

Methyl Methacrylate Polymerization Involving a Cobalt *ortho*-Iminobenzosemiquinone Complex: Determination of the Chain Transfer Constant

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Abstract—We studied the effect of bis[4,6-di-*tert*-butyl-*N*-(2,6-dimethylphenyl)-*ortho*-iminobenzosemiquinono]cobalt(II) on the kinetics of the bulk polymerization of methyl methacrylate at 70°C and on the molecular-weight characteristics of the polymer synthesized. The effective chain transfer constant in the polymerization of methyl methacrylate in the presence of the complex in benzene at 70°C was determined by the Mayo method and by linearizing the macromolecule chain length distribution. The constants obtained were compared with the same parameters available from the literature for a number of known chain-transfer agents, viz., dodecyl mercaptan and cobalt porphyrin and oxime complexes.

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One of the topical problems faced by modern macromolecular chemistry is that of designing novel promising methods for the synthesis of polymers with tailor-made characteristics and properties. In this context, in recent decades the conception of controlled free-radical polymerization catalyzed by metal complexes has been actively developed. This polymerization allows preparation of polymers having definite values of molecular weight (MW) and polydispersity, as well as macromolecular design and creation of polymers with certain topology (synthesis of block, branched, and comb- and star-shaped polymers, dendrimers, etc.) [1–9].

For this purpose, various catalytic and initiating systems based on the transition and nontransition elements, including cobalt complexes [1, 2, 5–7], are used. Polymerization of a wide range of monomers in the presence of cobalt complexes with different ligand environments proceeds via different mechanisms, including catalytic chain transfer (CCT) [10–13], reversible inhibition (RI) with cobalt–carbon bonding (also referred to as cobalt mediated radical polymerization) [6, 14], and degenerate chain transfer (DCT) polymerization [6, 15, 16]. Of great importance for any given polymerization mechanism to be realized is not only the structure of the metal complex, but also the nature of monomer. The monomer nature effect is most pronounced in the case of polymerization involving cobalt porphyrin, oxime, and acetylacetonato complexes. For such monomers as vinyl acetate, acrylonitrile, and various acrylates, the typical mechanism is either degenerate chain transfer or reversible inhibition. Methyl methacrylate (MMA), α -methylstyrene, and methacrylonitrile tend to chain transfer by hydrogen

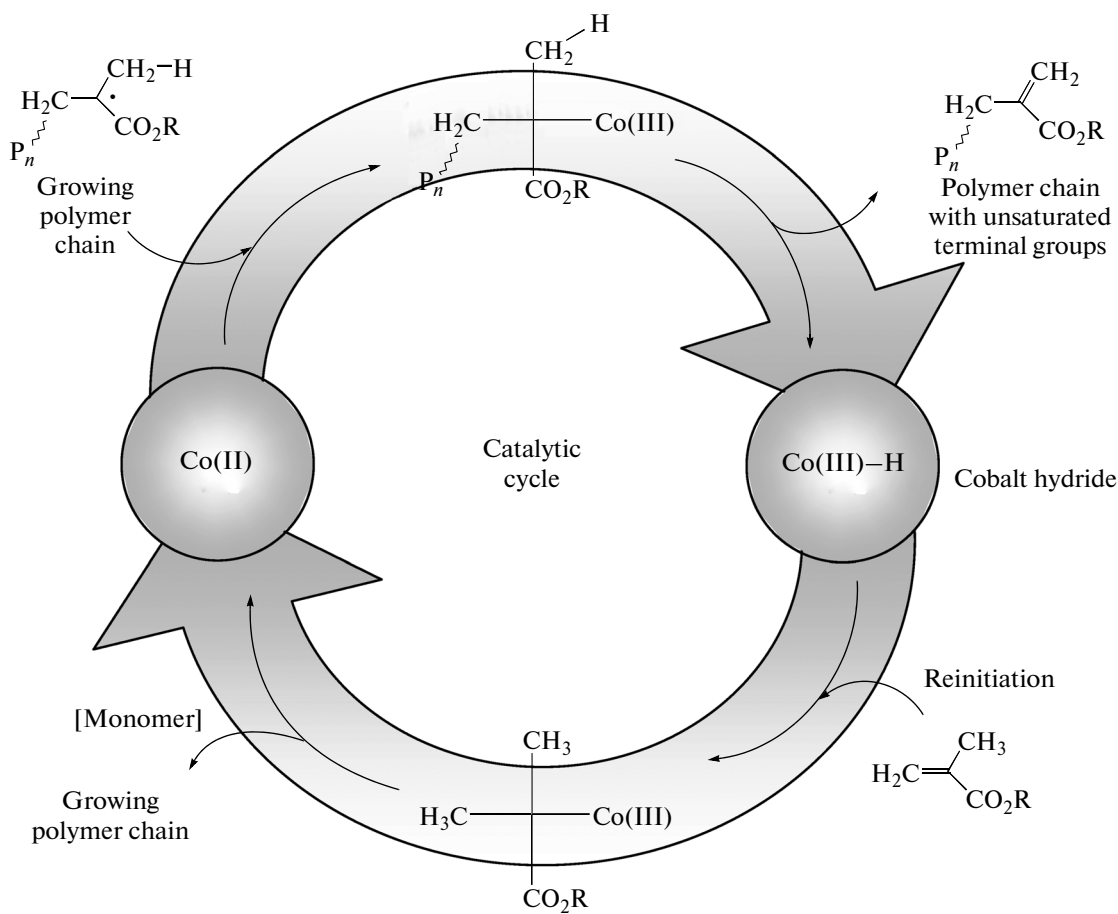
abstraction, and the polymerization of these monomers proceeds by the catalytic chain transfer mechanism.

The common CCT mechanism for methyl methacrylate includes several steps (Scheme 1) [12, 13].

In the first step, the cobalt(II) complex reacts with the polymeric radical to give a cobalt(III) alkyl complex which undergoes a β -hydride shift from the methyl group to the cobalt atom resulting in the formation of a polymer chain with unsaturated terminal groups and cobalt hydride. The catalytic cycle is closed by hydrogen-atom transfer from cobalt(III) hydride to monomer, yielding a growing radical which is subsequently involved in the chain propagation step. A remarkable fact is that, if the transfer rate is low, the growing radicals are terminated on the Co(II) complex, yielding a Co(III) complex. Under certain conditions, the Co(III) complex can reinitiate polymerization; i.e., the RI or DCT mechanisms are realized [6, 14–16].

The most active catalytic chain transfer agents, are cobalt complexes, such as porphyrin and cobaloximes, for which the typical chain transfer constants are about 10^2 – 10^4 [12, 13].

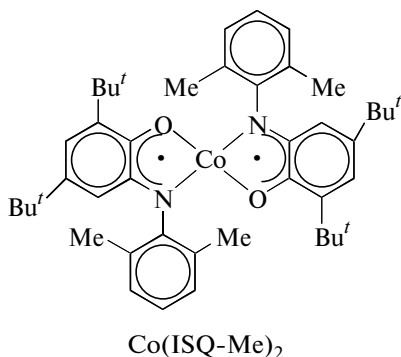
At the same time, the nature of the metal complex catalyst can play a significant role in the polymerization of methacrylic monomers. For example, based on the data from [17, 18], one can assume that, in MMA polymerization involving tris(triphenylphosphine)cobalt halides or cobalt acetate via the atom transfer radical polymerization mechanism, the contribution from CCT is minimal, which is evidenced by the good agreement between the experimental molecular-weight characteristics of poly(methyl methacrylate) (PMMA) and the theoretical ones calculated taking into account



Scheme 1. CCT mechanism in MMA polymerization in the presence of cobalt complexes

only atom transfer radical polymerization. Note that there is an example of MMA polymerization in the presence of dinuclear cobalt complexes proceeding by the reversible inhibition mechanism [19]. Thus, the ligand environment of the cobalt atom has also an effect on the polymerization mechanism.

The aim of the present work is to study the features of azobisisobutyronitrile (AIBN)-initiated polymerization of MMA in the presence of bis[4,6-di-*tert*-butyl-*N*-(2,6-dimethylphenyl)-*ortho*-iminobenzosemiquinono]-cobalt(II) ($\text{Co}(\text{ISQ-Me})_2$) containing two reactive sites, namely, the transition metal atom and the redox-active ligand.



The ligand of the above-mentioned cobalt complex can undergo a one-electron redox transition. This unique capability of the *ortho*-iminobenzosemiquinone ligands can have a dramatic effect on the mechanism of MMA polymerization in the presence of $\text{Co}(\text{ISQ-Me})_2$ [20, 21]. For this reason and for the purpose of gaining a deep insight into the mechanism of MMA polymerization involving $\text{Co}(\text{ISQ-Me})_2$, we estimated the constant of chain transfer to this complex.

EXPERIMENTAL

Starting Compounds

Commercially available MMA (Aldrich) was washed with 10% sodium hydroxide and distilled water, dried over calcium chloride, and distilled in vacuo to collect the fraction with a boiling point of 38°C/15 Torr. $\text{Co}(\text{ISQ-Me})_2$ was prepared according to an earlier described procedure [22]. Commercially available dodecyl mercaptan ($\text{C}_{12}\text{H}_{25}\text{SH}$, Arkema) was used as received. AIBN (Aldrich) was recrystallized from methanol at 50°C [23]. Benzene, hexane, dichloromethane, and ethyl acetate were dried over calcined calcium chloride and distilled under atmospheric pressure. Tetrahydrofuran (THF) was dried over an alkali and was dis-

tilled from sodium metal. The physicochemical properties of all of the compounds were in agreement with the literature [24].

Experimental Procedure

For the determination of the chain transfer constant, samples were prepared as follows. AIBN initiator (45.9 mg) was dissolved in a mixture (14 mL) of MMA and benzene (50 : 50, v/v). Portions of $\text{Co}(\text{ISQ-Me})_2$ (0, 2.3, 4.5, 9.0, 11.3, and 22.6 g) were placed into separate tubes, and a solution of AIBN (1.6 mL, 2×10^{-2} mol/L) was added to each tube to obtain solutions with $\text{Co}(\text{ISQ-Me})_2$ concentrations of 0.2×10^{-3} , 4×10^{-3} , 8×10^{-3} , 1×10^{-2} , and 2×10^{-2} mol/L, respectively.

The kinetics of MMA polymerization in the presence of the cobalt complex and dodecyl mercaptan was studied in the bulk of monomer, which serves as the solvent. When performing polymerization in the presence of $\text{Co}(\text{ISQ-Me})_2$, a 1×10^{-2} mol/L solution of AIBN (18.6 mg of AIBN in 12 mL of MMA) was preliminary prepared. A tube was loaded with $\text{Co}(\text{ISQ-Me})_2$, and the prepared solution (1.6 mL) of AIBN in the monomer was added to obtain a solution of $\text{Co}(\text{ISQ-Me})_2$ at a concentration of 2.4×10^{-3} mol/L. For polymerization in the presence of $\text{C}_{12}\text{H}_{25}\text{SH}$, the starting solutions were prepared as follows: AIBN (18.6 mg, 1×10^{-2} mol/L) and $\text{C}_{12}\text{H}_{25}\text{SH}$ (5.8 mg, 2.4×10^{-3} mol/L) were dissolved in MMA (12 mL). The prepared solution (1.6 mL) of AIBN and dodecyl mercaptan was placed in a tube.

The tube contents were degassed three times by repeating the freeze-thaw cycle until a residual pressure of 2×10^{-2} Torr, and then the tube was sealed. The polymerization kinetics at 70°C was monitored by gravimetric and thermoanalytical methods [25]. After the preset time elapsed, the sealed tube was withdrawn from the device and was cooled with liquid nitrogen to terminate polymerization, and the resulting polymer was precipitated in hexane. To purify the polymers from the remaining monomer, initiator, and $\text{Co}(\text{ISQ-Me})_2$ (or $\text{C}_{12}\text{H}_{25}\text{SH}$), the samples were reprecipitated from ethyl acetate or THF and were dried to constant weight at a reduced pressure. The conversion x was calculated via the formula

$$x = \frac{m_{\text{polymer}}}{m_{\text{monomer}}} \times 100\%,$$

where m is the weight of polymer or monomer.

The molecular weight and molecular-weight distribution (MWD) of polymers were determined by gel permeation chromatography (GPC) on a KNAUER liquid chromatograph (Germany) equipped with a cascade of Phenomenex columns (300 mm \times 7.8 mm, phenogel, 10 μm) having a pore diameter of 10^5 and 10^3 Å and two (refractive index and UV) detectors. The

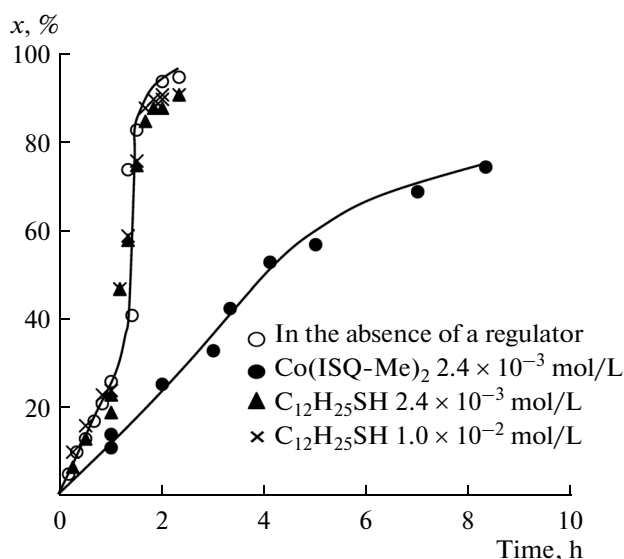


Fig. 1. MMA conversion in the presence of AIBN (1×10^{-2} mol/L) at 70°C as a function of the polymerization time.

eluent was THF, and the column temperature was $25.0 \pm 0.1^\circ\text{C}$. Calibration was performed using narrow-polydispersity PMMA standards [26].

RESULTS AND DISCUSSION

In recent decades, metal complexes with quinone ligands have found wide application in polymerization processes. Their effects can be conventionally divided into catalytic (defined by individual properties of the central metal atom) [27–29] and controlling ones (defined not only by the nature of the element, but also by specific properties of the redox-active ligands) [8, 20, 21, 30–32].

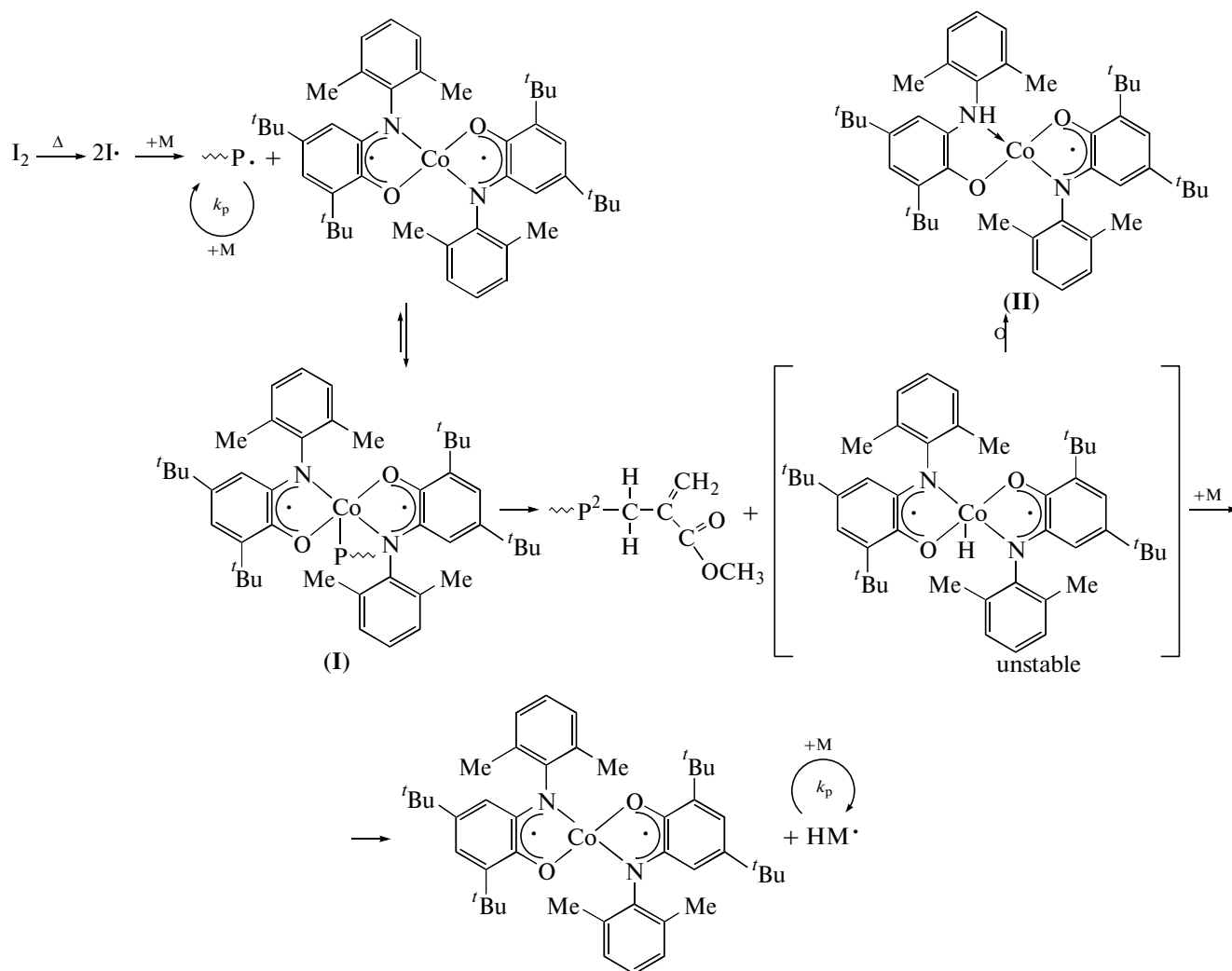
We showed that the addition of the cobalt complex influences the process kinetics and the molecular-weight characteristics of synthesized samples. In the study of the polymerization rate by the gravimetric (Fig. 1) and thermoanalytical (Fig. 2) methods, it was established that the presence of $\text{Co}(\text{ISQ-Me})_2$ in the system results in degeneration of the gel effect that is observed under conditions of conventional free-radical polymerization of MMA using the classical initiator AIBN. At the same time, the addition of the cobalt complex even in small amounts causes a significant decrease in the polymerization rate.

The $\text{Co}(\text{ISQ-Me})_2$ additives also influence the molecular-weight characteristics of the synthesized samples. For example, in the polymerization of MMA at 70°C , the MW of the polymer increases linearly with an increasing monomer conversion (Fig. 3, curve 1). However, the curve does not pass through the origin of coordinates, which can be due to the fact that pentacoordinated cobalt complex I (Scheme 2) containing a

polymeric radical and acting as the main regulator in the polymerization of MMA forms slowly at the initial step of polymerization. In addition, the slope of the straight line is less than that in polymerization via the “ideal” controlled mechanism. The polydispersity of PMMA increases as the monomer conversion increases (Table 1). These facts suggest simultaneous realization of several parallel mechanisms.

As noted above, depending on the nature of compounds and monomer used, as well as on the conditions of polymerization in the presence of cobalt complexes,

three different mechanisms, viz., CCT, RI, and DCT, can be realized. Since the polymerization of methacrylic monomers in the presence of cobalt complexes proceeds mainly via the CCT mechanism [12, 13], it seemed necessary to study the features of this process in the polymerization of MMA involving $\text{Co}(\text{ISQ-Me})_2$, particularly for quantitatively estimating the efficacy of the above-mentioned complex as a catalytic chain transfer agent (Scheme 2). It should be noted that it is chain transfer that contributes significantly to the decrease in the MW of polymers in controlled polymerization [33].



Scheme 2. Mechanism of MMA polymerization involving $\text{Co}(\text{ISQ-Me})_2$

The efficacy of a chain transfer agent is characterized by the chain transfer constant C_{tr} , which is defined as the ratio of the rate constant of chain transfer to the added regulator to the chain propagation rate constant:

$$C_{\text{tr}} = \frac{k_{\text{tr}}}{k_{\text{pr}}}, \quad (1)$$

where k_{tr} is the rate constant of chain transfer to the agent introduced and k_{pr} is the chain propagation rate constant.

Note that the catalytic chain transfer agents differ significantly from the normal chain transfer agents in that they have large values of C_{tr} and are not consumed during the reaction:

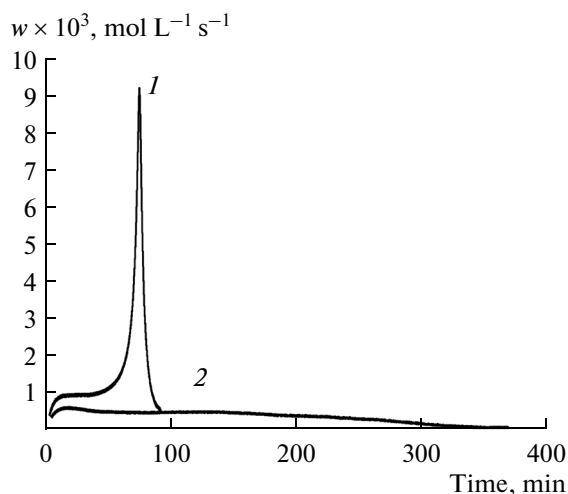
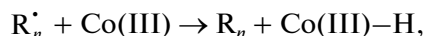
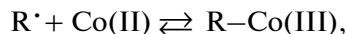


Fig. 2. Differential MMA polymerization curves at different concentrations of $\text{Co}(\text{ISQ-Me})_2$, mol/L: (1) 0 and (2) 2.4×10^{-3} . $[\text{AIBN}] = 1 \times 10^{-2}$ mol/L, 70°C .



where R_n^* is a growing polymer radical and R_1^* is a nonmacromolecular active radical.

However, if a chain transfer agent is capable to interact with propagating chains in other ways, for example, through reversible or irreversible termination,



the actual concentration of the chain transfer agent will be lower than the added concentration, and the effective chain-transfer constant is typically determined in this case:

$$C_{\text{tr}}^{\text{eff}} = C_{\text{tr}} \frac{[\text{Co}(\text{II})]}{[\text{Co}(\text{II})]_0}, \quad (2)$$

where $C_{\text{tr}}^{\text{eff}}$ is the effective (apparent) chain-transfer constant, C_{tr} is the chain transfer constant, $[\text{Co}(\text{II})]$ is the actual concentration of $\text{Co}(\text{II})$, and $[\text{Co}(\text{II})]_0$ is the initial concentration of $\text{Co}(\text{II})$.

In the present work, the effective constant of chain transfer to the cobalt complex in MMA polymerization in benzene at 70°C was determined using two techniques, viz., the Mayo method [34] and linearization of the macromolecule chain length distribution [35]. The conventional Mayo method is based on determination of the average MW of polymers (degree of polymerization) as a function of the ratio between the concentrations of chain transfer agent and monomer.

$$DP_n^{-1} = DP_{n0}^{-1} + C_{\text{tr}} \frac{[\text{Co}(\text{II})]}{[\text{MMA}]}, \quad (3)$$

where DP_n and DP_{n0} is the degree of polymerization in the presence and in the absence of a chain transfer agent, respectively; C_{tr} is the chain transfer constant;

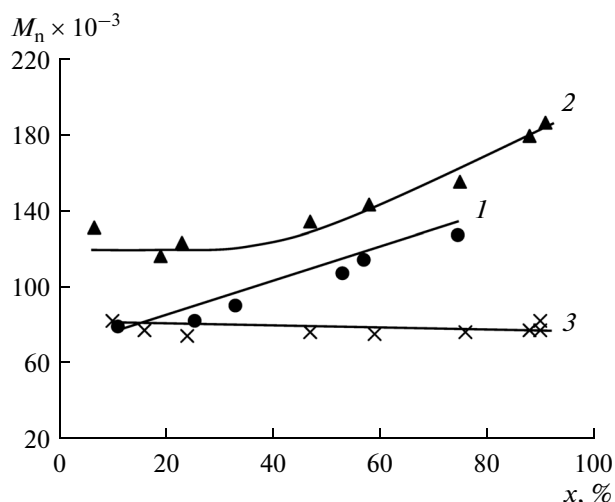


Fig. 3. Number-average MW of PMMA as a function of the monomer conversion in the presence of different regulators: (1) $\text{Co}(\text{ISQ-Me})_2$ (2.4×10^{-3} mol/L), (2) $\text{C}_{12}\text{H}_{25}\text{SH}$ (2.4×10^{-3} mol/L), and (3) $\text{C}_{12}\text{H}_{25}\text{SH}$ (1×10^{-2} mol/L). $[\text{AIBN}] = 1 \times 10^{-2}$ mol/L, 70°C .

$[\text{Co}(\text{II})]$ is the concentration of $\text{Co}(\text{ISQ-Me})_2$; and $[\text{MMA}]$ is the initial concentration of MMA.

Based on Eq. (3), the chain transfer constant is determined.

The average degree of polymerization is conventionally determined from the number-average MW (M_n):

Table 1. Polydispersity of PMMA synthesized in the presence of AIBN (1×10^{-2} mol/L) and different regulators at 70°C

Regulator	Regulator concentration, mol/L	Conversion, %	M_w/M_n
—	—	13	1.90
		36	2.78
		92	7.23
$\text{Co}(\text{ISQ-Me})_2$	2.4×10^{-3}	11	1.91
		33	1.88
		57	1.99
		75	2.07
$\text{C}_{12}\text{H}_{25}\text{SH}$	2.4×10^{-3}	13	2.08
		47	2.65
		58	2.91
$\text{C}_{12}\text{H}_{25}\text{SH}$	1×10^{-2}	91	3.10
		10	2.22
		47	1.95
		63	2.03
		91	2.04

Table 2. Experimental data on MMA polymerization in the presence of Co(ISQ-Me)₂ used in the calculation of the chain transfer constant ([AIBN] = 2 × 10⁻² mol/L, 70°C, 4–8% conversion)

[Co(II)], mol/L	$\frac{[\text{Co(II)}]}{[\text{MMA}]}$	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	DP_n		$-\Lambda = C_{tr}/m_0$
					M_n	M_w	
0	—	62	109	1.75	620	545	1.0×10^{-7}
2×10^{-4}	4.2×10^{-5}	65	115	1.76	650	575	7.0×10^{-6}
2×10^{-3}	4.2×10^{-4}	50	90	1.79	500	450	1.0×10^{-5}
4×10^{-3}	8.5×10^{-4}	47	89	1.89	470	445	1.0×10^{-5}
8×10^{-3}	1.7×10^{-3}	41	76	1.85	410	380	1.7×10^{-5}
1×10^{-2}	2.1×10^{-3}	39	75	1.90	390	375	1.8×10^{-5}
2×10^{-2}	4.2×10^{-3}	27	50	1.85	270	250	3.0×10^{-5}

$DP_n = M_n/m_0$. However, in the calculation of the degree of polymerization using the M_n value, there can be a great error caused by the fact that the baseline position in gel permeation chromatography is ambiguous, which has a significant effect on the determination of M_n [36–39]:

$$DP_n = \frac{M_w}{2m_0}, \quad (4)$$

where DP_n is the degree of polymerization and m_0 is the MW of the monomer.

Based on the data obtained we plotted the function $[DP]^{-1} = f([\text{Co}]/[\text{MMA}])$ (Table 2, Figs. 4a, 4b) and determined the chain transfer constant from the slope of straight line.

An alternative method of determination of the chain transfer constant is linearization of the macromolecule chain length distribution [35] at high MWs. The number distribution $P(M)$ is calculated based on the MWD determined by GPC. The chain transfer constant is determined using the equation

$$\lim_{M \rightarrow \infty} \frac{d \ln(P(M))}{dM} = \Lambda = -C_{tr} \frac{[\text{Co(II)}]}{[\text{MMA}]} \frac{1}{m_0}, \quad (5)$$

where $P(M)$ is the number-average molecular-weight distribution, C_{tr} is the chain transfer constant; $[\text{Co(II)}]$ is the concentration of Co(ISQ-Me)₂, and m_0 is the MW of the monomer.

The number distribution $\ln(P(M)) = f(M)$ is shown in Fig. 5. From the slope of the linear dependence in the high-molecular-weight region, Λ values proportional to $-C_{tr}/m_0$ were determined. From the dependence of Λ on $[\text{Co(II)}]/[\text{MMA}]$ (Fig. 6) at different concentrations

of Co(ISQ-Me)₂, chain transfer constants were calculated from the slope of the $C_{tr} = -\Lambda m_0$ curve.

Calculation by the Mayo method		Calculation by linearization of the macromolecule chain length distribution
Via the equation $DP_n = M_n/m_0$	Via Eq. (4) $DP_n = M_w/2m_0$	
0.49	0.50	0.56

The Mayo and linearization methods are identical in their nature. With both methods, the constants of chain transfer to the cobalt *ortho*-iminobenzosemiquinone complex in MMA polymerization at 70°C are of the same order and are comparable with one another within the limits of the experimental error.

Comparing our constants of chain transfer to the cobalt complex in MMA polymerization to those reported in [40–42], it should be noted that the constants determined by us differ significantly from the constants of chain transfer to porphyrin and oxime complexes (Table 3). With account taken of the data obtained and the reactivity of the cobalt *ortho*-iminobenzosemiquinone complex, the CCT mechanism involving pentacoordinated complex **I** that forms in the polymerization medium (Scheme 2) seems unlikely. For example, if the cobalt hydride complex formed, it would rearrange under these conditions into aminophenoxide **II**, whose electronic absorption spectrum (EAS) differs from that of the starting metal complex. However, during the experiment, the EAS remained unchanged. Thus, the data obtained suggest that, in MMA polymerization at 70°C in the presence of Co(ISQ-Me)₂, catalytic chain transfer is not the dominant process. Note that the concentration of the complex added has a slight effect not only on the molecular weight of PMMA but also on the polydispersity of the synthesized samples (Table 2).

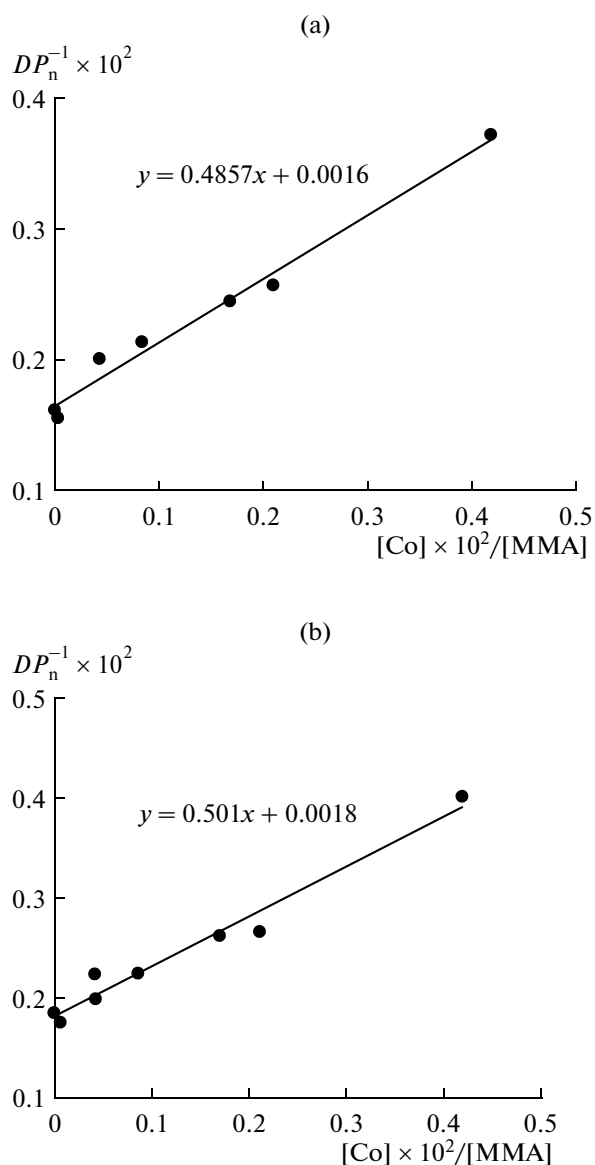


Fig. 4. Plots for determination of the chain transfer constants by the Mayo method using the degrees of polymerization calculated according to the equations (a) $DP_n = M_n/m_0$ and (b) $DP_n = M_w/2m_0$.

However, our constant of chain transfer to the cobalt complex is comparable to the constant of chain transfer to such common transfer agents as mercaptans; therefore, one cannot exclude chain transfer to the cobalt complex caused by the ligand environment. One known fact regarding the effect of some chain transfer agents on the polymerization rate should be mentioned here: when using high concentrations of mercaptans, a partial degeneration of the gel effect and its shift to higher conversions are observed [43]. This is due to the decrease in the MWs of the polymers, which affects the autoacceleration step. For this reason, we deemed necessary to study, under the analogous conditions, the effect of $C_{12}H_{25}SH$, which is

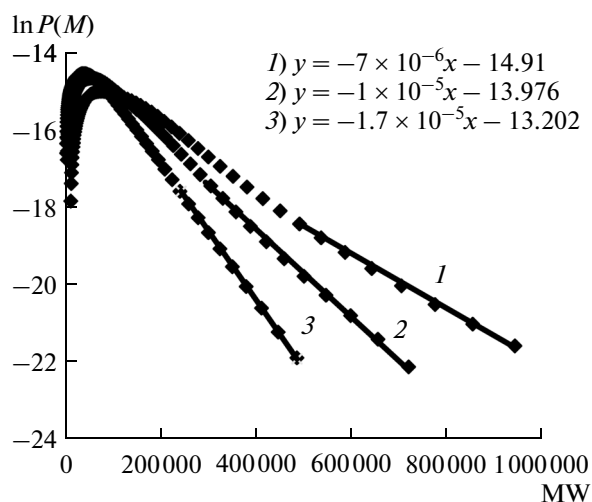


Fig. 5. $\ln P(M)$ versus $f(M)$ at different concentrations of $[Co(ISQ-Me)_2]$, mol/L: (1) 2×10^{-4} , (2) 2×10^{-3} , and (3) 8×10^{-3} . $[AIBN] = 2 \times 10^{-2}$ mol/L

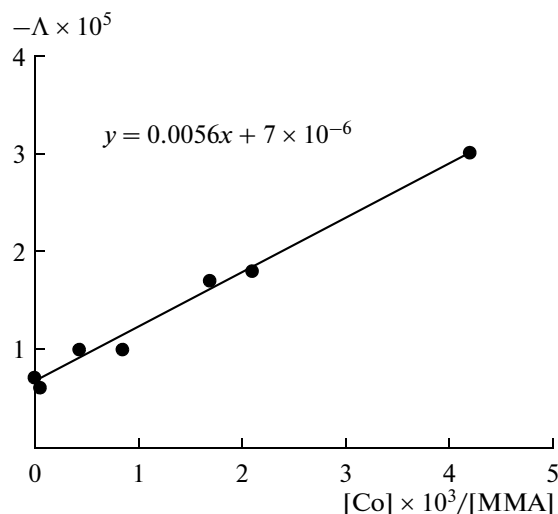


Fig. 6. $-\Lambda = f([Co(II)]/[MMA])$ plot used in the determination of the chain transfer constant by linearizing the macromolecule chain length distribution. $[AIBN] = 2 \times 10^{-2}$ mol/L.

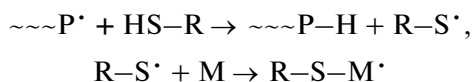
characterized by virtually the same chain transfer constant as $Co(ISQ-Me)_2$ (Table 3). An analysis of the polymerization of MMA in the presence of such regulators as $C_{12}H_{25}SH$ and $Co(ISQ-Me)_2$ suggests that the metal atom and ligand environment have a noticeable effect on the reaction mechanism. For example, the addition of dodecyl mercaptan in amounts comparable with those of the cobalt complex, as distinct from the addition of the latter, has no effect on the polymerization rate of MMA (compare the curves designated ● and ▲ in Fig. 1). A fourfold increase in the amount of dodecyl mercaptan (up to 1×10^{-2} mol/L, a concentration comparable to that of the initiator) also causes

Table 3. Chain transfer constants in MMA polymerization at 60°C

Compound	C_{tr}	Reference
MMA	1×10^{-5}	[34]
CBr ₄	0.27	[34]
Cobalt oxime complex (COBF)	$(24-40) \times 10^3$	[33]
Cobalt porphyrin complex (CoP)	3.6×10^3	[35]
C ₁₂ H ₂₅ SH	0.7	[36]

no decrease in the polymerization rate at the autoacceleration step (Fig. 1, curve designated ×).

Dodecyl mercaptan and the cobalt complex have different effects on the molecular-weight characteristics of PMMA (Fig. 3, Table 1). Mercaptans are classical chain transfer agents and are involved in polymerization according to the scheme



Upon the addition of dodecyl mercaptan at a low concentration, the MW of PMMA decreases significantly relative to that of the polymer synthesized using the classical initiator, viz., AIBN (MW = 465 000, and the conversion is 92%). The MW remains unchanged up to a conversion of 25%, but at higher monomer conversions there is an increase in the MW (Fig. 3, curve 2), in contrast to what is observed in polymerization involving the cobalt complex. An increase in the C₁₂H₂₅SH concentration has a more significant effect on the molecular-weight characteristics of PMMA. For example, the addition of dodecyl mercaptan at high concentrations allows preparation of the polymer with a lower and constant MW, irrespective of the monomer conversion (Fig. 3, curve 3). Likewise, C₁₂H₂₅SH and Co(ISQ-Me)₂ have different effects on the polydispersity index. When the polymer is synthesized in presence of 2.4×10^{-3} mol/L of mercaptan, i.e., at a concentration comparable with that of the cobalt complex, and the monomer conversion is high, the polydispersity indices of the resulting samples have large values (Table 1). Only a fourfold excess of dodecyl mercaptan concentration over that of the cobalt complex has the same effect on the molecular-weight characteristics of PMMA (Table 1).

Thus, comparison the MMA polymerization rates and molecular-weight characteristics of PMMA obtained in the presence of the cobalt *ortho*-iminobenzosemiquinone complex to the same data obtained with dodecyl mercaptan showed that the effect of the cobalt complex is not due to the chain transfer process but is likely due to its reaction with the

growing radical accompanied by the formation of pentacoordinated complex I (Scheme 2).

Thus, in the present work the polymerization of MMA in the presence of Co(ISQ-Me)₂ was studied and the effective constants of chain transfer to Co(ISQ-Me)₂ were determined by the Mayo method and by linearization of the macromolecule chain length distribution. The values obtained agree well with one another and are about 0.5–0.6, being comparable within the limits of experimental error. These values were compared with earlier published data on the constants of chain transfer involving effective chain transfer agents, such as dodecyl mercaptan and cobalt porphyrin and oxime complexes. The significant difference between the chain transfer constants for the complex under study, on the one hand, and for the cobalt porphyrin and oxime complexes, on the other hand, suggests that no catalytic chain transfer occurs in MMA polymerization at 70°C in the presence of Co(ISQ-Me)₂.

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