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Bis-catecholate complexes of the IV group elements in the radical polymerization of styrene: ESR studies

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The main features of the radical polymerization of styrene in the presence of germanium(IV) and tin(IV) bis-catecholate complexes were studied in the temperature range 70—110 °C. Depending on the initial composition and structure, as well as on the reaction conditions, the complexes used can play the role of inhibitors or regulators directing the polymerization process. The ESR data in the styrene medium showed formation of germanium and tin *o*-semiquinolate derivatives, that indicates a direct involvement of the organoelement additives into the propagation step. The polymers synthesized in the presence of the bis-catecholate complexes of the IV group elements can be used as macroinitiators of styrene polymerization.

Key words: bis-catecholate complex, *o*-semiquinone complex, germanium(IV), tin(IV), styrene, radical polymerization, electron spin resonance.

Nowadays, radical polymerization with the use of coordination and organometallic compounds as regulating agents is one of the most intensively pursued lines of development in synthetic chemistry of polymeric compounds.[1—3] Studies in this field facilitate design of new efficient initiators-regulators of polymerization processes, which give one an opportunity to obtain materials with desired properties. In particular, it was shown that introduction of transition metal complexes to the reaction system allows one to change molecular-weight characteristics of the synthesized polymeric materials and kinetic parameters of polymerization.[1—3] A key role in this case is played by the ability of the central metal atom to easily and reversibly change the extent of oxidation both in the reaction with organohalogene compounds and with the growing radicals.

In the literature, there are virtually no examples when complexes of nontransition elements are used as regulators of the polymeric chain growth. At the same time, due to specificities of the ligand surrounding compounds of nontransition elements can be involved in a number of cases into the reactions with different radicals, including polymeric ones, to purposefully tune their reactivity. For instance, by the introduction of redox-active ligands to a nontransition metal complex, these compounds acquire an ability to be involved into the reactions of oxidative addition[4—6] and reductive elimination,[7,8] thus mimicking the behavior of transition metal derivatives. Unlike compounds of transition elements, a redox-active ligand is the oxidation-reduction center in these complexes, rather than a metal atom.

Complexes of nontransition elements with the redox-active ligands, for example, based on 3,6-di-*tert*-butylpyrocatechol, are not only promising reactants for the radical particles to be trapped with subsequent identification of the products by ESR,[4—8] but also can be used as regulators of propagation in polymerization processes.[9—11]

The purpose of the present work was to study the main features of the synthesis of polystyrene in the presence of germanium and tin bis-catecholate complexes with different ligand surrounding. This work also included ESR study of the paramagnetic adduct structures formed in the polymerization process as a result of the reaction of propagation radicals with the metal complexes of interest.

The following objects were chosen for the study: bis(3,5-di-*tert*-butylcatecholato)germanium(IV) (**1**), bis(3,6-di-*tert*-butylcatecholato)germanium(IV) (**2**), bis(3,6-di-*tert*-butylcatecholato)tin(IV) (**3**), bis(3,6-di-*tert*-butyl-4-methoxycatecholato)tin(IV) (**4**), and bis(3,6-di-*tert*-butyl-4-chlorocatecholato)tin(IV) (**5**) ditetrahydrofuranates. Asobis(isobutyronitrile) (AIBN) was an initiator.

Results and Discussion

The ESR studies of the reaction of germanium and tin bis-catecholates with carbon-centered radicals in styrene

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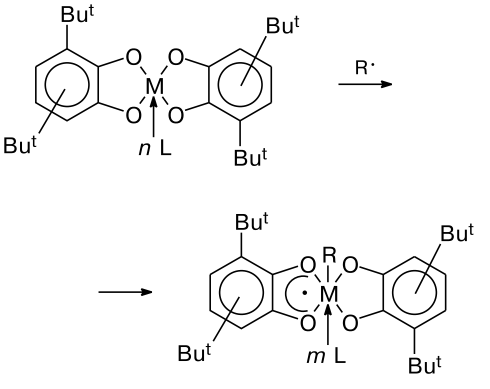
in the temperature range 70—90 °C showed formation of mono-*o*-semiquinolate derivatives of the IV group elements (Scheme 1, Figs 1—3).

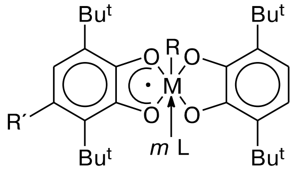
Scheme 1



R is the initiating or oligomeric radical;
L is the solvate ligand (molecule of THF or monomer);
M = Ge, Sn; *n* = 1, 2; *m* = 1, 2

The shape of the spectra recorded for the derivatives of complexes **1** and **3** virtually did not change with time.

In the case of complex **2**, the signal in the ESR spectrum in the initial step corresponds to the formation of germanium mono-*o*-semiquinolate complexes (see Fig. 2, *a*). The observed superposition of the triplet 1 : 2 : 1 and the quintiplet 1 : 4 : 6 : 4 : 1 suggests that germanium radical derivatives with different geometry are present in the reaction mixture.[12] However, after the system was warmed for 6 h, a weak signal (see Fig. 2, *b*) with the hyperfine splitting only on one proton is observed at both 70 and 90 °C. This corresponds to the appearance of germanium radical complex in the system, in which the proton at position 4 of the semiquinone fragment is replaced by an alkyl substituent.



R, R′ are the initiating or oligomeric radicals

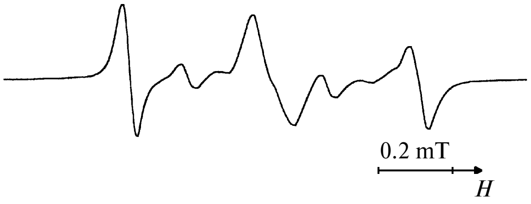


Fig. 1. The ESR isotropic spectrum observed during polymerization of styrene in the presence of complex **3** (0.1 mol.%) and AIBN (0.1 mol.%). $T = 70$ °C. The parameters of ESR spectrum: a_i(H) = 0.36 mT, a_i(H) = 0.44 mT, $g_i = 2.0032$.

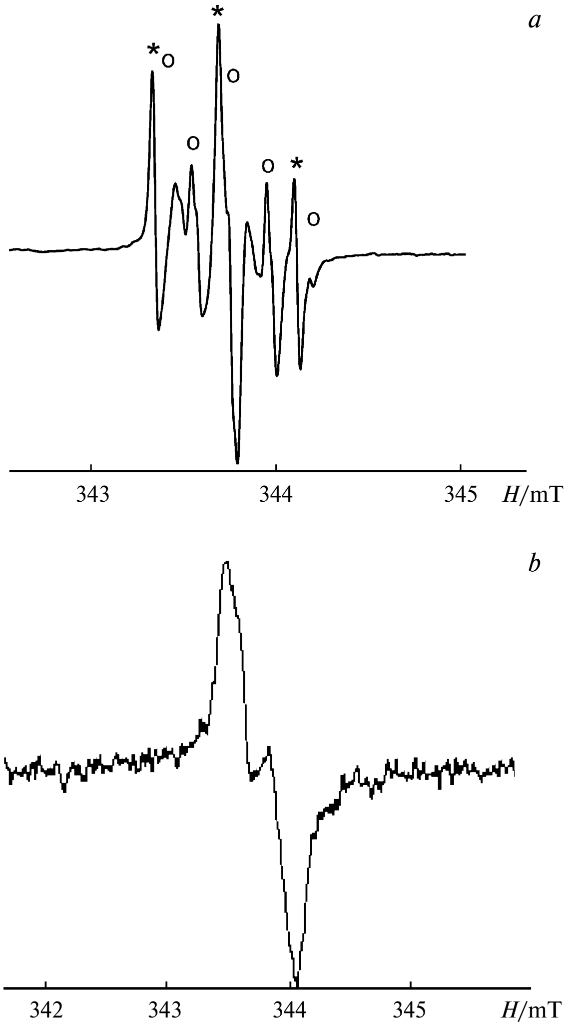


Fig. 2. The isotropic ESR spectrum for the styrene—complex **2**—AIBN system: $T = 70$ °C, 20 min reaction time, the parameters of ESR spectrum a_i(H) = 0.37 mT, a_i(H) = 0.41 mT, $g_i = 2.0045$; a_i(4H) = 0.17 mT, $g_i = 2.0043$ (*a*); $T = 90$ °C, 6 h reaction time, the parameters of ESR spectrum a_i(H) = = 0.39 mT, $g_i = 2.0042$ (*b*). The triplet and quintiplet lines are marked with asterisks and circles, respectively.

The formation of such a derivative, possibly, includes the reaction of germanium *o*-semiquinolate complex with an alkyl radical (Scheme 2, path *A*) leading to a "dead" macromolecule and substituted germanium catecholate complex.

The transfer of the alkyl radical to the ring of *o*-semiquinone fragment can also proceed through the formation of a biradical complex (see Scheme 2, path *B*) with subsequent intramolecular migration of the hydrocarbon substituent.[13]

The compound obtained can be also involved into the reaction with radicals similarly to the initially unsubstituted catecholate complex (Scheme 3).

To sum up, regulation of polymerization process with the use of complex **2** is possible by several mechanisms occurring in parallel.

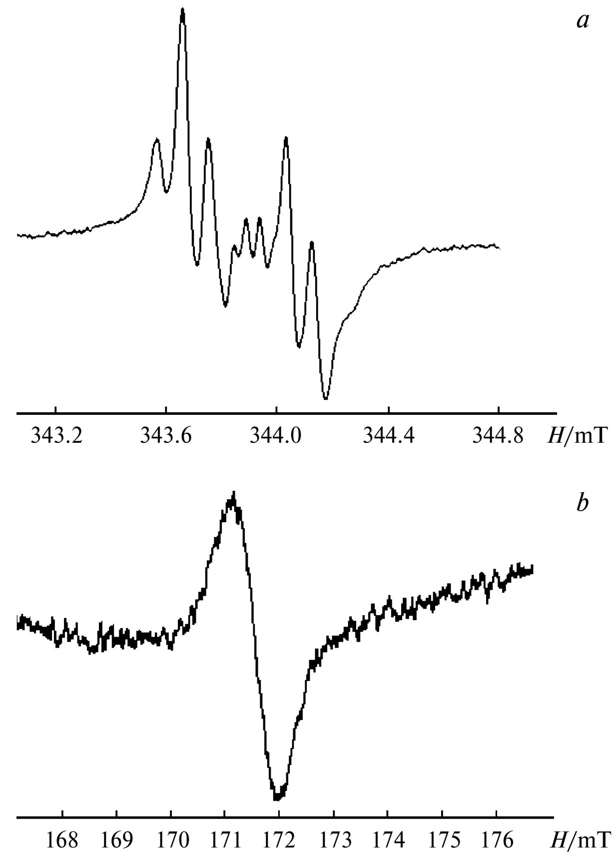


Fig. 3. The ESR spectra for the styrene—complex **4**—AIBN system: the isotropic spectrum, $T = 90$ °C, 10 min reaction time (*a*); the signal of the ESR spectrum in the frozen solvent matrix corresponding to the transition $\Delta m_s = 2$, $T = 150$ K (*b*).

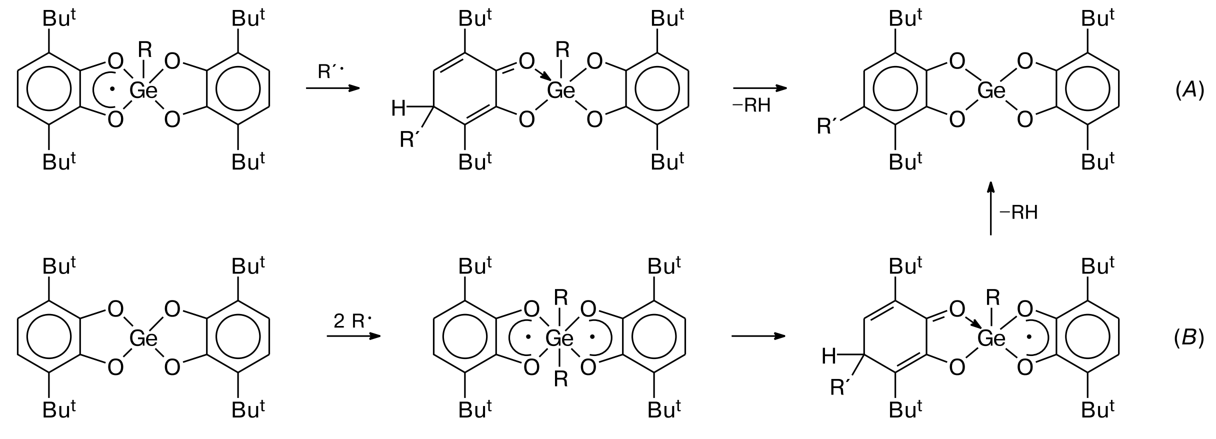
In the case of complex **4**, formation of the tin bis-*o*-semiquinone complexes was observed at both 70 and 90 °C together with the metal monosemiquinone derivatives (see Fig. 3, *a*). The evidence in favor of this fact is the appearance of a signal in the frozen glass-like solvent matrix at $H \approx 172$ mT, which corresponds to the forbidden transition $\Delta m_s = 2$ (see Fig. 3, *b*) characteristic of a biradical particles. It should be noted that intensity of the signal for the bis-*o*-semiquinolate derivative decreases with the elevation of temperature. When the styrene—AIBN—complex **5** system was warmed, a signal corresponding to the formation of bis-*o*-semiquinolate complexes was also observed in the ESR spectrum, however, its intensity only increases with time. The presence of additional substituent at position 4 of the catecholate fragment of complexes **4** and **5**, possibly, facilitates an increase in stability of the formed metal *o*-semiquinone derivatives due to the additional steric shielding of the radical ligand. This, in turn, should exhibit a stronger inhibiting effect on the polymerization process of styrene as compared to complex **3**.

Formation of *o*-semiquinolate derivatives in the monomeric medium indicates a possibility of the direct involvement of the used germanium and tin bis-catecholate complexes into the reaction with active initiating and/or oligomeric radicals, that eventually should affect kinetic laws of the styrene polymerization and molecular-weight characteristics of the polymer formed in their presence.

The germanium bis-catecholate complexes **1** and **2** used in the work differ only in the positions of the *tert*-butyl substituents in the quinone ligand, however, their behavior is however considerably different under polymerization conditions.

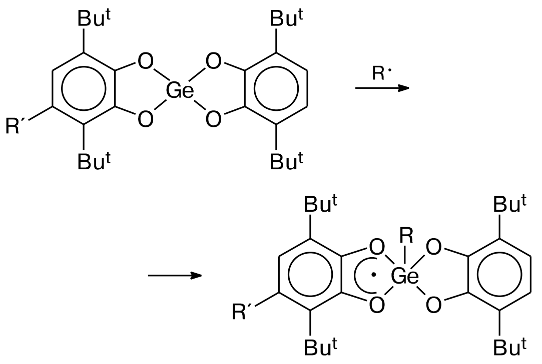
Thus, introduction of complexes **1** and **2** into the system leads to a significant reduction in the yield of the polymer: the limiting degree of styrene conversion at 70 °C is ~40% (Fig. 4, *a*). Complex **1** only retards polymerization, whereas in the case of complex **2**, an appreciable (~7 h) induction period appears. Reduction in the yield of polystyrene (PS) indicates a partial acceptance of the initiating (or oligomeric) radicals by the metal complexes virtually without subsequent elimination of the "trapped"

Scheme 2



R, R' are the initiating or oligomeric radicals

Scheme 3



radical. The different rates of styrene polymerization with participation of complexes **1** and **2**, possibly, are related not only to the specific features of the structure of **1** in solution,[14] but they also can be associated with the reactions of *o*-semiquinolate derivatives **2** proceeding as indicated in Schemes 2 and 3.

When complex **3** is used, the limiting degree of styrene conversion is somewhat higher (~60%), which confirms the lower stability of the formed tin *o*-semiquinolate adducts as compared to the analogous germanium derivatives. This fact is in good agreement with the known patterns of variations of the element—carbon bond energies in compounds of the IV group: the Ge—C bond energy,[15] as a rule, is higher than that of the Sn—C.

At 90 °C, polymerization of styrene in the presence of germanium and tin bis-catecholates occurs without the gel-effect, the conversion increases to ~80—90% (see Fig. 4, *b*). The total rate of styrene polymerization in the presence of complex **3** is higher than the rate of polymerization involving analogous germanium compounds.

Polymerization of styrene in the presence of compounds **4** and **5** was performed in order to evaluate the role of the quinone ligand composition in the tin bis-catecholate complex. It was found that the presence of both an electron-donating and electron-withdrawing substituents in the quinone ligand leads to a considerable increase in the inhibiting property of tin bis-catecholates. Thus, the highest styrene conversion observed in the presence of complex **4** is lower than in the case when complex **3** is used and is equal to ~30 and ~70% at 70 and 90 °C, respectively (see Fig. 4, *a* and *b*). The rate of styrene polymerization involving complex **5** in the temperature range under study is very low, and even at 90 °C the yield of the polymer is not high: styrene conversion does not exceed 30%.

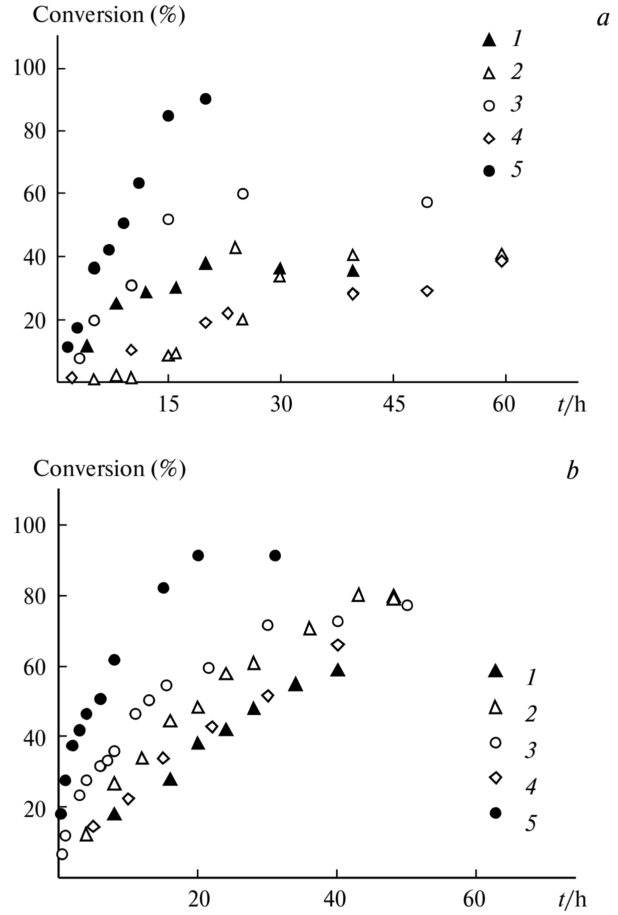


Fig. 4. The dependence of the PS yields from the polymerization time at 70 (*a*) and 90 °C (*b*) in the presence of complexes **1** (*1*), **2** (*2*), **3** (*3*), **4** (*4*) and in the absence of the metal complex (*5*). AIBN (0.1 mol.%) as an initiator, 0.1 mol.% of the complexes added.

Introduction of each from bis-catecholate complexes used leads to the change in the molecular-weight characteristics of obtained PS. The average number molecular weight (MW) of the polymer synthesized in the presence of complexes **1**—**4** at 70 °C proportionally increases with conversion (Fig. 5, *a*), thus indirectly indicating participation of the metal complexes in the propagation step of the styrene polymerization. It is interesting that polydispersity coefficients (M_w/M_n (M_w and M_n are the average weight and average number molecular masses, respectively)) of the PS samples obtained using complexes **1** and **2** are high enough (2.8—3.2), in contrast to such values recorded for the samples obtained with complexes **3** and **4** (~2.0). This can indicate that several parallel processes occur in the reaction system involving germanium bis-catecholate complexes.

At 90 °C, dependencies of MW on conversion for the PS samples synthesized in the presence of germanium and tin bis-catecholates are significantly different. Thus, introduction of complexes **1**, **3**, and **4** into the polymerization system leads to a linear growth in the polymer average number MW with the increase in the conversion (see Fig. 5, *b*).

When complex **2** is used, the polymer average number MW remains virtually unchanged with conversion (~60000).

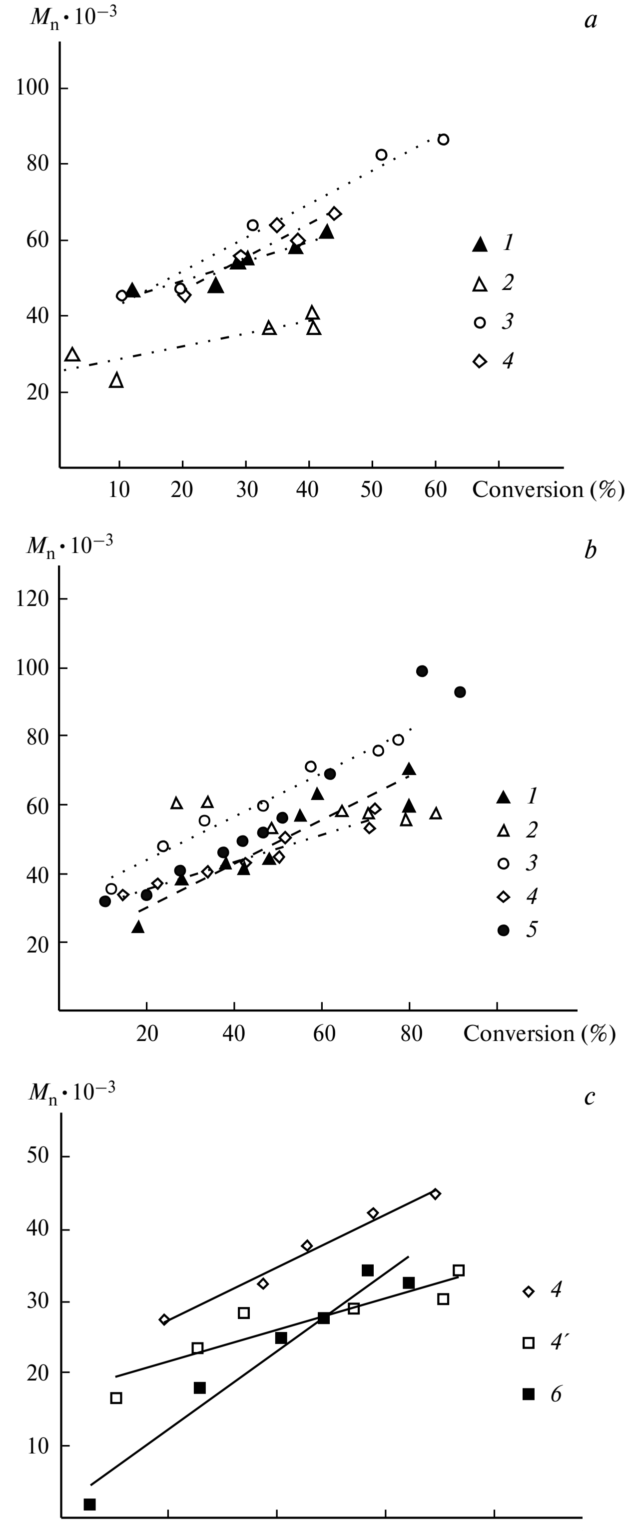


Fig. 5. The dependence of the average number molecular weight of PS (M_n) on conversion at 70 (*a*), 90 (*b*), and 110 °C (*c*) in the presence of complexes **1** (*1*), **2** (*2*), **3** (*3*), **4** (*4*), in their absence (*5*), and without initiator in the presence of complexes **4** (*4′*) and **5** (*6*). AIBN (0.1 mol.%) as an initiator, 0.1 mol.% of the complexes added.

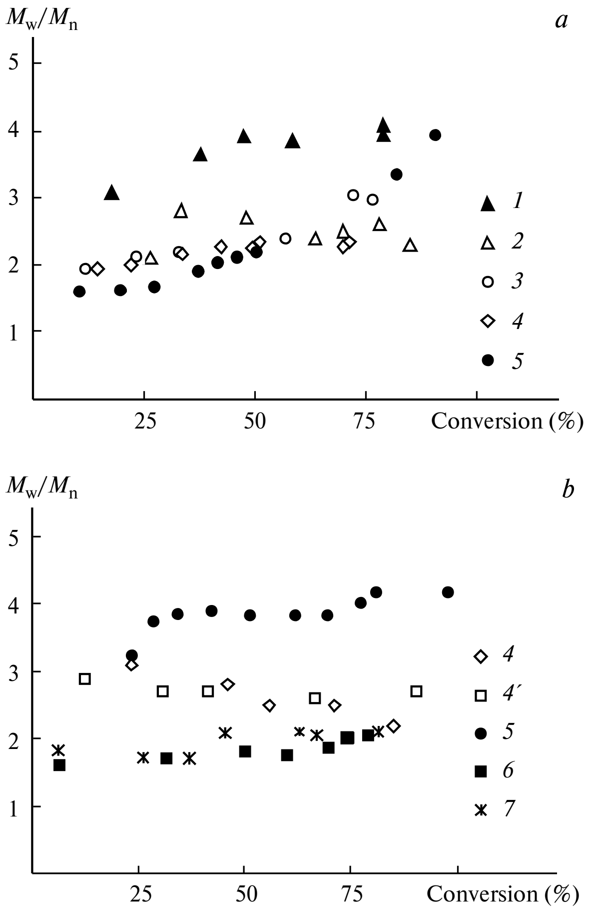


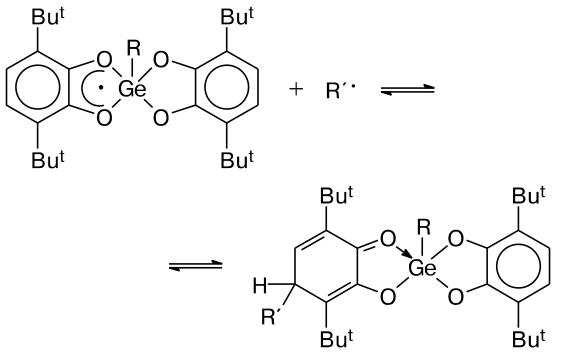
Fig. 6. The dependence of the polydispersity coefficient of PS (M_w/M_n) on conversion at 90 (*a*) and 110 °C (*b*) in the presence of complexes **1** (*1*), **2** (*2*), **3** (*3*), **4** (*4*), in their absence (*5*), without initiator in the presence of complexes **4** (*4′*) and **5** (*6*), and during autopolymerization of styrene (*7*). AIBN (0.1 mol.%) as an initiator, 0.1 mol.% of the complexes added.

It should be noted that the change in temperature from 70 to 90 °C leads to the reduction in the M_w/M_n value for the PS samples obtained in the presence of complex **2** (Fig. 6, *a*). It is obvious that when the temperature is raised, one of the parallel reactions involving complex **2** or its derivatives predominates. In particular, it cannot be ruled out that the reactions of radical species with *o*-semiquinolate adducts **2** acquire reversible character (Scheme 4).

Similar scheme has been suggested earlier[16] to account for the effect of copper(I) *o*-semiquinolate complex on the process of styrene polymerization.

In the reaction system, compounds **4** and **5** form the most stable *o*-semiquinolate derivatives, that allows one to somewhat extend the temperature range of their application. In fact, at 110 °C introduction of complex **4** leads to the reduction in the rate of either polymerization of styrene initiated by AIBN or its autopolymerization. In this case, the presence of complexes **4** and **5** (see Fig. 5, *c*) facilitates a linear growth of the average number MW

Scheme 4



of the polymer with the increase in the conversion of styrene (in contrast to PS obtained by thermal initiation, whose MW remains virtually unchanged and is close to ~230000—250000).

Polydispersity coefficients of the PS samples obtained with complex **4** either in the presence of initiator AIBN or in its absence somewhat decrease with an increase in the monomer conversion (see Fig. 6, *b*). This trend is characteristic of the processes of regulated polymerization.[1—3] In the case when complex **5** was used, the M_w/M_n values agree with those for the polymer obtained by autopolymerization (see Fig. 6, *b*).

The mechanism of chain growth following the scheme of reversible inhibition, in which organometallic compounds can also be included, assumes that the polymer isolated at any step can serve as an initiator of polymerization of a new portion of the monomer.[1—3] In our case, macroinitiators, *i.e.*, *o*-semiquinolate derivatives of the IV group elements bearing a polymeric radical, were obtained by polymerization of styrene involving germanium and tin bis-catecholate complexes (0.1 mol.%) and AIBN (0.1 mol.%).

The experimental data on postpolymerization at 70—110 °C are given in Table 1. The data show that the *o*-semiquinolate adducts of each of the complexes used can initiate polymerization of styrene.

The curves of the molecular-weight distribution (MWD) of polystyrene initiators and obtained postpolymers are unimodal (Fig. 7, *a*), unlike the MWD curves of postpolymers synthesized using tin monocatecholate *o*-semiquinolate derivatives.[9] In this case, the MWD curves of postpolymers are displaced to the region of higher MW with the increase in polymerization time (see Table 1 and Fig. 7, *a*). No considerable changes are observed for the M_w/M_n values of the postpolymer samples, that indicates involvement of virtually entire macroinitiator into the further polymerization.

Postpolymerization of styrene on the germanium *o*-semiquinolate derivatives obtained using complex **2** at

Table 1. Results of postpolymerization of styrene on macroinitiators obtained in the presence of germanium and tin bis-catecholate complexes **1—5**

Complex	Polymer	T/°C	t/h	C_{mi} (wt.%)	Conversion (%)	$M_n \cdot 10^{-3}$	M_w/M_n
1	PS-initiator	90	—	—	28*	42	3.7
	Postpolymer	90	30	22	55	76	4.0
2	PS-initiator	70	—	—	41*	37	2.8
	Postpolymer	70	30	29	5	42	3.1
	Postpolymer	70	60	29	33	50	3.6
	PS-initiator	90	—	—	34*	62	2.7
	Postpolymer	90	15	25	30	59	3.5
	Postpolymer	90	30	25	59	66	3.1
3	PS-initiator	90	—	—	32*	39	2.4
	Postpolymer	90	15	24	9	61	2.8
	Postpolymer	90	30	24	40	73	3.0
4	PS-initiator	70	—	—	38*	60	2.1
	Postpolymer	70	30	28	9	67	2.9
	PS-initiator	90	—	—	43*	43	2.7
	Postpolymer	90	30	30	59	57	2.5
	PS-initiator	110	—	—	46*	38	2.8
	Postpolymer	110	7	32	24	42	3.9
	Postpolymer	110	15	32	43	68	3.4
5	PS-initiator	110	—	—	35*	24	2.0
	Postpolymer	110	8	26	44	70	2.5
	Postpolymer	110	15	26	61	92	2.2

Note. C_{mi} is the concentration of macroinitiator, M_n and M_w are the average number and average weight molecular masses, respectively.

* The conversion of polystyrene used as a macroinitiator.

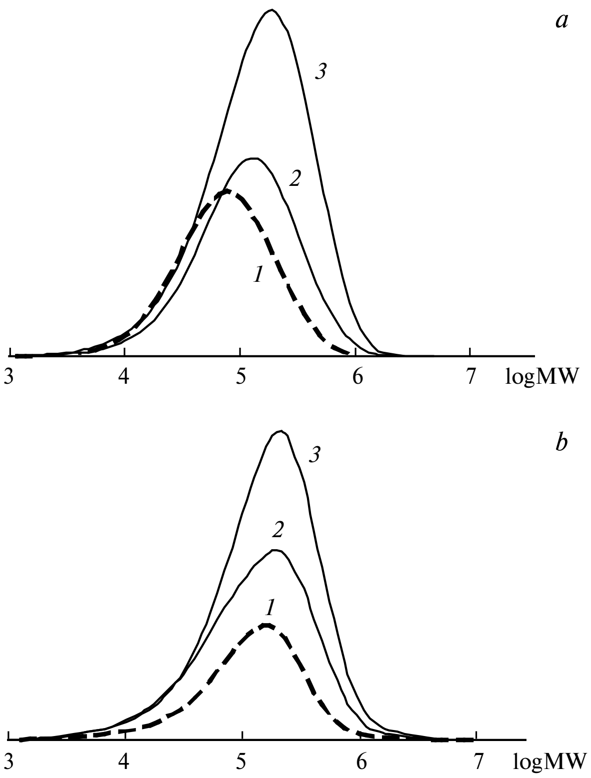


Fig. 7. The curve of MWD of polymers obtained in the presence of complexes **3** (*a*) and **2** (*b*) at 90 °C: PS as initiator (*1*), postpolymers (*2, 3*) at the conversion of styrene introduced into the polymerization system of 9 (*2*) and 40% (*3*) (*a*); 30 (*2*) and 59% (*3*) (*b*).

90 °C is the only exception. In this case, despite a high conversion of styrene, virtually no increase in the MW of postpolymer and displacement of the MWD curves to the high-molecular-weight region are observed with the growth in the conversion (see Fig. 7, *b*). Possibly, this observation is due to a considerable contribution of side reactions involving germanium *o*-semiquinolate derivatives in both the step of generation of macroinitiator and the further postpolymerization.

In conclusion, the ESR data showed that the radicals emerged in the process of styrene polymerization in the presence of tin and germanium bis-catecholate complexes are able to react with the indicated metal complexes to form *o*-semiquinolate derivatives. This ability directly affects kinetic specificities of the polymerization and molecular-weight characteristics of polystyrene. The polymers synthesized can serve as macroinitiators, thus indicating a direct involvement of the nontransition element complexes into the elementary steps of radical polymerization. This involvement can particularly occur by the successive steps of acceptance and elimination of polymeric radicals. The differences in the rates of the synthesis of macromolecules, the average number molecular weights, and polydispersity coefficients of the polymeric samples obtained in the presence of germanium and tin bis-catecholate complexes reflect different accepting ability of the bis-catecholates with respect to the carbon-centered radicals in the monomeric medium, as well as reactivity of the *o*-semiquinolate derivatives formed.

Experimental

Styrene, the initiator, and the solvents were purified by the conventional methods.**[17—20]** Germanium and tin bis-catecholate complexes were obtained according to the procedures described earlier.**[4—8,21—23]** Physicochemical constants of all the compounds agreed with the literature data.

Samples for the studies were prepared as follows: styrene, AIBN, and metal complex in certain ratios were placed into glass tubes, which were thrice degassed, freezing the tubes in liquid nitrogen, to the residual pressure ~1.3 Pa. The tubes with solutions were unsealed and placed into a thermostat for the strictly defined time intervals.

Kinetics of polymerization was controlled by gravimetric method. The polymer samples were purified from the monomer and initiator impurities by double reprecipitation from chloroform, then they were dried at reduced pressure until the weight was constant.

Molecular-weight characteristics of the polymers obtained were determined by GPC.**[24,25]** Chromatographic analysis of polymers was performed on a Knauer apparatus with a linear column (Phenomenex, USA). An RI Detektor K-2301 differential refractometer was used as a detector, THF as an eluent. Polystyrene narrow-dispersed standards were used for the calibration.

Postpolymerization of styrene was carried out according to the procedure described earlier**[10]** based on the initially synthesized polystyrene macroinitiators. The macroinitiators were obtained by polymerization of styrene in the presence of the IV group element catecholate complexes under study (0.1 mol.%) and AIBN (0.1 mol.%) for the time corresponding to ten half-lives of AIBN (this allows one to assume that under such conditions the radical initiator in the system is completely decomposed). Since tin and germanium *o*-semiquinolate derivatives are susceptible to the air oxygen, the macroinitiator was separated from the monomer by lyophilic drying of the solution in chloroform.

ESR spectra were recorded on a Bruker-EMX radiospectrometer (9.75 GHz). Diphenylpicrylhydrazyl ($g = 2.0037$)**[26]** was used as an internal standard to determine the *g*-factor.

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