# Radical polymerization of methacrylic esters involving various tin(IV) monocathecholate complexes

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The effect of tin(IV) monocathecholate $36CatSnR_2 \cdot nTHF$ (36Cat is 3,6-di-*tert*-butylcatehol dianion; R = Me, Et, Ph, or Cl; $n = 1$ and 2) on the radical polymerization of methyl methacrylate and *n*-butyl methacrylate was studied. The role of the complexes in the synthesis of the corresponding polymers is mainly determined by the structure of tin *o*-semiquinone derivatives formed directly in the polymerization process. Tin(IV) monocatecholates can control the synthesis of polymers *via* the mechanism of reversible inhibition and, in certain cases, exert an accelerating effect on the polymerization of methacrylic monomers like Lewis acids.

**Key words:** radical polymerization, ESR spectroscopy, catecholate complex, *o*-semiquinone complex, tin(IV), methyl methacrylate, *n*-butyl methacrylate.
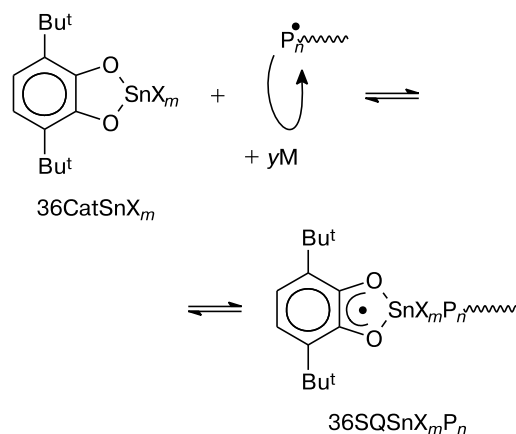
Complexes of non-transition elements based on sterically hindered pyrocatechols are unique traps for the fixation of radical species followed by the identification of the formed paramagnetic products by ESR spectroscopy.[1,2] This property makes it possible to use them as original agents for controlled synthesis of macromolecules.[3—5] It was established that the radical polymerization of styrene and methyl methacrylate (MMA) initiated by azoisobutyronitrile (AIBN) in the presence of various germanium(IV) and tin(IV) biscatecholates is controlled *via* the scheme of reversible inhibition[3—5] (Scheme 1).

The key role in control of polymer synthesis involving catecholate complexes of non-transition elements belongs to the redox-active ligands rather than to the metal atom, as it takes place in transition element compounds actively used in the recent years as controlling agents.[6—8] As a result of consecutive reactions of accepting and elimination of growing radicals by metal complexes, polymerization can be carried out without a gel effect and also the molecular mass of macromolecules can be increased during the processes and block copolymers can be obtained.[3]

The formation of the corresponding paramagnetic germanium(IV) and tin(IV) *o*-semiquinolate derivatives in the system was detected by ESR spectroscopy.[3—5] It was found that, if the initial metal complex contains two catecholate ligands, only one of them is involved in reactions with initiating/growing radicals in most cases.[3,5]

The purpose of this work is to study the influence of the ligand environment of the metal atom on the controlling ability of the tin(IV) monocatecholate complexes of different structures in the radical polymerization of methacrylic esters. The objects of the study were dimethyl- ($36CatSnMe_2 \cdot THF$), diethyl- ($36CatSnEt_2 \cdot THF$), diphenyl- ($36CatSnPh_2 \cdot THF$), and dichloro-(3,6-di-*tert*-butylcatecholato)tin(IV) ($36CatSnCl_2 \cdot 2THF$) tetrahydrofuranates.

**Scheme 1**



36Cat is 3,6-di-*tert*-butylpyrocatecholate dianion (catecholate ligand); 36SQ is 3,6-di-*tert*-butyl-*o*-semiquinolate ligand; X = Et, Ph, 36Cat
$m = 1, 2$
$P_n$ is growing macroradical; M is monomer molecule

36CatSnR$_2$ · $n$THF
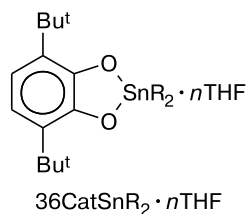
R = Me, Et, Ph, Cl
$n$ = 1, 2

## Results and Discussion

It was found that the character of influence of the tin(IV) monocatecholate complexes on the kinetic regularities of polymerization of methacrylic esters and molecular mass characteristics of polymethacrylates depends on the initial composition of the complex and conditions of the process (Figs 1—4). The variation of temperature and the metal complex to initiator ratio makes it possible to distinctly fix significant differences in effects of complexes 36CatSnMe$_2$·THF, 36CatSnEt$_2$·THF, 36CatSnPh$_2$·THF, and 36CatSnCl$_2$·2THF on the polymerization of MMA and $n$-butyl methacrylate (BMA).

The introduction of tin dimethyl catecholate (36CatSnMe$_2$·THF) in an equimolar concentration exerts almost no substantial effect on MMA and BMA polymerization at 70 °C (see Fig. 1, *a*, Fig. 2, curve *2*). The gel effect characteristic of uncontrolled polymerization processes is observed even in a fourfold excess of complex 36CatSnMe$_2$·THF over the initiator during the polymerization of the indicated above monomers. In spite of the retention of the gel effect, the time when it is observed insignificantly increases (compared to the process occurring without a metal complex) and varies depending on the concentration of tin(IV) dimethyl catecholate.

The polymerization of MMA and BMA involving 36CatSnEt$_2$·THF also proceeds with the gel effect (see Fig. 1, *b*; Fig. 2, curves *3*, *4*). In the initial stage (below ~15—20% conversion), the time dependence of the monomer conversion is almost the same in the whole range of concentrations of the introduced complex and does not differ from a similar dependence for radical polymerization without a metal complex. However, as the 36CatSnEt$_2$·THF/AIBN ratio increases, the time interval after which the gel effect is observed decreases and its intensity increases (see Fig. 1, *b*, curves *1* and *3*, curves *5—7*).

The time of gel effect onset decreases in the case of MMA polymerization at 50 °C already at the equimolar ratio 36CatSnEt$_2$·THF/AIBN (see Fig. 1, *b*, curves *5* and *6*). An increase in the concentration of the complex does not further change the process rate. However, at 70 °C complex 36CatSnEt$_2$·THF with the initiator in an equimolar ratio exerts no effect on the general kinetic regularities of MMA polymerization (see Fig. 1, *b*, curves *1* and *2*). A twofold increase in the concentration of tin(IV) diethyl catecholate results in an increase in the MMA polymer-
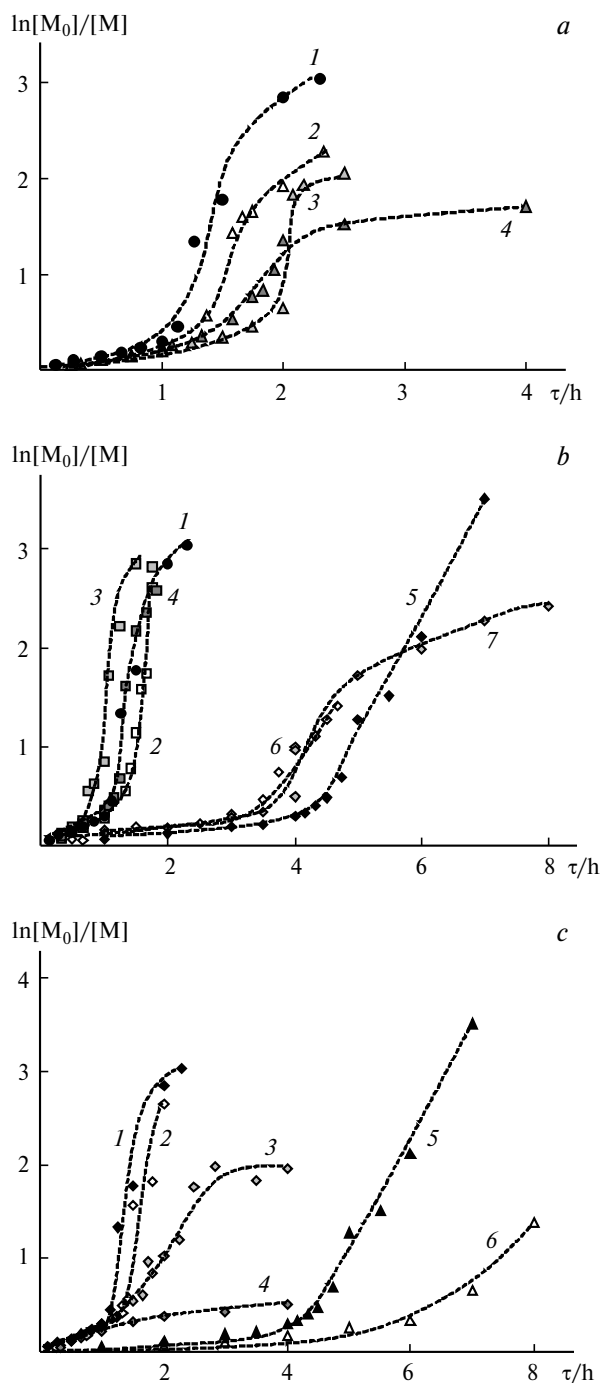


**Fig. 1.** Dependences of ln[M$_0$]/[M] of MMA on the polymerization time in the presence of complexes 36CatSnMe$_2$·THF (*a*), 36CatSnEt$_2$·THF (*b*), and 36CatSnPh$_2$·THF (*c*). Concentration of the complexes, mol.%: *a*, 0 (*1*), 0.1 (*2*), 0.2 (*3*), and 0.4 (*4*); *b*, 0 (*1, 5*), 0.1 (*2, 6*), 0.2 (*3, 7*), and 0.4 (*4*). AIBN initiator (0.1 mol.%). *T*, °C: *a*, 70; *b*, 70 (*1—4*), 50 (*5—7*); *c*, 70 (*1—4*), 50 (*5, 6*).

ization rate at the stage of gel effect and shortens the time of gel effect onset. At the ratio 36CatSnEt$_2$·THF/AIBN = = 4 : 1, the time dependence of the polymer yield in the semilogarithmic coordinates approaches a similar depen-
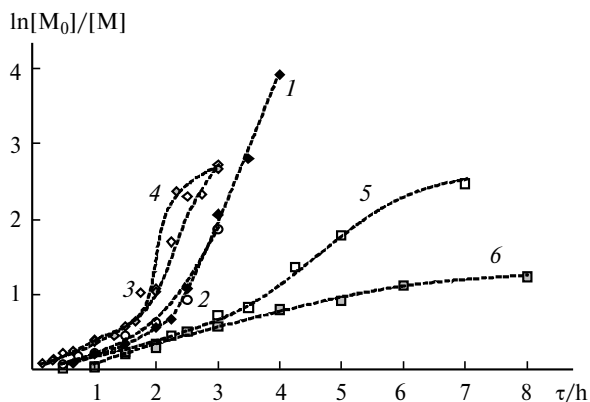
**Fig. 2.** Dependences of $\ln[M_0]/[M]$ of BMA on the polymerization time in the presence of complexes $36CatSnMe_2 \cdot THF$ (*2*), $36CatSnEt_2 \cdot THF$ (*3, 4*), and $36CatSnPh_2 \cdot THF$ (*5, 6*). Concentration of the complexes, mol.%: 0 (*1*), 0.1 (*2, 3, 5*), and 0.2 (*4, 6*). $T = 70\ °C$. AIBN initiator (0.1 mol.%).

dence in the case of polymerization involving one initiator only (without additives of the tin complex).

In the case of synthesis of polybutyl methacrylate (PBMA) at 70 °C, just an equimolar ratio of the initiator and $36CatSnEt_2 \cdot THF$ increases the polymerization rate at the stage of gel effect (see Fig. 2, curves *1* and *3*), and the increase in the metal complex concentration exerts no effect on the kinetic regularities of polymerization (see Fig. 2, curves *3* and *4*).

When compounds $36CatSnPh_2 \cdot THF$ and $36CatSnCl_2 \cdot 2THF$ are used, the polymerization time increases to attain high conversions at 70 °C and the limiting conversion decreases proportionally to the increase in the concentration of the complexes for both syntheses of polymethyl methacrylates (PMMA) and PBMA (see Fig. 1, *c*; Fig. 2, curves *1, 5*, and *6*). For the synthesis of PBMA, just an equimolar ratio of the metal complex to initiator suppresses autoacceleration characteristic of classical processes of radical polymerization. The absence of a gel effect indicates that the radicals are accepted in the system by the introduced complexes $36CatSnPh_2 \cdot THF$ and $36CatSnCl_2 \cdot 2THF$.[3—5]

The introduction of the tin(IV) monocatecholate complexes changes the molecular mass characteristics of polymethyl methacrylates (see Figs 3—5). When using the tin(IV) dimethyl catecholate complex, the number average molecular masses (MM) of the PMMA and PBMA samples almost do not differ from MM of the polymers synthesized without additives of tin compounds in the presence of AIBN as a radical initiator (see Fig. 3, *a*). The S-shaped dependence of the MM of the polymers on the monomer conversion characteristic of processes of usual radical polymerization with the gel effect is retained regardless of the amount of introduced $36CatSnMe_2 \cdot THF$.

For a certain ratio of $36CatSnPh_2 \cdot THF$ to AIBN, the numerical mean MM of polymethacrylates increases with



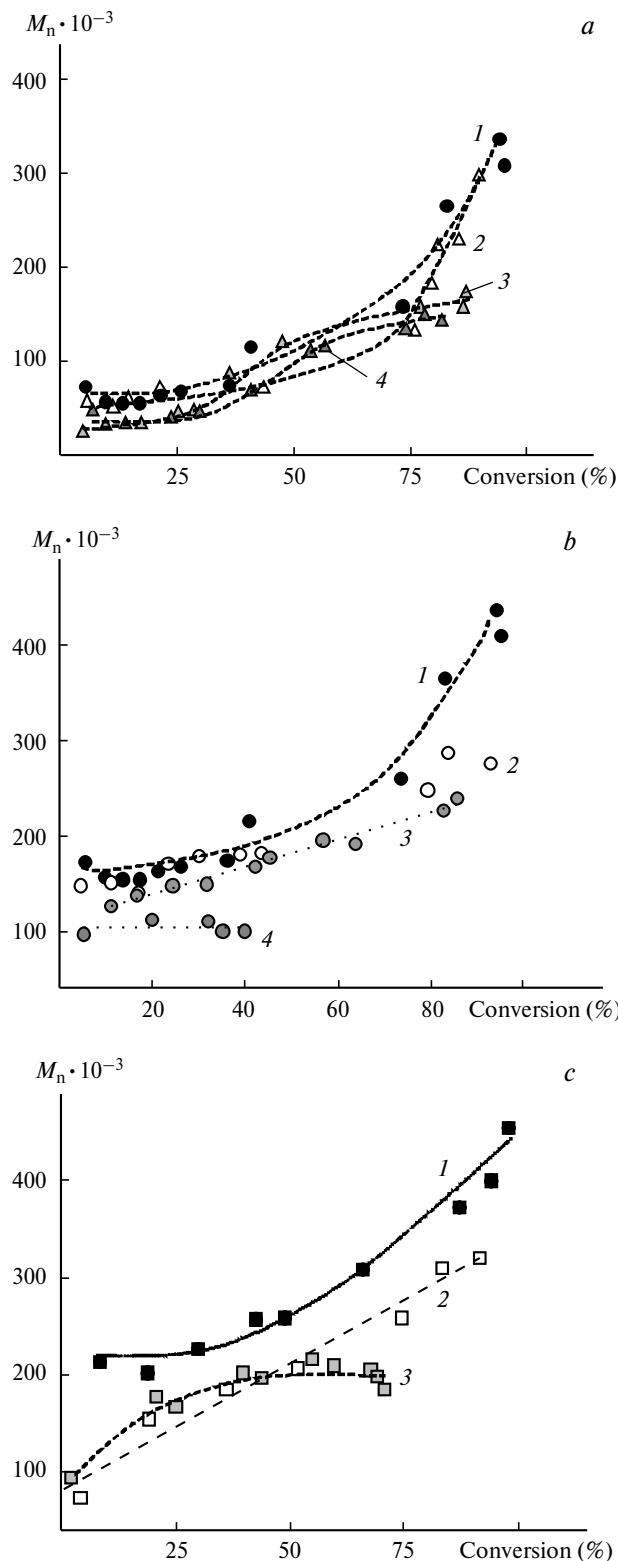**Fig. 3.** Numerical mean MM of polymers PMMA (*a, b*) and PBMA (*c*) *vs* conversion. $T = 70\ °C$. AIBN initiator (0.1 mol.%). Complexes: $36CatSnMe_2 \cdot THF$ (*a*), $36CatSnPh_2 \cdot THF$ (*b, c*). Concentration of the complexes, mol.%: *a*, 0 (*1*), 0.1 (*2*), 0.2 (*3*), and 0.4 (*4*); *b*, 0 (*1*), 0.1 (*2*), 0.2 (*3*), and 0.4 (*4*); *c*, 0 (*1*), 0.1 (*2*), and 0.2 (*3*).
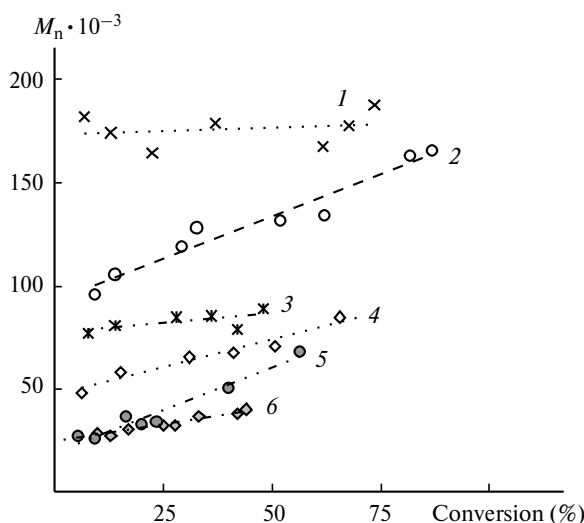
**Fig. 4.** Numerical mean MM of polymethacrylates PBMA (*1*, *3*) and PMMA (*2*, *4—6*) *vs* conversion. *T*, °C: 70 (*1*, *2*, *5*) and 90 (*3*, *4*, *6*). AIBN initiator (0.1 mol.%). Concentration of 36CatSnCl$_2$·2THF, mol.%: 0.1 (*1—4*) and 0.2 (*5*, *6*).

an increase in the monomer conversion (see Fig. 3, *b*, *c*). A higher concentration of the tin(IV) diphenyl catecholate complex is needed for MMA than that for BMA. A gradual increase in the concentration of 36CatSnPh$_2$·THF decreases the limiting conversion of (meth)acrylates (see Fig. 1, *c*) and also results in an unchanged value of numerical mean MM for poly(meth)acrylate samples (see Fig. 3, *b*, curve *4*; Fig. 3, *c*, curve *3*).

The linear increase in the MM of the PMMA samples is observed with an increase in the conversion for the polymerization involving 36CatSnCl$_2$·2THF regardless of the concentration of the complex (see Fig. 4, curves *2* and *5*). In the case of BMA, the numerical values of MM remain almost unchanged (see Fig. 4, curves *1* and *3*). These regularities are retained for the temperature increase to 90 °C (see Fig. 4, curves *3*, *4*, and *6*).

The molecular mass distribution (MMD) curves for the poly(meth)acrylate samples obtained when using complexes 36CatSnMe$_2$·THF, 36CatSnPh$_2$·THF, and 36CatSnCl$_2$·2THF are unimodal for all temperature and concentration ranges indicated above.

The shape of the MMD curves of the PMMA samples synthesized in the presence of the tin(IV) diethyl catecholate complex at 70 °C depends on the concentration of the complex. At the 36CatSnEt$_2$·THF to AIBN ratio equal to 1 : 1 and 4 : 1, the MMD curves at the initial polymerization stage are bimodal and become unimodal with an increase in the conversion (see Fig. 5, *a, c*).

For a twofold excess of the 36CatSnEt$_2$·THF complex over AIBN, the MMD curves of PMMA are unimodal at the initial polymerization stages (see Fig. 5, *b*). The second mode with a higher MM appears with time, and its fraction increases proportionally to the increase in the
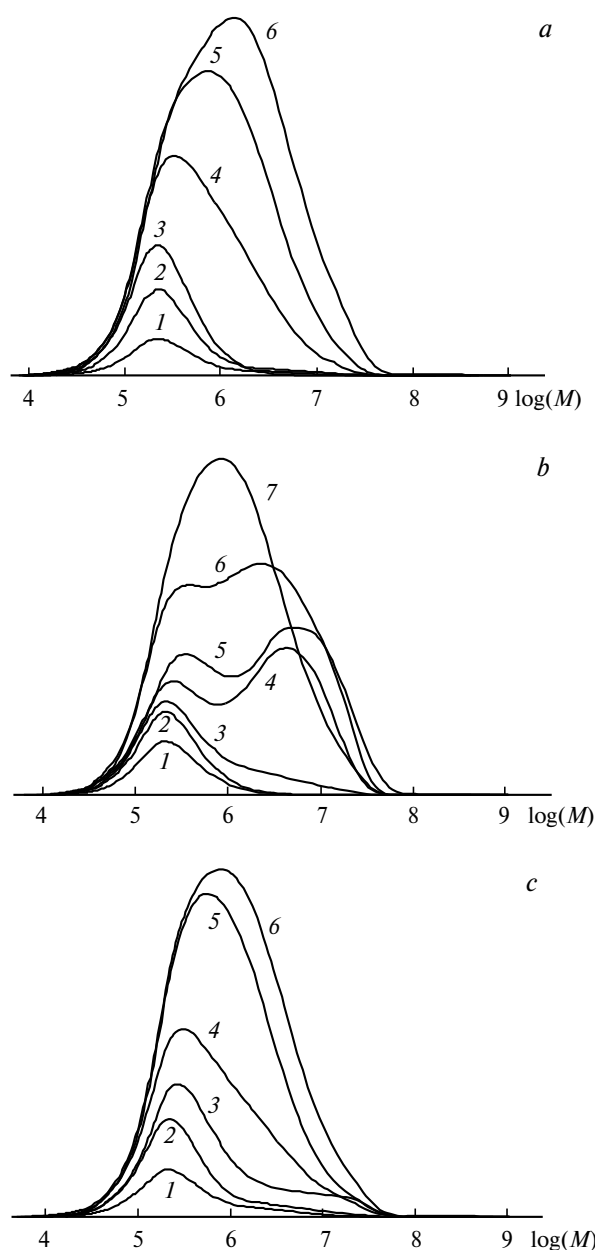


**Fig. 5.** MMD curves for polymer PMMA. *T* = 70 °C. AIBN initiator (0.1 mol.%). Concentration of 36CatSnEt$_2$·THF, mol.%: 0.1 (*a*), 0.2 (*b*), and 0.4 (*c*). Conversion of MMA, wt.%: *a*, 7 (*1*), 16 (*2*), 24 (*3*), 54 (*4*), 79 (*5*), and 93 (*6*); *b*, 11 (*1*), 17 (*2*), 25 (*3*), 47 (*4*), 57 (*5*), 82 (*6*), and 94 (*7*); *c*, 10 (*1*), 20 (*2*), 31 (*3*), 49 (*4*), 80 (*5*), and 92 (*6*).

conversion of MMA. This fact indicates macromolecules in the system with the direct participation of 36CatSnEt$_2$·THF grow *via* two parallel mechanisms, and the role of one of them becomes predominant with time. It should be mentioned that the introduction of 36CatSnEt$_2$·THF does not decrease the numerical values of MM of the polymers. This indirectly indicates that the number of reaction centers in the system does not increase

and, hence, the time of gel effect onset shifts due to the coordination of growing macroradicals with the metal complex rather than due to the stimulation of initiator decomposition.

The MMD curves for PMMA obtained at 70 °C with the participation of AIBN only are unimodal, and the polydispersity coefficients ($M_w/M_n$) increase with an increase in the conversion from 1.7 to 7.6. The numerical values of the polydispersity coefficients of PMMA in the case of using 36CatSnMe$_2$·THF (0.1 mol.%) at 70 °C change from 2.0 to 6.3 at a concentration of the complex of 0.1 mol.%. The numerical values of a similar parameter for PMMA obtained with the participation of 36CatSnPh$_2$·THF are 2.0—5.0, 1.9—4.2, and 1.8—2.0 for the concentration of the complex 0.1, 0.2, and 0.4 mol.%, respectively. When using complex 36CatSnCl$_2$·2THF/AIBN, the polydispersity coefficients of PMMA change in the range 1.6—2.0 up to the limiting conversions at both 70 and 90 °C.

In the case of BMA polymerization involving 36CatSnPh$_2$·THF, the polydispersity coefficients of PBMA change slightly compared to the polymer obtained in the presence of AIBN without the metal complex at 70 °C and remain in a range of 2.0—2.7. When using the 36CatSnCl$_2$·2THF/AIBN system at 90 °C, these values decrease to 1.6—1.9.

Substantial differences in the influence of the tin(IV) monocatecholate complexes on the polymerization of MMA and BMA are evidently related to the difference in both the rate constants of the growth of the corresponding macroradicals and the accepting ability of the used complexes toward the macroradicals. According to the literature data and earlier studies,[1—5] in polar media tin(IV) monocatecholates are capable of forming several types of *o*-semiquinolates with different compositions and arrangements of the alkyl radicals in the coordination sphere of the metal (I—V, Table 1). For the polymerization of (meth)acrylic esters, the monomer can be considered as a polar solvent (for example, compared to styrene), whose macromolecule can coordinate to the metal atom.

At the initial stage of MMA and BMA polymerization involving each complex used, the ESR spectrum contains signals indicating the formation of tin(IV) *o*-semiquinone complexes, and the composition and structure of intermediates somewhat differ. Unfortunately, it is impossible to determine quantitatively the concentration of intermediates with a sufficient accuracy because of a significant broadening of the spectral lines during polymerization due to an increase in viscosity in the system. However, the data on the composition and structure of tin(IV) *o*-semiquinolates formed at the initial stage make it possible to explain the regularities observed for polymerization involving tin(IV) monocatecholates. The parameters of the obtained spectra, each of which is characterized by a hy-
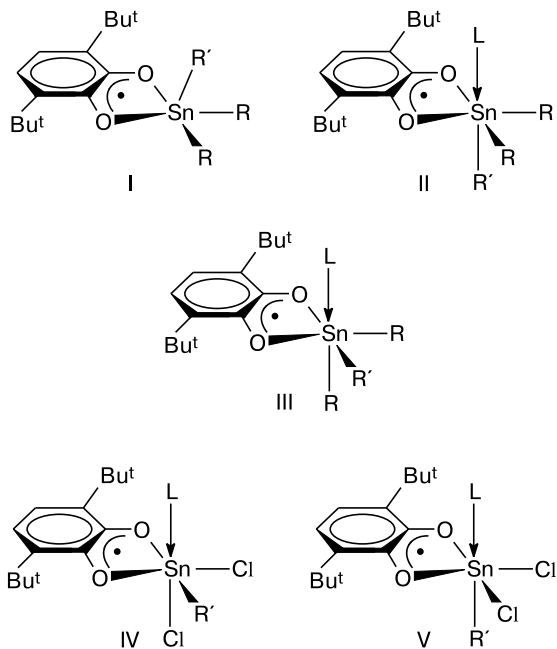


R = Alk, Ar

R′ is initiating or growing macroradical.

perfine coupling (HFC) of an unpaired electron with two protons of the *o*-semiquinone ring and magnetic tin isotopes $^{117}$Sn and $^{119}$Sn (for $^{117}$Sn, 7.68%, $I = 1/2$, $\mu_N = 1.000$; for $^{119}$Sn, 8.58%, $I = 1/2$, $\mu_N = 1.046$),[9] are presented in Table 2.

In the case of MMA and BMA polymerization in the presence of 36CatSnMe$_2$·THF and 36CatSnEt$_2$·THF, the spectra are detected in which the main signal is a doublet (1 : 1) of doublets (1 : 1) (Fig. 6, *a*). This fact along with the value of HFC constants on the magnetic metal isotopes[1,2,10,11] indicate the formation of predominantly hexacoordinated tin(IV) *o*-semiquinolates of

**Table 1.** Possible structure of tin(IV) *o*-semiquinolates (SQ) formed upon radical accepting and the corresponding shape of the main signal in the ESR spectrum

| Type of SQ | Structural features | Spectrum shape |
|---|---|---|
| I | Equivalent protons of *o*-semiquinolate ligand, pentacoordinated complex | Triplet |
| II | Equivalent protons of *o*-semiquinolate ligand, hexacoordinated complex | Triplet |
| III | Nonequivalent protons of *o*-semiquinolate ligand, hexacoordinated complex | Doublet of doublets |
| IV | Halogen in apical position of complex, hexacoordinated complex | Triplet of quartets |
| V | Both halogens in *o*-semiquinolate ligand plane, hexacoordinated complex | Triplet |

**Table 2.** Characteristics of the ESR spectra of the tin $o$-semiquinolate complexes formed upon radical accepting by the catecholate derivatives $36CatSnR_2 \cdot nTHF$*

| Monomer | R | Type of main signal | $a_i$/mT | $g_i$ | Shape of SQ spectrum |
|---|---|---|---|---|---|
| MMA | Me | Doublet of doublets | 0.33 (H), 0.41 (H), 0.15 ($^{117,119}$Sn) | 2.0038 | III |
| MMA | Et | Doublet of doublets | 2.58 (H), 4.66 (H), 0.28 ($^{117,119}$Sn) | 2.0044 | III |
| MMA | Ph | Doublet of doublets (determined) | 0.32 (H), 0.42 (H), 0.85 ($^{117,119}$Sn) | 2.0037 | III |
| MMA | Cl | Triplet of quartets | 0.39 (2H), 0.61 ($^{117,119}$Sn), 0.06 ($^{35,37}$Cl) | 2.0034 | IV |
| BMA | Me | Doublet of doublets | 0.33 (H), 0.40 (H), 0.22 ($^{117,119}$Sn) | 2.0038 | III |
| BMA | Et | Doublet of doublets | 0.32 (H), 0.41 (H), 0.18 ($^{117,119}$Sn) | 2.0039 | III |
| BMA | Ph | Triplet + | 0.37 (2H), 1.16 ($^{117,119}$Sn) | 2.0039 | I |
|  |  | doublet of doublets | 0.32 (H), 0.42 (H), 0.85 ($^{117,119}$Sn) | 2.0037 | III |
| BMA | Cl | Triplet of quartets | 0.39 (2H), 0.59 ($^{117,119}$Sn), 0.06 ($^{35,37}$Cl) | 2.0038 | IV |

\* Temperature 70 °C, reaction time 8—20 min.
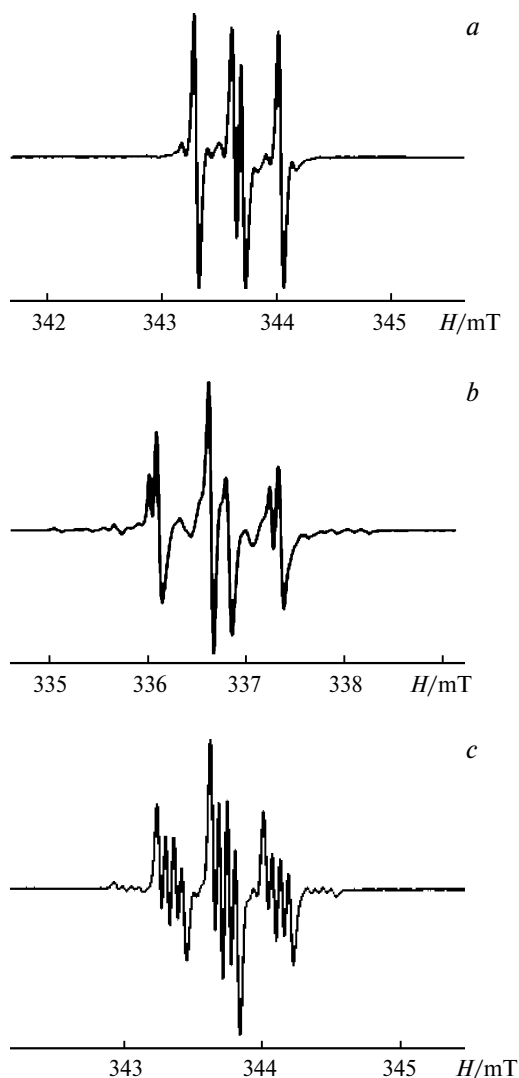


**Fig. 6.** Isotropic ESR spectra of the system BMA + 0.1 mol.% AIBN + 0.1 mol.% $36CatSnR_2 \cdot nTHF$, where R = Me ($a$), Ph ($b$), and Cl ($c$). $T = 70$ °C, reaction time 10—20 min. Selected parameters of the spectra are presented in Table 2.

type III (see Table 1) containing the coordinated donor ligand in the composition.

The ESR spectrum observed at the initial BMA polymerization at 70 °C in the presence of the $36CatSnPh_2 \cdot$ $\cdot THF$/AIBN system (see Fig. 6, $b$) is a superposition of two signals: triplet and doublet of doublets. These spectra can be assigned to the formation of penta- (of type I) and hexacoordinated (type III) tin(IV) complexes in the reaction mixture. A similar combination of signals in the ESR spectra was detected when the influence of $36CatSnPh_2 \cdot$ $\cdot THF$ on styrene polymerization was studied.[4]

In the case of MMA polymerization involving the $36CatSnPh_2 \cdot THF$/AIBN system, a signal is detected being a superposition of several signals from at least three difference tin $o$-semiquinolates. Only one of them was reliably characterized: a doublet of doublets, indicating that complexes of type III are formed.

At the initial stage of polymerization of (meth)acrylic esters in the presence of $36CatSnCl_2 \cdot 2THF$, the ESR spectrum contains similar signals: triplets (1 : 2 : 1) of quartets (1 : 1 : 1 : 1), indicating the formation of hexacoordinated tin(IV) $o$-semiquinolate complexes (see Fig. 6, $c$). The quartet splitting in the observed spectra is caused by the presence of the halogen atom (for $^{35}$Cl, 75.77%, $I = 3/2$, $\mu_N = 0.8218$; for $^{37}$Cl, 24.23%, $I = 3/2$, $\mu_N = 0.6841$)[9] in the apical position of the octahedral environment of the tin atom in $o$-semiquinolate of type IV.

Under the conditions of a multiple excess of the monomer over a controlling additive in the polymerized mixture, THF is evidently replaced in the initial tin catecholate complexes by a methacrylic ester molecule. Therefore, a molecule of the MMA (or BMA) molecule acts as ligand L in structures I—V.

According to published data,[12] the acceleration of polymerization of polar monomers is one of specific features of complex radical polymerization involving Lewis acids, Tin salts (for example, $SnCl_4$ and some other) are used to control both the composition of copolymers and tacticity

of polymer samples.[12,13] The MMD curves of the polymers synthesized with the addition of tin halides are complicated as in the above described samples with the tin catecholate complexes. The main explanation of the increase in the polymerization rate is a change in the reactivity of the macroradicals and polymerization mechanism due to the simultaneous coordination in the sphere of the metal of the growing radical and monomer molecule.[12]

According to the ESR data, under polymerization conditions, complexes $36CatSnMe_2 \cdot THF$ and $36CatSnEt_2 \cdot \cdot THF$ form predominantly hexacoordinated *o*-semiquinolates of type III (see Table 1). This type of coordination polyhedron will be characterized by the direct closeness of ligand L (in a medium of methacrylic ester as a monomer) and growing macroradical R´. This fact can result in the interaction of the accepted polymer radical with the monomer directly in the coordination sphere of the metal, which finally increases the polymerization rate of (meth)acrylates at the stage of gel effect (mechanism of complex radical polymerization[12,13]). The parallel growth of macroradicals in the coordinated and non-coordinated states appears as a bimodality of the MMD curves (see Fig. 5). Thus, contrary to expectations, for the processes involving $36CatSnEt_2 \cdot THF$ in a medium of MMA, the formation of the *o*-semiquinolate derivatives favors an increase in the polymerization rate. In the case of tin(IV) dimethyl catecholate, the growth of macromolecules in the coordinated and non-coordinated states evidently occurs in parallel, but these processes are comparable due to the high stability of the corresponding metal *o*-semiquinone derivatives.[14]

The formation of *o*-semiquinolates in the case of $36CatSnPh_2 \cdot THF$ and $36CatSnCl_2 \cdot 2THF$ makes it possible to control the macromolecule length at a certain ratio of monocatecholate to initiator in the polymerization of MMA and BMA by consecutive reactions of accepting and elimination of polymer radicals. In the case of primarily more sterically hindered $36CatSnPh_2 \cdot THF$, an addition coordination of the monomer molecule seems to be impossible for the formation of the *o*-semiquinone derivatives. This is also indicated by polymerized mixtures of paramagnetic species with the pentacoordinated metal atom observed in the ESR spectrum. A gradual decrease in the polymerization rate of MMA and BMA and their limiting conversion in polymerization involving $36CatSnPh_2 \cdot THF$ and $36CatSnCl_2 \cdot 2THF$ are related to a sufficiently high stability of the corresponding *o*-semiquinones[14] and an increase in the role of side processes with the participation of *o*-semiquinones as they are accumulated.

In particular, the transformation of alkyl-containing tin(IV) *o*-semiquinolates can proceed *via* two routes.[15,16] The first route is bimolecular dealkylation (see Scheme 1, backward reaction), which makes it possible to carry out styrene polymerization involving tin(IV) monocatecholates

in the reversible inhibition mode.[4] The second route of conversion is the disproportionation of the formed radical metal complexes (Scheme 2).

**Scheme 2**



36SQSnR₃

36CatSnR₂
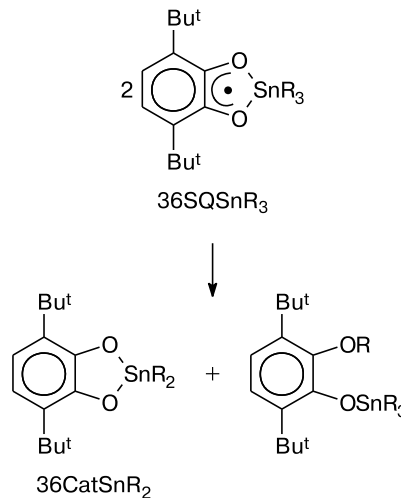
An increase in the concentration of the tin(IV) *o*-semiquinolate derivatives in the course of the process and the introduction of a monocatecholate excess over the initiator increase the probability of their transformation by disproportionation, and a gradual removal of the growing radicals from the reaction zone results in polymerization decay.

It should be mentioned that, in the processes involving tin(IV) diphenylcatecholates, the corresponding *o*-semiquinolates can also eliminate the phenyl radical: this is a unique reaction of "chain transfer" (Scheme 3).

**Scheme 3**
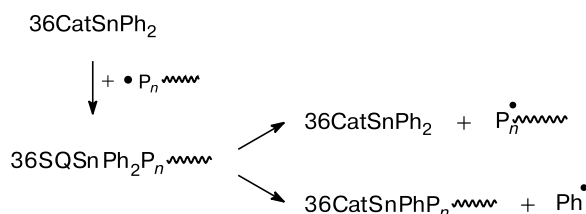


This reaction along with a gradual decomposition of the initiator in the system, *i.e.*, not simultaneous nucleation of growing radicals is a reason for an increase in the polydispersity coefficients of the polymer samples with an increase in the synthesis time, which in several cases results in constant values of numerical mean MM of poly-(meth)acrylates.

Thus, the accepting ability of tin(IV) monocatecholates toward carbon-centered radicals in polar monomeric media depends on their initial composition and spatial struc-

ture and the growing radical itself. The differences in composition and structure of the formed tin *o*-semiquinolate complexes play the key role in the controlled synthesis of polymers based on methacrylic esters in the presence of the complexes used. Depending on the composition, tin(IV) monocatecholates also can act as controlling agents of radical polymerization providing the linear growth of the molecular mass with conversion and as Lewis acids accelerating polymerization.

## Experimental

Methacrylic esters (MMA and BMA), initiator, and solvents used were purified using earlier described methods.[17−19] Tin(IV) monocatecholate complexes were synthesized according to described procedures.[1,20] The physicochemical constants of all compounds used corresponding to published data.

The samples were prepared as follows: the initiator and metal complexes taken in a certain ratio were placed in glass ampules and degassed three times to remove oxygen by freezing—thawing out the ampules in liquid nitrogen and pumping out air. Polymerization was carried out at a residual pressure of ~1.3 Pa.

The polymerization kinetics was controlled by gravimetry. To purify polymers from residues of unreacted monomer and initiator, the samples were reprecipitated from a dichloromethane solution and dried under reduced pressure to a constant weight.

The molecular mass characteristics of the obtained polymers were determined by GPC using a standard procedure.[21] Chromatographic analysis of the polymers was carried out on a Knauer setup with a cascade of linear columns ($10^3$—$10^5$, Phenomenex, USA). A RI Detektor K-2301 differential refractometer was used as a detector. THF served as an eluent. Narrow-dispersion PMMA standards were applied for calibration.

ESR spectra were recorded on a Bruker-EMX radiospectrometer (working frequency 9.75 GHz). Diphenylpicrylhydrazyl ($g = 2.0037$) was used as a standard for the determination of the *g* factor.[22]

## References

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