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Metallocene Catalysis in the Complex-Radical Polymerization of Methyl Methacrylate

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Abstract—The initiation stage of methyl methacrylate polymerization in the presence of benzoyl peroxide–metallocene (MC) systems is considered, with MC = Cp_2Fe, $(C_5Me_5)_2Fe$, $(AcC_5H_4)(C_5H_5)Fe$, Cp_2TiCl_2, Cp_2ZrCl_2, and $(C_5Me_5)_2ZrCl_2$. The decomposition of benzoyl peroxide in the presence of a metallocene proceeds via the formation of its complex with the metallocene. The catalytic effect of the metallocenes on the initiation of methyl methacrylate polymerization is due to the formation of a metallocene–benzoyl peroxide complex and its decomposition yielding primary radicals. The chain propagation stage is metallocene-dependent, which is explained by the formation of complex sites. Their formation pathway and structures are analyzed using quantum-chemical calculations.

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The study of radical polymerization in the presence of initiating systems containing Cp_2Fe and benzoyl peroxide (BP) showed that Cp_2Fe increases the polymerization rate of methyl methacrylate (MMA) [1]. According to Puzin et al. [1], in the presence of ferrocene initiation can proceed as follows:

$$(PhCOO)_2 \rightarrow 2PhCOO^{\bullet}, \qquad (I)$$

$$\begin{gathered}(C_5H_5)_2Fe + (PhCOO)_2 \\ \longrightarrow (C_5H_5)_2Fe^{+\bullet} + PhCOO^- + PhCOO^{\bullet}.\end{gathered} \qquad (II)$$

In this scheme, metallocene (MC) exhibits reductive properties in its redox reaction with BP.

We believed that use of MCs with various redox potentials would affect the initiation rate and, correspondingly, the initial polymerization rate. In this work, we also studied the influence of the MC nature on the chain propagation stage, for it was shown earlier that ferrocene affects the kinetics of MMA polymerization [2]. The chain initiation and propagation stages of MMA polymerization were studied at different temperatures in the presence of the following MCs: ferrocene (FH), acetylferrocene (AcFc), decamethylferrocene (Cp_2^*Fe), titanocene dichloride (**Cp_2TiCl_2**), zirconocene dichloride (**Cp_2ZrCl_2**), and decamethylzirconocene dichloride (**$Cp_2^*ZrCl_2$**).

EXPERIMENTAL

Bulk MMA polymerization was carried out in the temperature range from 40 to 80 ± 0.05°C at a BP concentration of 1.0×10^{-3} mol/L. The monomer was purified from the stabilizer by shaking it with a 10% KOH solution, washed with water until neutral, dried over $CaCl_2$, and distilled twice in vacuo.

The polymerization kinetics was studied by the dilatometric method. The reaction mixture, in a dilatometer, was pumped to a residual pressure lower than 1.33 Pa [3].

The metallocenes FH, Cp_2ZrCl_2, and Cp_2TiCl_2 were received from Sigma Aldrich. Cp_2^*Fe, $Cp_2^*ZrCl_2$, and AcFc were synthesized at the Institute of Applied Physics, Russian Academy of Sciences (Nizhni Novgorod) were.

Quantum-chemical calculations were performed using the PRIRODA-06 program [4, 5], in which Gaussian basis sets are used to solve the Kohn–Sham equations and electron density is expanded in an auxiliary basis set to calculate the Coulomb and exchange-correlation energies. We used the PBE density functional [6] and a three-exponent basis set consisting of contracted orbital sets of Gaussian type functions: (5*s*1*p*)/[3*s*1*p*] for H, (11*s*6*p*2*d*)/[6*s*3*p*2*d*] for C and O, (15*s*11*p*2*d*)/[10*s*6*p*2*d*] for Cl, (17*s*13*p*8*d*)/[12*s*9*p*4*d*] for Fe and Ti, and (20*s*16*p*11*d*)/[14*s*11*p*7*d*] for Zr. The auxiliary basis sets were uncontracted sets of Gaussian type functions with dimensions of (5*s*2*p*) for H, (10*s*3*p*3*d*1*f*) for C and O, (14*s*3*p*3*d*1*f*1*g*) for Cl, (18*s*6*p*6*d*5*f*5*g*) for Fe and Ti, and (22*s*5*p*5*d*4*f*4*g*) for Zr. This method makes it possible to reproduce well the geometric parameters of the compounds examined, which was demonstrated earlier [7, 8]. The geometric parameters of the structures were optimized without symmetry constraints. The type of the stationary point on the potential surface

Table 1. Initiation rates and the initial rates of MMA polymerization at different temperatures in the presence of metallocenes*

T, K	W, mol L^{-1} min^{-1}						
	BP	Cp_2Fe	$(C_5Me_5)_2Fe$	$(AcC_5H_4)(C_5H_5)Fe$	Cp_2TiCl_2	Cp_2ZrCl_2	$(C_5Me_5)_2ZrCl_2$
313	$\frac{-}{1.4}$	$\frac{-}{15.0}$	$\frac{-}{2.5}$	$\frac{-}{5.8}$	$\frac{-}{2.5}$	$\frac{-}{1.0}$	$\frac{-}{1.4}$
323	$\frac{2.7}{1.8}$	$\frac{15.6}{25.5}$	$\frac{2.7}{4.0}$	$\frac{6.8}{9.6}$	$\frac{-}{2.7}$	$\frac{-}{2.2}$	$\frac{-}{2.5}$
328	$\frac{-}{3.5}$	$\frac{-}{38.8}$	–	–	–	–	–
333	$\frac{2.8}{5.6}$	$\frac{30.5}{41.8}$	$\frac{4.7}{6.3}$	$\frac{8.7}{16.2}$	$\frac{1.2}{7.4}$	$\frac{0.4}{5.0}$	$\frac{-}{5.6}$
343	$\frac{-}{11.3}$	$\frac{36.0}{51.0}$	$\frac{8.1}{11.7}$	$\frac{27.8}{34.8}$	$\frac{-}{13.1}$	$\frac{-}{12.0}$	$\frac{-}{11.2}$
353	$\frac{-}{26.8}$	$\frac{-}{85.4}$	$\frac{-}{20.4}$	$\frac{-}{40.1}$	$\frac{-}{25.9}$	$\frac{-}{26.1}$	$\frac{-}{22.9}$

* The numerator is the initiation rate of polymerization $W_{\text{init}} \times 10^6$, and the denominator is the initial polymerization rate $W_{\text{in}} \times 10^3$.

energy was determined by calculating the Hessian matrix.

RESULTS AND DISCUSSION

Initiation Stage

The electrochemical potential of FH, AcFc, and Cp_2^*Fe is 0.41, 0.68, and −12 V, respectively [9, 10]. Therefore, Cp_2^*Fe is the strongest reducing agent of the metallocenes used in the work. The electrochemical potential of Cp_2ZrCl_2 is +1.86 V [11], much higher than those of the ferrocenes. The electrochemical potentials of Cp_2TiCl_2 and $Cp_2^*ZrCl_2$ were not determined, but it can be assumed that they are also higher than unity. Thus, according to reaction (II), Cp_2^*Fe would be expected to exert the most significant effect on the decomposition of BP. In fact (Table 1), the highest initiation rates in MMA polymerization (W_{init}) are observed in the presence of ferrocene, regardless of the reaction temperature. They considerably exceed the polymerization rate in the system containing BP only. The second strongest accelerator of polymerization is AcFc, and $Cp_2^*Fe_2$ occupies the third place. The data on the influence of the metallocenes on W_{init} and on the initial polymerization rates (W_{in}) correlate.

Based on the linear dependences of log W_{in} on $1/T$, we calculated the total activation energies of polymerization: $E_{\text{a.p}} = 1/2E_{\text{init}} + (E_{\text{p}} - 1/2E_{\text{f}})$, where E_{f} is the formation energy (Table 2). As can be seen, the smallest values of $E_{\text{a.p}}$ are observed in the presence of the BP–FcH system. Somewhat larger values were observed for the BP–AcFc systems, which are followed by BP–$Cp_2^*Fe_2$ and BP–Cp_2TiCl_2, whereas for the BP–Cp_2ZrCl_2 and BP–$Cp_2^*ZrCl_2$ systems, $E_{\text{a.p}}$ is close to the values obtained for the polymerization in the presence of BP.

The increase in the initiation rate and the comparatively low activation energies of MMA polymerization in the presence of MC indicate the catalytic activity of the latter in the decomposition of BP. However, the order in which the MCs can be arranged according to the degree of their influence on the initiation rate and activation energy of the initial polymerization stages suggests that the catalytic effect of the MCs on BP decomposition does not correlate directly with their reducing power.

It is known from the literature that metal compounds can catalyze the decomposition of diacyl peroxides. In particular, the reactions of BP with Fe(II) compounds proceed via a one-electron transfer mechanism through the complex formation stage [13]:

Table 2. Activation energies of MMA polymerization initiated by BP in the presence of MC ([BP] = [MC] = 1 × 10^{-3} mol/L)

Admixture	$E_{\text{a.p}}$, kJ/mol
BP	81.6 [12]
Cp_2Fe	37.5
$(AcC_5H_4)(C_5H_5)Fe$	47.5
$(C_5Me_5)_2Fe$	48.0
Cp_2ZrCl_2	76.1
$(C_5Me_5)_2ZrCl_2$	65.0
Cp_2TiCl_2	57.5

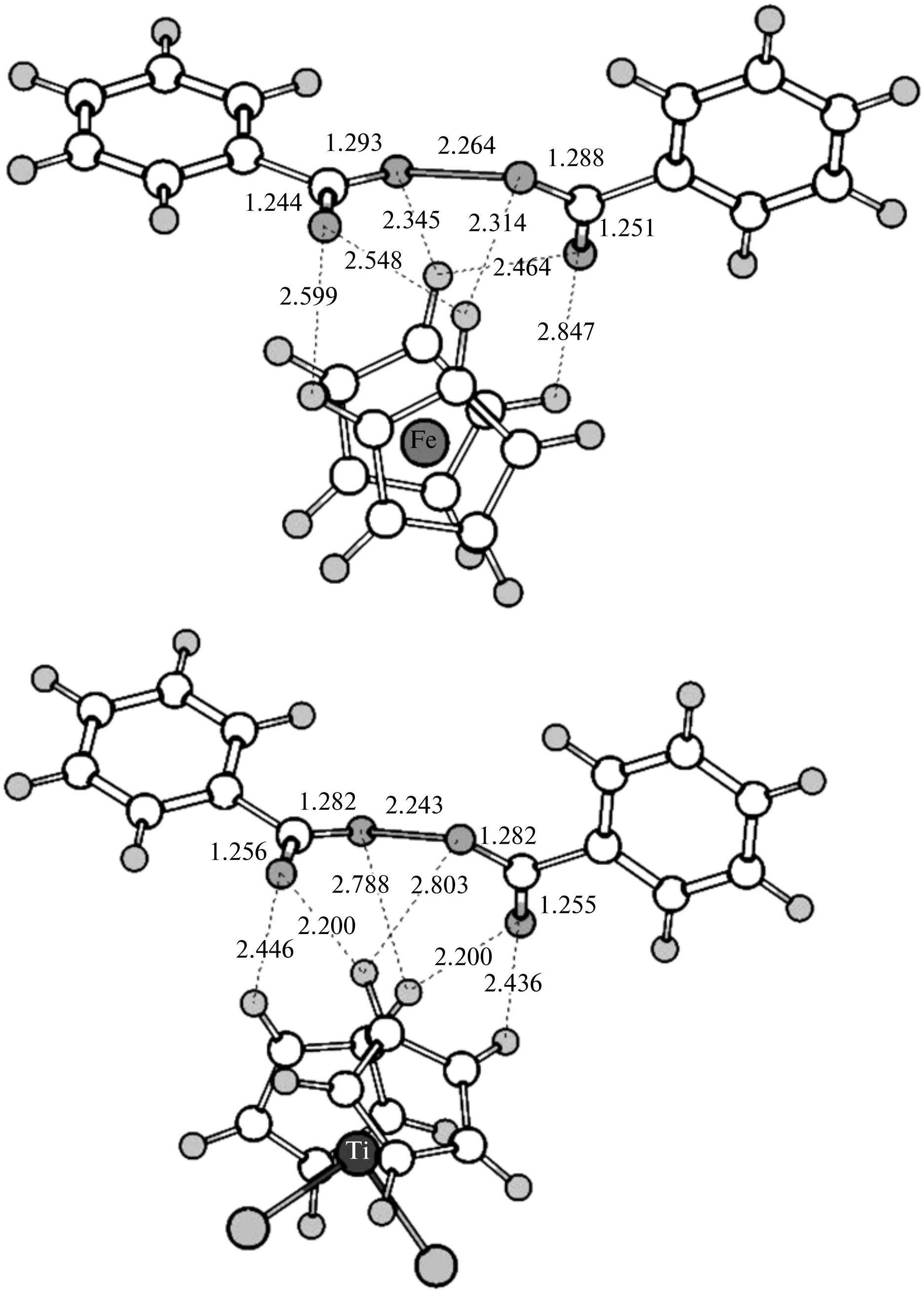


Fig. 1. Structures of the FH–BP and Cp_2TiCl_2–BP complexes. Interatomic distances are in Å.

$$Fe^{2+} + (PhCOO)_2 \rightarrow [\text{complex}] \rightarrow Fe^{3+} + PhCOO^- + PhCOO^{\bullet}. \quad \text{(III)}$$

It is assumed that the electron transfer to the peroxide is preceded by the coordination of BP with iron. There are reports on the spectral investigation of the formation of the 1 : 1 ferrocene–BP complex [14]. This complex is stable between –20 and +20°C. As the temperature is further increased, it decomposes, becoming capable of initiating MMA polymerization. However, the structure of the complex remains unknown. The iron atom in the ferrocene molecule is coordinatively saturated and, therefore, cannot form a coordination bond with, for example, a lone electron pair of oxygen. The structures of the MC–BP complexes were determined by quantum-chemical calculations. The complexes of BP with Fc and Cp_2TiCl_2 are shown in Fig. 1. As can be seen, these complexes form due to the interaction of the oxygen atoms of BP with hydrogen atoms of the cyclopentadienyl rings. The formation of the MC complexes with BP is accompanied by a considerable extension of the peroxide bond

Table 3. Changes in energy in the formation and decomposition of the MC–BP complexes, calculated by the PBE/3z method

Reaction	Energy, kJ/mol				
	Cp_2Fe	AcFc	$(C_5Me_5)_2Fe$	Cp_2TiCl_2	Cp_2ZrCl_2
$MC + (PhCOO)_2 \rightarrow [MC\cdots(PhCOO)_2]$	14	28	–15	64	77
$[MC\cdots(PhCOO)_2] \rightarrow MC^{+\bullet} + PhCOO^- + PhCOO^\bullet$	159*	–	–	–	–
$[MC\cdots(PhCOO)_2] + MMA \rightarrow [MC\cdots PhCOO]^\bullet + PhCOO\text{–}MMA^\bullet$	–87	–92	–84	–104	–108
$[MC\cdots PhCOO]^\bullet + MMA \rightarrow MC + PhCOO\text{–}MMA^\bullet$	–31	–39	–5	–64	–72

* Determined by single calculations of the energy of the reactants in ethanol (polarized continuum model). This value is 424 kJ/mol, when the solvent effect ignored.

(its length in the free BP molecule is 1.432 Å) and by a transition to the triplet state.

Table 3 lists the changes in energy for the formation of MC–BP complexes and for their subsequent decomposition. The probability of the formation of these complexes does not correlate directly with the electrochemical potentials of the MCs. However, the lower the electron donating power of the MC, the higher the energy required for the formation of the MC–BP complex. The decomposition of the complexes involves monomer molecules and results in the formation of radicals and regeneration of the MC molecule. The change in energy in the decomposition of the MC–BP complexes shows that the probability of these reactions also depends on the MC nature. The overall effect is determined by the ratio between the probabilities of formation and decomposition of the complex. The formation of the BP complexes with Cp_2ZrCl_2, $Cp_2^*ZrCl_2$, and Cp_2TiCl_2 requires a considerably higher energy than the formation of the complexes with the ferrocenes. This means that the equilibrium in the formation of the MC–BP complexes should be significantly shifted to the initial components. Nevertheless, the energy consumed in the formation of such a complex is still lower than the energy necessary for the unassisted decomposition of BP (125 kJ/mol [13]). Thus, the effect of the metallocenes on the initiation stage of MMA polymerization, i.e., the acceleration of initiator decomposition is due to the possibility of the formation of the MC–BP complex and its decomposition yielding primary radicals.

Chain Propagation Stage

The presence of an MC in the polymerization system affects both the initial polymerization rate and the general shape of the kinetic curves. While the dependence of the polymer yield on the reaction time in classical free-radical polymerization processes remains unchanged as process conditions are varied, the presence of an MC can smooth the gel effect.

If BP is the only initiator in the polymerization system, an increase in the polymerization temperature leads to a natural increase in the rate of the process. In addition, polymerization occurs with a clearly pronounced gel effect, whose maxima shift to shorter polymerization times (Fig. 2), but to higher conversions. As can be seen from Fig. 2, there is no gel effect when ferrocene is used in combination with BP in the temperature range from 55 to 60°C, and it is smoothed at 50, 65, and 70°C. In addition, the gel effect onset time is the same at any polymerization temperature.

In the presence of Cp_2^*Fe, which has electron-donating substituents in the cyclopentadienyl ring, the gel effect is insignificant and the maxima are small and blurred (Fig. 3).

When the cyclopentadienyl ring has the electron-withdrawing substituent acetyl, a pronounced gel effect is observed (Fig. 4) and the polymerization rate maximum time depends on the temperature, as in the case of BP used alone.

The metallocenes Cp_2ZrCl_2, $Cp_2^*ZrCl_2$, and Cp_2TiCl_2 exert almost no effect on the polymerization kinetics observed in the presence of BP alone.

The absence of the gel effect and its smoothing indicate that, under the given conditions, quadratic-law chain termination obeys a linear law or is absent at all. According to published data [15], the chlorine-containing metal complexes can control the radical polymerization rate by reversibly reacting with the growth radicals. However, it was shown [16] that

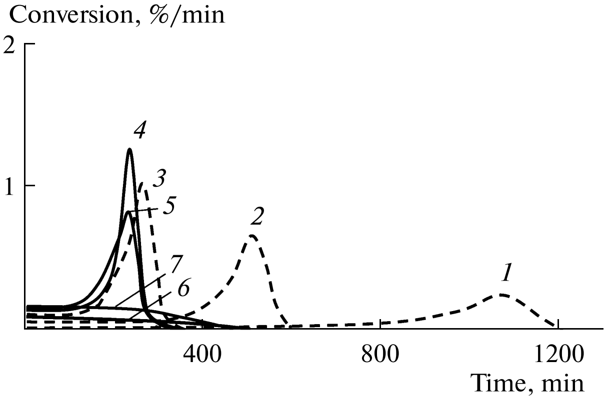


Fig. 2. Differential curves of MMA polymerization in the presence of (*1*–*3*) BP and (*4*–*7*) BP–FH at the polymerization temperatures (*4*) 40, (*1, 5*) 50, (*6*) 55, (*2, 7*) 60, and (*3*) 70°C; [BP] = [FH] = 1 × 10^{-3} mol/L.

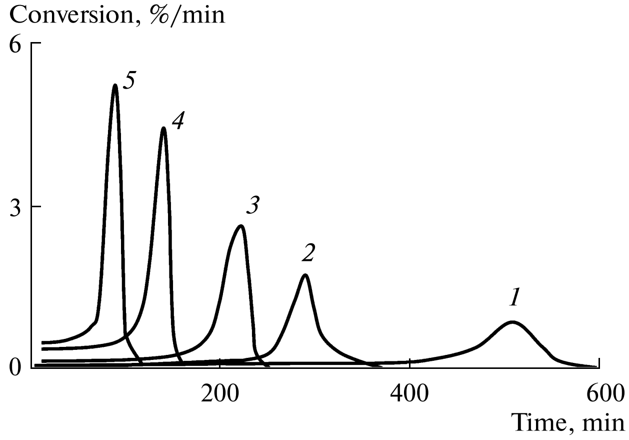


Fig. 4. Differential curves of MMA polymerization in the presence of BP–AcFc at the polymerization temperatures (*1*) 40, (*2*) 50, (*3*) 60, (*4*) 70, and (*5*) 80ºC; [BP] = [AcFc] = 1 × 10^{-3} mol/L.

Cp_2TiCl_2 can participate in the reversible transfer of a chlorine atom (reaction **1** in Scheme 1). It can also be directly involved in elementary events of monomer addition to the growing chain via the coordination–radical mechanism in the $Cp_2Ti^{\bullet}(R)(MMA)$ intermediate resulting from consecutive reactions **2**–**4** (Scheme 1). The activation barrier to the addition of MMA to the polymer chain on this active site is 21 kJ/mol (Scheme 1).

We believe that ferrocene can also form a complex active polymerization site with similar structure. An analysis of possible reactions of Cp_2Fe with poly(methyl methacrylate) (PMMA) radicals and MMA molecules made it possible to find the energetically most probable processes and to suggest the following active site formation pathway (Scheme 2).

The calculated activation energy of MMA addition to the polymer chain in the $CpFe(R)(MMA)_2$ complex is 15 kJ/mol, close to the E_a of chain propagation for conventional free-radical MMA polymerization (19 kJ/mol [12).

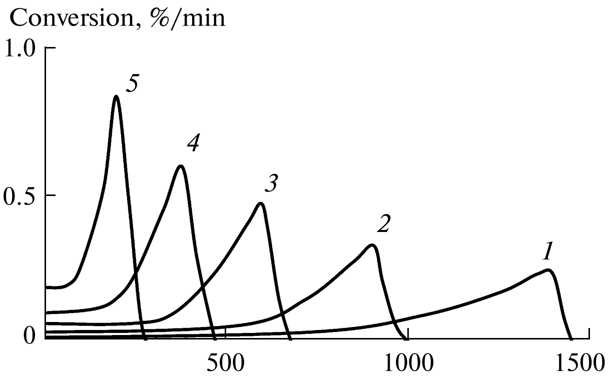


Fig. 3. Differential curves of MMA polymerization in the presence of BP–Cp_2^*Fe at the polymerization temperatures (*1*) 40, (*2*) 50, (*3*) 60, (*4*) 70, and (*5*) 80°C; [BP] = [Cp_2^*Fe] = 1 × 10^{-3} mol/L.

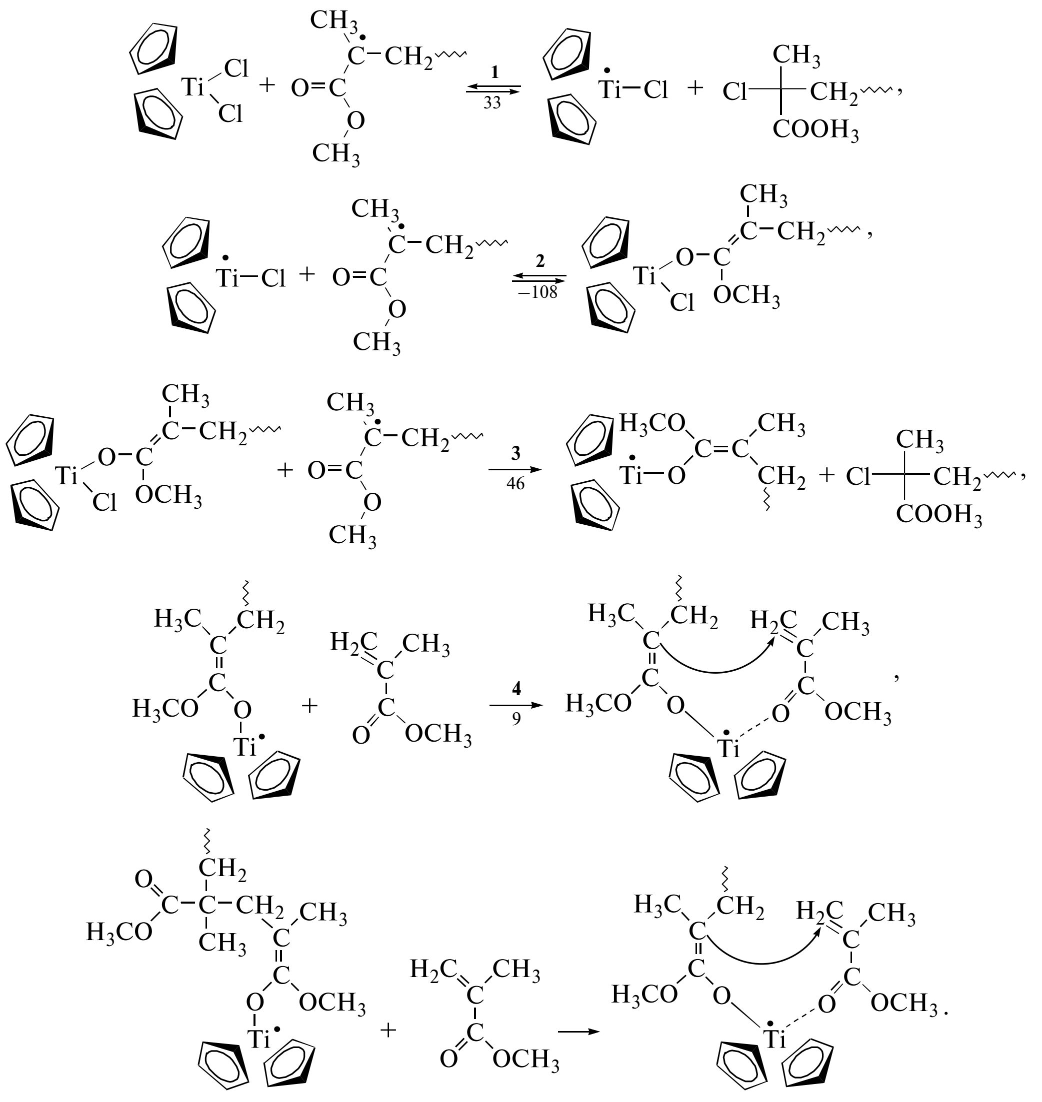
As can be seen from Schemes 1 and 2, the energy required for the formation of the complex active sites is low. Since these reactions are still endothermic, the elementary events of chain propagation occur mainly on the free radicals, and part of them interacts with MC (FH, Cp_2TiCl_2) and turns into complex sites of polymerization. An increase in the polymerization temperature within certain limits should naturally increase the probability of the formation of complex sites of chain propagation.

The chain propagation reactions involving the MCs considered in this work are similar to the chain propagation reactions under ion-coordination polymerization conditions. This provides good reason for introduction of the term "coordination–radical polymerization." This chain propagation mechanism (in which the carbonyl groups of the radical and monomer are simultaneously coordinated to the metal atom of the complex-forming molecule) was proposed as early as the 1970s, when the radical polymerization of vinyl monomers in the presence of Lewis acids was extensively studied [17].

The complex sites cannot participate in the quadratic-law termination reactions. Therefore, their presence in the polymerization system affects not only the chain propagation stage, but also the chain termination stage, and this can be the reason why the gel effect is smoothed.

Thus, a specific feature of the initiation of MMA polymerization in the presence of the MC–BP systems is the formation of a charge-transfer complex between the initiator and MC. According to the quantum-chemical calculations performed in this study, the polymerization process is accelerated in the presence of MC due to the free-radical decomposition of

Reactions of Cp_2TiCl_2 with macroradicals and monomer molecules making it possible to control MMA radical polymerization [16]



Scheme 1.

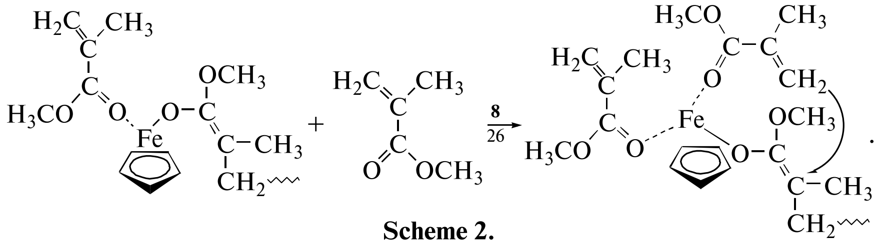
(Hereafter, the numbers under arrows are the heats of reactions in kJ/mol)

Reactions of Cp_2Fe with macroradicals and monomer molecules resulting in the formation of the complex site of MMA polymerization

$$Cp_2Fe + R^{\bullet} \xrightarrow[3]{5} CpFe^{\bullet}(C_5H_5R),$$

$$CpFe^{\bullet}(C_5H_5R) + R^{\bullet} \xrightarrow[11]{6} CpFe(C_5H_5R)(R),$$

$$CpFe(C_5H_5R)(R) + MMA \xrightarrow[34]{7} C_5H_5R + CpFe(MMA)(R),$$



Scheme 2.

the complex involving monomer molecules. The probability of formation and decomposition of the complex depends on the nature of the MC used. Ferrocene and acetylferrocene catalyze peroxide decomposition most efficiently, which is due to the low positive heat of formation of the corresponding complexes and the high exothermicity of their decomposition. When titanocene dichloride and zirconocene dichloride are used, the formation of a complex with the initiator requires considerable energy and, hence, their influence on peroxide decomposition is weak.

The effect of the MCs is also manifested at the chain propagation stage. Under certain conditions, depending on the MC nature, complex sites incapable of participating in quadratic-law chain termination form, which results in the smoothing of the gel effect and ensures that polymerization occurs in a controlled regime.

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