 1 and then dropped almost to zero. Moreover, it was assumed[178,179] that not only BBu^n_3 but also *p*-benzoquinone was consumed (Scheme 3).

With the increase in the concentration of 2,5-di-*tert*-butyl-*p*-benzoquinone, the rate increased insignificantly to reach its maximum at the ratio [BBu^n_3] : [quinone] = 2.6 : 1 and then, after a slight decrease, remained virtually unchanged, which could be associated with either the MMA copolymerization with quinone or the incorporation of quinone into the macromolecule as the end group.

Using the UV and IR spectroscopic methods, it was shown that PMMA radicals attacked benzoquinone and chloranil preferentially on the C=C bond, whereas their interaction with 2,5-di-*tert*-butyl-*p*-benzoquinone preferentially proceeded on the C=O bond. The formed aryloxy radicals reacted with BBu^n_3 to generate a butyl radical capable of carrying on the polymerization. According to Dodonov and co-workers,[179] the chain termination occurred as the result of its transfer to boroalkyl rather than by the reactions of dimerization and disproportiona-

Scheme 3



tion. Note that the latter statement was not rigorously proved.

In the MMA polymerization initiated by CPC at 30 °C, in the presence of BBu^n_3, the decrease in the inhibiting activity was also observed for duroquinone, 1,4-naphthoquinone and 9,10-anthraquinone.[176]

It was shown that PMMA samples synthesized in the presence of the BBu^n_3–quinone system were more stable with respect to thermooxidative destruction as compared with the polymer synthesized in the absence of this system.[178] In this case, the polymer stability depended on the activity of quinones used. For more active quinones (*p*-benzoquinone and chloranil), the polymer was less stable with respect to thermooxidative destruction; the higher polymer stability was observed for the less active duroquinone, 1,4-naphthoquinone and 9,10-anthraquinone.

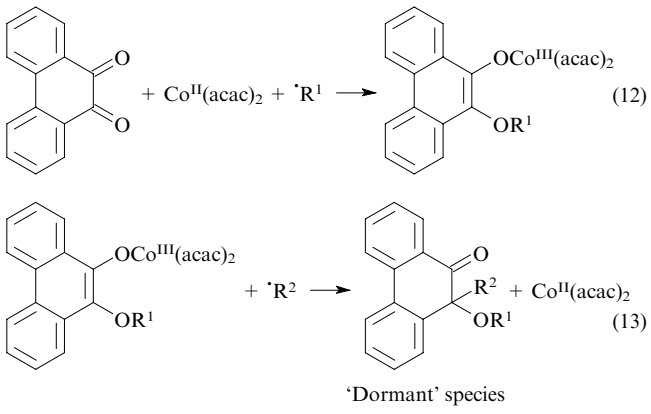
According to Dodonov *et al.*,[180, 181] the BBu^n_3–*p*-quinone systems are capable of sustaining the MMA polymerization initiated by CPC at 30 °C in the living chain mode. Indeed, for spatially impeded 2,5-di-*tert*-butyl- and butyl-*p*-benzoquinones, the dependences of the yield of polymer on the polymerization time and also of the viscosity-average MW on the conversion were linear. On the other hand, for the *p*-benzoquinone systems, the pronounced gel effect was observed, which to a certain extent contradicted the main relationships of the polymerization in the living-chain mode. Despite the mentioned specific features, the MWD of obtained PMMA samples was sufficiently wide; for 2,5-di-*tert*-butyl- and butyl-*p*-benzoquinones, the MWD had the pronounced bimodal character. This was associated with the simultaneous occurrence of both the controlled and the common polymerization processes in this system (see Scheme 3).[181]

To substantiate the proposed mechanism, based on prepolymers primarily obtained in the presence of the proposed system, the postpolymers were synthesized at elevated temperatures (up to 45–80 °C). The molecular weight distributions for polymer samples were bimodal, but one of the modes shifted to higher molecular weights with conversion.

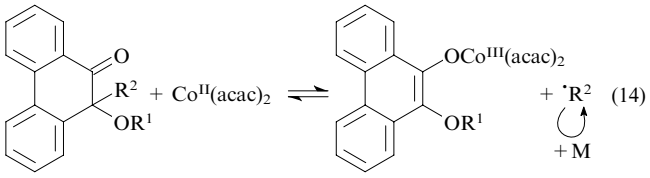
4. Controlled radical polymerization involving the quinone–metal complex system

In 2005, Belgian scientists put forward[182] an unusual approach to the controlled polymerization of ST in the presence of the quinones–transition metal acetylacetonates system, which was referred to as the Quinone Transfer Radical Polymerization (QTRP), *i.e.*, the radical polymerization with the transfer of the quinone fragment. It was shown[182] that the use of cobalt(II) acetylacetonate and 9,10-phenanthraquinone (9,10-PQ) in the molar ratio 1 : 100 allowed PS with MW of up to 30 000–60 000 and the narrow MWD (M_w/M_n = 1.3–1.5) to be synthesized at 100 °C. Moreover, the MW of PS samples in the limited interval (up to 40% conversion) proportionally increased with conversion, which pointed to the presence of controlled synthesis. This was found to occur only in the presence of a binary system phenanthraquinone–cobalt complex; the use of individual components of the system did not allow polymers with the narrow MWD to be synthesized.

Based on the obtained results, a stepwise mechanism of polymerization in the presence of the 9,10-PQ–$Co(acac)_2$ (acac is acetylacetonate) composition was put forward.



Here, R^1 and R^2 are either the initiating radicals formed in the system at the ST polymerization or the oligomeric PS radicals.



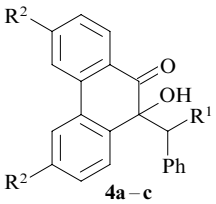
(14)

To prove that the chain was terminated precisely on quinone molecules in the presence of the 9,10-PQ–$Co(acac)_2$ binary system at 100 °C, a low-molecular PS macroinitiator was synthesized. It was shown that the further polymerization in this macroinitiator in the absence of cobalt complexes produced PS with bimodal MWD. The presence of the bimolecular mode pointed to the uncontrolled autopolymerization process in this system. On the other hand, the introduction of catalytic amounts of $Co(acac)_2$ led to unimodal MWD and the MW of synthesized PS samples higher as compared with the earlier synthesized macroinitiator. Thus, it was found that $Co(acac)_2$ simultaneously served as a mediator in the formation of a 'dormant' adduct [reactions (12), (13)] and could activate the polymerization by the 'pseudoliving' mechanism [reaction (14)].

Similar relationships of the QTRP process were also revealed for the ST polymerization in the presence of 9,10-phenanthraquinone and acrylacetonates of other metals, namely, $Ni(acac)_2$, $Mn(acac)_2$, $Mn(acac)_3$, $Al(acac)_3$.[183]

The effect of the nature of quinone on the peculiarities of the ST polymerization by the QTRP mechanism were also studied.[184] Systems based on Co(acac) and containing di-*tert*-butyl- and tetrachloro-*o*-benoquinones were found to be inefficient in the ST autopolymerization processes. The PS samples obtained in their presence did not differ from PS samples synthesized by autopolymerization at 100 °C as regards their MW and MWD. The substitution of more active 3,6-dimethoxy-9,10-phenanthraquinone (3,6-MPQ) for phenantraquinone[184] resulted in the decrease in the polydispersity index to 1.2 for $Co(acac)_2$ and 1.1 for $Al(acac)_3$. In this case, the dependence of MW on the degree of conversion was linear up to deep degrees (~65%) as compared with systems based on phenanthraquinone. The increase in the temperature to 120 °C for the 3,6-MMPQ–$Co(acac)_2$ system allowed the ST autopolymerization to be carried out without any induction period; moreover, the polymer MW still increased linearly with conversion. A certain broadening of MWD (M_w/M_n = 1.4–1.6) was probably associated with the changes in the concentration of initiating radicals, which enhanced the contribution of the uncontrolled polymerization.

To prove the proposed mechanism, the authors of the above study carried out the QTRP process for ST, which involved model compounds, namely, 9(10*H*)-phenanthrenones **4a–c**, synthesized outside the polymerization system.[185]



4a–c

R^2 = H: R^1 = H (**a**), Me (**b**);
R^1 = Me, R^2 = OMe (**c**).

9(10*H*)-Phenanthrenones **4a–c** are the analogues of the dormant species synthesized *in situ* at the ST autopolymerization in the presence of 9,10-PQX–$Co(acac)_2$ composition, which act as the initiators of the ST polymerization in the presence of catalytic amounts of $Co(acac)_2$ in the system [see reaction (14)].

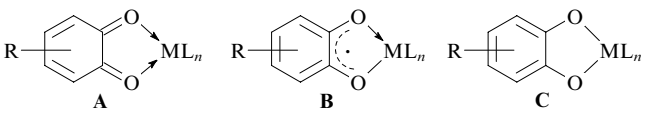
Systems **4a**–$Co(acac)_2$, **4b**–$Co(acac)_2$ and **4c**–$Co(acac)_2$ allow the controlled ST polymerization to be carried out at 100 °C without any induction period. In the process, the yield of PS was much higher than for polymerization in the presence of the phenanthraquinone–$Co(acac)_2$ system and the polymer MW increased directly with the degree of conversion up to deep degrees.[185] The MWD was unimodal, the M_w/M_n ratio varied within 1.6–1.8 [for systems **4a**–$Co(acac)_2$ and **4b**–$Co(acac)_2$) and within 1.2–1.3 (for system **4c**–$Co(acac)_2$].

The ^1H NMR spectroscopic studies[185] of both low- and high-molecular PS revealed the presence of fused aromatic structures incorporated into macromolecules, which also confirmed the proposed mechanism of ST polymerization in the presence of phenanthraquinone–metal acetyacetonate systems.

V. Catecholate and semiquinolate metal complexes in the controlled polymerization of vinyl monomers

Various quinone-based binary compositions are very promising as the initiating and regulating agents of radical polymerization. It is noteworthy that the controlled process with their participation is based on the possibility of the formation of semiquinolate[174,175] or phenoxyl[180,181] adducts as the result of interaction of system components.

Indeed, a characteristic feature of quinones is their trend for participation in redox processes. Their use as the ligands in metal complexes opens up wide prospects in several research directions. A quinone ligand can exist in several forms easily transformable into one another, which allows it to enter different reactions without substantial changes in the structure and the composition of the complex itself. The following three types of coordination of quinone ligands with the metal atom were mentioned: coordination of a neutral form (**A**), coordination of a monoreduced species as a radical anion (**B**), coordination of direduced form as pyrocatechol dianion (**C**).



SQ-Complexes Cat-Complexes

L are other ligands.

Among the mentioned complexes, it is the semiquinone (SQ) and catecholate (Cat) complexes of transition and non-transition metals that find the widest application in various fields of chemistry. To date, several examples are known where the polymerization of olefins and other monomers involves compounds containing quinone ligands in their composition. Then, the effect of such complexes can be conditionally divided into catalytic (due to individual properties of the central metal atom) and regulating (caused not only by the nature of the central element but also by specific properties of redox-active ligands).

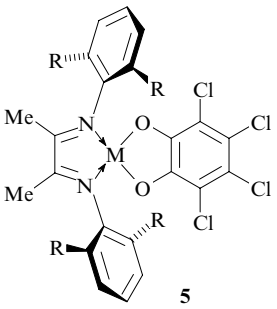
Thus, the possibility of carrying out ethylene polymerization in the presence of nickel(II) (2,3-dimethyl-1,4-diphenyl-1,4-diazabuta-1,3-diene)-3,5-di-*tert*-butylcate-

cholate with methylalumoxane (MAO) as the cocatalyst in the wide temperature interval was demonstrated.[186]

Later, Abakumov *et al.* in cooperation with US scientists[187] studied the polymerization of α-olefins with the addition of MAO in the presence of LMX complexes, where L is the bidentate or tridentate neutral ligand, M is the transition metal (Co, Ni, Pd, Fe), X is the catecholate ligand.

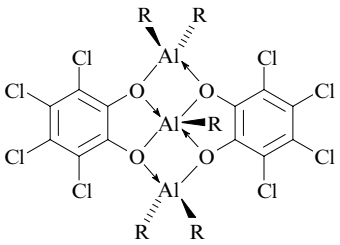
Catalysts based on group 8, 9 and 10 transition metals, suitable for the polymerization of ethylene, α-olefins, diolefins, substituted olefins and alkynes were described in a patent.[187] For the ethylene homo-polymerization in different solvents (methylene chloride, toluene and diethyl ether) in the presence of nickel and cobalt catalysts in the temperature range of 40–80 °C, polyethylene with the MW from 2000 to 160 000 and the polydipersity index of 1.18–3.06 was obtained. The smallest polydispersity indices of polyethylene corresponded to the Co catecholate complexes (1.18–1.44).

A later study by Spanish scientists[188] has shown that the systems including nickel and palladium α-diimine tetrachlorocatecholate complexes **5** with aluminium alkylcatecholates **6** are the active catalytic systems for olefin polymerization.



5

M = Ni, Pd; R = Me, Pr^i.

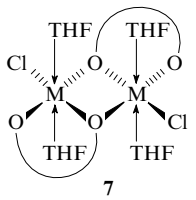


6

R = Me, Et.

Comparing the catalytic properties of systems based on α-diimine catecholates and halide complexes as the precatalysts with different activators [modified methylalumoxane (MMAO) and aluminium alkylcatecholates] showed that the presence of catecholate ligands in both components of the catalyst favoured the smallest quantitative ratio transition metal : aluminium, which offered a certain advantage. Particularly, the catalyst stability increased, especially, for palladium complexes. In the presence of these complexes, the ethylene polymerization at elevated pressure and 30 °C was sufficiently fast. The activities of proposed catalytic systems were estimated. The catalyst activity was shown to substantially increase with the introduction of large amounts of MMAO and comparatively low amounts of co-catalysts **6**. Generally, the catalytic systems based on α-diimine catecholates of Ni and Pd produced polyethylene in the wide MW range (from 20 000 to 440 000) and the polydispersity index from 2.0 to 5.7.[188]

US scientists studied[189] the possibility of using catecholate metal complexes (by the example of Al and Zn binuclear complexes **7**) as the catalysts of polymerization by the ring opening mechanism (Ring-Opening Polymerization, ROP). However, such structures were assumed to be insufficiently efficient in the polymerization of propylene oxide due to steric factors.

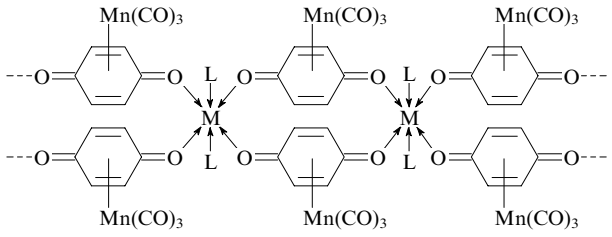


7

M = Al, Zn;

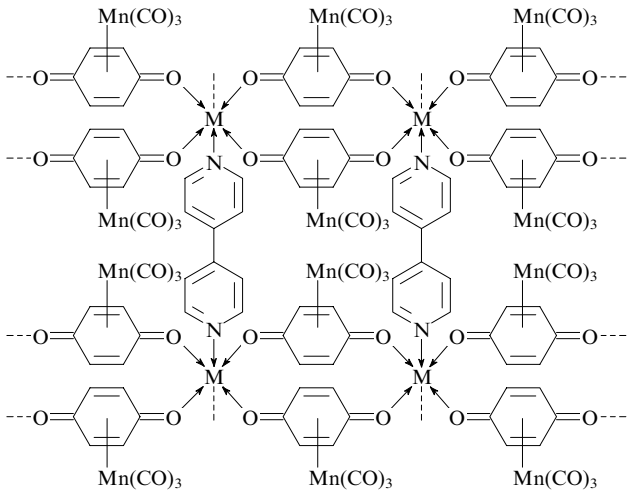
O O is 3,5-di-*tert*-butylcatecholate.

It deserves mention that a series of metal complexes including redox-active ligands in combination with mono- and bidentate ligands allowed the supramolecular coordination polymer structures to be formed. Structures **8**–**10** can serve as the examples.[190–193]



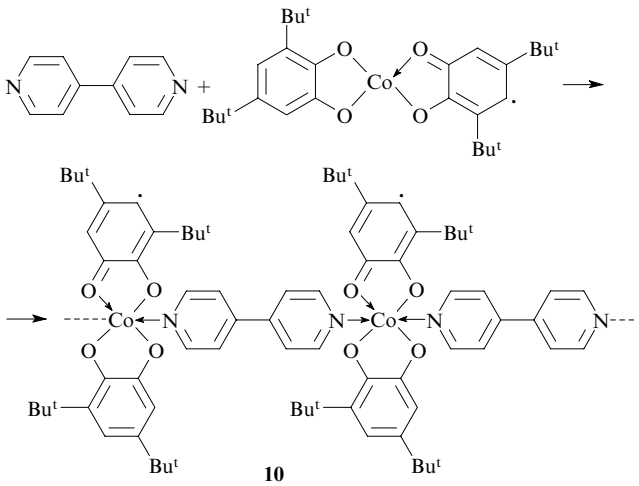
8

M = Mn, Co, Ni, Cd; L = DMSO, Py.



9

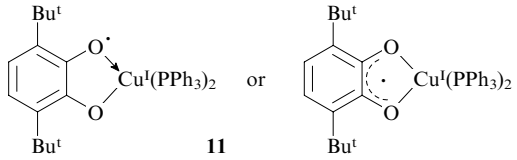
M = Mn, Co, Ni, Cd.



10

Such supramolecular structures can be used in the initiation of charge transfer reactions, in the catalysis, ion exchange, optics, as the magnetic materials, *etc*. It is noteworthy that the rational approach to designing such structures including their nanosized versions may involve the targeted variation of parameters such as the coordination number and the oxidation state of the metal nucleus in the complex and also of the steric factors of the ligand surrounding.

Metal complexes with redox-active ligands were recently used as the regulators of polymerization for a wide range of monomers. Semchikov and co-workers [194–197] studied the effect of bis(triphenylphosphino)-(3,6-di-*tert*-butylbenzosemiquinone-1,2)copper(I) (**11**) in the processes of homo- and copolymerization of different vinyl monomers.



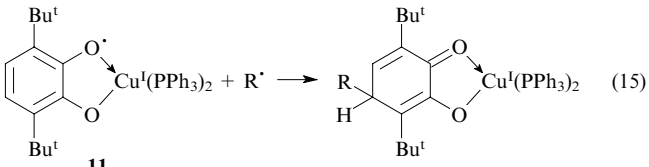
11

Compound **11** was found [194] to efficiently inhibit the polymerization of ST and butyl methacrylate (BMA) initiated by AIBN. The length of the induction period increased directly with the complex concentration. However, upon the end of the induction period, the ST and BMA polymerization rate was not equal to the rate in the absence of semiquinolate complexes. This means that compound **11** is not the ideal inhibitor.

The AIBN-initiated ST polymerization in the temperature interval of 95–125 °C (Ref. 194) in the presence of compound **11** demonstrated the linear increase in polystyrene MW with conversion. Moreover, the MW of the polymer synthesized with participation of a semiquinolate complex was considerably lower that the MW of the polymer obtained by common AIBN-initiated polymerization. The somewhat lower polydispersity indices were also observed ($M_w/M_n \approx 1.7-1.8$).

In the general form, the involvement of compound **11** in the polymerization was described by the following reactions.

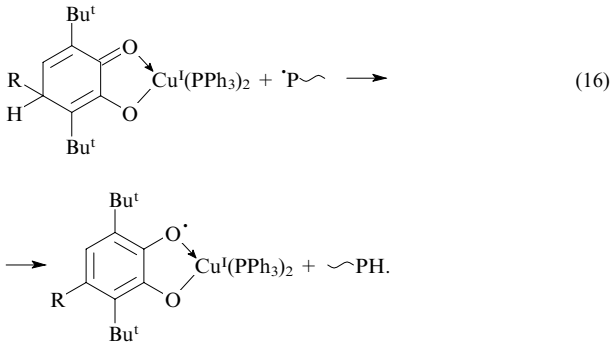
Primary inhibition, *i.e*., the reaction that affords a 'dormant' adduct due to the scavenging of initiating radicals.



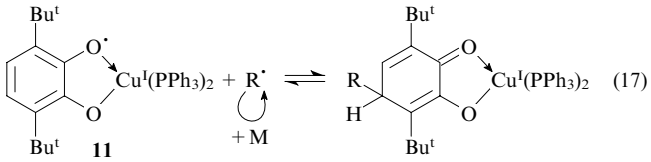
11 'Dormant' species (15)

The variation in the concentration of semiquinolate complex **11** during the induction period, detected by the EPR method, confirmed the correctness of the proposed scheme.

The reaction of secondary inhibition



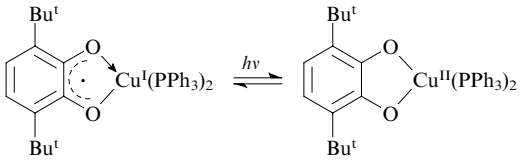
It was assumed [194] that with the increase in the temperature, reaction (15) became reversible which allowed the regulation of the polymer chain propagation according to the following equation:



11

The polydispersity indices higher as compared with the autopolymerization were associated with both the reactions of the propagating radical recombination and the competitive reactions of chain propagation and termination involving compound **11** [reactions (15)–(17)].

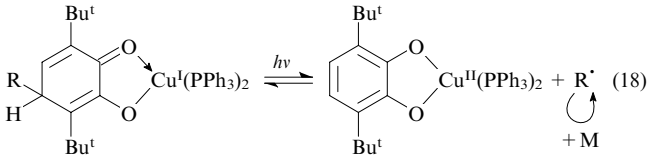
Studying the peculiarities and properties of complex **11** as a representative of *o*-semiquinone complexes of transition metals revealed its trend for intramolecular transformations with the electron transfer between the radical-ion ligand and the central copper atom in response to an external impact. For example, as the result of absorption of UV radiation, the metal atom gives an electron to the ligand, which is accompanied by the changes in the structure and the reactivity of this complex.



SQ-Complex of Cu^I Cat-Complex of Cu^{II}

Varying the polymerization conditions allowed the temperature of the PS synthesis in the presence of complex **11** to be lowered down. Thus it was shown [194, 195] that PS samples synthesized under UV radiation at 25 °C had a narrow MWD (~1.32). The effect of the semiquinolate complex on the polymerization was attributed to the photoinduced intramolecular electron transfer accompanied by the $Cu^I \rightarrow Cu^{II}$ transformation.

In contrast to AIBN-initiated ST polymerization, its photopolymerization proceeds by the following mechanism:



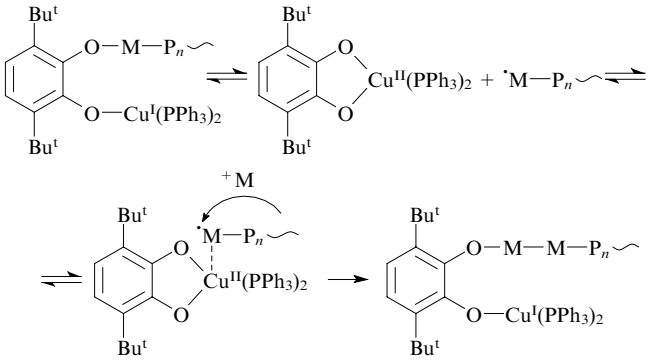
To confirm the regulating abilities of the semiquinone complex under the conditions of UV irradiation, the block copolymers ST–BMA [195] and ST–vinylpyrrolidone [196] were synthesized from the primarily synthesized low-molecular PS chains containing the labile radical–complex **11** bond. The analysis of block copolymer samples revealed the absence of pure PS, which suggested that the whole macroinitiator was involved in the polymerization reaction.

However, the proposed equations of thermal [reaction (17)] and photopolymerization [reaction (18)] in the presence of complex **11** cannot be considered as unambiguous. Several factors revealed in the analysis of the tacticity of PMMA synthesized under these conditions and also in studying the copolymerization of monomers of different nature in the presence of complex **11**,[197, 198] pointed indirectly to the coordination interaction of this complex with the propagating radicals. Thus, a decrease in the isotriad fraction in PMMA synthesized by photopolymerization was observed in the presence of a semiquinolate complex as compared with the polymer grown as the result of polymerization with initiators. The decrease in the probability of *meso*-addition was associated [195] with the possible formation of a donor–acceptor complex of compound **11** with reagents.

Complex **11** was observed [197, 198] to affect the relative activities of co-monomers in the thermal and photoinitiated copolymerization of ST with BMA, MMA, butyl acrylate, 2,2,3,3-tetrafluoropropyl methacrylate and vinylpyrrolidone. For all systems listed, except for ST–MMA, the polarity of the electron-acceptor co-monomer was observed to increase upon the addition of the copper semiquinolate complex into the system.

The obtained relationships were explained [195, 197, 198] by the possible coordination of the propagating macroradical on the semiquinolate complex due to the donor–acceptor interaction between the carbonyl oxygen atom of the ester group and the copper atom of the catecholate complex. As the result of coordination, the electron density additionally shifted to the carbonyl group through the π–π-conjugation system, which led to an increase in the positive partial charge on the radical and had a direct effect on its reactivity.

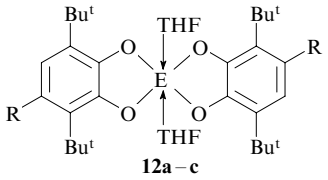
The general scheme of the process is as follows:



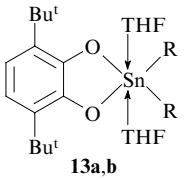
M is monomer.

Thus, the semiquinolate complex allows controlling not only the termination but also the propagation of the polymer chain.

The activity of several catecholate complexes of group 14 elements was studied.[199–204] Both symmetrical biscatecholates **12a–c**,[199–201, 203, 204] and monocatecholate complexes of tin **13a**,**b** [202] served as the scavengers of free radicals.



12a–c



13a,**b**

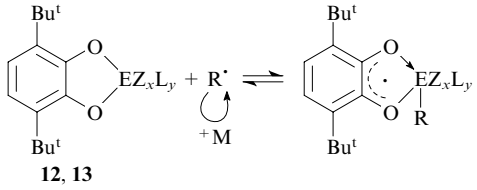
E = Sn: R = H (**a**), OMe (**b**); E = Ge, R = H (**c**).

R = Et (**a**), Ph (**b**).

Tin catecholate complexes tin proved to be efficient scavengers of short-lived and stable radicals to form *o*-semiquinone derivatives.[205, 206] In fact, such complexes can serve as the spin traps of active organic radicals to afford stable radicals of the semiquinolate type and can be suitable models in studying the mechanism of polymerization of vinyl monomers in the presence of such systems.

Indeed, it was shown that in the monomer medium, complex **12a** could also accept the propagating radicals to form mono-*o*-semiquinolte derivatives.[199] Moreover, the similar formation of semiquinolate derivatives in the ST polymeriation was observed by the EPR method for tin monocatecholate complexes **13a**,**b** [202] and also for germanium derivative **12c**.[201]

The role of compound **12a** as the scavenger of propagating radicals was studied for the MMA and ST polymerization.[199, 200] For the ratio metal complex : AIBN = 1 : 1, the polymerization of MMA and ST proceeded up to deep degrees of conversion in a wide temperature range (70–100 °C). Moreover, no pronounced acceleration was observed and the MW of polymers increased linearly with conversion. The polydispersity indices of PMMA and PS synthesized in the presence of complex **12a** were somewhat lower as compared with samples obtained with participation of conventional initiators (M_w/M_n = 2.1–2.6). It was assumed that under certain conditions, the formed tin semiquinolate complexes could eliminate the propagating macroradicals thus providing the possibility of reinitiation of polymerization [reaction (19)].



12, **13** (19)

E = Sn or Ge; R is initiating or propagating macroradical; Z is Cat (catecholate), Ph or Et; L is ligand (THF or monomer); M is monomer molecule.

To prove this assumption, block copolymers of ST and MMA were synthesized based on macroinitiators prepared in the presence of complex **12a**.[200] The quantitative yield and the composition of formed block copolymers depended on the nature of the primarily used macroinitiator and the temperature conditions.

The specific features of ST polymerization were also studied in the presence of compound **12c** in the temperature range of 70–90 °C.[201] The obtained data suggested that the introduction of the germanium catecholate complex in the system gave rise to the induction period and inhibited the polymerization. At 90 °C, the ST polymerization in the

presence of this complex proceeded without gel effect and was accompanied by the linear increase in polystyrene MW with conversion. The polydispersity indices of PS samples synthesized in the presence of compound **12c** were high (M_w/M_n = 2.8 – 3.4), albeit somewhat lower as compared with a polymers synthesized in the absence of this complex.

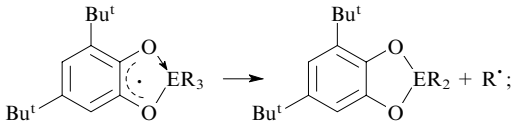
Such relationships were also observed for monocatecholate complexes **13a**,**b**.[202] The introduction of these complexes were shown to result in a decrease in the total rate of ST polymerization and a decrease in the MW of the synthesized polymer. Varying the complex : initiator ratio and also the temperature mode allowed the polydispersity index of synthesized PS and the limiting conversion to be changed. For 70 – 90 °C, the polymer MW increased monotonously with conversion, which indirectly pointed to the fragmentary growth of macromolecules; however, the polydispersity index of synthesized samples was sufficiently high ($M_w/M_n > 2.0$). The direct evidence for the chain re-initiation was obtained for postpolymerization of ST based on PS macroinitiators synthesized in the presence of complex **13b**. It was shown that a part of the macroinitiator remained active and capable of continuing polymerization upon the addition of a new portion of monomer, as evidenced by the increase in conversion up to 50% – 60% and the higher number-average MW of the postpolymer as compared with macroinitiator.

On the whole, studying the nature of catecholate complexes of group 14 elements and monomers has shown[203, 204] that compound **12a** is the most efficient regulator of MMA polymerization that allows the polymerization in the autoacceleration stage to be slowed down and the polymers with the desired molecular-weight characteristics to be synthesized. The other tested complexes (**12b**,**c**, **13a**,**b**) failed to efficiently regulate the MMA polymerization in the temperature range of 50 – 100 °C. Compounds **12b**,**c** exhibited the stronger inhibiting ability in the MMA polymerization as compared with complex **12a** and virtually completely suppressed the process even at high temperatures (90 – 110 °C). In contrast to biscatecholates, monocatecholate derivatives **13a**,**b** did not affect the MMA polymerization rate and the molecular-weight characteristics of the synthesized polymer.

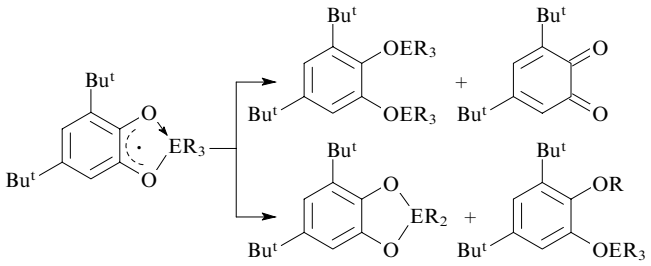
Thus, based on the research results, it was assumed[199 – 204] that in the presence of catecholate complexes of tin and germanium, the mechanism of controlled synthesis of PMMA and PS can take place. The controlled polymerization proceeds as the result of successive reactions of acceptance and elimination of propagating radicals by a metal complex [reaction (19)]. On the whole, this process was confirmed by the possibility of synthesizing post- and block copolymers (PMMA-b-PS and PS-b-PMMA) by using macroinitiators obtained in the presence of the mentioned catecholate complexes. However, the thus synthesized polymers were characterized by the sufficiently broad MWD. This was associated with the gradual decomposition of AIBN in the system, *i.e.*, with the non-simultaneous formation of propagating radicals, and also with the possible side reactions of formed tin *o*-semiquinolate complexes.

Thus, it is well known that alkyl derivatives of *o*-semiquinolates of group 14 elements can undergo transformations by the following two directions:[207, 208]

1) homolytic rupture of the metal – carbon bond, which can be formally described by the following equation:



2) disproportionation:



ER$_3$ = SiMe$_3$, GeEt$_3$, SnPh$_3$, *etc.*

The ratio of reactions of polymer radical elimination, dealkylation and disproportionation depends on the temperature of the process and the length of radicals in the *o*-semiquinolate complex.[207] With the increase in the temperature and the radical size, the probability of elimination increases.

In fact, systems of this type were the first complexes of non-transition metals to be used in processes of controlled polymerization. This approach is based on the introduction of redox-active ligands capable of existing in different oxidation states into the complex. In line with this, the catecholate complexes of non-transition metals are capable of entering the reactions of oxidative addition and reductive elimination thus simulating the behaviour of transition metals. However, in contrast to transition metal compounds, the redox centre in these compounds is a redox-active ligand rather that the central atom.

VI. Conclusion

This review summarizes the literature data on the targeted regulation of the kinetic parameters of polymerization and the molecular-weight characteristics of polymers synthesized in the presence of phenols and quinoid compounds including their organoelement derivatives. The wide practical use of radical polymerization in the commercial synthesis of polymer materials makes extremely important the problem of suppression of the gel effect and also of the targeted impact on the molecular-weight distribution of high-molecular compounds aimed at the improvement of their characteristics. In line with this, it seems promising to use the competitive reactions in the stage of gel effect by adding different inhibitors including phenols, quinones and binary systems based on the latter compounds. However, the majority of known regulators of polymerization, *i.e.*, phenols and quinones, have a serious drawback, namely, they efficiently work only for polymerization of a limited circle of monomers. Moreover, in some cases, these compounds tend to copolymerization by being incorporated into the polymer chain and also by being involved in different side processes; thus, they exert an unpredictable effect on the molecular-weight characteristics of macromolecules.

Of much higher interest is the use of binary systems based on phenols and quinones in regulating the kinetic parameters of polymerization and the molecular-weight

characteristics of polymers. Such systems can perform different functions, namely, serve as the synergistic inhibiting mixtures; they are used as photosensitizers in the polymerization of vinyl monomers, exhibit extraordinary properties in the presence of organoelement compounds and metal complexes, act as regulators of homo- and copolymerization. Thus, the targeted choice of the second component allows the properties of these systems to be sharply modified and the desired characteristics of synthesized polymer materials to be achieved.

In the past decades, attention was focused on studying the boundary of organometal chemistry and polymer chemistry. The results of these studies open up wide prospects for synthesizing macromolecules with desired properties due to the individual properties of both the metal atom and the ligands involved in the composition. Thus for quinone-based complexes used as the chain propagation controllers, the key role can be played not only by the electronic structure of the metal atom but also by the redox properties of ligands. The joint use of metal complexes and phenol-type inhibitors including quinones and their derivatives attracts keen interest as regards both the theory and the practical use, because phenol inhibitors are the main stabilizers used in the long-term storage and transportation of monomers. The use of organometallic and metal complex compounds allows the polymer synthesis to be carried out without preliminary cleaning of monomers from inhibitors, thus directly affecting the polymerization kinetics and the molecular-weight characteristics of polymers and also, in some cases, making possible the living chain polymerization.

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