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Influence of 5,15-bis(4′-*tert*-butylphenyl)-2,8,12,18-tetra(*n*-butyl)-3,7,13,17-tetramethylporphyrin of Fe^{III} on methyl methacrylate and styrene radical polymerization

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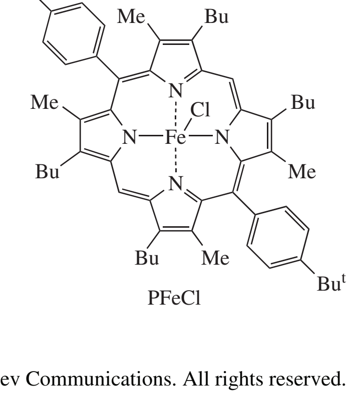
Controlled radical polymerization of methyl methacrylate and styrene initiated by azobisisobutironitrile or benzoyl peroxide in the presence of a chlorine-containing complex of Fe^{III} with 5,15-bis(4′-*tert*-butylphenyl)-2,8,12,18-tetra(*n*-butyl)-3,7,13,17-tetramethylporphyrin was investigated.

Controlled radical polymerization has recently become an important method for producing synthetic vinyl polymers. Compounds such as alkoxyamines, dithioesters, trithiocarbonates and xanthates were proposed as propagation regulators.[1] Organometal compounds of the general formula Mt^{n}YL, where Mt is a transition metal (Cu, Fe, Ru, Re, Ni, *etc.*); Y is a halogen anion (mainly chlorine or bromine); L is an organic ligand [mostly 2,2′-bipyridine, 4,4′-bi(5-nonyl)-2,2′-pyridine or triphenylphosphine] are of great interest. Their use underlies the most widely applicable methods of living radical polymerization – atom transfer radical polymerization (ATRP) and reverse atom transfer radical polymerization (RATRP), whose mechanisms are examined in detail by K. Matyjaszewski.[2–4] The main point of approach is reverse interaction of propagating radicals with additive – propagation regulator – results in suppression of bimolecular termination and uncontrolled increasing of polymer molecular mass.

The use of metal complexes of porphyrins in controlled radical polymerization could be very promising.[5] Thus, catalytic chain transfer to the monomer and catalytic inhibition were discovered in the polymerization of methacrylates carried out in the presence of cobalt porphyrins.[6–9] It was found that the cobalt complex of tetramesitylporphyrin initiates polymerization of acrylates leading to the formation of homopolymers and block copolymers.[10,11] In this case, a linear increase in the number-average molecular mass with conversion and low polydispersity coefficients are observed ($M_w/M_n \approx 1.1$). However, only few metal porphyrins, which are well-soluble in organic media, mainly, cobalt, rhodium, aluminum complexes, allowing the radical polymerization of vinyl monomers to occur under controlled mode, have been studied.[10–14]



PFeCl

The goal of this work was to study the bulk radical polymerization of methyl methacrylate (MMA) and styrene initiated by azobisisobutironitrile (AIBN) or benzoyl peroxide in the presence of chlorine-containing complex of 5,15-bis(4′-*tert*-butylphenyl)-2,8,12,18-tetra(*n*-butyl)-3,7,13,17-tetramethylporphyrin Fe^{III} (PFeCl). The above metal porphyrin has been first used for polymerization processes.†

The use of chlorine-containing porphyrin of Fe^{III} in the bulk radical polymerization of MMA initiated by AIBN at 60 °C leads to a decrease in the overall polymerization rate in comparison with the polymerization in the presence of AIBN only. A successive increase in the iron porphyrin concentration from 0.5 to 3.0 mmol dm^{-3} (concentration of AIBN, 1.0 mmol dm^{-3}) facilitates a process deceleration, considerable decrease in the auto acceleration and allows one to suppress undesirable gel effect [Figure 1(*a*)].

Polymethyl methacrylate (PMMA) synthesized in the presence of AIBN and iron porphyrin has homogeneous structure without

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† Methyl methacrylate (Fluka) and styrene (Fluka) were twice distilled under reduced pressure: bp 48 °C (140 Torr) and bp 52 °C (27 Torr), respectively. Benzoyl peroxide and AIBN were recrystallized three times from ethanol and dried at room temperature under a vacuum to constant weight. Purity of monomers and initiators was controlled by ^{1}H NMR spectroscopy.

Iron porphyrin was synthesized and purified as described elsewhere.[15]

Polymerization mixtures were placed in glass ampoules, degassed by three freeze–pump–thaw cycles to a residual pressure of 1.3 Pa, sealed and placed in a water (oil) bath at 60 or 100 (±0.1) °C. After the predetermined intervals, ampoules were cooled and unsealed. The obtained polymers were purified from residual initiator and additive by dissolving in acetone followed by precipitating with a 10–15-fold excess of methanol three times. The kinetics of bulk polymerization was studied by the dilatometric method.[16]

Molecular weight characteristics (M_n is the number-average molecular mass, M_w is the weight-average molecular mass and M_w/M_n is the coefficient of polydispersity) were determined by gel penetrating chromatography performed on a Waters GPC 2000 System chromatograph (eluent, THF; flow rate, 0.5 ml min^{-1}). Chromatographic columns were standardized with polystyrene standards ($M_w/M_n \le 1.2$).

^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AM-300 spectrometer at 25 °C. TMS was used as an internal standard. Contents of syndio-, hetero- and isotactic fragments were determined using ^{1}H NMR spectra.[17] Physicochemical characteristics of purified distilled solvents (MeOH, acetone, THF, glycerol and $CDCl_3$) satisfy the requirements.[18]

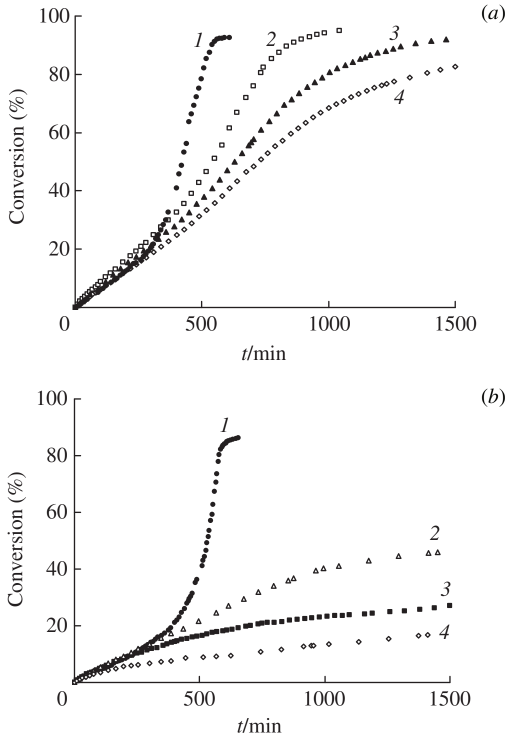


Figure 1 Conversion of MMA *vs.* polymerization time at 60 °C in the presence of (*a*) AIBN (1.0 mmol dm^{-3}) and PFeCl; (*b*) benzoyl peroxide (1.0 mmol dm^{-3}) and PFeCl; (*1*) 0, (*2*) 0.5, (*3*) 1.0 and (*4*) 3.0 mmol dm^{-3} of PFeCl.

any defects and colours from light brown to dark brown depending on iron porphyrin concentration. The molecular mass of polymers obtained at an additive to initiator mole ratio of 1:1 (concentration of AIBN, 1.0 mmol dm^{-3}) about 2–3 times less compared to the samples synthesized solely with azoinitiator. The number-average molecular mass M_n of the polymer depends linearly on monomer conversion beginning from 10% conversion, the polydispersity coefficients remain almost unchanged in the course of polymerization and amount 1.4–1.5 (Figure 2), which are smaller than in the case of common free-radical polymerization ($M_w/M_n \geq 2.0$).[1,2] Molecular weight distribution curves for PMMA are unimodal (Figure 3). In the presence of iron porphyrin the content of syndiotactic fragments in the PMMA chains increases by 3–5% compared to polymers synthesized solely with AIBN: 59–61% syndiotactic sequences against 55–56%.

Obtained data evidence features of the living process.[1,2] The revival of macromolecules can probably occur *via* the RATRP (Scheme 1).

Note that along with living macromolecules there are ‘dead’ macromolecules due to bimolecular termination of macroradicals in simultaneous free-radical polymerization. Thereof M_n–conversion curve intercepts on an ordinate axis (Figure 2, curve *1*).

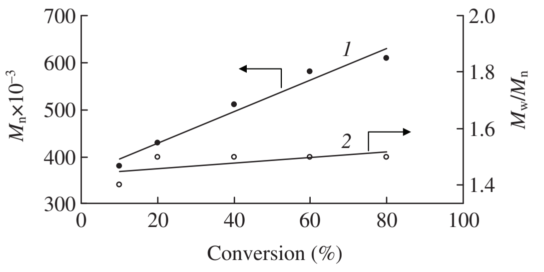


Figure 2 (*1*) M_n and (*2*) M_w/M_n of PMMA produced in the presence of AIBN and PFeCl as a function of monomer conversion. [PFeCl] = [AIBN] = = 1.0 mmol dm^{-3}. Polymerization temperature is 60 °C.

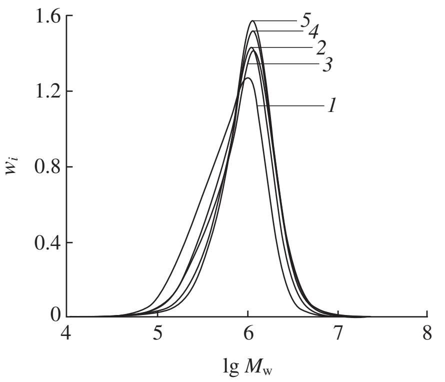
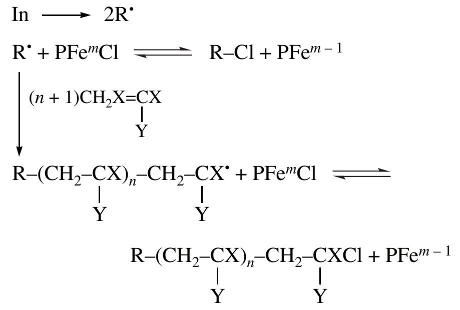


Figure 3 Molecular weight distribution curves of PMMA obtained in the presence of AIBN and PFeCl. Conversion (%): (*1*) 10, (*2*) 20, (*3*) 40, (*4*) 60 and (*5*) 80. [AIBN] = [PFeCl] = 1.0 mmol dm^{-3}. Polymerization temperature is 60 °C; w_i is the mass fraction of macromolecules with certain molecular mass.



Scheme 1

The bulk polymerization of styrene initiated by AIBN in the presence of iron porphyrin at 100 °C occurs practically in the same manner as the process without metal porphyrin [Figure 4(*a*)]. An increase in the additive concentration leads to insignificant reduction in the overall polymerization rate. It was mentioned that living radical polymerization regulators may not affect poly-

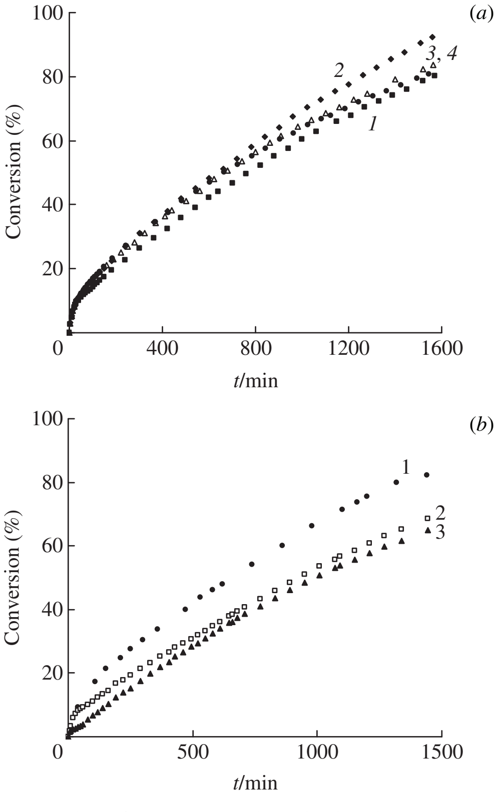


Figure 4 Conversion of styrene *vs.* polymerization time at 100 °C in the presence of (*a*) 1.0 mmol dm^{-3} AIBN and (*1*) 0, (*2*) 0.5, (*3*) 1.0 and (*4*) 3.0 mmol dm^{-3} of PFeCl; (*b*) 1.0 mmol dm^{-3} benzoyl peroxide and (*1*) 0, (*2*) 1.0 and (*3*) 3.0 mmol dm^{-3} PFeCl.

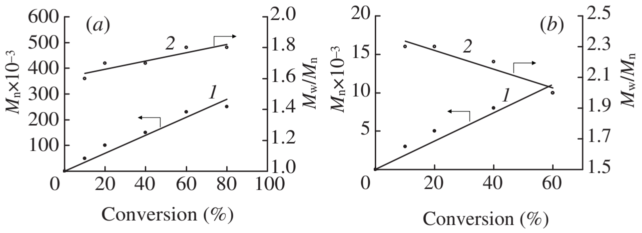


Figure 5 (*a*) (*1*) M_n and (*2*) M_w/M_n of polystyrene produced in the presence of AIBN and PFeCl as a function of monomer conversion. [PFeCl] = [AIBN] = 1.0 mmol dm^{-3}. (*b*) (*1*) Mn and (*2*) M_w/M_n of polystyrene produced in the presence of benzoyl peroxide and PFeCl as a function of monomer conversion. [Benzoyl peroxide] = [PFeCl] = = 1.0 mmol dm^{-3}. Polymerization temperature is 100 °C.

merization rate.[19] Note that there is a unique combination of initiating system components and temperature for each monomer to carry out successful living polymerization.[1]

Polystyrene obtained in the presence of iron porphyrin had the same properties (homogeneity, colour, molecular characteristics) as PMMA. So, the molecular mass of polystyrene decreases about 2–3 times compared to the samples synthesized solely with AIBN. The M_n of the polymers increases linearly on conversion, the polydispersity coefficients change insignificantly in the polymerization course and amount 1.6–1.8 [Figure 5(*a*)]. Molecular weight distribution curves are unimodal and shift to higher molecular masses with conversion.

It is known that acryl and methacryl monomers show higher activity than styrene in polymerization processes.[16] Apparently, the difference in the kinetic features of styrene or MMA polymerization in the presence of iron porphyrin may be due to different coordination ability of these unsaturated monomers to transition metal atom of porphyrin. In the case of MMA polymerization, PFeCl can coordinate with monomer (or macro radical) that result in tacticity changes. Nevertheless, the general trend of polymerization is the same, and overall mechanism is probably RATRP.

If benzoyl peroxide is used as an initiator in the polymerization of MMA, the addition of iron porphyrin leads to essential deceleration of the process. The ultimate yield of PMMA did not exceed 15% for 25 h at 3.0 mmol dm^{-3} PFeCl concentration (concentration of benzoyl peroxide, 1.0 mmol dm^{-3}) [Figure 1(*b*)]; *i.e.*, polymerization decelerates vastly right after the decomposition of benzoyl peroxide. The rate of the benzoyl peroxide-initiated styrene polymerization in the presence of iron porphyrin decreases also, but not as sharp as in the case of MMA polymerization [Figure 4(*b*)]. As was mentioned,[4] organometal compounds can react with peroxide initiators forming complexes of different stability that hinders in living polymerization. Apparently, chlorine-containing iron porphyrin can coordinate with benzoyl peroxide. The nature of monomer, which plays an important role, should be taken into consideration. Complexation of metallocenes (ferrocene, zirconocene dichloride, diindenylzirconocene dichloride and titanocene dichloride) with MMA *via* coordination of central metal atom of organometal compound with oxygen atom of carbonyl group of monomer was proved by spectral methods.[20–22] Apparently considerable deceleration of MMA polymerization in the presence of benzoyl peroxide and iron porphyrin caused by participation of monomer in complexation of initiator and additive, which does not occur in the styrene polymerization under the same conditions. The benzoyl peroxide-initiated polymerization of styrene performed in the presence of iron porphyrin exhibits features of the living process to a greater extent compared to MMA polymerization. This is confirmed by molecular characteristics of obtained polystyrene, namely, a linear increase of M_n on conversion [Figure 5(*b*)].

Thus, on the basis of experimental data general features and peculiarities of MMA and styrene polymerization in the presence of peroxide initiator or azo-initiator and chlorine-containing iron porphyrin were determined. General features are signs of controlled macrochain propagation *via* RATRP in the polymerization of MMA and styrene in the presence of AIBN and PFeCl, namely, a linear increase of M_n on conversion, narrow molecular weight distribution (< 2.0), and a decrease in the overall polymerization rate with an increase of the additive concentration. Peculiarities are inhibition of MMA polymerization in the presence of benzoyl peroxide and iron porphyrin (while the polymerization of styrene occurs to high monomer conversion under the same conditions), and differences in kinetic features of the AIBN-initiated MMA polymerization from styrene polymerization in the presence of PFeCl.

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References

1 A. V. Yakimanskii, *Vysokomol. Soedin*., 2005, **47**, 1241 (in Russian).
2 K. Matyjaszewski and J. Xia, *Chem. Rev.*, 2001, **101**, 2921.
3 J. S. Wang and K. Matyjaszewski, *Macromolecules*, 1995, **28**, 7901.
4 K. Matyjaszewski, M. Wei, J. Xia and N. E. McDermott, *Macromolecules*, 1997, **30**, 8161.
5 O. I. Koifman and T. A. Ageeva, *Porfirinpolimery* (*Porphyrinpolymers*), Izdatel'stvo fiziko-matematicheskoi literatury, Moscow, 2006, p. 195 (in Russian).
6 B. R. Smirnov, I. M. Bel'govskii, G. V. Ponomarev, A. P. Marchenko and N. S. Enikolopyan, *Dokl. Akad Nauk SSSR*, 1980, **254**, 127 (in Russian).
7 B. R. Smirnov, V. D. Plotnikov, B. V. Ozerkovskii, V. P. Roschupkin and N. S. Enikolopyan, *Vysokomol. Soedin., Ser. A*, 1981, **23**, 2588 (in Russian).
8 B. R. Smirnov, L. M. Pushchaeva and V. D. Plotnikov, *Vysokomol. Soedin*., 1989, **37**, 2378 (in Russian).
9 *Porfiriny: struktura, svoistva, sintez* (*Porphyrins: Structure, Properties, Synthesis*), ed. N. S. Enikolopyan, Nauka, Moscow, 1985, p. 333 (in Russian).
10 B. B. Wayland, G. Poszmik and S. L. Mukerjee, *J. Am. Chem. Soc*., 1994, **116**, 7943.
11 Zh. Lu, M. Fryd and B. B. Wayland, *Macromolecules*, 2004, **37**, 2686.
12 B. B. Wayland, G. Poszmik and M. Fryd, *Organometallics*, 1992, **11**, 3534.
13 M. Kuroki, T. Aida and S. Inoue, *J. Am. Chem. Soc*., 1987, **109**, 4737.
14 Y. Hosokawa, M. Kuroki, T. Aida and S. Inoue, *Macromolecules*, 1991, **24**, 824.
15 K. M. Smith, *Porphyrins and Metalloporphyrins*, Elsevier, Amsterdam–London–New York, 1975.
16 G. P. Gladyshev, *Polimerizatsiya vinilovykh monomerov* (*Polymerization of Vinyl Monomers*), Nauka, Alma-Ata, 1964, p. 322 (in Russian).
17 R. C. Ferguson, *J. Am. Chem. Soc., Polym. Prepr*., 1985, **6**, 182.
18 A. J. Gordon and R. A. Ford, *The Chemist's Companion. A Handbook of Practical Data, Techniques and References*, Wiley-Interscience, New York, 1972, p. 542.
19 C. Barner-Kowollik, J. F. Quinn, T. L. U. Nguyen, J. P. A. Heuts and T. P. Davis, *Macromolecules*, 2001, **34**, 7849.
20 R. M. Islamova, G. R. Sadykova, Yu. I. Puzin, L. V. Spirikhin, V. A. Kraikin and Yu. B. Monakov, *Vysokomol. Soedin*., 2008, **50**, 938 (*Polym. Sci., Ser. B*, 2008, **50**, 128).
21 R. M. Islamova, Yu. I. Puzin, R. Kh. Yumagulova, A. A. Fatykhov, L. V. Parfenova, U. M. Dzhemelev and Yu. B. Monakov, *Vysokomol. Soedin*., 2006, **48**, 1101 (*Polym. Sci., Ser. B*, 2006, **48**, 712).
22 Yu. I. Puzin, E. M. Prokudina, R. Kh. Yumagulova, R. R. Muslukhov and S. V. Kolesov, *Dokl. Ross. Akad. Nauk*, 2002, **386**, 69 [*Dokl. Phys. Chem.* (*Engl. Transl.*), 2002, **386**, 211].

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