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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Preparation of Poly(Methyl Methacrylate) in the Presence of Ferrocenyl-Containing Fe(II) Semi- and Clathrochelates

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Abstract—The effect of ferrocenyl-containing semi- and clathrochelates on radical polymerization of methyl methacrylate, initiated by benzoyl peroxide, and on molecular characteristics of the polymer formed was examined.

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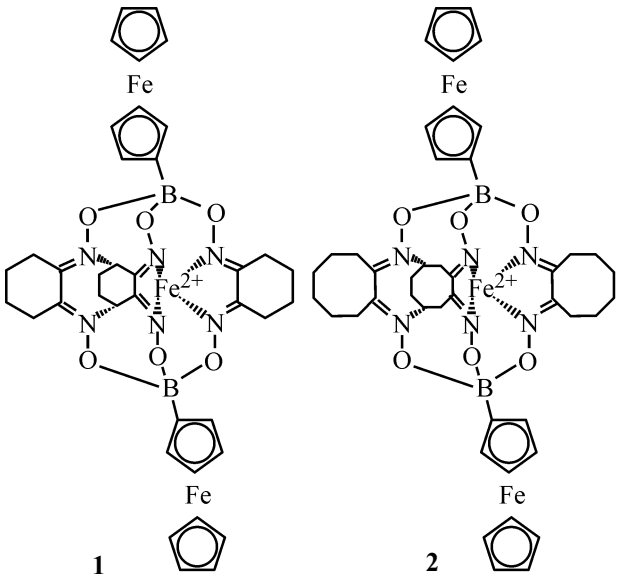
Vinyl polymers, and primarily poly(methyl methacrylate) (PMMA), are widely used in various branches of industry. PMMA is produced on the large-tonnage scale. Its production process is mainly based on radical polymerization. However, the process still involves certain problems. The major problem is low initial rate of the process. Spontaneous rate growth in the course of the polymerization leads to undesirable gel effect. Nonuniform course of the polymerization impairs the physicochemical characteristics of the forming product: In the gel effect step, its uniformity is distorted, the polydispersity increases, and the heat resistance decreases [1]. Therefore, determination of the conditions for performing radical polymerization in the controllable mode is an important problem of polymer chemistry.

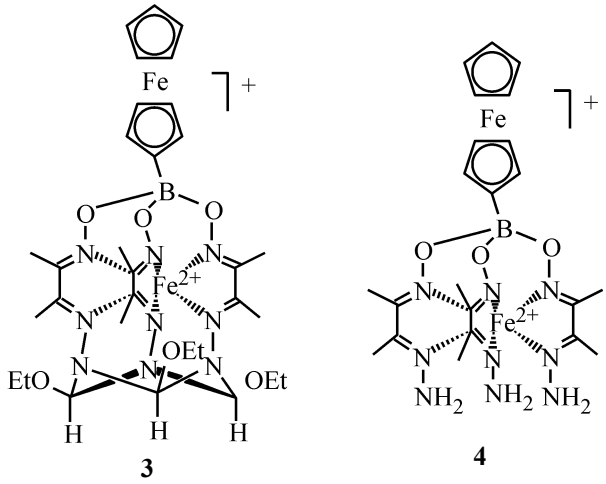
The polymerization rate and molecular characteristics of PMMA can be controlled by several methods. One of them under the conditions of a radical process is based on the use of modifying additives, in particular, of metal-containing compounds (Lewis acids [2], pseudoliving process agents [3], organometallic compounds [4]). Among organometallic compounds, metallocenes are particularly interesting and promising. The effect of ferrocene and of zirconocene, diindenylzirconocene, and titanocene dichlorides on polymerization of methyl methacrylate (MMA) was examined in [5–8]. These metal complexes in combination with diacyl peroxides (benzoyl and lauryl peroxides) allow the radical polymerization to be performed at a high rate and the molecular characteristics of the resulting PMMA to be controlled. At the same time, with azobis(isobutyronitrile) as initiator, these compounds do not noticeably affect the polymerization. Therefore, it is of particular interest to examine the effect of improved modifiers, in particular, of ferrocenyl-containing polynuclear iron(II) semi- and clathrochelates. We expected that unique properties of clathrochelate complexes with encapsulated metal ion [9] would allow enhancement of the effect of the modifying additive and development of new high-performance initiating systems.

In this study we examined the effect exerted by a new class of modifying additives, ferrocenyl-containing Fe(II) semi- and clathrochelates, on radical polymerization of MMA initiated by benzoyl peroxide (BP).

EXPERIMENTAL

Methyl methacrylate (Fluka) was double-distilled under reduced pressure (bp 48°C/140 mm Hg) before use. Benzoyl peroxide was triply recrystallized from ethanol and vacuum-dried at room temperature to constant weight. Ferrocenyl-containing semi- and clathrochelates





1–4 (see below) were prepared and purified by procedures described in [10, 11]. The purity of the substances used was monitored by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.

For polymerization in the bulk, the reaction mixture was poured into an ampule, the solution was degassed by triple freezing–pumping (to 1.3 Pa)–thawing cycle, and the ampule was sealed and placed in a thermostat preheated to 30, 45, or 60°C (±0.1°C). The ampule was kept in the thermostat until appropriate degree of conversion was attained. Then the ampule was cooled and opened. The polymeric product obtained was dissolved in acetone and precipitated with a 10–15-fold excess of methanol. The samples were purified by triple reprecipitation to remove the residual initiator and modifying additive. The process kinetics at low (with the starting monomer as seal liquid) and high (with glycerol as seal liquid) conversions was studied by dilatometry [12].

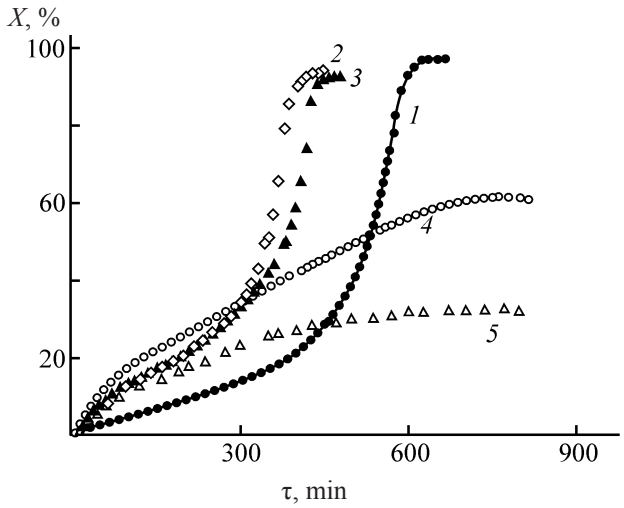


Fig. 1. Conversion X at 60°C as a function of time τ of MMA polymerization in the presence of (*1*) BP and (*2–5*) BP + ferrocenyl-containing clathrochelates. [BP] = 1×10^{-3} M. Clathrochelate, M: (*2*) $2, 5 \times 10^{-5}$; (*3*) $1, 5 \times 10^{-5}$; (*4*) $2, 1 \times 10^{-4}$; and (*5*) $1, 8 \times 10^{-5}$.

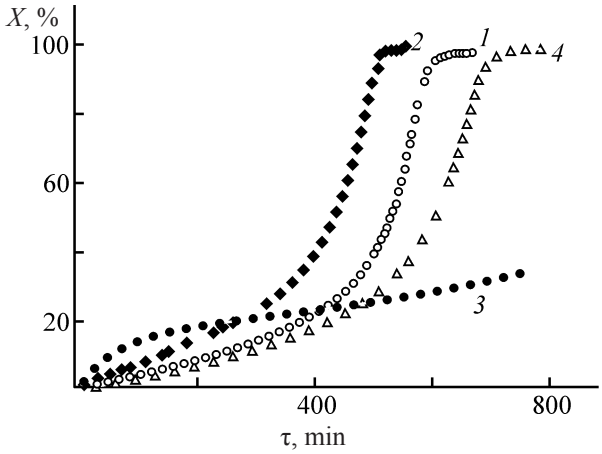


Fig. 2. Conversion X at 60°C as a function of time τ of MMA polymerization in the presence of complex 3 and BP. [BP], M: (*1–3*) 1×10^{-3} and (*4*) $5.0 \times\times 10^{-4}$. Concentration of 3, M: (*2, 4*) 1.0×10^{-4} and (*3*) 5.0×10^{-4}.

The molecular-weight characteristics of the polymers were determined by gel permeation chromatography with a Waters GPC 2000 System liquid chromatograph (eluent tetrahydrofuran, flow rate 0.5 ml min^{-1}). The system of columns was calibrated against polystyrene references with $M_w/M_n \leq 1.2$.

The ^1H NMR spectra of polymer solutions in $CDCl_3$ were recorded at 25°C with a Bruker AM-300 spectrometer relative to tetramethylsilane as internal reference. The content of syndio- hetero-, and isotactic sequences in the macromolecules was determined from the ^1H NMR spectra [13].

Table 1. Characteristics of MMA polymerization in the presence of clathrochelate 1 and BP at various temperatures

T, °C	[Additive] × 10^5, mol l^{-1}	[BP] × 10^3, mol l^{-1}	$W_0 \times 10^3$, mol l^{-1} s^{-1}	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n
		Clathrochelate (1)				
60	0	1.0	0.67	196	98	2.0
45	1.0	1.0	0.78	190	113	1.7
30	5.0	1.0	5.07	52	29	1.8
	10.0	1.0	5.87	42	20	2.1
	20.0	1.0	4.28	57	24	2.4
	10.0	0.5	4.35	59	29	2.0
	0.5	0.1	2.88	117	58	2.0
	5.0	0.05	1.82	187	93	2.0
	0	1.0	0.18	274	137	2.0
	10.0	1.0	2.72	43	25	1.7
	0	1.0	0.05	340	170	2.0
	10.0	1.0	1.63	44	25	1.8
		Clathrochelate (2)				
60	10.0	1.0	–	50	24	2.0
		Clathrochelate (4)				
60	80.0	1.0	–	35	18	1.9

Table 2. Microstructure of PMMA prepared in the presence of BP and various clathrochelates. [BP] = 1 × 10^{-3} M, monomer conversion 5–10%, 60°C

Additive	[Additive] × 10^4, mol l^{-1}	Content of triad, %		
		syndio	*setero*	*iso*
–	–	56	42	2
1	0.8	65	31	4
2	1.0	66	30	4
3	5.0	62	34	4
4	8.0	60	35	5

The heat resistance of PMMA was evaluated by thermal analysis using a Q-1000 derivatograph (MOM, Hungary). Samples (100 mg) were heated in air at a rate of 5 deg min^{-1}.

The physicochemical characteristics of the purified distilled solvents (methanol, acetone, tetrahydrofuran, deuterochloroform) and of glycerol used as seal liquid were in agreement with published data [14].

The use of complex **1** in combination with the peroxy initiator in bulk polymerization of MMA allows the process to be performed with a high initial rate W_0 in the examined temperature range (30–60°C). For example, in the presence of the initiating system **1**–BP at 30°C, W_0 increased by a factor of approximately 30. The apparent activation energy of the process was as low as 48 ± 3 kJ mol^{-1}, compared to 75 ± 5 kJ mol^{-1} for the polymerization initiated by BP only. It should be particularly noted that introduction of a ferrocenyl-containing clathrochelate complex into the polymerization system allows the initiator consumption to be decreased by a factor of 10–20, with the main process parameters preserved (Table 1). The consumption of the modifying additive is lower by 1–2 orders of magnitude compared to that of metallocenes [5–8].

Ferrocenyl-containing clathrochelates **1** and **2** have similar structure, differing only in the size of the edge alicyclic fragment, and their effect on MMA polymerization is essentially similar. Complex **2** is more soluble in organic solvents (including MMA) than complex **1**, which allows intensification of the bulk polymerization. The maximum attainable concentration of complex **1** in the monomer at 25°C is 4 × 10^{-4} M, whereas for clathrochelate **2** it is as high as 1.0 × 10^{-3} M.

Experiments on MMA polymerization in the presence of complexes **1** and **2**, performed to high conversions,

showed that, at clathrochelate concentrations of (1–5) × 10^{-5} M and fixed BP concentration of 1 × 10^{-3} M, the overall process rate increased relative to the process initiated by BP only. However, at concentrations of the macrobicyclic complexes of 8 × 10^{-5} M and higher, the gel effect was suppressed, which may be due to a decrease in the molecular weight of the forming polymer (Fig. 1).

The molecular characteristics of the polymers obtained in the presence of the initiating systems **1**–BP and **2**–BP are shown in Table 1. The molecular weight of PMMA in the presence of a clathrochelate decreases relative to the samples prepared with initiation by BP only. By varying the component concentrations at various temperatures, it is possible to obtain both high- and low-molecular-weight samples, i.e., to control their molecular weight; the polydispersity indices M_w/M_n are close to 2.0.

In the microstructure of the polymers prepared using ferrocenyl-containing clathrochelates **1** and **2** at 60°C, the content of syndiotactic structures increases by approximately 10% (Table 2), which favorably affects the polythermal characteristics of the synthesized PMMA. The decomposition onset temperature for the polymers prepared in the presence of complex **1** and BP increases by 40–45°C relative to the corresponding characteristic of PMMA prepared with initiation by BP only (267–269 and 224°C, respectively).

The MMA polymerization initiated by BP in the presence of oxime–hydrazonate semi- and clathrochelates **3** and **4**, as well as in the presence of trisdioximate complexes **1** and **2**, occurs at a high rate, and with complex **3** 98–100% conversion of the monomer is attained in approximately 8 h (Fig. 2, curve *2*). At a concentration of **3** of 5 × 10^{-4} M and higher, the gel effect degenerates. The use of macrobicyclic compound **3** allows the initiator consumption to be decreased by a factor of 2 (Fig. 2, curve *4*). PMMA prepared in the presence of complexes **3** and **4** has lower molecular weight than the samples synthesized in the presence of BP only (Table 1); The content of syndio triads in the polymer chains increases by 6% (Table 2).

Figure 3 shows that, in the presence of oxime–hydrazonate complexes, the process rate is higher than with α-dioximate clathrochelates. With respect to the effect exerted on MMA polymerization, the complexes can be ranked in the following order: 4 > 3 > 2 > 1.

We believe that high performance of the initiating systems based on the semi- and clathrochelates (increase in process rate, decrease in apparent activation energy, decrease in initiator consumption) is due to their interaction

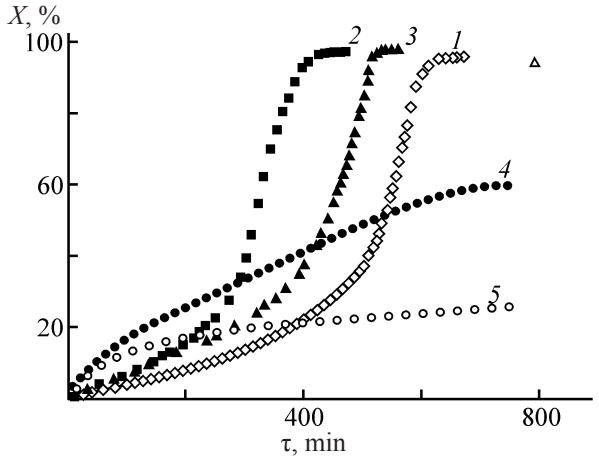


Fig. 3. Conversion X at 60°C as a function of time τ of MMA polymerization in the presence of BP and ferrocenyl-containing semi- and clathrochelates. [BP] = 1 × 10^{-3} M; concentration of complexes 1–4 1 × 10^{-4} M. Additive: (*1*) none, (*2*) 4, (*3*) 3, (*4*) 2, and (*5*) 1.

with a radical particle, resulting in delocalization of the unpaired electron on the highly conjugated clathrochelate core and ferrocenyl substituents, and also in a decrease in the O–O bond energy. Hence, decomposition of the initiator in the presence of the ferrocenyl-containing semi- and clathrochelates requires considerably lower energy consumption. Previously formation of a charge-transfer complex between ferrocene and BP was proved by spectroscopic methods [6]. The control of the PMMA characteristics (molecular weights, polydispersity, microstructure, heat resistance) may also be due to the above-described coordination-chemical activation and stabilization processes, i.e., the ferrocene-containing clathrochelate complex affects not only the initiation step but also the chain propagation and termination steps. The most probable mechanism of the process is the coordination radical mechanism [2, 3].

CONCLUSION

The use of ferrocenyl-containing semi- and clathrochelates allows the methyl methacrylate polymerization to be performed at a high rate at temperatures close to room temperature, with decreased initiator consumption and formation of polymers with controllable molecular-weight characteristics.

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REFERENCES

1. Nikolaev, A.F., *Sinteticheskie polimery i plasticheskie massy na ikh osnove* (Synthetic Polymers and Plastics Based on Them), Moscow: Khimiya, 1964.
2. Kabanov, V.A., Zubov, V.P., and Semchikov, Yu.D., *Kompleksno-radikal'naya polimerizatsiya* (Coordination Radical Polymerization), Moscow: Khimiya, 1987.
3. Matyjaszewski, K. and Xia*, J., Chem. Rev.*, 2001, vol. 101, no. 9, pp. 2921–2990.
4. Grishin, D.F. and Semenycheva, L.L., *Usp. Khim.,* 2001, vol. 70, no. 5, pp. 486–510.
5. Puzin, Yu.I., Yumagulova, R.Kh., and Kraikin, V.A., *Eur. Polym. J.,* 2001, vol. 37, no. 9, pp. 1801–1812.
6. Islamova, R.M., Sadykova, G.R., Puzin, Yu.I., et al., *Vysokomol. Soedin., Ser. B*, 2008, vol. 50, no. 5, pp. 938–944.
7. Islamova, R.M., Puzin, Yu.I., Yumagulova, R.Kh., et al., *Vysokomol. Soedin., Ser. A*, 2006, vol. 48, no. 7, pp. 1101–1107.
8. Kolesov, S.V., Yumagulova, R.Kh., Prokudina, E.M., et al*., Vysokomol. Soedin., Ser. B,* 2003, vol. 45, no. 2, pp. 324–328.
9. Voloshin, Y.Z., Kostromina, N.A., and Kramer, R., *Clathrochelates: Synthesis, Structure and Properties,* Amsterdam: Elsevier, 2002.
10. Voloshin, Ya.Z., Makarov, I.S., Vologzhanina, A.V., et al., *Izv. Ross. Akad. Nauk, Ser. Khim*., 2008, no. 6, pp. 1191–1198.
11. Voloshin, Ya.Z., Makarov, I.S., Vologzhanina, A.V., et al*., Izv. Ross. Akad. Nauk, Ser. Khim*., 2008, no. 6, pp. 1199–1206.
12. Gladyshev, G.P., *Polimerizatsiya vinilovykh monomerov* (Polymerization of Vinyl Monomers), Alma-Ata: Nauka, 1964.
13. Ferguson, R.C., *Polym. Prepr*., 1985, vol. 26, no. 1, pp. 182–183.
14. Gordon, A.J. and Ford, R.A., *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*, New York: Wiley, 1972.