

Amines as activators of the controlled polymer synthesis in the presence of ruthenacarboranes

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Using polymerization of a series of acrylic monomers of various structure in the presence of ruthenium complexes as an example, it was shown that introduction of amines into the polymerization system allows to overcome one of the significant drawbacks of the controlled polymer synthesis under the radical initiation conditions, connected with the low rate of the polymerization. The influence of the amine nature on the peculiarities of the controlled polymer synthesis in the presence of ruthenacarboranes has been studied and amine was found to act as a reducing agent converting ruthenium in a complex to the lowest oxidation state and regenerating the true polymerization catalyst.

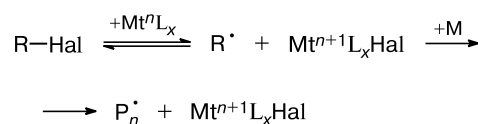
Key words: metallocarborane catalysis, *closo*-ruthenacarboranes, atom transfer radical polymerization, controlled synthesis, polymers, amines, AGET ATRP.

Presently, controlled radical polymerization (CRP) presents one of the high-priority trends in the development of the synthetic chemistry of polymers. It opens the way to obtain a series of various perspective polymer materials having given characteristics, including nanoscale and supramolecular structures.^{1,2} The fundamental distinction of CRP from the processes of a classical radical polymerization is the substitution of a undesired irreversible bimolecular termination by a reversible interaction of the growing macroradical with the agents specially introduced thereto. Among the CRP methods, of special importance is a process proceeding along the mechanism with an atom transfer.^{2–4} This methodology (referred to as Atom Transfer Radical Polymerization, ATRP), is based on the known reaction of the radical addition of alkyl halides to the double bond of alkenes.⁵ As this takes place, the reversible interaction of the growing macroradical (P_n^\bullet) with a metal complex in a highest oxidation state ($Mt^{n+1}L_xHal$) occurs with a halogen atom transfer to the end of the polymer chain and shifting the latter to a sleep mode (Scheme 1).

A wide range of monomers capable of reacting under these conditions, as well as the possibility to perform "tuning" of the metal complex polymerization catalyst through

* Based on the materials of the XXVI International Chugaev Conference on Coordination Chemistry (October 6–10, 2014, Kazan).

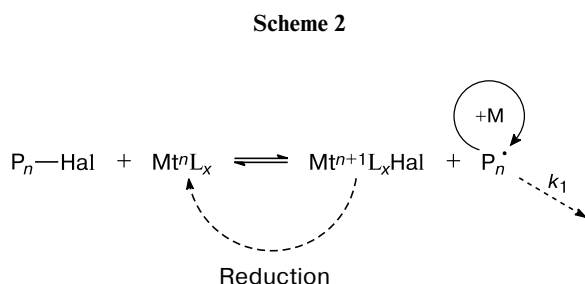
Scheme 1



changing the metal nature and its ligand environment, may be attributed to the benefits of polymerization along the mechanism with an atom transfer.

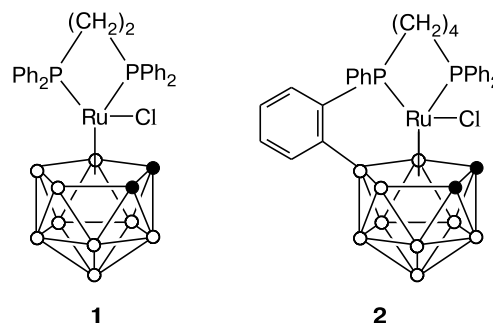
One of the main elements of this "tuning" is the development of effective procedures for controlled radical polymerization based on metal containing catalysts in low concentrations. Investigations in this field are of extreme importance in view of practical application of such systems to obtain polymers with given molecular weight characteristics and structure. Thus, decreasing the catalyst concentration allows one to reduce significantly the costs of the catalyst and of the subsequent purification of the polymer therefrom, however, results in lowering the process rate and the lost of the control, being manifested mainly in an increase in polydispersity indexes of the samples obtained. Therefore, one of the main challenges is the development of effective methods and approaches allowing one to perform the polymerization process with an acceptable rate along with a minimum possible catalyst concentration, as well as the search for optimal ratios of

the catalyst and activator concentrations. One of the possible ways to solve the said problem is the introduction of various reducing agents capable of converting the catalyst to an active form, which favours the increase in the polymerization rate, into the polymerization system comprising the transition metal complexes (Scheme 2).



It has been just this idea which was used as a basis for one of the modern trends of the ATRP, connected with using activators generated by electron transfer (AGET). Today, examples of implementation of this mechanism upon performing the controlled processes in the presence of copper and iron complexes are known.^{6–10} Such regularities are observed also for the processes catalyzed by systems based on ruthenium and amine complexes.^{11–13} Obviously, amines may act as reducing agents in these reactions, however, mechanism of their activating action is presently unknown.

In the present study, we have examined the influence of amines of different structure on the polymerization of a series of methacrylic monomers, namely, methylmethacrylate (MMA), ethylmethacrylate (EMA), isobornylmethacrylate (IBMA) and *tert*-butylmethacrylate (TBMA), in the presence of carborane ruthenium complexes **1** and **2**, and also investigated the reaction between ruthenacarboranes and amines by a cyclic voltammetry (CVA) and ESR techniques.



Results and Discussion

Ruthenacarborane catalysts **1** and **2**, as well as the other carborane complexes of ruthenium, have been successfully used previously in the synthesis of polyMMA in the "living" chain mode,¹⁴ however, like the majority of the CRP, polymerization of MMA in this case was characterized by a low rate. In this connection, it was of importance and urgency to study the possibility of carrying out a controlled synthesis of macromolecules with rates comparable to those of a classical radical polymerization, using low amounts of a catalyst (at a level of hundredths of a percent relative to a monomer) by varying the initiator concentration and introducing the corresponding activating agents.

The samples of polyMMA obtained without introducing amines in the presence of 0.01 mol.% of *closo*-ruthenacarborane catalysts **1** and **2** (Table 1) exhibit polydispersity indices that are relatively high for the CRP processes ($M_w/M_n > 1.5$). This points to an insufficient level of the chain growth control and may be connected with the undesired contribution of a thermal self-initiation of the polymerization (the synthesis proceeds within more than 80 h at 80 °C) and/or processes of the bimolecular chain termination. Absolute values of molecular weights (MM) therewith differ upward from the theoretical values,

Table 1. Dependence of an amine addition and CCl_4 initiation on polyMMA synthesis in the presence of *closo*-ruthenacarboranes **1** and **2** synthesis at 80 °C (component concentrations, mol.%: [ruthenacarborane] = 0.01, CCl_4 = 0.25, [amine] = 0.04).

Ruthenacarborane complex	Amine	Time/h	<i>P</i> (%)	$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-3}$	M_w/M_n
1	No amine	>80	24	73.1	130.1	1.8
	Pr^iNH_2	60	82	32.6	46.6	1.4
	Ph_2NH	80	43	23.8	36.0	1.5
	$\text{C}_5\text{H}_5\text{N}$	80	53	32.3	48.6	1.5
	Ph_2NCH_3	80	41	25.9	40.0	1.5
2	No amine	80	26	11.8	17.6	1.6
	Pr^iNH_2	60	72	24.9	33.8	1.3
	Ph_2NH	80	45	23.2	32.0	1.4
	$\text{C}_5\text{H}_5\text{N}$	80	40	23.0	33.3	1.4
	Ph_2NCH_3	80	41	21.1	29.7	1.4

which also testifies the occurrence of side reactions in the system, differing from the ideal "living" polymerization.

Introduction of amines into the system was found to result in the polymer yield duplication over the given period of time and in a significant increase in the polymerization rate as well as in an increase in the degree of the control over the process being represented as a significant narrowing of the molecular-weight distribution (MWD) of the samples synthesized. Most samples have polydispersity indices (M_w/M_n) of less than 1.5, which is typical of processes proceeding under the controlled mode.^{1–3} It should be noted that the most narrow disperse polymers were obtained using *ortho*-phenylenecycloboronated complex **2** as a catalyst.

Under these conditions, aromatic amines and pyridine proved to be less effective compared to aliphatic amines. The main reason for the different behaviour of the aromatic and aliphatic amines appear to be the conjugation between the lone-electron pair of the nitrogen atom and the aromatic nucleus, as well as the larger size of aromatic substituents compared to their aliphatic analogues, which likely hampers the interaction between an amine and ruthenacarborane catalyst. Since the system based on the complex **2** and isopropylamine proved to be most effective under the above conditions, a detailed study of the polymerization process directed to the determination of the activator optimal concentration, was performed just on this example.

Figure 1 illustrates the monomer conversion versus MMA polymerization time relationship under changes of the amine concentration from 0.04 to 4.0 mol.%. It is evident from the data shown that polymerization occurs evenly without a self-acceleration at any selected concentration of an amine. An increase the amine concentration results in a rise of the polymerization rate. How-

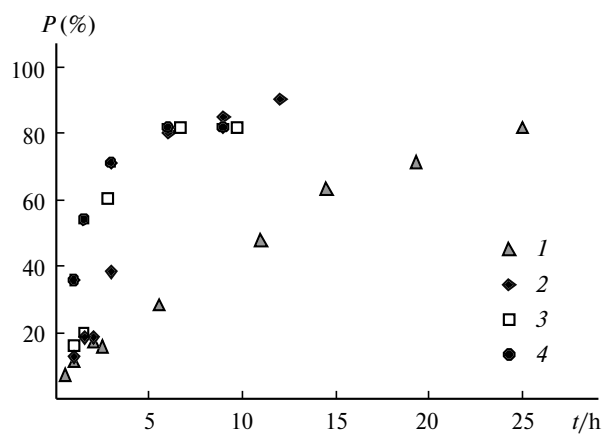


Fig. 1. Monomer conversion-time relationship for the MMA polymerization initiated by the Pr^iNH_2 —complex **2**— CCl_4 system with different amine concentrations at 80 °C. Component concentrations, mol.%: $[\mathbf{2}] = 0.01$; $[\text{CCl}_4] = 0.25$; $[\text{Pr}^i\text{NH}_2] = 0.04$ (**1**), 0.4 (**2**), 0.8 (**3**), 4.0 (**3**).

ever, with using Pr^iNH_2 at a concentration more than 0.4 mol.%, no further growth of the process rate is observed.

MWD curves recorded for the polymer samples obtained are unimodal, the distribution maximum being sequentially shifted to the high molecular weight region with the rise of the monomer conversion degree. Figure 2 depicts relationships of the molecular weight and polydispersity indices of the samples versus the monomer conversion at various concentrations of Pr^iNH_2 . A linear increase of the MW with the rise of the monomer conversion in the presence of an amine at any of the concentrations examined is observed. At the low concentration of the amine there is a good correlation between experimental and theoretical MW values. However, on rising the concentration of Pr^iNH_2 up to 4.0 mol.%, a 1.5-fold excess over theoretical MW value is observed. High activator concentration is likely to result in the formation of a great number of active chains at the polymerization onset thus favouring the increase in the rate and proportion of the irreversible termination. This in turn leads to a decrease in the amount of chains carrying the polymerization and, consequently, to the elongation of the forming chains, *i.e.* to the MW growth. These data correlate well with higher values of the polydispersity indices ($M_w/M_n > 2$) for samples obtained with using activators at a concentration of 4.0 mol.%. Carrying out the process at lower concentrations of Pr^iNH_2 is accompanied by the decreasing of the polydispersity indices at the rise of the conversion, which is typical for the processes of the controlled radical polymerization.

Similar experiments were performed with other methacrylic monomers — analogues of MMA, namely, ethyl-

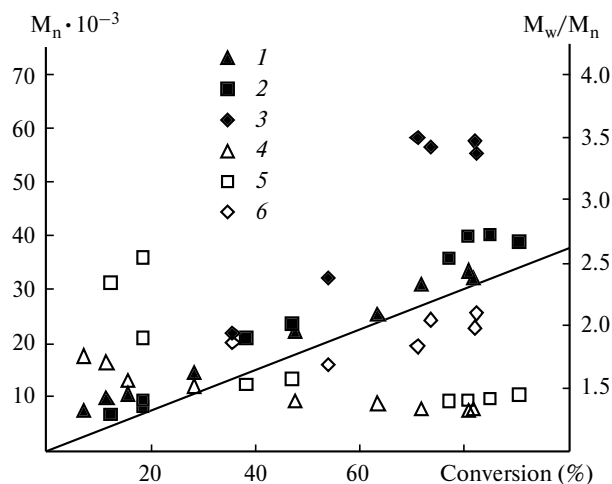


Fig. 2. Number-average molecular weight (M_n , **1–3**) and polydispersity indices (M_w/M_n , **4–6**) dependence for the polyMMA samples obtained with different amine concentrations at 80 °C, of the monomer conversion. Component concentrations, mol.%: $[\mathbf{2}] = 0.01$; $[\text{CCl}_4] = 0.25$; $[\text{Pr}^i\text{NH}_2] = 0.04$ (**1**, **4**), 0.4 (**2**, **5**), 4.0 (**3**, **6**). A straight line is a theoretical MW value.

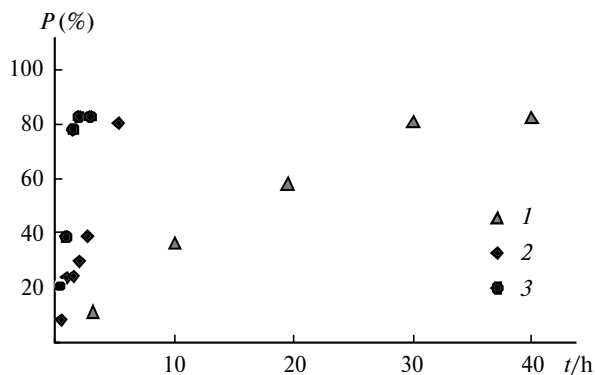


Fig. 3. Conversion-time relationship for the EMA polymerization initiated by Pr^iNH_2 -complex **2**- CCl_4 catalytic system at $T = 80^\circ\text{C}$. Component concentrations, mol.%: $[\text{2}] = 0.01$; $[\text{CCl}_4] = 0.25$; $[\text{Pr}^i\text{NH}_2] = 0.04$ (1), 0.4 (2), 4.0 (3).

methacrylate (EMA), *tert*-butylmethacrylate (TBMA) and isobornylmethacrylate (IBMA). Figure 3 shows the conversion-time relationship for the EMA polymerization. A small induction period is observed in the conversion dependence. Obviously, its appearance is caused by the proceeding of the catalyst activation reaction at the initial stage of the process. It should be noted, that the process of EMA polymerization proceeds with lower rate compared to the above MMA polymerization, being relevant to the values of propagation constants for these monomers.^{15,16}

Consecutively rising the amine concentration from 0.4 to 4.0 mol.% results in an increase of the conversion over the given periods of time, which yet causes the MWD broadening. This is especially evident for the highest concentration of an amine, when polydispersity indices exceed 1.7, and molecular weights of the polymers obtained exceed the theoretical ones, which is explained by the irreversible termination on the initial polymerization stage (Fig. 4).

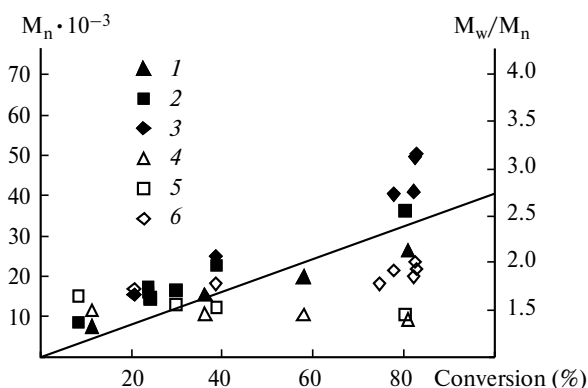


Fig. 4. Number-average molecular weight (M_n , 1–3) and polydispersity indices (M_w/M_n , 4–6) for the PEMA samples obtained with different amine concentrations at 80°C , of the monomer conversion. Component concentrations, mol.%: $[\text{2}] = 0.01$; $[\text{CCl}_4] = 0.25$; $[\text{Pr}^i\text{NH}_2] = 0.04$ (1, 4), 0.4 (2, 5), 4.0 (3, 6). A straight line is a theoretical MW value.

Polymerization of the other methacrylic monomers IBMA and TBMA using the composition based on ruthenacarborane **2** and isopropylamine proceeds without autoacceleration to the high degrees of conversion. The polymers obtained are characterized by unimodal MWD curves. Figure 5 represents the MWD curves of the polymers synthesized, obtained by GPC method, wherein the shift of the distribution maximum to the high molecular weight region on increasing the monomer conversion, is clearly manifested. From the data obtained, it follows that the GPC curves corresponding to the samples analyzed do not show the high-polymeric fractions which suggests the absence of the undesired intermolecular cross-linking during polymerization.

As is seen from the data of the Figure 6, the polymerization is characterized by a linear increase in the polymer MW with the growth of the monomer conversion, which is typical for the CRP processes.^{1–3} It should be noted that experimental values of the number-average MW are slightly different from the theoretical ones calculated on the basis

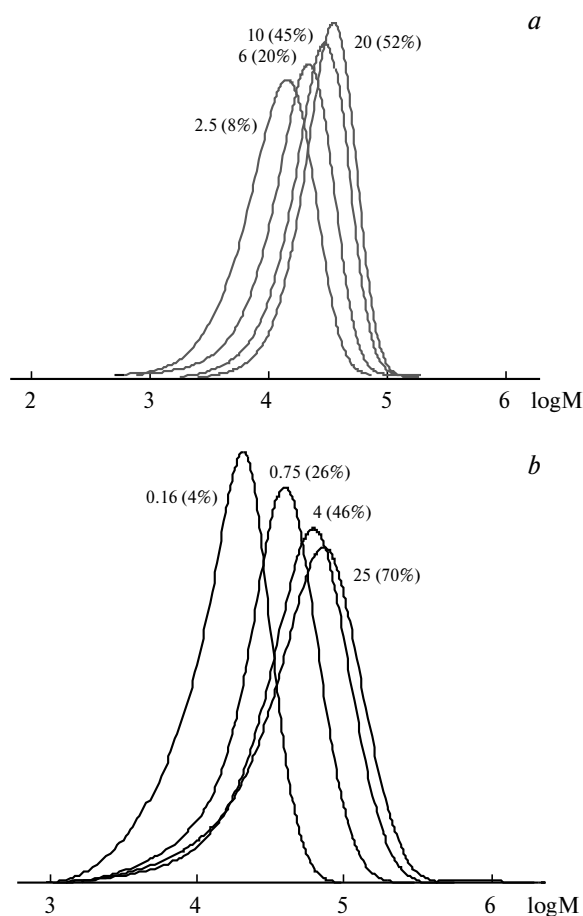


Fig. 5. MWD curves for the PTBMA (a) and PIBMA (b) synthesized in the presence of complex **2** at 80°C . Component concentrations, mol.%: [isopropylamine] = 0.04; $[\text{1}] = 0.01$; $[\text{CCl}_4] = 0.25$. Numbers on the curves—polymerization time (hours), in parentheses—monomer conversion degree.

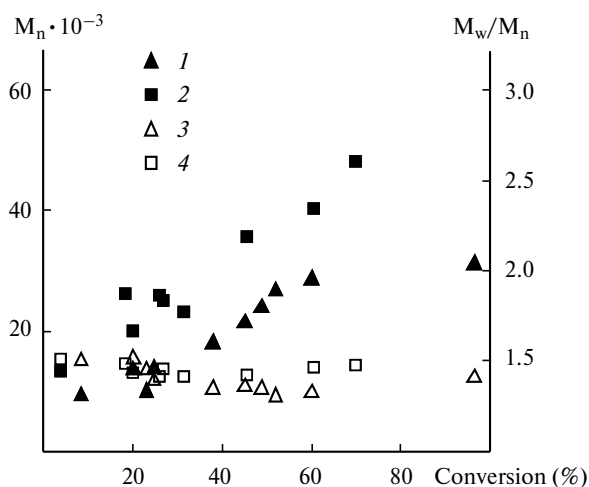


Fig. 6. Number-average MW (M_n , 1, 2) and polydispersity indices (M_w/M_n , 3, 4) dependence for the PTBMA (1, 3) and PIBMA (2, 4) synthesized in the presence of complex **2** at 80 °C, of the monomer conversion. Component concentrations, mol.%: $[CCl_4] = 0.25$; $[2] = 0.01$; $[isopropylamine] = 0.04$.

of an assumption that the polymer chain is generated by one molecule of an initiator. However the above deviation is insignificant and relates to the formation of a "dead" polymer in the system, fitting well the experimental characteristics of the molecular-weight distribution (M_w/M_n) of the samples obtained ranging from 1.3–1.6. Noteworthy is the decrease of the polydispersity index as the conversion rises which is also the feature of a controlled polymerization process.

Polymerization of IBMA under the action of the Pr^iNH_2 —complex **2**— CCl_4 catalytic system proceeds somewhat faster compared to the synthesis of polyTBMA (see Fig. 6). The MW values of the samples obtained increase linearly with an increase of the conversion, however as for the polymerization of TBMA, experimental MW values are lower than theoretically calculated ones. The polydispersity value for the polymers synthesized is about 1.5, being considerably lower than values obtained on polymerizing the same monomer, e.g. with binuclear ruthenium complex $[(1,3,5-Pr^i_3C_6H_3)Ru(\mu-Cl)_3RuCl(C_2H_4)-(PCy_3)]$ (see Ref. 17).

A good evidence for the IBMA polymerization to proceed along the ATRP mechanism is the data derived from the MALDI mass spectrometry technique. The spectrum consists of one set of signals spaced 222 Da apart, corresponding to the IBMA unit. Based on the analysis of the m/z absolute values of the macrocations detected it may be deduced that the macromolecules formed comprise trichloromethyl group in the head and chlorine atom in the tail of the chain. This fact is in full accordance with the proposed mechanism of the polymerization. Thus, the calculated m/z value of the polymer comprising 27 IBMA units of $CCl_3(C_{14}H_{22}O_2)_{27}ClNa$ composition is 6180 Da,

corresponding to the value of 6181 Da, observed in the spectrum.

Thus, the data obtained testify that the introduction of amines into the polymerization system based on *closo*-ruthenacarborane **2** increases significantly the polymerization rate of the methacrylic monomers. In this case, a linear increase of the molecular weight correlates well with theoretical values and results of MALDI-mass spectrometry analysis of the polymers gives an additional confirmation to the ATRP mechanism of the process.

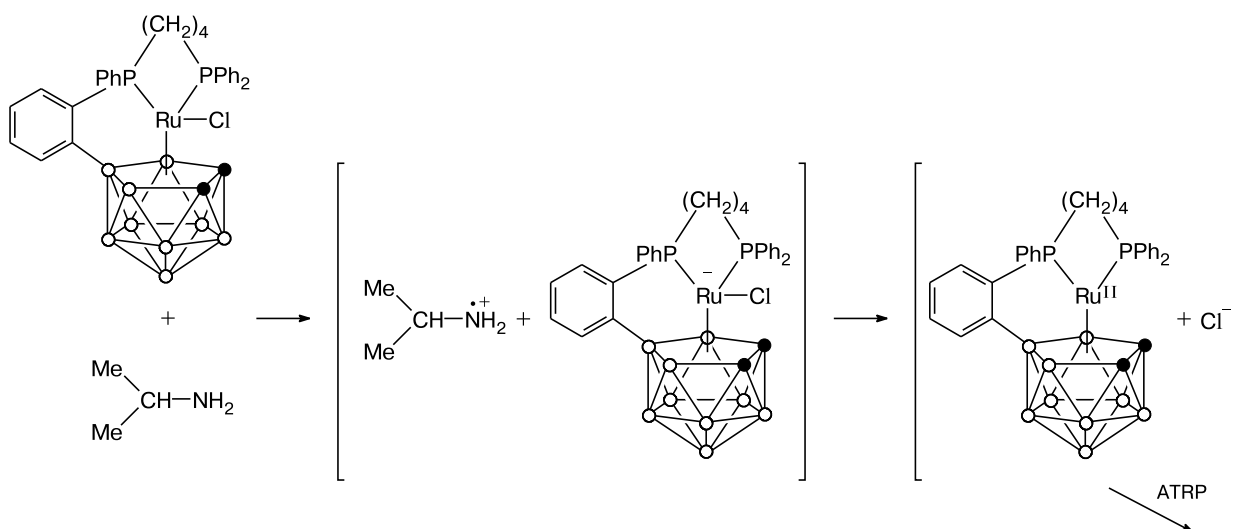
The results of our experiments suggest that amines are effective activators of the controlled radical polymerization catalyzed by carborane ruthenium complexes. The behaviour observed is similar to that typical for the polymerization proceeding along the AGET ATRP mechanism. Thus, under that logic, in the systems under consideration, an amine acts to transform the ruthenacarborane catalyst to an active form wherein the metal atom has the oxidation state of +2. Amines are known to be reducing agents and under certain conditions may readily undergo oxidation. Thus, in a series of papers,^{18–21} oxidation of amines by chloride oxide, permanganate anion and a number of other oxidizing agents was examined in details. In the above reactions, an initial stage of the process is the one-electron oxidation of an amine affording the nitrogen-containing cation-radical. In the above system, on polymerizing methacrylic monomers in the presence of amines, one-electron reduction of the parent Ru^{III} complex takes place yielding an active anion-radical and subsequently, the 16-electron Ru^{II} complex; the latter catalyzes the ATRP polymerization according to the Scheme 3 given below.

It should be noted, that some examples of the reduction of ruthenium(III) compounds by aliphatic amines including that in the course of catalytic cycles^{22,23} has been described earlier, however for the carborane ruthenium complexes and the other metallocarboranes such variant is considered for the first time.

To confirm experimentally the mechanism proposed by us we used the ESR method and cyclic voltammetry (CV). Figure 7 illustrates an anisotropic ESR spectrum of the paramagnetic complex **2** measured in the solid toluene—methylene chloride matrix. The ESR spectrum of the sample obtained after heating the complex **2** with isopropylamine shows no signal suggesting the formation of a diamagnetic ruthenium complex in the system. Unfortunately, an extremely low stability gives no possibility to isolate the reaction product in the individual state and to unambiguously identify it in the solid state.

Electrochemical study of the reaction of the complex **2** with isopropylamine also provides evidence for the formation of diamagnetic products during the course thereof. Figure 8 presents cyclic voltammograms measured for the complex **2** in 1,2-dichloroethane solution before and after adding isopropylamine into the system. From the previous data it follows that for the starting complex **2** a reversible

Scheme 3



transition corresponding to the reduction of the Ru^{III} complex to the Ru^{II} one is observed.²⁴ Introduction of an amine into the system results in a decrease of the intensity of the

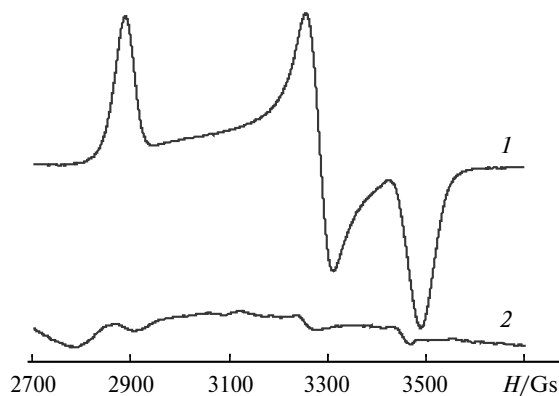


Fig. 7. Anisotropic ESR spectra measured at 150 K in toluene: 1 is pure complex 2; 2 is a sample of the complex 2 and Pr³NH₂ after heating.

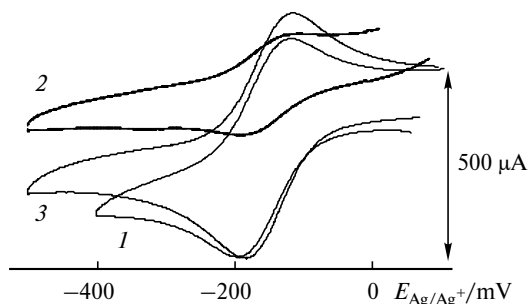


Fig. 8. Cyclic voltammograms measured for the initial complex 2 (1) in 1,2-dichloroethane and after amine (2), carbon tetrachloride (3) addition.

signal corresponding to the reductive transition of the complex 2, suggesting its reduction by the amine. On adding an equimolar amount of CCl₄ to the system, a reduction peak reappears on the CV curve which may result from the regeneration of the starting complex.

Thus, on the basis of the experimental results and the literature data analysis, it may be deduced that polymerization of methacrylic monomers in the presence of *closo*-ruthenacarborane catalysts and amines proceeds via a AGET ATRP mechanism. The true catalysts of the process therewith are particles containing bivalent ruthenium. During the study, the most effective in terms of the control of the process and its rate was shown to be the use of an excess of amine in 40 : 1 ratio relative to the catalyst. Proposed catalytic systems based on carborane complexes of ruthenium and amines show high potency in the controlled radical polymerization of methacrylic esters of various structure, allowing their application for the synthesis of homo- and copolymers with given molecular-weight characteristics.

Experimental

Closo-ruthenacarboranes used were synthesized according to the previously reported procedure^{25,26} under argon atmosphere. All the solvents used for dissolution and precipitation of polymers were thoroughly dried and distilled prior to use. Monomers (Sigma) were distilled *in vacuo* immediately prior to use. 0.1 M solution of CCl₄ in toluene was used as a polymerization initiator. Physical and chemical constants of all the compounds used in the present work correspond to the literary data.

The method of sample preparation and carrying out the polymerization is described in the study.¹² Molecular weight characteristics of the polymers were determined by the gel-permeation chromatography (GPC) in THF solution on Knauer apparatus

having a cascade of two columns (Phenomenex, Phenogel with the pore size of 10^3 and 10^5 Å). The apparatus was calibrated using narrow disperse polyMMA standards (Waters) having number average MW values (M_n) from 0.4 to 2000 kDa. The MW values of the polymers were determined with regard to the universal calibration according to the Mark—Kuhn—Houwink equation. Upon calculation, the following constants were used: $K = 7.5 \cdot 10^{-3}$, $a = 0.72$ (for polyMMA²⁷); $K = 3.8 \cdot 10^{-3}$, $a = 0.748$ (for polyIBMA²⁸); $K = 5.84 \cdot 10^{-3}$, $a = 0.76$ (for polyTBMA²⁹); $K = 9.7 \cdot 10^{-3}$, $a = 0.714$ (for polyEMA³⁰). The analysis of polymers by the MALDI-TOF mass spectrometry was performed in a linear mode on a «Bruker Microflex LT» apparatus using DCTB as a matrix according to a previously reported procedure.¹² ESR-studies were performed on a «Bruker EMX» apparatus. Electrochemical experiments were carried out by cyclic voltammetry in a three-electrode cell with platinum electrodes using a potentiostat IPC Pro. Tetrabutylammonium tetrafluoroborate was used as a supporting electrolyte; potentials measurements were made with respect to the silver pseudoelectrode.²⁴

The authors show appreciation to A. V. Piskunov (IOMC RAS) for the ESR measurements.

The work was financially supported by the Ministry of Education and Science of the Russian Federation (project No 736).

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Received February 2, 2015;
in revised form March 30, 2015