

Radical polymerization of methyl methacrylate in the presence of benzoyl peroxide, ferrocene and zirconocene dichloride

Yurii B. Monakov, Regina M. Islamova,* Anna K. Frizen,
Olesya I. Golovocheva and Svetlana V. Nazarova

Institute of Organic Chemistry, Ufa Scientific Center of the Russian Academy of Sciences, 450054 Ufa, Russian Federation. Fax: +7 347 235 6166; e-mail: puzin@anrb.ru

DOI: 10.1016/j.mencom.2011.07.012

The controlled radical polymerization of methyl methacrylate initiated by the ferrocene–zirconocene dichloride–benzoyl peroxide system was found to occur as a living radical process with an increased concentration of syndio-triads in the resulting poly(methyl methacrylate).

Metallocenes have been used in the radical polymerization of vinyl monomers more than thirty years. The influence of ferrocene (FC), titanocene (TC), zirconocene (ZRC), diindenylzirconocene (IZRC) dichlorides^{1–5} and others^{6,7} have been investigated in detail. Metallocenes in combination with peroxide compounds form initiating systems for polymerization at lowered temperatures. At the same time, FC forms the most active initiating system with benzoyl peroxide (BP). The initial rate of methyl methacrylate (MMA) polymerization in the presence of FC and BP increased by a factor of 10, and the effective activation energy decreased from 75–80 to 48–40 kJ mol⁻¹, as compared with polymerization initiated by peroxide without metal complex addition.¹ It was found by spectroscopic and quantum chemical methods⁵ that a strong increase in the rate results from the formation and following rapid decomposition of a FC–BP charge transfer complex.

Chlorinated metallocenes in combination with peroxides form less active initiating systems, as compared with FC. Note that the concentration of syndiotactic fragments in PMMA increases by 5–10% in the presence of FC, TC, ZRC or IZRC.^{1–4} It is most likely that polymerization in the presence of metallocenes occurs by a complex-radical mechanism. This was confirmed by quantum-chemical calculations (formation of intermediates of monomer and growing macroradical⁹) and spectroscopic methods (interaction of monomer and metal complex additives^{2–4}).

However, the presence of chlorine atoms in TC, ZRC, IZRC *etc.* do not exclude living radical polymerization by reverse atom transfer and/or reverse inhibition mechanisms.^{6,8,9} Polymerization in a living manner was not observed in the metallocene (FC, ZRC, IZRC)–BP initiating systems.^{1–5} It can be expected that a combination of chlorinated metallocenes with FC, which facilitate rapid dissociation of diacyl peroxides into radicals, provides optimal conditions for the controlled growth of macrochains by a living radical polymerization mechanism. The goal of this study was to investigate the radical polymerization of MMA initiated by BP in the presence of FC and ZRC.[†]

In MMA polymerization in the presence of two metallocenes, the rate of the process at the initial stages of conversion (5–10%) increased strongly, as compared with that of BP and the ZRC–BP system, or decreased, as compared with the FC–BP system [Figure 1(a)]. With raising FC concentration to 3.0 mmol dm⁻³ (ZRC and BP concentrations of 1.0 mmol dm⁻³), the total rate of polymerization increased, whereas the total rate slowed down with raising ZRC concentration under analogous conditions [Figure 1(b)].

The polydispersity coefficient (M_w/M_n) decreased to 1.3–1.4 with increasing FC concentration to the ratio FC:ZRC:BP = 3:1:1

(the concentration of BP was 1.0 mmol dm⁻³) at an initial degree of conversion (5–10%), and it was no higher than 2.0–2.1 at higher conversions (Figure 2). The number-average molecular weight (M_n) of the polymer increases linearly with monomer conversion (Figure 2). The undesirable gel effect that narrows M_w/M_n and the linear dependence of M_n on conversion suggest the living growth of a polymer chain in the presence of FC and ZRC additives.^{8,9} This suggestion is confirmed by quantum-chemical calculations.

The reactions of FC with MMA and BP, as well as with the poly(methyl methacrylate) propagating radicals, were investigated earlier.^{5,17,18} FC catalyzes the decomposition of BP. Moreover, a part of elementary propagation acts may occur in the coordination

[†] MMA (Fluka) was twice distilled under reduced pressure (bp 48 °C, 140 Torr). Benzoyl peroxide was recrystallized three times from methanol and dried at room temperature in a vacuum. FC and ZRC (Fluka) were used without further purification.

For bulk polymerization, the reaction mixtures were placed in glass ampoules, the solution was degassed by freeze–pump–thaw cycles repeated three times to a residual pressure of 1.3 Pa and the ampoules were sealed and placed in a thermostat (± 0.1 °C). After the reaction, the ampoules were cooled and unsealed. The resulting polymer was dissolved in acetone and precipitated with a 10- to 15-fold amount of methanol. The process kinetics was studied by dilatometry and gravimetry according to well-known methods.¹⁰

The molecular-weight characteristics were determined by gel penetration chromatography on a Water GPS 2000 System liquid chromatograph equipped with a differential refractometer and HT-3, HT-4 and HT-6 columns. The eluent was THF; flow rate of 0.5 ml min⁻¹. The system of columns was calibrated against polystyrene standard with a polydispersity of ≤ 1.2 .

Syndiotactic sequences in PMMA were determined according to a published procedure.¹¹

The quantum-chemical calculations were performed using the Priroda-06 program.^{12,13} The generalized gradient approximation for the exchange-correlation functional by Perdew, Burke, and Ernzerhof was employed.¹⁴ The electronic configurations of the molecular systems were described by the orbital basis sets of contracted Gaussian-type functions of size (5s1p)/[3s1p] for H, (11s6p2d)/[6s3p2d] for C and O, (15s11p2d)/[10s6p2d] for Cl, and (20s16p11d)/[14s11p7d] for Zr, which were used in combination with the density-fitting basis sets of uncontracted Gaussian-type functions of size (5s2p) for H, (10s3p3d1f) for C and O, (14s3p3d1f1g) for Cl, and (22s5p5d4f4g) for Zr. The quantum-chemical method reproduces well the geometries of zirconocenes, as demonstrated previously.^{15,16} The structures were optimized without symmetry restriction. Analytical second derivatives were used to determine the type of a stationary point. The enthalpies of reactions ($\Delta_r H^0$) were determined at 298 K. The Et⁺C(Me)(COOMe) species (R⁺) was used as a model of poly(methyl methacrylate) propagating radical.

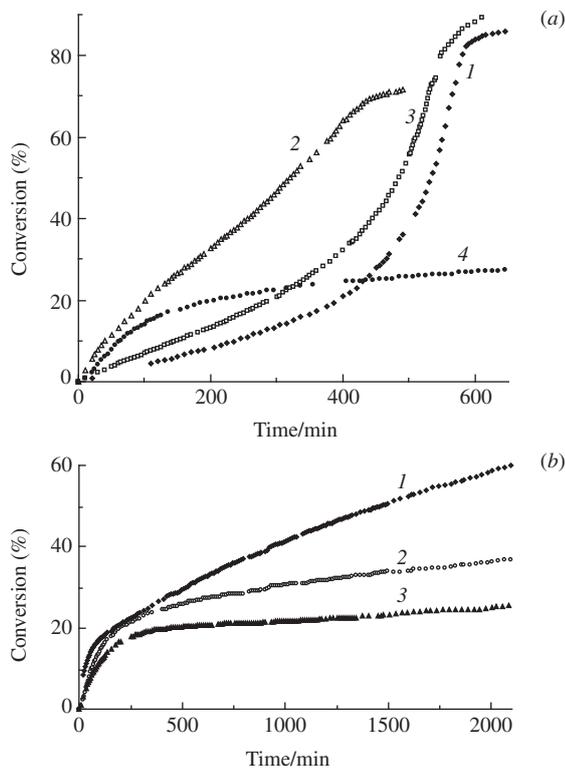


Figure 1 Kinetic curves of MMA polymerization at 60°C, initiated by (a) (1) BP, (2) FC–BP system, (3) ZRC–BP system and (4) FC–ZRC–BP system. [FC] = [ZRC] = [BP] = 1.0 mmol dm⁻³; (b) FC–ZRC–BP system, the FC:ZRC:BP ratios are (1) 3:1:1, (2) 1:1:1 and (3) 1:3:1, [BP] = 1.0 mmol dm⁻³.

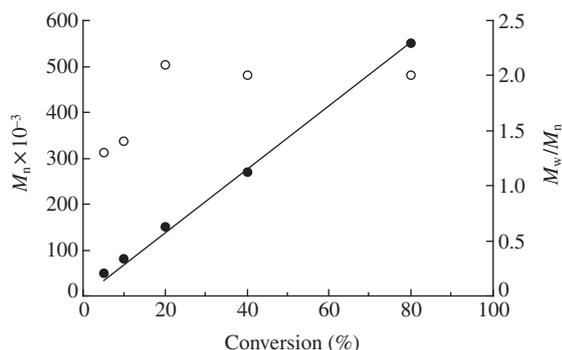
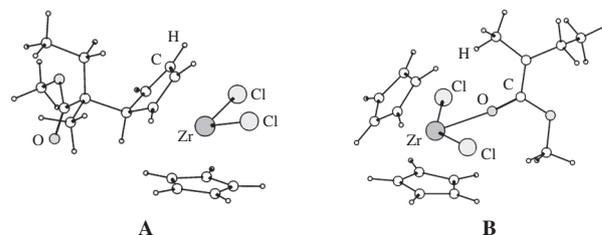


Figure 2 Dependence of M_n (closed circles) and M_w/M_n (open circles) of PMMA obtained in the presence of FC, ZRC and BP at 60°C on the conversion of the monomer. [BP] = [FC] = [ZRC] = 1.0 mmol dm⁻³.

sphere of Fe *via* a complex-radical mechanism, *i.e.*, FC influences not only the initiation stage but also chain propagation. It is evident that the polymerization of MMA in the presence of both FC and ZRC is determined by the reactions of FC with PMMA radicals and MMA molecules and by analogous reactions with the participation of ZRC. According to the results of calculations,¹⁹ the reaction $\text{Cp}_2\text{ZrCl}_2 + \text{R}^* \rightarrow \text{R-Zr}^*\text{Cp}_2\text{Cl}_2$, which leads to Zr–C bond formation, is impossible. The heat of the chlorine atom transfer reaction $\text{Cp}_2\text{ZrCl}_2 + \text{R}^* \rightarrow \text{Cp}_2\text{Zr}^*\text{Cl} + \text{RCl}$ is 138 kJ mol⁻¹; *i.e.*, its probability is too small. However, the addition of R* to the carbon atom of the cyclopentadienyl ring is probable: $\text{Cp}_2\text{ZrCl}_2 + \text{R}^* \rightarrow \text{CpZr}^*\text{Cl}(\text{C}_5\text{H}_5\text{R})$. The heat of this reaction is 37 kJ mol⁻¹.¹⁹ Since the reactions of ZRC with R* are endothermic, the equilibrium between the active free radicals and the ‘dormant’ chains will be shifted to the left. Thus, the reasons for the absence of a dramatically expressed regulating effect of ZRC upon the MMA polymerization initiated by BP become clear.

It is evident that the living character of MMA polymerization in the presence of the FC–ZRC–BP initiating system is caused

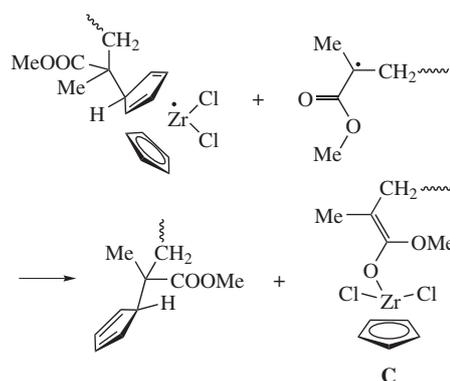


by the interaction of ZRC with the polymerization mixture components. The reaction intermediates are responsible for the controlled polymerization process. The presence of FC allows the fast formation of initiating radicals to occur; the further transformations of intermediate **A** are unclear.

During the investigation of primary reactions between ZRC and PMMA radicals, it was found that the zirconium atom is capable of adding the carbonyl group of R* to yield intermediate **B**.

The calculated value of $\Delta_r H^0$ for this reaction is 34 kJ mol⁻¹. Thus, the formation of intermediates **A** and **B** is approximately equiprobable. Species **A** and **B** are metalloradicals: in both cases, the spin density at the Zr atom is about 1 a.u.

We analyzed the interaction of **A** and **B** with both PMMA radicals and MMA molecules. Based on the calculated values of $\Delta_r H^0$, the most energetically favorable reactions were revealed. During the interaction of **A** with R*, the dissociation of the cyclic diene ligand C₅H₅R occurs ($\Delta_r H^0 = 141 \text{ kJ mol}^{-1}$) (Scheme 1).



Scheme 1

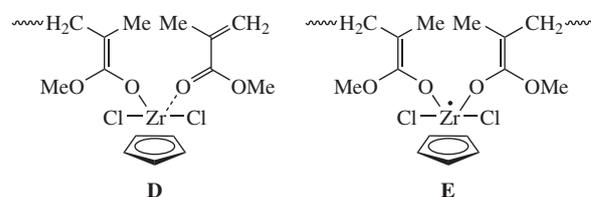
The carbonyl groups of MMA and R* can coordinate to the metal in CpZrCl₂(R) (**C**) to give **D** and **E**, respectively.

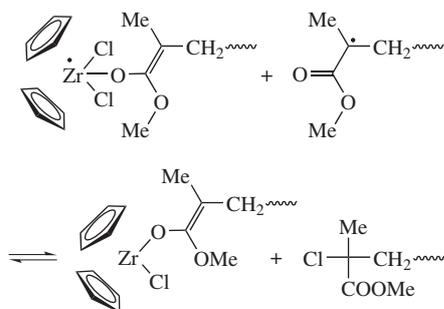
Complex **B** can take part in chlorine atom transfer ($\Delta_r H^0 = 98 \text{ kJ mol}^{-1}$) (Scheme 2).

The addition of the PMMA radical to the Cp ring of **B** can occur to cause the deprivation of C₅H₅R and formation of **C**.

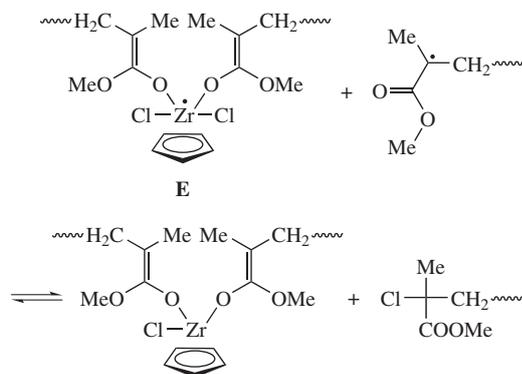
Intermediate **E** is active in the chlorine atom transfer reaction ($\Delta_r H^0 = 55 \text{ kJ mol}^{-1}$) (Scheme 3).

It is well known that fast initiation is necessary for the successful controlled radical polymerization.⁸ Evidently, the fast decomposition of a charge-transfer FC–BP complex occurs in the presence of FC and ZRC in the polymerization mixture. Thus, the generation of free radicals is quick (practically simultaneous). As a result, sufficient amounts of intermediates **B** and **E**, which are responsible for ATRP, are formed already at the initial stage of polymerization. However, in the case of the ZRC–BP initiating





Scheme 2



Scheme 3

system, the decomposition of the initiator proceeds more slowly, and conventional radical polymerization predominates. Thus, the cooperative action of FC, ZRC and BP provides suitable concentrations of complexes **B** and **E** for ATRP.

Note that FC and ZRC control macrochain growth and stereochemistry. The concentration of syndio-triads in PMMA obtained using the FC–ZRC–BP system increased by ~7%, as in the case of the FC–BP and ZRC–BP systems (Table 1). It was shown^{1–5} that the microstructure of PMMA synthesized using two metallocenes changed due to the formation of intermediate complexes with the monomer and radicals. In particular, the interaction between ZRC and MMA was studied.^{2,4} We investigated the complexation of FC with the monomer by IR spectroscopy. An absorption band at 1730 cm⁻¹ was shifted to 1737 cm⁻¹, and bands at 1737, 1722 and 1707 cm⁻¹ were observed upon mixing FC with an excess of MMA (Figure 3). It is obvious that a coordination bond between iron atoms and carbonyl oxygen is formed. Quantum-chemical calculations⁵ confirmed the possibility of this interaction.

Based on quantum-chemical calculations, the structures of the complex-radical active sites were proposed for FC and TC.^{17,20} According to the results of our calculations, the addition of MMA to a propagating radical occurs in an analogous manner in the coordination sphere of zirconium in **D**. The enthalpy of activation for this chain propagation reaction (28 kJ mol⁻¹) is close to the enthalpy of the free-radical addition of MMA to R* (~20 kJ mol⁻¹). Therefore, changes in the microstructure of PMMA synthesized in the presence of ZRC are caused by the complex-radical mechanism.

Table 1 Microstructure of PMMA obtained in the presence of FC–ZRC–BP systems at 60 °C. [BP] = 1.0 mmol dm⁻³. Conversion of PMMA was 10%.

[FC]/ mmol dm ⁻³	[ZRC]/ mmol dm ⁻³	Triads content (%)		
		syndio	hetero	iso
0	0	56	42	2
1.0	0	65	35	–
0	1.0	64	36	–
1.0	1.0	63	33	4

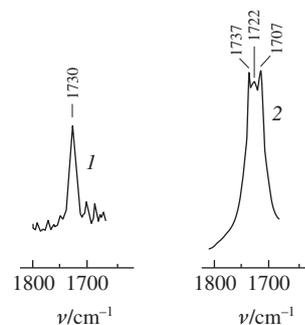


Figure 3 IR spectra of (1) MMA and (2) FC and MMA mixture. [FC] = 10.0 mmol dm⁻³, [MMA] = 10.0 mol dm⁻³. Temperature, 25 °C; solvent, CCl₄.

Thus, on the addition of FC and ZRC in the polymerization of MMA initiated by benzoyl peroxide, the features of living radical growth were observed. Furthermore, stereoregular functions remained because elementary propagating acts can occur in the coordination spheres of Fe and Zr atoms.

The study was supported by a Federal special programme (state contract no. 02.740.11.0648). The calculations were performed on the cluster supercomputer at the Institute of Organic Chemistry of the Ufa Scientific Center of the RAS.

References

- Yu. I. Puzin, R. Kh. Yumagulova and V. A. Kraikin, *Eur. Polym. J.*, 2001, **37**, 1801.
- Yu. I. Puzin, E. M. Prokudina, R. Kh. Yumagulova, R. R. Muslukhov and S. V. Kolesov, *Dokl. Akad. Nauk*, 2002, **386**, 69 [*Dokl. Phys. Chem. (Engl. Transl.)*, 2002, **386**, 211].
- S. V. Kolesov, R. Kh. Yumagulova, E. M. Prokudina, R. R. Muslukhov, Yu. I. Puzin, S. I. Kuznetsov and I. A. Ionova, *Vysokomol. Soedin.*, 2003, **45**, 324 (in Russian).
- R. M. Islamova, Yu. I. Puzin, R. Kh. Yumagulova, A. A. Fatykhov, L. V. Parfenova, U. M. Dzhemilev and Yu. B. Monakov, *Vysokomol. Soedin.*, 2006, **48**, 1101 (*Polym. Sci., Ser. A*, 2006, **48**, 712).
- A. K. Friesen, *PhD Thesis*, Ufa, 2007.
- E. L. Grogneć, J. Claverie and R. Poli, *J. Am. Chem. Soc.*, 2001, **123**, 9513.
- D. F. Grishin, L. L. Semenicheva, E. V. Telegina, A. S. Smirnov and V. I. Nevodchikov, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 482 (*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 505).
- A. V. Yakimanskii, *Vysokomol. Soedin.*, 2005, **47**, 1241 (in Russian).
- K. Matyjaszewski and J. Xia, *Chem. Rev.*, 2001, **101**, 2921.
- G. P. Gladyshev and K. M. Gibov, *Polimerizatsiya pri glubokikh stepeniyakh prevrashcheniya i metody ee issledovaniya (Polymerization at High Conversions and Methods for its Investigation)*, Nauka, Moscow, 1974, p. 244 (in Russian).
- R. C. Ferguson, *J. Am. Chem. Soc., Polym. Prepr.*, 1985, **6**, 182.
- D. N. Laikov, *PRIRODA, Electronic Structure Code*, Version 6, 2006.
- D. N. Laikov and Yu. A. Ustynyuk, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 804 (*Russ. Chem. Bull., Int. Ed.*, 2005, **54**, 820).
- J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- I. E. Nifant'ev, L. Yu. Ustynyuk and D. N. Laikov, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 1168 (*Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 1164).
- E. Yu. Pankratyev, T. V. Tyumkina, L. V. Parfenova, L. M. Khalilov, S. L. Khursan and U. M. Dzhemilev, *Organometallics*, 2009, **28**, 968.
- A. K. Friesen, S. L. Khursan, S. V. Kolesov and Yu. B. Monakov, in *Success in Chemistry and Biochemistry: Mind's Flight in Time and Space*, ed. G. E. Zaikov, N. M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, 2009, vol. 4, p. 497.
- A. K. Frizen, S. L. Khursan, S. V. Kolesov and Yu. B. Monakov, *Khim. Fiz.*, 2009, **28**, 87 (*Russ. J. Phys. Chem., Ser. B*, 2009, **3**, 674).
- A. A. Shchepalov and D. F. Grishin, *Izv. Akad. Nauk, Ser. Khim.*, 2007, 1690 (*Russ. Chem. Bull., Int. Ed.*, 2007, **56**, 1752).
- A. K. Friesen, S. L. Khursan and Yu. B. Monakov, *Izv. Vuzov, Khimiya Khim. Tekhnol.*, 2010, **53**, 70 (in Russian).

Received: 15th December 2010; Com. 10/3643