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Mechanism of methyl methacrylate polymerization initiated by benzoyl peroxide and ferrocene in the presence of oxygen

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The role of the ferrocenium radical cation and Cp_2Fe^+–$O^\bullet$ radical in the initiation of methyl methacrylate polymerization in the absence and presence of oxygen was demonstrated.

The ferrocene (Cp_2Fe)–benzoyl peroxide (BP) initiating system is often used for the polymerization of vinyl monomers. The polymerization of methyl methacrylate (MMA) in the presence of ferrocene derivatives is affected by the nature of the initiator. In the case of BP, the reaction was accelerated.[1] The reaction between Cp_2Fe and BP leads to the formation of iron(II) benzoate, which catalyzes the decomposition of BP.[2,3] According to published data,[4] the formation of active centres in the initiating system occurs through charge-transfer complexes, which easily decompose in the presence of a monomer. Ferrocene is involved in macrochain propagation by a complex–radical mechanism.

It was found[1] that Cp_2Fe reacts with BP through the formation of the ferrocenium cation and Fe^{III} by the following reactions:

$$Cp_2Fe + [PhC(O)O]_2 \rightarrow [Cp_2Fe^+]PhC(O)O^- + PhC(O)O^\bullet$$

$$Cp_2Fe^+ + PhC(O)O^\bullet \rightarrow Fe^{2+} + PhC(O)O^- + 2C_5H_5$$

$$Fe^{2+} + [PhC(O)O]_2 \rightarrow Fe^{3+} + PhC(O)O^- + PhC(O)O^\bullet$$

Immediately after the homogenization of the components, a green complex appeared, and the BP radical was obtained.[2] The green colour gradually changed to yellow due to the decomposition of ferrocenium to ferrocene and the second radical:

$$[Cp_2Fe^+]PhC(O)O^- \rightarrow Cp_2Fe + PhC(O)O^\bullet$$

The role of the ferrocenium radical cation in the initiation mechanism of MMA polymerization in the presence of BP and ferrocene is unclear. Here, we discuss the results of a spectrophotometric study of the interaction of BP with Cp_2Fe and the mechanism of MMA polymerization initiated by reaction products.

In isooctane, Cp_2Fe and BP ($[Cp_2Fe]_0 = [BP]_0 = 5$ mmol dm^{-3}) are not spent at 285 K during 120 min. The addition of MMA to a solution of Cp_2Fe in isooctane ($[Cp_2Fe]_0 = 5$ mmol dm^{-3}; $[MMA]_0 = 50$ mmol dm^{-3}) leads to an increase in the molar absorption coefficient of Cp_2Fe. A weak complex of Cp_2Fe with MMA can be formed in cyclohexane ($K = 0.1$).[5]

Ferrocene reacts with BP in ethanol and acetonitrile in the entire test temperature range. In the UV spectra, an absorption band due to the ferrocenium cation appears at 611 nm[6,7] (Figures 1S and 2S, see Online Supplementary Materials).

The ferrocenium cation has a signal in the EPR spectra.[8] In the EPR spectra of mixed solutions of Cp_2Fe and BP, we observed a signal due to $Cp_2Fe^{+\bullet}$. Figure 3S (see Online Supplementary Materials) shows the absorption spectrum of a blue solution of $Cp_2Fe^{+\bullet}$ and the product of its reaction with O_2. We believe that the salt of the ferrocenium radical cation $[Cp_2Fe^{+\bullet}]PhCO_2^-$ **1** was originally formed in a vacuum. Then, the diamagnetic [μ-(peroxy-O:O′)]diferrocenium benzoate $[Cp_2Fe^+$–OO–$^+FeCp_2][PhC(O)O^-]_2$ **2**, which has an absorption band at $\lambda_{max} = 611$ nm, was formed in the presence of oxygen. The peaks in the ^{1}H NMR spectrum do not have a broadening because of the absence of paramagnetic particles (Fe^{2+}, Fe^{3+}) from the test sample of **2**. The results of time-dependent DFT calculations performed for this compound are consistent with the experimental spectrum (Figure 3S). The UV-VIS spectra of Fe^{2+} and Fe^{3+} peroxides exhibited an absorption band at 600–700 nm.[9]

The transformation of the ferrocenium radical cation in the presence of oxygen was described.[10,11] The first detection and characterization of a similar Fe^{III} intermediate was performed by the oxidation of iron porphyrins.[12]

The reaction between ferrocene (5 mmol dm^{-3}) and BP (1.25 mmol dm^{-3}) proceeds similarly when MMA is used as a solvent (Figure 4S, see Online Supplementary Materials).

The absorbance at 611 nm gradually increased to reach a steady-state peak after 55 min. The experiment in MMA was stopped after 210 min due to the strong increase of viscosity as a result of polymerization in air. Since the thermal decomposition of BP at this temperature is negligible and does not initiate the polymerization of MMA, we have assumed that the resulting compound **2** is the initiator of polymerization.

Investigation of MMA polymerization in the presence of Cp_2Fe and BP (molar ratio of 4 : 1) in air by dilatometry showed that polymerization proceeds to a high conversion at a high rate (Figure 1, curve *1*). The kinetics of polymerization under anaerobic and aerobic conditions differed only slightly (Figure 1, curves *1*, *2*), initial polymerization rates are 45.8 and 46.0 mmol dm^{-3} min^{-1}, respectively. Apparently, the interaction of ferrocene with BP leads to the formation of **2**, which initiates polymerization. The degassing by freeze-pump-thaw cycles repeated three times does not affect the polymerization mode. In that case, the rate of polymerization is lower than that of polymerization with an access of air (Figure 1, curve *3*). In the absence of oxygen, the maximum concentration of the ferrocenium radical cation salt was 2 mmol dm^{-3}, and the maximum concentration of **2** in the presence of air was 1 mmol dm^{-3}. Figure 1 shows that the initiating capability of **2** is higher than that of BP (curves *2* and *4*).

Thus, the polymerization of MMA in the presence of ferrocene and BP proceeds under both anaerobic and aerobic conditions. We assume that, in the former case, the initiator is the salt $[Cp_2Fe^{+\bullet}]PhCO_2^-$ **1** and BP radicals, and, in the latter case it is [μ-(peroxy-O:O′)]diferrocenium **2**.

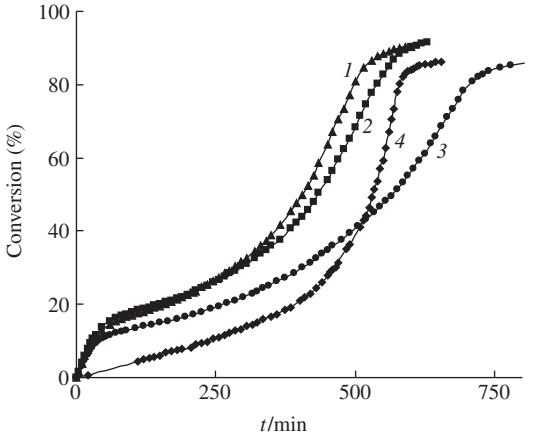


Figure 1 Conversion *vs.* time for the polymerization of MMA in the presence of (*1*)–(*3*) ferrocene and BP and (*4*) only BP at 60 °C. [Cp_2Fe] = 4 mmol dm^{-3}, [BP] = 1 mmol dm^{-3}. Polymerization conditions: (*1*) with access for air; (*2*), (*4*) standard method of polymerization mixture preparation; (*3*) without oxygen.

Compound **2** was educed during the reaction of ferrocene and BP in isooctane with access for air at room temperature. Its ^{1}H NMR spectrum in ethanol-d_6 revealed one singlet at δ 5.35 ppm for the cyclopentadienyl ring and two signals of the benzoate anion at δ 6.55 and 7.05 ppm. The IR spectra show the characteristic bands of the benzoate anion at 1653 (ν_{as}), 1400 (ν_s), 1250 (ν_{as}, aromatic ring), 720 (δ_{C-H} out of plane, aromatic ring), 675 (δ_{C-H}, aromatic ring) cm^{-1}, ferrocene at 476 cm^{-1} for Fe–C stretch and absorption bands at 800–1100 cm^{-1} for both. Iodometric titration shows the presence of one peroxide group.

It was found that [μ-(peroxy-O:O′)]diferrocenium **2** initiated the polymerization. A maximum monomer conversion of ~95% was achieved for 18–19 h (Figure 2, curve *1*), the polymerization of MMA initiated by BP occurred for 12–13 h (Figure 2, curve *3*). Ferrocene itself does not affect the polymerization (Figure 2, curves *4*, *5*). During storage the activity of **2** decreases and the polymerization proceeds at a lower rate (curve *2*).

The polymerization of MMA initiated by **2** in the presence of DPPH or *tert*-butanol (0.1 mmol dm^{-3}) was performed in order to determine the nature of activity centres. No induction period was observed during both of these polymerizations. Thus, we assume that the process is not purely radical or purely ionic but ion-radical, moreover living ion-radical process.

The rate of polymerization increases if the activity centre contains oligomer molecules (Figure 2, curve *6*).[13] This fact

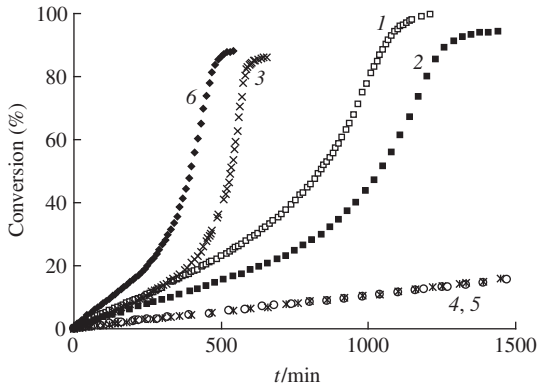


Figure 2 Conversion *vs.* time for the polymerization of MMA at 60 °C, standard method of preparation of polymerization mixture, [Cp_2Fe] = [BP] = = [**2**] = [($MMA_{10}Cp_2Fe^+O$)PhC(O)O$^-$] = 0.02 wt%: (*1*) 0.3 mmol dm^{-3} of **2**, freshly prepared; (*2*) 0.3 mmol dm^{-3} of **2** after storage for a week; (*3*) BP (1.0 mmol dm^{-3}); (*4*) Cp_2Fe (1.1 mmol dm^{-3}); (*5*) without initiator (thermal polymerization of MMA); (6) ($MMA_{10}Cp_2Fe^+O$)PhC(O)O$^-$ (0.15 mmol dm^{-3}).

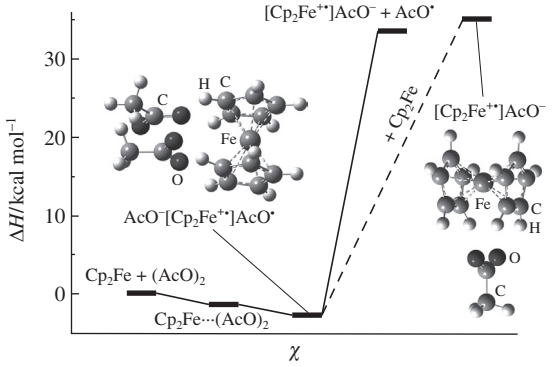
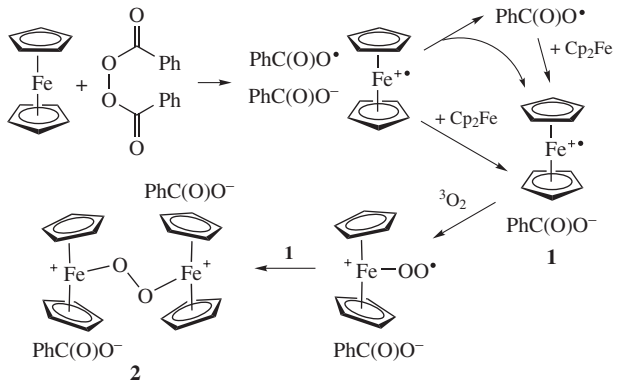


Figure 3 Energetic diagram for the ferrocene–diacetylperoxide system calculated at the mPW1K/6-31+G(d,p) level of theory.

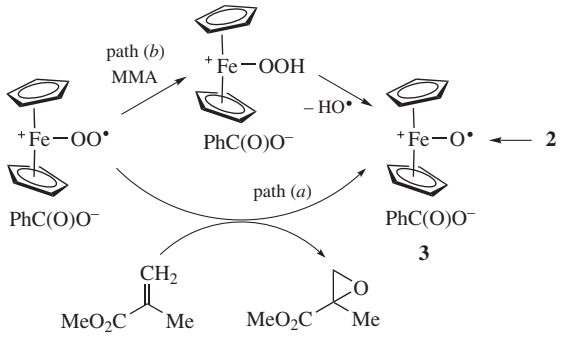
confirms that MMA polymerization proceeds in a living manner. The oligomer activity centre was prepared by a reaction of ferrocene (5 mmol dm^{-3}) with BP (5 mmol dm^{-3}) in the presence of MMA (50 mmol dm^{-3}) in isooctane. Voluminous blue-gray sediment, which is stable in a solid state, was educed from the reaction mixture. There are no signals in the EPR spectrum of the sediment, whereas its ^{1}H NMR spectrum in ethanol-d_6 revealed characteristic signals for isotactic PMMA[14] at δ 1.15 (Me), 3.5 (OMe), 2.18 (very weak, CH_2) ppm, and weak signals of the cyclopentadienyl ring at δ 8.04 ppm and two signals of benzoate anion at δ 7.46, 7.57 ppm. The IR spectra show the characteristic bands of the benzoate anion at 1653 (ν_{as}), 1400 (ν_s), 1250 (ν_{as}, aromatic ring), 720 (δ_{C-H} out of plane, aromatic ring), 675 (δ_{C-H}, aromatic ring), ferrocene at 478 cm^{-1} for Fe–C stretch and absorption bands at 800–1100 cm^{-1} for both. There is an absorption band due to the stretching vibrations of C=O at 1720 cm^{-1} and the stretching vibrations of COMe at 1270 cm^{-1} characteristic of MMA. The absorption band of the C=C bond at 1640 cm^{-1} is not observed in the IR spectrum of the oligomer.

We have calculated the energy of intermediates for ferrocene oxidation by diacetyl peroxide at the mPW1K/6-31+G(d,p) level (Figure 3). Peroxide and ferrocene form a weak complex (ΔH = = –1.3 kcal mol^{-1}), which is transformed by redox reaction in the complex of ferrocenium cation with AcO^- and $AcO^\bullet$. This complex either gives the free acetyl radical or reacts with another ferrocene molecule. The formed free acetyl radical can react with ferrocene giving [$Cp_2Fe^{+\bullet}$]AcO^-, the enthalpy of this reaction is –1.8 kcal mol^{-1}. Thus, the second step of the process can proceed as the destruction of the complex to form a free acetyl radical, which oxidizes ferrocene to [$Cp_2Fe^{+\bullet}$]AcO^- or as the direct reaction of $AcO^\bullet$[$Cp_2Fe^{+\bullet}$]AcO^- with ferrocene.

Based on the experimental data, we proposed the most probable reaction scheme (Schemes 1–4). Experimentally, we found that the interaction of ferrocene with BP rapidly affords the salt of the ferrocenium radical cation **1**, which in the presence of oxygen

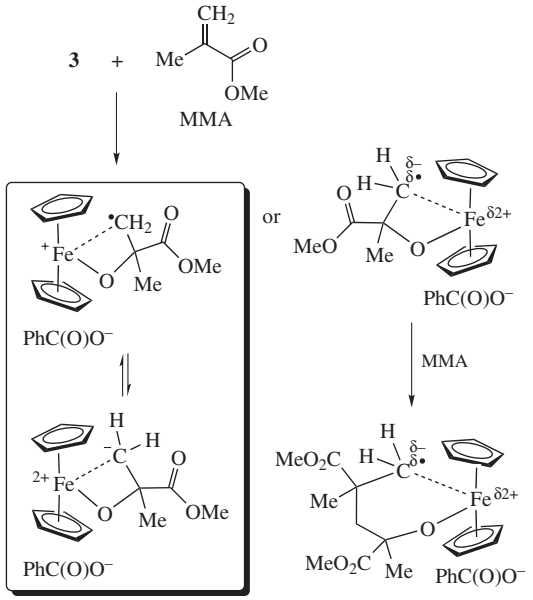


Scheme 1

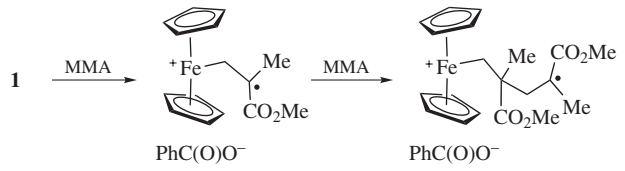


Scheme 2

quickly forms [μ-(peroxy-O:O′)]diferrocenium **2** (Scheme 1). The latter is unstable and decomposes through peroxy bond cleavage (Scheme 2). In the bulk polymerization of MMA, the Cp_2Fe^+–OO$^\bullet$ radical can react with the monomer. The first pathway is the oxidation of the monomer [path (*a*)], and the second is H-atom abstraction from MMA [path (*b*)] with the formation of an unstable hydroperoxide and a C-centered radical of MMA. In both cases under aerobic conditions, the Cp_2Fe^+–O$^\bullet$ radical **3** is generated. This radical reacts with the monomer to form the reaction center, where the electron density is delocalized between the carbon atom and the iron cation; the chain growth occurs due to the insertion of the monomer into the delocalized C···Fe bond (Scheme 3). The ferrocenium radical cation **1** initiates the polymerization in the absence of oxygen (Scheme 4).



Scheme 3



Scheme 4

In conclusion, the role of the ferrocenium radical cation and Cp_2Fe^+–O$^\bullet$ radical in the initiation of MMA polymerization in the absence and presence of oxygen was demonstrated and the formation of the [μ-(peroxy-O:O′)]diferrocenium was experimentally proved.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2013.01.020.

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