

Radical Polymerization of Methyl Methacrylate in the Presence of *N,N*-Dimethyl-*N*-(methylferrocenyl)amine

Y. B. Monakov,¹ Y. I. Puzin,^{1,2} A. V. Zaikina,¹ E. I. Yarmukhamedova,¹
A. A. Fatykhov,¹ G. E. Zaikov³

¹Institute of Organic Chemistry of the Ufa' Reseach Center of RAS, Prospect Octyabrya 71, Ufa 450054, Russian Federation

²Ufa' State Petroleum Technological University, Kosmonavtov str. 1, Ufa 450054, Russian Federation

³Institute of Biochemical Physics of RAS, Kosygina 4, Moscow 119991, Russian Federation

Received 29 March 2006; accepted 12 June 2006

DOI 10.1002/app.24982

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The specific features of free-radical polymerization of methyl methacrylate in the presence of a new initiating system, benzoyl peroxide-*N,N*-dimethyl-*N*-(methylferrocenyl)amine, are studied. Mutual influence of ferrocenyl- and amine groups on kinetic parameters of polymerization and on the microstructure of the resulting

polymers is found. It is shown that the polymer obtained in the presence of this initiating system has predominantly syndiotactic structure. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 724–727, 2007

Key words: radical polymerization; metallocene

INTRODUCTION

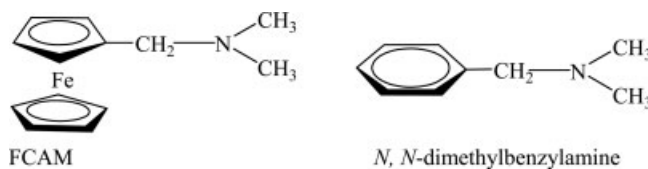
A polymer formed by free-radical polymerization is enriched in syndiotactic sequences owing to a slight difference in activation energies of syndio- and isotactic attachment of a monomer to the growing macroradical (this difference comprises ~ 4 kJ/mol¹). The content of heterotactic sequences increases with temperature, thus reducing the syndiotacticity of the polymer chain as a whole.

The use of some initiating systems allows one to influence the polymer properties, including microstructure, in the course of free-radical polymerization. For example, in the presence of ferrocene–benzoyl peroxide system, polymerization rate increases and at the same time the resultant poly(methyl methacrylate) (PMMA) and polystyrene have a lower molecular mass, a narrower molecular-mass distribution and an increased content of syndiotactic sequences.² On the other hand, in the presence of amines, the rate of per-

oxides decomposition markedly increases when compared with the reaction without amines.^{3,4} Experiments with initiating systems based on heteroaromatic diketocarboxylic acids showed that the influence of nitrogen-containing compounds on the polymer microstructure is so high that this effect manifests itself at concentrations that are one or two orders of magnitude lower than the peroxide concentration and exceeds the effect of metallocene systems.^{2,5,6}

However, the peroxide–tertiary amine systems are characterized by a significant initial acceleration of the polymerization process followed by deceleration with increasing monomer conversion,⁷ thus making polymer production problematic. It can be expected that the presence of both metallocene and nitrogen-containing groups in the initiating system will allow one to preserve their stereo regulation function with a simultaneous increase in the polymerization rate.

In this work, the effect of *N,N*-dimethyl-*N*-(methylferrocenyl)amine (FCAM) on free-radical polymerization of methyl methacrylate (MMA) is considered. FCAM contains both ferrocenyl- and tertiary amine groups:



An initiating system containing FCAM can behave as a system with ferrocene and as a system with tertiary amines. Two functional groups can simultane-

Correspondence to: Y. B. Monakov (monakov@anrb.ru).

Contract grant sponsor: Russian Fund for Basic Research, Lenin prospect 32a, Moscow, 119991, Russian Federation; contract grant sponsor: 05-03-32087a.

Contract grant sponsor: Leading Scientific Schools, Rosnauka, Tverskaya 11, str. 11, Moscow, 125009, Russian Federation; contract grant number: NSh-728.2003.3.

Contract grant sponsor: Chemistry and Science Department of Materials of RAS, Lenin prospect 32a, Moscow, 119991, Russian Federation; contract grant number: 10,002-251/OXNM-04/125-141/200404-050.

Journal of Applied Polymer Science, Vol. 103, 724–727 (2007)
© 2006 Wiley Periodicals, Inc.

TABLE I
Polymerization of MMA in the Presence of FCAM (Benzoyl Peroxide (BPO)
at 1×10^{-3} mol/L) as Initiator)

T ($^{\circ}\text{C}$)	[FCAM] (10^3 mol/L)	W_0 (10^3 mol/ L min)	P_n (10^{-3})	Reaction order with respect to FCAM	Reaction order with respect to BPO
60	–	3.8	17.1	0.22	0.21
	0.25	24.1	3.4		
	1.0	32.7	2.5		
45	–	1.1	22.8	0.30	0.33
	0.25	11.3	3.6		
	1.0	17.0	2.4		
30	–	0.3	25.4	0.34	0.29
	0.25	3.4	2.9		
	1.0	6.0	3.2		
0	0.25	0.3	6.7	0.41	0.04
	1.0	1.3	4.5		

ously affect the free-radical polymerization, thus influencing both the polymerization process and the polymer microstructure. Kinetic parameters of polymerization in the presence of ferrocene have been described.² For comparison with influence of amine group of FCAM on polymerization process, the effect of *N,N*-dimethylbenzylamine on free-radical polymerization of MMA was investigated.

EXPERIMENTAL

Methyl methacrylate (MMA) was separated from the stabilizer by shaking with 5–10% KOH solution, washed with water up to a neutral reaction, dried over CaCl_2 , and distilled twice in vacuum. Benzoyl peroxide (BPO) after multiple recrystallizations from methanol had $T_m = 108^{\circ}\text{C}$ (with decomposition). FCAM was prepared and purified using the procedure described in Ref. 8. *N,N*-dimethylbenzylamine was received from Aldrich and was used without purification. The kinetic curves of bulk polymerization were obtained by the dilatometric method.⁹

Content of iso- and syndiotactic sequences in the macromolecules was determined using ^1H NMR spec-

troscopy on a "Bruker" AM-300 spectrometer operating at 300 MHz¹⁰; for this purpose, the polymer obtained at low conversions (up to $\sim 5\%$) was used. Deuteriochloroform CDCl_3 was used as the solvent.

Intrinsic viscosity of benzene solutions of poly(methyl methacrylate) (PMMA) was measured in a modified suspended-level viscometer at $25 \pm 0.05^{\circ}\text{C}$. The polymer samples for these measurements were taken at low monomer-to-polymer conversions (up to $\sim 5\%$), reprecipitated twice from benzene solutions into hexane, and dried in vacuum at 40°C to a constant weight. Molecular mass of PMMA was calculated through the relationship $[\eta] = KM^{\alpha}$, where $K = 0.94 \times 10^{-4}$; $\alpha = 0.76$.¹¹

RESULTS AND DISCUSSION

The kinetic studies of MMA polymerization initiated by the BPO-FCAM system showed that this system differs from the BPO-ferrocene² and BPO-amines systems,^{3,4,7,12} which have been discussed earlier. The initial rate of polymerization was found to be dependent upon the concentration BPO and FCAM. The introduction of FCAM additive into the initiating system

TABLE II
Polymerization of MMA in the Presence of *N,N*-dimethylbenzylamine (Benzoyl
Peroxide (BPO) at 1×10^{-3} mol/L) as Initiator)

T ($^{\circ}\text{C}$)	[<i>N,N</i> -dimethyl- benzylamine] (10^3 mol/L)	W_0 (10^3 mol/ L min)	P_n (10^{-3})	Reaction order with respect to <i>N,N</i> -dimethyl- benzylamine	Reaction order with respect to BPO
60	–	3.8	17.1	0.1	0.4
	0.25	3.8	11.1		
	1.0	3.6	11.8		
	4.0	5.5	13.3		
45	–	1.1	22.8	0	0.4
	0.25	1.2	29.2		
	1.0	1.0	26.0		
30	–	0.3	25.4	0	0.3
	0.25	0.3	31.5		
	1.0	0.3	27.3		

causes an increase in the initial rate of MMA polymerization when compared with the polymerization rate in the absence of the additive (Table I). The orders of the reaction with respect to the initiators, BPO and FCAM, were calculated (Table I). The total order of the reaction is close to 0.5, which indicates the formation of free-radical type initiating system. Analogous values were obtained earlier for ferrocene-BPO system.² The estimated activation energy of MMA polymerization initiated by the BPO-FCAM system is equal to 45.7 ± 2.5 kJ/mol and close to the activation energy for the BPO-ferrocene system (48.3 ± 1.5 kJ/mol²). The data on kinetic investigation of MMA polymerization in the presence of BPO-*N,N*-dimethylbenzylamine initiating system is shown in Table II. The activation energy of polymerization initiated by the BPO-*N,N*-dimethylbenzylamine was calculated. This value is equal to 130 ± 2.5 kJ/mol and exceeds the activation energy for usual MMA free-radical polymerization initiated by BPO. Thus, the kinetic parameters of polymerization in the presence of BPO-FCAM system are similar to those characteristic of systems with ferrocene.² One can conclude that the ferrocenyl group of FCAM plays the decisive role in polymerization.

Figure 1 shows the kinetic curves of MMA radical polymerization at 60°C initiated by BPO in the presence of FCAM and *N,N*-dimethylbenzylamine. The addition of FCAM results in a sharp increase in the initial polymerization rate, however, then the rate decreases and attains a constant value. This feature is most pronounced when the concentration of FCAM exceeds that of BPO. In this case, the process is slowed down at comparatively lower monomer conversion (Fig. 1, curves 2 and 3). Such a polymerization pattern is typical of peroxide-tertiary amines systems,¹² including the BPO-*N,N*-dimethylbenzylamine system.

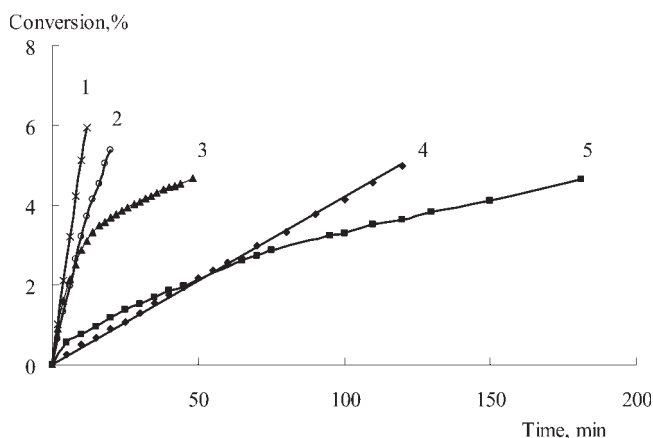


Figure 1 MMA conversion versus polymerization time at 60°C: [BPO] = 1×10^{-3} mol/L, [ferrocene] = 1×10^{-3} mol/L (1); [BPO] = 1×10^{-3} mol/L, [FCAM] = 1×10^{-3} mol/L (2); [BPO] = 1×10^{-3} mol/L, [FCAM] = 4×10^{-3} mol/L (3); [BPO] = 1×10^{-3} mol/L (4); [BPO] = 1×10^{-3} mol/L, [*N,N*-dimethylbenzylamine] = 4×10^{-3} mol/L (5).

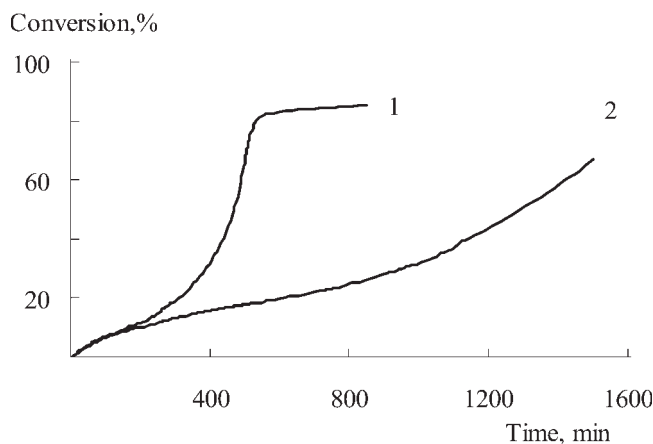


Figure 2 Kinetic curves of MMA polymerization in the presence of FCAM at 45°C up to high conversion of monomer to polymer. [FCAM] $\times 10^3 = 0.5$ (1) and 1.0 (2) mol/L, [BPO] = 1×10^{-3} mol/L.

In spite of the lower rate, polymerization of MMA in the presence of FCAM is not completed at low conversions and shows the presence of a gel effect. As the additive concentration is raised, the time required for completion of polymerization becomes longer (Fig. 2).

The use of FCAM as a component of the initiating system entails a sharp decrease in the average degree of polymerization (P_n) of the resulting polymer (Table I). This influence on polymer's molecular mass is typical of metallocenes.² On the other hand, in the presence of *N,N*-dimethylbenzylamine, molecular mass increases for polymer obtained at 45 and 30°C (Table II).

PMMA synthesized in the presence of initiating system with FCAM demonstrates a predominantly syn-

TABLE III
Effect of FCAM on the PMMA Microstructure

T (°C)	[BPO] (10^3 mol/L)	[FCAM] (10^3 mol/L)	Content of triads (%)		
			Syndio-	Hetero-	Iso-
60	1.0	—	56.1	42.0	1.9
	1.0	0.25	58.0	35.8	6.2
	1.0	1.00	56.9	36.4	6.7
	1.0	2.00	56.8	36.8	6.4
	0.5	1.00	60.0	33.8	6.2
	2.0	1.00	59.0	34.3	6.7
45	1.0	—	65.2	32.4	2.4
	1.0	0.50	63.7	33.4	2.9
	1.0	1.00 ^a	62.0	34.4	3.6
	1.0	1.00 ^b	62.2	34.5	3.3
	1.0	2.00	63.6	33.4	3.0
30	1.0	—	65.6	30.5	3.9
	1.0	1.00	68.3	29.7	2.0
20	1.0	1.00	69.4	28.8	1.8
	1.0	2.00	71.6	26.8	1.6

^a Conversion 40%.

^b Conversion 80%.

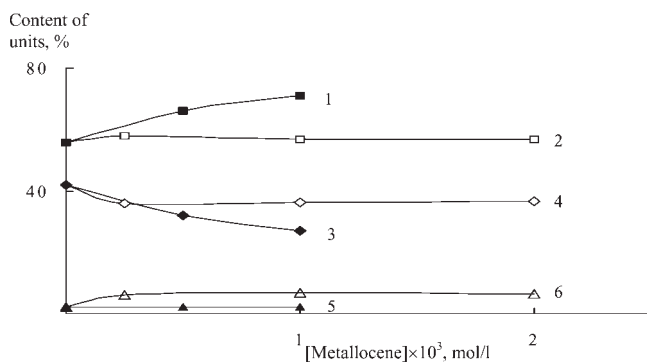


Figure 3 Content of syndio- (1, 2), hetero- (3, 4), and isotactic (5, 6) units of PMMA obtained at 60°C in the presence of initiation systems containing BPO (1×10^{-3} mol/L) as a function of concentration of ferrocene (1, 3, 5) or FCAM (2, 4, 6).

diotactic structure (Table III), although with a significant amount of isotactic sequences. It is seen that the content of iso- and heterotactic sequences increases with temperature, whereas the number of syndiotactic triads decreases. It is significant that the microstructure of the polymer chain is virtually independent of conversion.

Figure 3 shows how the microstructure of PMMA changes with the synthesis conditions. For comparison, the earlier published data⁶ on the effect of ferrocene on the triad composition of polymer produced under similar conditions are presented in the same figure. It can be concluded that the presence of an amino group favors the isotactic sequences formation and hinders the accumulation of syndiotactic triads. On the contrary, the presence of ferrocene leads to the formation of syndiotactic sequences.

Unfortunately, we could not find any published data on the microstructure of PMMA obtained in the presence of BPO-amines systems. Syntheses of syndiotactic PMMA in the presence of systems consisting of BPO with cetylpyridinium chloride¹³ and with 3,6-bis(*o*-carboxybenzoyl)-*N*-isopropylcarbazole⁵ have been described. In both cases, the concentration of isotactic triads is fairly low. It can be suggested that, in the absence of other function groups, the amine group favors the formation of a macromolecule enriched in syndiotactic sequences.

Ferrocene is known to accelerate BPO decomposition² and the formation of an intermediate complex of metallocenes with BPO primarily affects the carbonyl group.⁶ It can be expected that the complex with FCAM is more stable than the individual complex of BPO with ferrocene and with amine. It is well-known that, during free-radical polymerization of vinyl monomers in the presence of a complexing agent, the effect of this agent on the kinetic parameters of the process is related to its direct participation in elementary acts of chain propagation,¹⁴ and this affects the stereoisomerism of the polymer chain to some extent.

Taking into account that the polymerization process is mainly influenced by the ferrocene group, one can assume that it is the presence of this group that favors the formation of syndiotactic sequences, in accordance with the published data.² Apparently, the presence of amine group somewhat hinders syndiotactic addition to the growing chain, thus increasing the content of isotactic sequences. The same molecule of the complexing agent can participate in elementary events of chain propagation by migrating to the terminal unit of the growing chain.

CONCLUSIONS

The specific features of free-radical polymerization of methyl methacrylate in the presence of a new initiating system, BPO-FCAM, are studied. Both functional groups of FCAM affect the polymerization of MMA and, with the increasing of the additive concentration, the inhibiting effect of amine group grows in the course of polymerization. The ferrocene component plays decisive role at low monomer conversions, the kinetic parameters of polymerization are close to those characteristic of systems with ferrocene. A decrease in the content of syndiotactic sequences and an increase in the number of isotactic sequences, which are observed in the case of simultaneous presence of metallocene and amine groups, are indicative of the mutual influence of these groups on each other's activity in the interaction with BPO.

References

1. Encyclopedia of Polymers, Vol. 2; Sovetskaya Entsiklopediya: Moscow, 1974.
2. Puzin, Y. I.; Yumagulova, R. Kh.; Kraikin, V. A. *Eur Polym J* 2001, 37, 1801.
3. Chalt'ikyan, O. A.; Atanasyan, E. N.; Sarkisuyan, A. A. *Doklady Akademii Nauk Arm SSR* 1952, 15, 41.
4. Miluytinskaya, R. I.; Bagdasar'yan, K. S. *Zhurnal Phis Khimii* 1960, 34, 405.
5. Puzin, Y. I.; Galinurova, I. E.; Kuznetsov, S. I.; Fatykhov, A. A.; Monakov, Y. B. *V'isokomolec Soed A* 2002, 44, 1752.
6. Puzin, Y. I.; Proculina, E. M.; Yumagulova, R. K.; Musluhchov, R. R.; Kolesov, S. V. *Doklady Akademii Nauk* 2002, 386, 69.
7. Pravednicov, A. N.; Stavrova, S. D.; Chikhacheva, I. P.; Ephremova, E. P.; Eremina, M. G.; Budanova, E. N. *Plasticheskie Massy* 1980, 12, 10.
8. *Sintez'i Organicheskikh Preparatov* (Translated by A. F. Plate); Mir: Moscow, 1964.
9. Gladyshev, G. P. *Vinyl Monomers Polymerization*; Nauka: Alma-Ata, 1964.
10. Shapiro, Y. I. *Bull Magn Reson* 1985, 7, 27.
11. Raficov, S. R.; Pavlova, S. A.; Tverdokhlebova, I. I. *Methods Determination of Polymer Molecular Weight and Polydispersity*; Izdatel'stvo Akad Nauk SSSR: Moscow, 1962.
12. Epimakhov, Y. K.; Galibei, V. I.; Khudyakova, U. A. *V'isokomolec Soed B* 1985, 27, 464.
13. Trubicina, S. N.; Margaritova, M. F.; Medvedev, S. S. *Doklady Akademii Nauk SSSR* 1966, 166, 381.
14. Kabanov, V. A.; Zubov, V. P.; Semchicov, Y. D. *Complex-Radical Polymerization*; Khimiya: Moscow, 1987.