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Bis(3,6-di-*tert*-butylcatecholato)tin(IV) ditetrahydrofuranate in radical polymerization of methyl methacrylate

E. V. Kolyakina,[a] ***L. B. Vaganova,***[a] ***A. V. Lado,***[b] ***A. V. Piskunov,***[b] ***V. K. Cherkasov,***[b] ***and D. F. Grishin***[a]*

[a]Chemistry Research Institute, N. I. Lobachevsky State University of Nizhny Novgorod,
23 prosp. Gagarina, 603950 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 65 8162. E-mail: grishin@ichem.unn.ru
[b]G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
49 ul. Tropinina, 603950 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 62 7497. E-mail: pial@iomc.ras.ru

The effect of bis(3,6-di-*tert*-butylcatecholato)tin(IV) ditetrahydrofuranate (**1**) on the kinetic parameters of methyl methacrylate polymerization and on the molecular weight characteristics of polymers prepared was studied. According to EPR data, complex **1** can accept and eliminate the growing macroradicals in monomer media. This allows the lifetimes of the growing polymer chains to be controlled. The optimal temperature range for accomplishing controlled synthesis of polymer in the presence of complex **1** was determined.

Key words: tin(IV) catecholate complexes, methyl methacrylate, radical polymerization.

At present, the concept of controlled radical polymerization has found wide application in synthetic polymer chemistry.[1—5] The possibility of using various polymer chain growth regulators predetermined the emergence of various research avenues, such as iniferter-controlled polymerization, stable free-radical polymerization, atom transfer radical polymerization, and reversible addition-fragmentation polymerization.

A recently developed original method[6—12] involves various quinones, binary systems based on them, and metal complexes with quinone ligands as chain growth regulators. The semiquinone and catecholate complexes of both transition and main group metals based on sterically hindered pyrocatechol derivatives are quite promising for searching novel efficient chain growth regulators.[13—15]

Main group and transition metal complexes with various quinones are of interest for synthetic polymer chemistry because they can accept free carbon-centered radicals to give corresponding stable *o*-semiquinone derivatives[14,15] and then eliminate them.[16,17] It is logical to assume that these intermediate spin adducts can be active in controlled synthesis of polymers.

The aim of this work was to study the effect of bis(3,6-di-*tert*-butylcatecholato)tin(IV) ditetrahydrofuranate (**1**) on the kinetics of radical polymerization of methyl methacrylate (MMA) initiated by azoisobutyric acid dinitrile (AAD) and on the molecular weight characteristics of polymers prepared.

Results and Discussion

Catecholate tin complexes can accept short-lived and stable radicals to form *o*-semiquinone derivatives.[13,14] In particular, complex **1** efficiently accepts O-, C-, N-, and S-centered radicals in various solvents to give mono- or bis-semiquinone derivatives.

To study the effect of complex **1** on the polymerization of MMA and to evaluate its ability to accept carbon-centered polymer radicals in monomer media, we carried out an EPR study of the intermediate reactive species formed in the reactions of the growing macroradicals with complex **1**.

We established that complex **1** efficiently accepts the chain growth macroradicals in the monomer medium to give an *o*-semiquinolate derivative. For comparison, Fig. 1 presents the EPR spectra of the *o*-semiquinone tin derivatives obtained in the MMA medium and in ethyl acetate (the latter can be treated as a model for hydrogenated analog of the acrylic monomer with the donor ability comparable to that of MMA) in the presence of AAD initiator.

No biradicals of *o*-semiquinone tin derivatives were detected under similar conditions. This is probably due to (i) great steric hindrances produced in the coordination sphere of the metal atom in the course of addition of the radical species and (ii) the fact that the radical species are incapable of displacing the solvent (THF or monomer) molecule from the complex. This makes the approach of the second radical difficult. The results ob-

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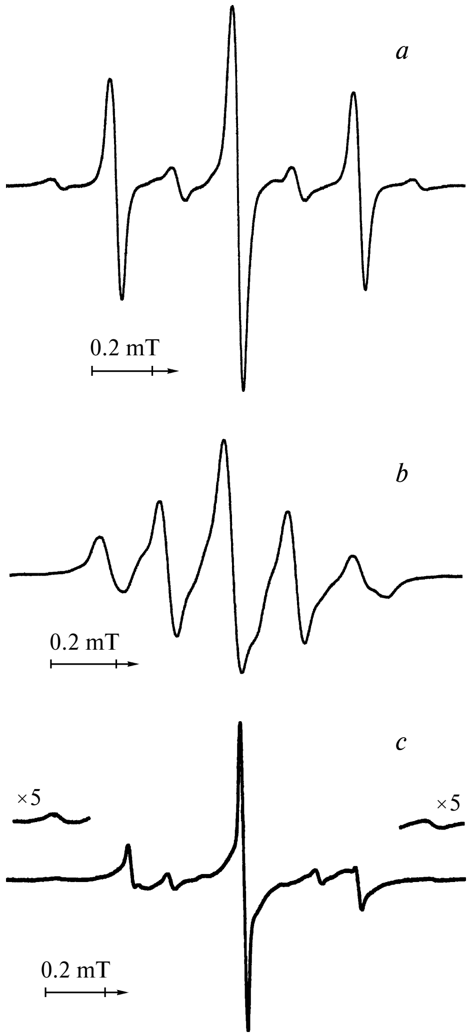


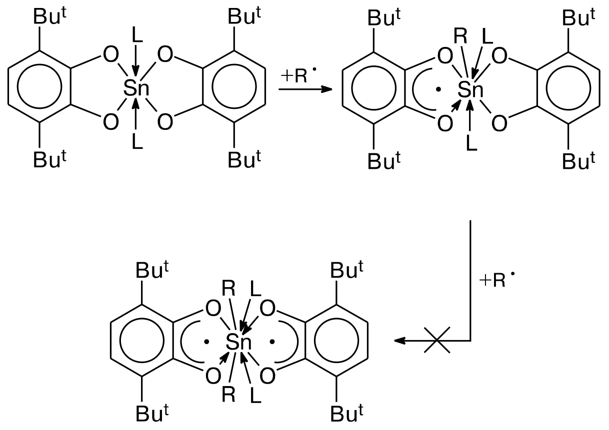
Fig. 1. EPR spectrum recorded in MMA medium (*a*, *b*) and in ethyl acetate (*c*) in the presence of complex **1** (0.1 mol.%) and AAD (0.1 mol.%) at 343 (*a*, *c*) and 353 K (*b*). HFC constants: *a*) a_i(2 H) = 0.40 mT, a_i(^{117,119}Sn) = 0.40 mT, g_i = 2.0032; *b*) a_i (4 H) = 0.19 mT, a_i (^{117,119}Sn) = 0.51 mT, g_i = 2.0035; *c*) a_i (2 H) = 0.37 mT, a_i(^{117,119}Sn) = 0.49 mT, and g_i =2.0037.

tained suggest that complex **1** interacts with the chain growth radicals in monomer medium only in the first stage (Scheme 1).

To choose optimal conditions for controlled synthesis of poly(methyl methacrylate) (PMMA), it was interesting to assess the stability of intermediate *o*-semiquinone derivatives at different temperatures by EPR spectroscopy.

In the temperature range 323—348 K the EPR spectrum exhibits a triplet with a component intensity ratio of 1 : 2 : 1 (see Fig. 1, *a*), which is due to the interaction of the unpaired electron with two equivalent protons. In addition, there is a satellite splitting on the magnetic isotopes of tin (^{117,119}Sn). Comparison of the HFC constants a_i(2 H) = 0.4 mT, a_i(^{117,119}Sn) = 0.4 mT, g_i = 2.0032 with

Scheme 1

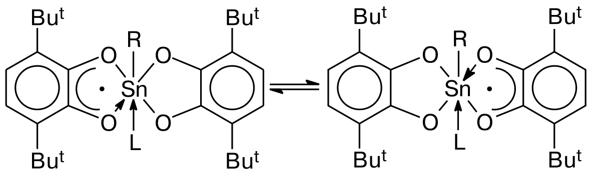


R stands for initiator radicals or macroradicals,
L stands for THF or monomer molecule.

the published data indicates the formation of an *o*-semiquinone tin(IV) derivative.[14,15] The magnitude of the HFC constant a_i(^{117,119}Sn) indicates the presence of tin(IV) complexes with a coordination number of six and more. The shape and parameters of the EPR spectrum recorded in ethyl acetate medium (see Fig. 1, *c*) are strongly different from those mentioned above. This difference points to another nature of the radical that adds to the tin complex. Namely, here we deal with the addition of the carbon-centered radical produced upon decompositon of AAD in contrast to fixation of the growing macroradical in the monomer medium.

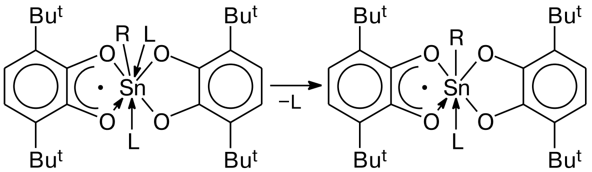
Yet another *o*-semiquinone tin(IV) complex is formed in the system at elevated temperatures (353—373 K). The species is characterized by a quintet EPR spectrum with a component intensity ratio of 1 : 4 : 6 : 4 : 1 (see Fig. 1, *b*). This splitting is due to the interaction of the unpaired electron with four equivalent protons of the quinone ligands. The HFC constant a_i(4 H) equal to 0.19 mT is nearly halved compared to that of the first complex. This is indicative of a fast, in the EPR time scale, transfer of the unpaired electron between two *o*-quinone ligands (Scheme 2).

Scheme 2



The HFC constant a_i(^{117,119}Sn) = 0.51 mT points to a smaller, compared to the first complex, value of the coordination number of the Sn atom, which can be explained by elimination of a neutral ligand from the *o*-semiquinone tin derivative formed in the first stage (Scheme 3).

Scheme 3



At T > 373 K, the signal of the *o*-semiquinone tin derivative disappears due to breakdown of the intermediate structures.

We also carried out an EPR study of the kinetics of accumulation and loss of the *o*-semiquinone tin(IV) derivatives in the MMA medium at 343 K over a period of 2 h. Initially, the signal amplitude increased, but the concentration of the intermediate species decreased with time and after ~15 min the system reached a steady state. The constant concentrations of the *o*-semiquinone derivatives in time show the potential ability of complex **1** to control the chain growth in MMA polymerization by acceptance of carbon-centered radicals and subsequent elimination of these species.

Based on the EPR data, one can assume that the temperature range 323—373 K is optimum for carrying out controlled polymerization; here, both acceptance and elimination of carbon-centered radicals (including polymer ones) are possible. In addition, the *o*-semiquinone tin derivatives and the additive (complex **1**) remain stable in contrast to the higher-temperature range (T >343 K).

To evaluate the effect of complex **1** on the kinetics and activation energy of MMA polymerization, we studied the temperature dependence of the initial rate of the process in the 323—348 K interval by dilatometry. As should be expected, the rate of the process monotonically increases with temperature both in the presence and in the absence of complex **1** (Table 1). However, by and large the introduction of complex **1** causes a considerable decrease in the polymerization rate throughout the whole temperature interval under study. The results obtained show that complex **1** inhibits MMA polymerization in the presence of AAD. Probably, reduction of the polymerization rate is due to initial acceptance of the polymerization-initiating radicals by the complex (see Scheme 1).

From the initial rates we calculated the activation energies of the processes mentioned above. The activation energy of conventional radical polymerization of MMA is somewhat lower than that of the process occurring in the presence of complex **1** (see Table 1).

To study the effect of complex **1** on the overall polymerization rate in more detail, we studied the yields of the polymer after specified time intervals at different temperatures (Table 2). The results obtained show that introduction of complex **1** causes a significant reduction of the overall polymerization rate and the limiting conversion at 323 and 333 K. In the high-temperature interval the effect of the additive on the polymerization rate is less pronounced; more pronounced is the effect of complex **1** on the polydispersity indices of the PMMA samples.

Table 1. Effect of complex **1** on the initial rate and activation energy of MMA polymerization (initiator AAD, 0.1 mol.%)

[**1**] (mol.%)	E_a /kJ mol^{-1}	T/°C	τ^a /min	$V^b \cdot 10^4$ /mol L^{-1} s^{-1}
0	76±5	50	0	1.3
		55	0	2.1
		60	0	3.3
		65	0	4.5
		70	0	7.0
0.1	87±6	55	~90	1.3
		60	~40	1.9
		65	~15	2.9
		70	~8	5.2
		75	~4	7.5

[a] Induction period.

[b] Polymerization rate.

In this connection it was interesting to study the effect of the concentration of complex **1** on the molecular weight characteristics of the polymers and on the rate of MMA polymerization. From the data in Table 3 it follows that an increase in the additive concentration causes the overall rates of the processes and the limiting conversion to abruptly decrease and the molecular weights (MW) and polydispersity indices of the PMMA samples to decrease at comparable conversions. Large amounts of complex **1** present in the system inhibit the polymerization of MMA.

Table 2. Effect of temperature on characteristics of MMA polymerization in the presence of complex **1** (initiator AAD, 0.1 mol.%)

T/°C	[**1**] (mol.%)	t/h	C* (%)	$M_\eta \cdot 10^{-3}$	M_w/M_n
50	—	2.0	7	1120	—
		6.0	80	—	—
	0.1	6.3	9	955	—
60	—	2.5	93	2690	2.8
	0.1	6.0	66	1344	2.9
70	—	2.4	99	1640	2.9
	0.1	6.0	83	700	2.6
80	—	1.3	97	1000	3.2
	0.1	6.0	79	588	3.1
100	—	0.5	95	307	3.4
	0.1	6.0	75	237	3.3

* Here and in Tables 3 and 4 C is the conversion.

Table 3. Effect of the concentration of complex **1** on the molecular weight characteristics of PMMA (initiator AAD, 0.1 mol.%; $T = 70$ °C)

[**1**] (mol.%)	t/h	C (%)	$M_{\eta} \cdot 10^{-3}$	$M_{\omega} \cdot 10^{-3}$	M_w/M_n
0.1	1	21	135	303	2.2
	4	56	159	383	2.4
	13	83	189	492	2.6
0.2	13	57	122	215	1.8
0.4	150	17	48	87	1.8
0.8	150	15	43	72	1.7

For instance, at 343 K the process stops after attainment of the limiting conversion at additive : initiator molar ratios of 4 : 1 and 8 : 1 (see Table 3). At a higher temperature (~373 K), the polymerization almost completely stops at low conversions at additive : initiator ratios of 2 : 1 and 4 : 1.

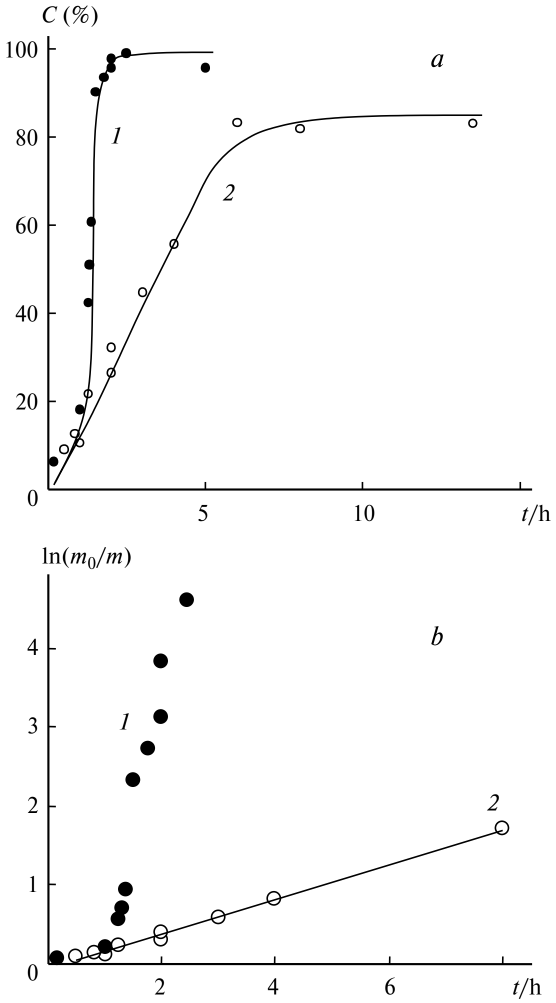


Fig. 2. Conversion (C) (a) and $\ln(m_0/m)$ (b) plotted *vs.* duration of MMA polymerization at 343 K and a concentration of complex **1** of 0 (*1*) and 0.1 mol.% (*2*). Initiator AAD (0.1 mol.%).

Being guided by the results obtained, we carried out further studies under kinetically optimal conditions for MMA polymerization, that is, the temperature range 343—373 K and the initiator : additive ratio 1 : 1.

The MMA conversion is plotted *vs.* duration of polymerization in the presence and in the absence of the additive in Fig. 2. In the presence of complex **1** the gel effect is partially removed and the monomer conversion (up to 60%) is linearly related to time.

Complex **1**, as additive, also affects the molecular weight characteristics of the polymers synthesized. For instance, the polymerization of MMA at 343 and 373 K is characterized by almost linear increase in the viscosity-average and number-average MW (M_{η} and M_n, respectively) of PMMA with an increase in the monomer conversion in contrast to the S-shaped curve characteristic of the MMA polymerization in the presence of a conventional initiator (Figs 3 and 4).

The molecular weight distribution curves of the PMMA samples synthesized in the presence of complex **1** are monomodal throughout the process. Complex **1** has little effect on the polydispersity indices of the polymers obtained (Table 4). This is probably due to concurrent occurrence of the controlled synthesis in the presence of complex **1** and competing reactions involving this complex[16,17] that lead to a large contribution of bimolecular chain termination.

Thus, we established that complex **1** has a strong effect on the kinetic parameters of radical polymerization of MMA in the temperature interval 323—373 K and on the molecular weight characteristics of the polymers synthesised in the presence of this additive.

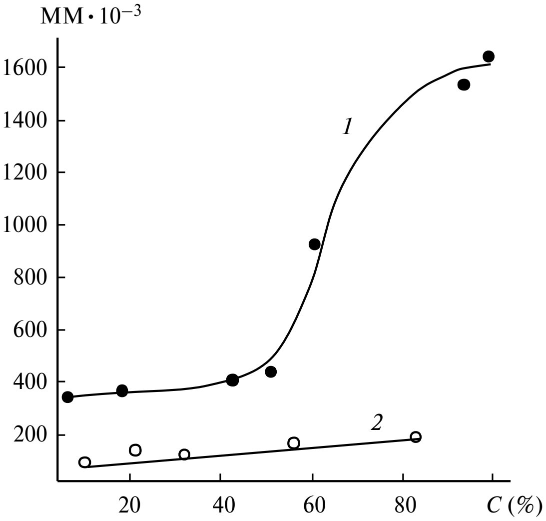


Fig. 3. Viscosity-average (*1*) and number-average (*2*) molecular weight of PMMA synthesized at 343 K plotted *vs.* conversion in the absence (*1*) and in the presence of complex **1** (0.1 mol.%) (*2*). Initiator AAD (0.1 mol.%).

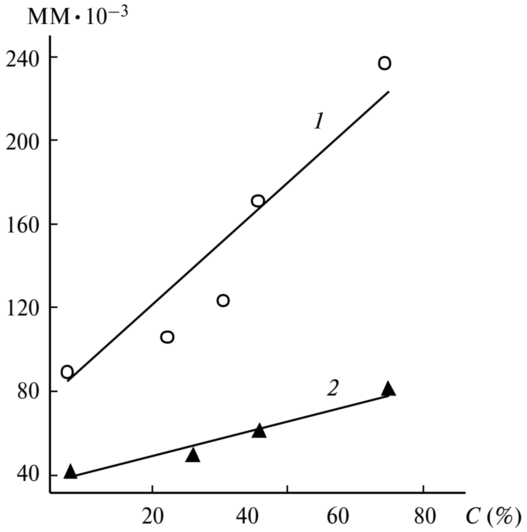


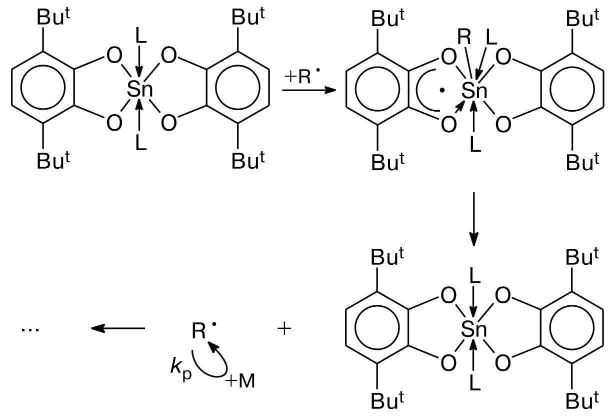
Fig. 4. Viscosity-average (*1*) and number-average (*2*) molecular weight of PMMA synthesized at 373 K in the presence of complex **1** (0.1 mol.%) plotted *vs.* conversion. Initiator AAD (0.1 mol.%).

Table 4. Molecular weight characteristics of PMMA synthesized in the presence of complex **1** (0.1 mol.%) (initiator AAD, 0.1 mol.%)

T/°C	C (%)	$M_\eta \cdot 10^{-3}$	M_w/M_n
70	10	89	2.1
	21	135	2.2
	56	159	2.4
	83	189	2.6
100	28	41	2.1
	46	49	2.5
	56	61	2.9
	75	81	3.3

Our EPR study revealed the ability of complex **1** to accept and eliminate macroradicals in MMA medium. Based on analysis of the published data on the reactivities of catecholate tin complexes and on the results obtained, it is logical to assume that chain growth in the MMA polymerization in the presence of complex **1** can be controlled in a fashion shown in Scheme 4.

Scheme 4



R is the initiator radical or macroradical, M is the monomer molecule; k_p is the rate constant for polymerization

The polymer (oligomer) radical that formed can again interact with complex **1** following Scheme 1.

The optimal temperature interval for controlled synthesis of PMMA in the presence of complex **1** is 343—373 K. We found that the molecular weights of the polymers obtained in the presence of complex **1** are linearly related to the monomer conversion. The introduction of the catecholate complex **1** considerably reduces the molecular weight, but has little effect on the polydispersity indices of the polymers synthesized.

Experimental

MMA samples were purified from stabilizer,[18] dried over anhydrous calcium chloride, and distilled at a reduced pressure. The initiator AAD and solvents were purified following known procedures.[19,20] Complex **1** was obtained as reported earlier.[15] The physicochemical constants of all compounds used in this work were in agreement with the published data.

The samples were prepared as follows: specified amount of monomer was placed in a glass tube and degassed by three freeze—thaw cycles in liquid nitrogen; polymerization was carried out at a residual pressure of ~1.3 Pa. The polymerization kinetics was monitored by dilatometry and gravimetriy. The polymer was poured in hexane, purified from the monomer and initiator residues by reprecipitation from the solution in chloroform, and then dried at a reduced pressure until constant weight.

EPR spectra were recorded on a Bruker ER-200D-SRC radiospectrometer (operating frequency ~9.5 GHz) equipped with a ER-4111VT thermostat. The g-factors were determined using diphenylpicrylhydrazyl ($g = 2.0037$) as reference.

The molecular weight characteristics of polymers were determined by viscosimetry and gel-permeation chromatography on a Knauer instrument with a linear column (Phenomenex, USA),[21] an RI Detektor K-2301 differential refractometer as detector, and chloroform as eluent. Narrow-disperse polystyrene standards were used for calibration. The average MW of PMMA were recalculated from calibration with the polystyrene standards to the PMMA samples under study using a conventional procedure.[22]

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