

# Effect of Amines on the Controlled Synthesis of Poly(methyl methacrylate) Catalyzed by Ruthenacarboranes

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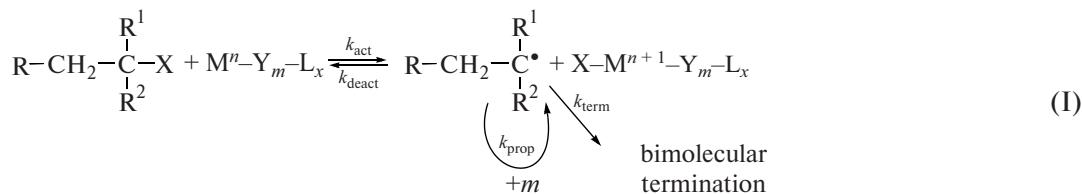
**Abstract**—The effects of amines on the activity of ruthenium catalysts in the controlled synthesis of poly(methyl methacrylate) are reported at 80°C. The introduction of *tert*-butylamine or triethylamine into the polymerization system raises the polymerization rate by 1–2 orders of magnitude without reducing the high degree of control over the chain propagation step. The “living” character of methyl methacrylate polymerization in the presence of ruthenacarboranes and amines is proved by the fact that, as the monomer conversion increases, the molecular weight of the resulting polymer increases linearly and the polydispersity index decreases. The polymer can serve as a macroinitiator for postpolymerization and block copolymer synthesis.

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The basic lines of advance of synthetic macromolecular chemistry are aimed at obtaining new polymers with better chemical and physicomechanical properties. One way of solving this problem by radical polymerization methods is by synthesizing polymers in the presence of a transition metal complex that can control chain propagation via the atom transfer radical polymerization (ATRP) mechanism [1, 2].

This approach is based on the well-known metal complex–catalyzed radical addition of alkyl halides to the double bond of olefins. This reaction was discov-

ered as early as the middle of the 20th century [3]. The recently suggested catalytic compositions based on complexes of various transition metals, including copper [4], nickel [5], iron [6], rhodium [7], molybdenum [8], palladium [9], and ruthenium [10–18], have opened up wide opportunities for controlled syntheses of macromolecular compounds using this reaction. The central metal atom in these metal complexes can react readily and, most importantly, reversibly with alkyl halides to yield carbon-centered radicals capable of participating in polymerization:



where  $M^n$  is a transition metal in the oxidation state  $n$ ,  $X$  and  $Y$  are chloride or bromide anions, and  $L$  is an organic ligand.

According to the literature [1, 2, 4], the rate of controlled radical polymerization depends on the ratio between the “dormant” and active chain times. In turn, this ratio is determined by the ratio between the activation and deactivation rate constants ( $k_{act}/k_{deact}$ , reaction (I)). At the same time, the molecular weight distribution (MWD) of the resulting polymer narrows

with a decreasing ratio of the propagation rate constant to the reversible termination rate constant ( $k_{prop}/k_{deact}$ ) [19]. Therefore, for an ATRP catalyst to be efficient, ensuring a high process rate at a small polydispersity index, it must cause rapid exchange between growing and dormant chains, thus maintaining a low concentration of growing macroradicals in the polymerization system.

Ruthenium compounds were among the first ATRP catalysts [10]. A rather large number of ruthe-

nium complex catalysts are known at present. They contain phosphine [10], cyclopentadienyl [14, 15], or carborane [12, 13] ligands and are used in the controlled synthesis of polymers.

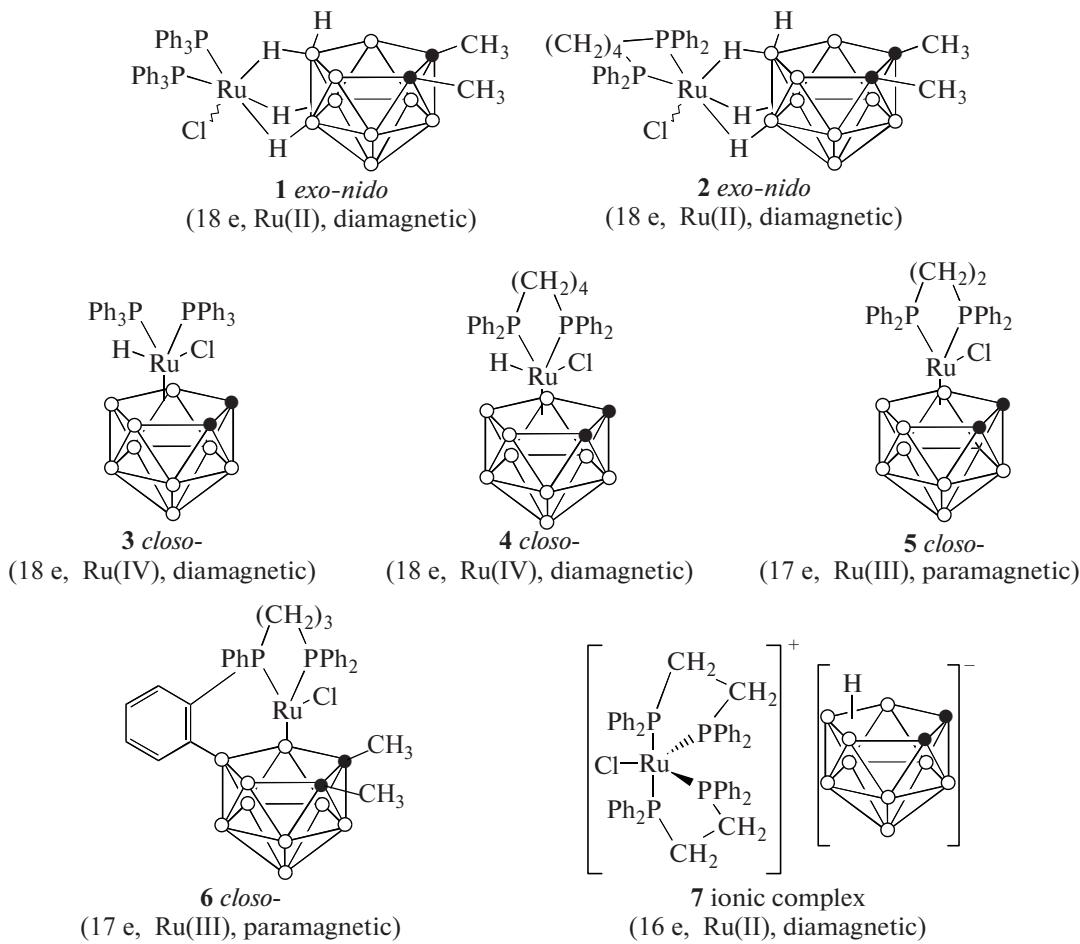
Interesting initiating systems based on ruthenium carborane complexes have recently been suggested for polymer synthesis by ATRP and reverse ATRP mechanisms [20, 21]. Ruthenacarboranes are more active than the cyclopentadienyl derivatives of ruthenium and do not require any Lewis acid cocatalyst. However, the rates of the controlled polymerization of methyl methacrylate (MMA) and styrene in the presence of ruthenacarboranes are low as compared to the rate of classical radical polymerization.

Note that the low rate, which is among the main drawbacks of “pseudoliving” radical polymerization, prevents commercialization of this process [1, 2, 4]. Because of this, one of the most challenging problems

of the synthetic chemistry of polymers is to accelerate polymerization and, at the same time, retain the high degree of control over the MWD.

It was demonstrated by the example of cationic carbene complexes of ruthenium [22] that amine admixtures increase the rates of controlled MMA and styrene polymerizations. The polydispersity of the resulting polymers remains at a level of 1.34–1.79, which is much lower than the values attained with azo compounds and peroxides—conventional radical initiators.

Here, using *tert*-butylamine and triethylamine as examples, we report the effect of nitrogen-containing compounds on the kinetics of the radical polymerization of MMA and the molecular weight characteristics of polymers synthesized in the presence of ruthenium carborane complexes (**1–7**):



## EXPERIMENTAL

The solvents to be used in macromolecule synthesis were dried over calcined calcium chloride and distilled. The physicochemical constants of the purified

solvents were in agreement with the reference data [23]. MMA was washed with 10% aqueous alkali to remove the inhibitor and then with distilled water until neutral to remove the alkali. Next, it was dried over calcium chloride and was purified by vacuum distilla-

**Table 1.** Effect of amines on the monomer conversion in MMA polymerization in the presence of ruthenium carborane complexes and carbon tetrachloride

Complex	Synthesis conditions					
	without an amine		with triethylamine		with <i>tert</i> -butylamine	
	time, min	conversion, %	time, min	conversion, %	time, min	conversion, %
<b>1</b>	4800	98	140	89	140	99
<b>2</b>	540	74	370	91	140	99
<b>3</b>	2700	88	370	87	140	97
<b>4</b>	6600	83	830	97	140	97
<b>5</b>	12000	39	370	91	140	95
<b>6</b>	6600	70	490	69	490	99
<b>7</b>	6600	71	140	99	140	99

Note: The reaction temperature is 80°C. Concentrations (mol %): ruthenacarborane, 0.125; CCl<sub>4</sub>, 0.25; amine, 0.500.

tion to collect the fraction with a boiling point of 38°C at 15 Torr [24]. Freshly distilled amines predried over solid potassium hydroxide were used in the reaction. The physicochemical constants of triethylamine and *tert*-butylamine were in agreement with reference data [25]. Carbon tetrachloride was used as the initiator of polymerization.

Appropriate amounts of the monomer, initiator, and catalyst (ruthenacarborane) were placed in a glass tube and were outgassed three times by freezing in liquid nitrogen. Thereafter, polymerization was performed at a residual pressure of 1.3 Pa. The polymerization kinetics was monitored gravimetrically at a constant temperature. After a strictly preset period of time, the ampule was withdrawn from the thermostat and the contents were frozen in liquid nitrogen to terminate polymerization. The resulting polymer was transferred into petroleum ether. To remove the residual monomer, initiator, and catalyst, the polymer was precipitated twice and was vacuum-dried to constant weight. Next, the MMA conversion was calculated. Postpolymerization was carried out in the same way.

The molecular weight characteristics of the polymers were determined by gel permeation chromatography (GPC) using a Knauer system (Germany) with a linear column (Phenomenex, USA). The detector was a differential refractometer (RI Detector K-2301). The eluent was chloroform. Calibration was carried out using a set of narrow-dispersion polyMMA standards in the molecular weight range from 2580 to  $9.81 \times 10^5$  (Waters). Chromatographic data were interpreted using the ChromGate program package.

Complexes **1–7** were synthesized from triphenylphosphine, 1,3-bis(diphenylphosphino)propane, and 1,4-bis(diphenylphosphino)butane (Strem Chemicals) via earlier reported procedures [20, 21, 26, 27] in an

argon atmosphere using absolutely dry solvents. The products were isolated and purified by column chromatography using silica gel (Merck, 230–400 mesh).

## RESULTS AND DISCUSSION

Amines markedly accelerate MMA polymerization in the presence of ruthenacarboranes. In particular, they shorten the maximum conversion time and raise the maximum polymer yield (Table 1). Note that this effect is observed in the presence of both *clos*o- and *exo-nido*-ruthenacarboranes. In nearly all cases, *tert*-butylamine, the most effective activator, ensures ~100% monomer conversion in a time shorter than 2.5 h.

It is very important for practice that the introduction of an amine into the polymerization system has a significant effect not only on the polymerization kinetics and polymer yield, but also on the molecular weight characteristics of the resulting polymer (Table 2). The strongest effect is observed when *exo-nido*-ruthenacarboranes are used as the catalyst. As follows from the data presented here, the polyMMA samples synthesized in the presence of ruthenacarboranes **1** and **2** in the absence of amines have polydispersity indices that are rather high for living polymerization. This is evidence that chain propagation is controlled to an insufficient extent. This can be due to the unfavorable contribution from thermal polymerization (the reaction proceeds at 80°C for a long time). The amines as activators of metal complexes **1** and **2** substantially shorten the polymerization time and make the MWD much narrower (Table 2). This is accompanied by a decrease in the absolute value of the molecular weight of the polymer.

Thus, the amines enhance the effectiveness of the *exo-nido*-carboranes as chain propagation controllers in radical polymerization.

Adding the amines to *closo*-ruthenacarboranes leads to a slightly broader MWD of polyMMA as compared to that observed in the absence of a nitrogen-containing compound. However, the polydispersity indices of most of the resulting samples are below or near 1.5, indicating that the process is controlled. Note that the polymers with the lowest polydispersity index were obtained with complexes **4** and **5** as catalysts, which are the most effective chain propagation controllers in the absence of amines as well.

In MMA polymerization in the presence of amines and complex **7**, which has an ionic structure, we observed the largest  $M_w/M_n$  values. At the same time, it is the complex that affords the most significant increase in the molecular weight of the polymer relative to the molecular weight observed in the absence of an amine (Table 2).

It was demonstrated by the example of *closo*-ruthenacarboranes that the possibility of controlling the MWD depends on steric factors. A comparison between the MWDs of the polyMMA samples obtained in the presence of compounds **3** and **4** suggests that the linking of the phosphine ligands by methylene groups is sterically most favorable for chain propagation control.

Of special interest is the effect of amines on MMA polymerization in the presence of 17-electron complexes. In the absence of an amine, the process occurs very slowly and stops at a low conversion. This is particularly true for compound **5**, with which the ultimate conversion does not exceed 40%. In the presence of an amine and ruthenacarborane **5**, the MMA conversion is close to 100%. Furthermore, this conversion is reached in a very short time (slightly longer than 2 h). It is particularly remarkable that the MWD of the polymers obtained in the presence of **5** remains very narrow ( $M_w/M_n \leq 1.3$ ).

The living character of MMA polymerization in the presence of the amines and ruthenacarboranes examined is proved by the linear dependence of

$\ln \frac{[M]_0}{[M]}$  on the reaction time (Fig. 1) and by the polymer molecular weight increasing linearly with increasing conversion (Fig. 2). Furthermore, a comparison between MWD curves obtained by GPC suggests that, as the MMA conversion increases, the mode shifts to higher temperatures and the MWD narrows (Fig. 3), which is typical of controlled radical polymerization processes [1, 2].

Further evidence of living polymerization occurring in the presence of the amines and ruthenium carborane complexes was provided by experimental data on MMA postpolymerization catalyzed by the ruthenacarborane **4** + *tert*-butylamine system. The initiator in these experiments was polyMMA synthesized under

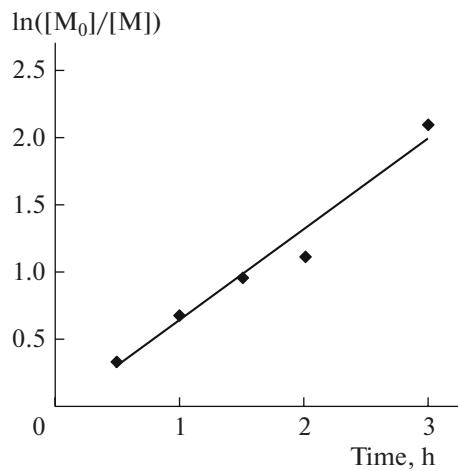
**Table 2.** Molecular weight characteristics of the polyMMA samples obtained in the presence of a ruthenium carborane complex, carbon tetrachloride, and an amine

Complex	Conversion, %	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_w/M_n$
Without an amine				
<b>1</b>	98	51.9	100.2	1.93
<b>2</b>	74	104.9	279.7	2.67
<b>3</b>	88	36.2	58.9	1.62
<b>4</b>	83	26.8	33.6	1.25
<b>5</b>	39	17.6	21.7	1.23
<b>6</b>	70	41.9	57.4	1.37
<b>7</b>	71	29.8	44.9	1.50
In the presence of triethylamine				
<b>1</b>	89	29.9	45.4	1.52
<b>2</b>	91	38.6	60.4	1.56
<b>3</b>	87	34.8	54.5	1.57
<b>4</b>	97	26.5	38.0	1.44
<b>5</b>	91	24.9	32.3	1.30
<b>6</b>	69	29.9	43.7	1.46
<b>7</b>	99	40.1	70.0	1.73
In the presence of <i>tert</i> -butylamine				
<b>1</b>	99	36.8	57.0	1.55
<b>2</b>	99	37.6	56.8	1.51
<b>3</b>	97	40.5	68.9	1.70
<b>4</b>	97	19.2	25.9	1.35
<b>5</b>	95	18.3	23.6	1.29
<b>6</b>	99	35.8	53.5	1.50
<b>7</b>	99	41.2	67.0	1.63

Note: The reaction temperature is 80°C. Concentrations (mol %): ruthenacarborane, 0.125;  $\text{CCl}_4$ , 0.25; amine, 0.500.

the above-described conditions (Table 1), purified from catalyst traces, and dried. After a new portion of the monomer, metallacarborane **4**, and the amine were added to the macroinitiator (polyMMA), the polymerization process resumed. The MWD mode of the resulting postpolymer was shifted to larger molecular weights (Fig. 3).

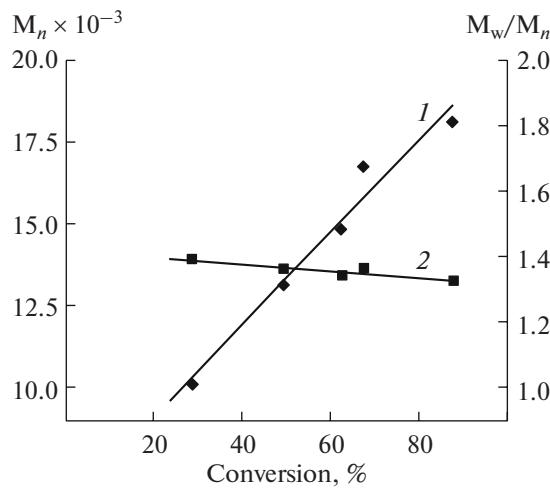
Note that, in some cases, the polydispersity index of polyMMA synthesized in the presence of a ruthenacarborane and an amine (Table 2) exceeds the critical level for controlled radical polymerization ( $M_w/M_n \approx 1.5$ ). As was noted above, this is likely due to the fact that the



**Fig. 1.**  $\ln([M_0]/[M])$  as a function of the time of MMA polymerization in the presence of complex **4**,  $\text{CCl}_4$ , and *tert*-butylamine at  $80^\circ\text{C}$ .

controlled living polymerization (main process) is accompanied by ordinary (uncontrolled) free-radical MMA polymerization occurring in the system owing to thermal activation at  $80^\circ\text{C}$ . At the same time these  $M_w/M_n$  values are far below the polydispersity indices of the polyMMA samples resulting from MMA polymerization in the same temperature range in the presence of peroxides or azo compounds as initiators ( $M_w/M_n > 2$ ) [28]. They are practically equal to the polydispersity indices of the samples obtained by living polymerization in the presence of other ruthenium complexes at a much lower process rate and a much lower ultimate conversion [10, 22].

For *closo*-ruthenacarboranes **4**–**6** as examples, we evaluated the effect of the amine-to-ruthenacarborane ratio on the synthesis of the macromolecules. As follows from our data (Table 3), varying the amine concentration between 0.125 mol % (which is equivalent to the amount of ruthenacarborane in the monomer mixture) and 0.500 mol % does not exert any signifi-



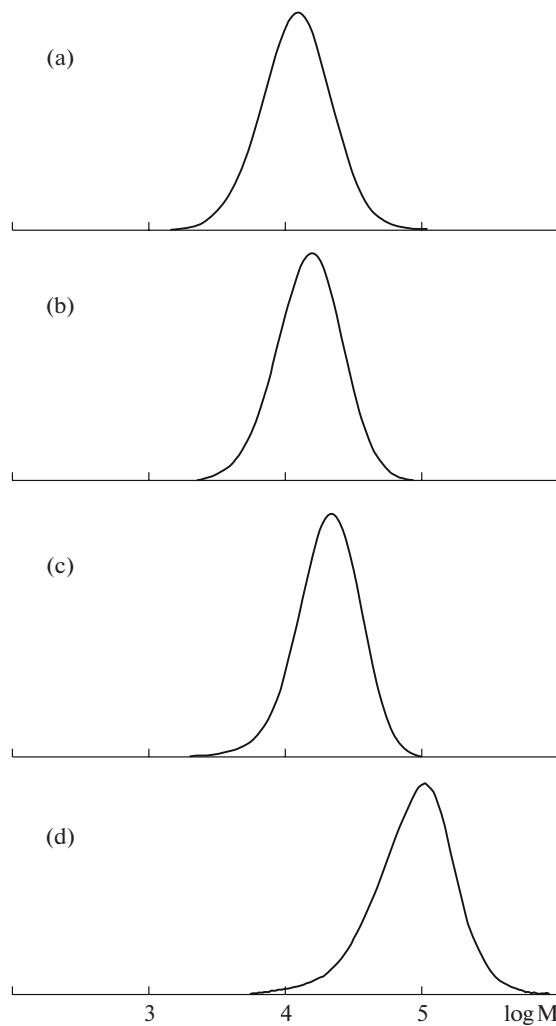
**Fig. 2.** (1) Number-average molecular weight  $M_n$  and (2) polydispersity index  $M_w/M_n$  as a function of the MMA conversion for polyMMA samples synthesized in the presence of complex **4**,  $\text{CCl}_4$ , and *tert*-butylamine at  $80^\circ\text{C}$ .

cant effect on the polymerization rate or the molecular weight characteristics of the resulting macromolecules. Within the experimental error, the polydispersity index (which is among the main measures of the degree of control of polymerization [1, 2]) is independent of the amine concentration in the above-specified range. These data in combination with the molecular weights of the samples synthesized at various amine concentrations indicate that the amine is not involved in the chain transfer step. This inference is confirmed by the fact that the primary amine (*tert*-butylamine), whose mobile hydrogen atoms at the nitrogen atom ensure a high chain transfer rate constant, and the tertiary amine (triethylamine), which has no mobile hydrogen atoms, exert nearly equal effects on MMA polymerization in the presence of the ruthenacarboranes. It is likely that the role of the amine is limited to the following: its molecule interacts with the ruthenacarborane in a 1 : 1 ratio and occupies a certain place in the coordination sphere of

**Table 3.** Effect of the *tert*-butylamine concentration on the monomer conversion and on the molecular weight characteristics of polyMMA

Complex	Amine concentration, mol %								
	0.125			0.250			0.500		
	conversion, %	$M_n \times 10^{-3}$	$M_w/M_n$	conversion, %	$M_n \times 10^{-3}$	$M_w/M_n$	conversion, %	$M_n \times 10^{-3}$	$M_w/M_n$
<b>4</b>	67	19.6	1.38	71	18.4	1.36	67	16.7	1.36
<b>5</b>	77	18.6	1.33	84	18.2	1.33	79	19.0	1.32
<b>6</b>	31	18.0	1.64	36	19.4	1.61	30	15.2	1.57

Note: The reaction temperature is  $80^\circ\text{C}$ . The synthesis time is 2 h. Concentrations (mol %): ruthenacarborane, 0.125;  $\text{CCl}_4$ , 0.25.



**Fig. 3.** MWD curves for polyMMA samples synthesized in the presence of complex **4**,  $\text{CCl}_4$ , and *tert*-butylamine at  $80^\circ\text{C}$ : (a) 28.6% conversion,  $M_n = 10.1 \times 10^3$ ,  $M_w/M_n = 1.39$ ; (b) 49.2% conversion,  $M_n = 13.1 \times 10^3$ ,  $M_w/M_n = 1.36$ ; (c) 87.6% conversion,  $M_n = 18.1 \times 10^3$ ,  $M_w/M_n = 1.34$ ; (d) postpolymer,  $M_n = 69.3 \times 10^3$ ,  $M_w/M_n = 1.54$ .

ruthenium. This is favorable for the transfer of a halogen atom to the metal center. Eventually, this accelerates the controlled synthesis of macromolecules. It can be assumed that the active complex responsible for the generation of radicals and for the controlled synthesis of macromolecules forms just in polymer synthesis (*in situ*). It soon enters into the chemical reaction with  $\text{CCl}_4$  according to the scheme described in [20] to yield polyMMA with a comparatively low polydispersity index.

Thus, the use of the ruthenacarborane-based compositions in combination with amines in the presence of  $\text{CCl}_4$  markedly raises the efficiency of the ruthenium carborane complexes in the controlled synthesis of macromolecules. The processes involving amines

yield polymers with a comparatively low polydispersity index and proceed at an exceptionally high rate for controlled radical polymerization up to  $\sim 100\%$  conversion.

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