

N-Aryl-*o*-iminobenzoquinones as Novel Regulators of Radical Polymerization

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Abstract—The effect of a number of quinoid compounds on methyl methacrylate polymerization initiated by azo-bis(isobutyronitrile) has been studied. It has been revealed that *N*-aryl-*o*-iminobenzoquinones, in contrast to *o*-benzoquinones, can provide radical polymerization of methyl methacrylate in controllable mode. The efficiency of the compounds as chain growth regulators has been found to depend on their composition and reaction conditions. It has been established that 4,6-di-*tert*-butyl-*N*-(2,6-diethylphenyl)-*o*-iminobenzoquinone and 4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzoquinone under radical initiation conditions provide the synthesis of poly(methyl methacrylate) with wide-range molecular weight, retaining polydispersity indices about ~1.4–1.8 up to deep conversions.

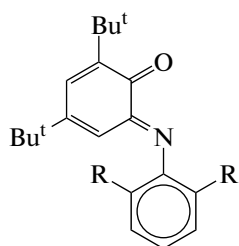
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Control of radical polymerization processes is the priority direction of synthetic macromolecular chemistry in recent years [1]. Reversible inhibition is a particular method for preparing polymers with prescribed molecular-weight characteristics. Attention of researchers to chain growth regulators is focused mainly on stable nitroxyl [2] and spatially hindered carbon-centered radicals, whereas phenoxyl derivatives of different structure are left out of consideration [3]. This is somewhat due to the fact that quinones and phenols as the sources of phenoxyl radicals are commonly used as compounds capable of retarding and completely suppressing polymerization. This property allows one to use them as inhibitors on storage and transportation of certain monomers.

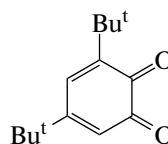
The products and mechanisms of quinone reactions with different radicals, including initiating ones,

in monomeric and non-monomeric media have been studied in sufficient detail [3]. The majority of studied compounds are *p*-quinones and their derivatives. The prospects for the use of *o*-quinones and their nitrogen-containing analogues as regulating agents in polymerization processes are poorly studied.

Therefore, the aim of this work is to compare the process of radical polymerization of methyl methacrylate (MMA) initiated by azo-bis(isobutyronitrile) (AIBN) with participation of certain spatially hindered *o*-quinones and *o*-iminoquinones and to develop on their basis new efficient regulators of molecular-weight characteristics for poly(methyl methacrylate) (PMMA). We used compounds **1–4** as the subjects of the study.



R = Me (**1**), Et (**2**), Prⁱ (**3**)



3,5-di-*tert*-butylbenzoquinone (**4**)

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o-Iminoquinones **1–3** were obtained by procedures [4, 5]. The monomer, initiator, and solvents were purified by standard methods. Physicochemical constants of all compounds correspond to the literature data. To

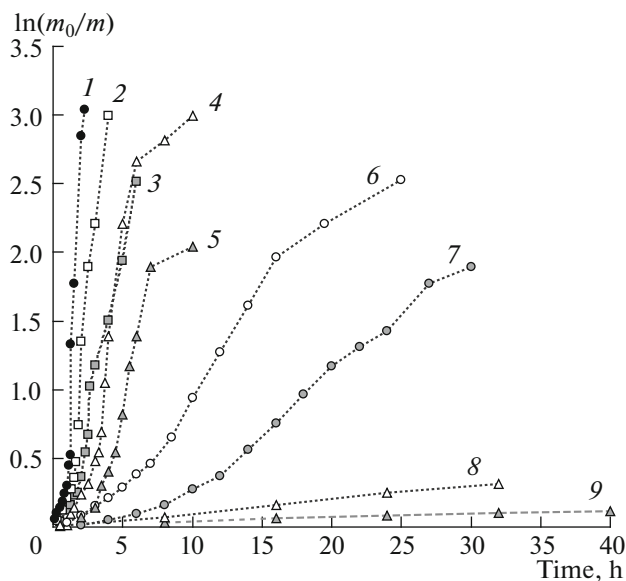


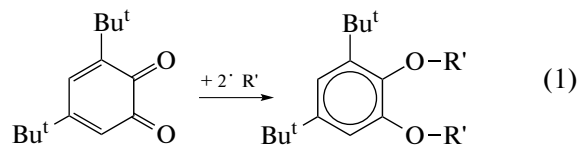
Fig. 1. Dependence of $\ln(m_0/m)$ of MMA on reaction time. AIBN concentration is 0.1 mol %. $T = 70^\circ\text{C}$. Additives: (2, 3) **1**, (4, 5) **2**, (6, 7) **3**, (8, 9) 3,5-di-*tert*-butylbenzoquinone. Additive concentration, mol %: (1) 0; (2, 4, 6, 8) 0.1; (3, 5, 7, 9) 0.2.

remove monomer residues, samples were precipitated twice from a methylene chloride solution and dried under reduced pressure until constant weight was obtained. The samples of the initiators for PMMA post-polymerization were prepared using different concentrations of the initiator and *o*-iminoquinones at 70°C , precipitated three times to remove residues of the initiator and unreacted *o*-iminoquinone. A weighed sample of the polymer was placed in an ampule and a calculated amount of pure MMA was added. After polymer dissolution, the ampule was triply degassed, sealed, and placed in a thermostat for a prescribed time. Molecular-weight characteristics were determined by GPC. PMMA standards with a narrow molecular weight distribution were employed for calibration. EPR spectra were recorded on a Bruker EMX spectrometer. Diphenylpicrylhydrazine ($g = 2.0037$) was used as a standard to determine g factor.

The bulk polymerization of MMA initiated by AIBN at 50 – 90°C shows classical behavior typical for radical processes: the presence of the gel effect, S-shaped dependence of the number-average molecular weight (M_n) of PMMA on conversion, and a considerable broadening of the molecular-weight distribution (MWD) curves in the course of process. The numerical values of molecular weights (MW) of PMMA increase stepwise in the ranges 160 000–440 000 and 70 000–120 000, while polydispersity indices (PI) vary within ~ 1.7 – 7.6 and ~ 1.6 – 5.0 for samples prepared at 70 and 90°C , respectively.

It was found that the character of influence of compounds **1**–**3** on the kinetic features of MMA polymer-

ization and molecular-weight characteristics of PMMA depend on the structure of *o*-iminoquinone and reaction conditions (Table 1, Fig. 1). In particular, the introduction of *o*-quinone **4** completely inhibits MMA polymerization initiated by AIBN (Fig. 1, dependences 8, 9). The limiting extent of MMA conversion at the ratio **4** : AIBN = 1 : 1 is no larger than 30%. This decrease in polymerization rate is caused by the fact that compound **4** irreversibly reacts with the radicals formed in the system:



R' is initiating or oligomeric radical.

At 70°C and equimolar ratio **4** : AIBN, M_n for PMMA varies in the range 8000–25 000, while polydispersity indices monotonically increase from 1.5 to 3.0.

Obviously, 3,5-di-*tert*-butyl-benzoquinone behaves as the inhibitor of polymerization. These results agree well with few literature data on the effect of *o*-quinones on the radical reactions and polymerization of methacrylic monomers [3, 6].

The introduction of *o*-iminobenzoquinones **1**–**3** also decreases total polymerization rate; the bulkier alkyl substituents in the aryl fragment, the lower the polymer yield over certain time interval. When compounds **1**–**3** are introduced into the polymerization system, the molecular weight of PMMA and the main value of polydispersity index also decrease as the concentration of *o*-iminoquinone increases.

The structure of the aryl fragment in *o*-iminobenzoquinones **1**–**3** and the temperature of polymer synthesis have a considerable effect on the kinetic features of MMA polymerization in their presence and on the molecular-weight characteristics of the polymer. Thus, at 50°C , the introduction of compounds **1** or **2** even in excess with respect to the initiator only flattens the gel effect and shifts it in time. On the contrary, *o*-iminoquinone **3**, even taken in an equimolar amount with the initiator, considerably inhibits polymerization: the yield of the polymer at 50°C is no higher than 10% in 60 h.

Upon MMA polymerization within 70 – 90°C using compound **1**, the gel effect is smoothed only with an increase in its concentration with respect to the initiator. At the same time, no auto acceleration of the reaction is observed in the presence of compounds **2** and **3** (Fig. 1) even at the equimolar *o*-iminoquinone : AIBN ratio. The time to achieve high conversions increases in accordance with *o*-iminoquinone : inhibitor ratio for each of the used compounds **1**–**3**. It should be noted that the MMA conversion upon the addition of compounds **1** or **2** at 50 – 70°C remains high and constitutes $\sim 90\%$. Increasing temperature to

Table 1. MMA polymerization with the use of compounds **1–4** and AIBN (0.1 mol %)

Regulator	$T, ^\circ\text{C}$	$C_{\text{add}}, \text{mol } \%$	Time, h	$P_{\text{MMA}}, \text{wt } \%$	$M_n \times 10^{-3}$	M_w/M_n
–	50	0	6	88	717	2.75
	70	"	1	26	175	2.67
	"	"	2	94	435	7.57
	90	"	0.25	34	69.8	1.64
	"	"	0.75	95	119	4.99
3,5-Di- <i>tert</i> -butylbenzoquinone (4)	70	0.1	8	7	9.9	1.94
	"	"	24	22	21.1	2.92
	90	0.1	5	20	17.9	3.05
1	50	0.1	10	27	271	2.89
	70	0.1	1	19	123	1.92
	"	"	4	88	261	4.69
	"	0.2	1	12	80	1.82
	"	"	4	78	183	2.54
2	50	0.1	10	3	46.0	1.36
	70	0.1	2	21	96.7	1.67
	"	"	4	75	197	1.95
	"	0.2	2	7	32.5	1.41
	"	"	6	75	131	1.56
	"	0.4	4	7	21.5	1.44
	"	"	12	74	116	1.43
3	90	0.1	1	82	108	1.91
	50	0.1	60	10	39.1	1.38
	70	0.1	4	19	42.2	1.51
	"	"	20	89	89.1	1.67
	"	0.2	4	5	13.0	1.50
	"	"	20	69	62.9	1.62
	90	0.1	1	47	54.0	1.63
	"	"	4	86	69.0	1.67
"	0.2	1	34	30.0	1.59	

90°C leads to a decrease of the ultimate conversion to 70–80% for each of compounds **1–3**.

The effect of compounds **1–3** on the molecular-weight characteristics of PMMA samples also depends on their structure and reaction conditions. Thus, at 50°C, the dependence of the number-average molecular weight of PMMA on conversion in the presence of compounds **1** or **2** is linear; however, polydispersity indices for PMMA samples monotonically increase with conversion at the equimolar ratio of the *o*-iminoquinone and the initiator in reaction mixture.

At 70°C in the presence of compound **1**, the dependence of number-average molecular weight M_n on the conversion at the ratio **1** : AIBN = 1 : 1 has an S-shaped form typical for non-controllable radical processes. An increase in the concentration of compound **1** leads to a linear growth of MW with MMA conversion.

The polydispersity index for PMMA when *o*-iminoquinone **1** is used in the polymerization process at 70°C increases in the range 1.8–4.7, 1.7–3.2, and 1.5–3.0 at the concentrations 0.1, 0.2, and 0.4 mol % of **1**, respectively (Table 1).

When compounds **2** and **3**, containing bulkier ethyl and isopropyl groups, are used as regulators, the linear growth of the polymer MW with conversion is observed at 70–90°C even at the equimolar *o*-iminoquinone : initiator ratio (Figs. 2a, 2b). An increase in the concentration of the *o*-iminoquinones leads to a decrease of the numerical values of MW, while the proportional growth of M_n with monomer conversion is retained. The polydispersity index of PMMA samples obtained in the presence of the equimolar mixture of compound **2** and the initiator varies in the range ~1.4–1.8, but increases up to ~2.2 at conversions

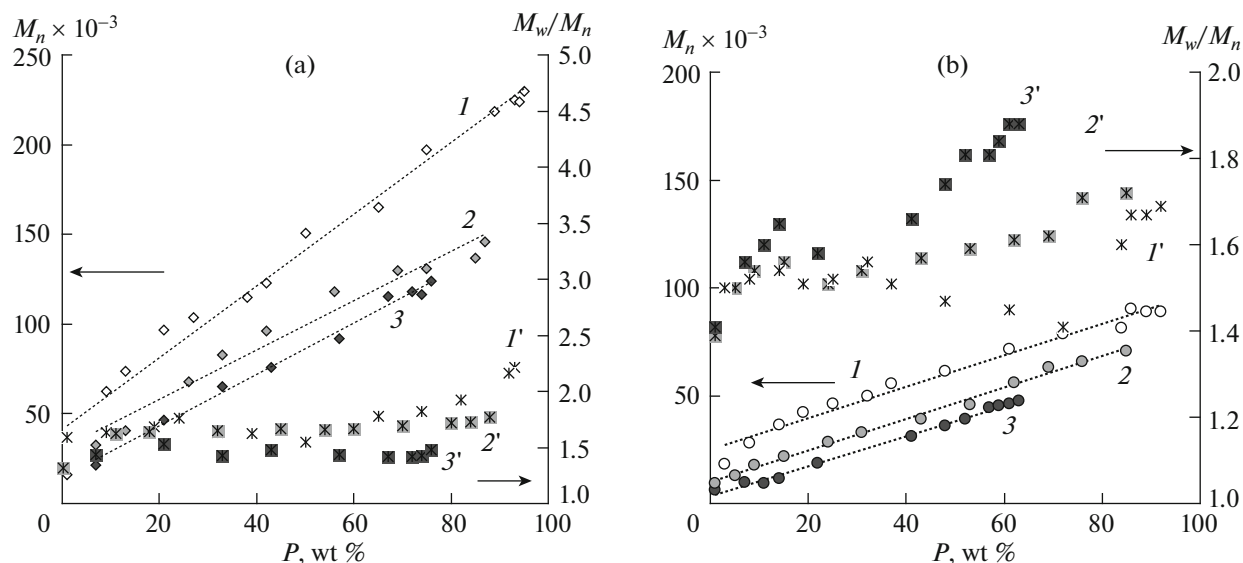


Fig. 2. Dependence of the (*I*–*3*) number-average molecular weight (*I*'–*3*') and polydispersity indices of PMMA on conversion. AIBN concentration is 0.1 mol %. Additives: (a) **2**, (b) **3**. Additive concentration, mol %: (*I*, *I*') 0.1, (*2*, *2*') 0.2, (*3*, *3*') 0.4.

higher than 80% (Fig. 2a, dependence *I*'). Once *o*-iminoquinone **2** is in excess, the value of polydispersity index is retained at the level ~1.4 up to deep conversions (Table 1, Fig. 2a, dependence *3*'). Polymer samples prepared in the presence of compound **3** have PI ~1.4–2.0 at both 70 and 90°C up to high conversions (Table 1, Fig. 2b, dependences *I*'–*3*').

The monitoring of reaction mixtures during polymerization in the presence of *o*-iminoquinone **3** by EPR spectroscopy allowed reliable identification for only one predominant signal, triplet (1 : 1 : 1) of doublets (1 : 1) corresponding to the coupling of unpaired electron *i* to magnetic nuclei ¹⁴N and ¹H ($a_i(^1\text{H}) = 0.38 \text{ mT}$, $a_i(^{14}\text{N}) = 0.39 \text{ mT}$, $g_i = 2.0039$, Fig. 3).

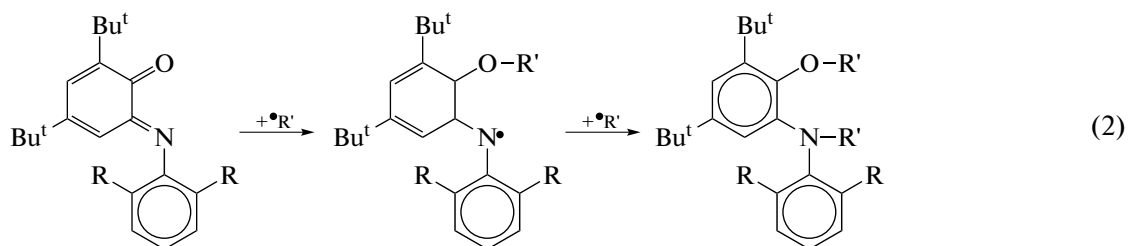
Table 2. The results of MMA post-polymerization at 70°C

Sample no.	Regulator	AIBN, mol %	Add., mol %	Characteristics of PMMA initiator				C_{MI} , wt %	<i>t</i> , h	P_{MMA} , wt %	Characteristics of post-polymerization products		
				<i>t</i> , h	P_{MI} , wt %	$M_n \times 10^{-3}$	M_w/M_n				$M_n \times 10^{-3}$	M_w/M_n	MWD shape
1	2	0.1	0.1	3	38	115	1.57	10	5	15	330	3.25*	2 modes
2	"	"	"	"	"	"	"	"	10	34	547	5.46*	2 modes
3	"	"	0.2	4.5	38	75.3	1.42	10	5	27	358	3.10*	2 modes
4	"	"	0.4	8	43	75.6	1.48	10	5	17	270	3.11*	2 modes
5	3	0.1	0.1	12	57	77.6	1.39	10	5	10	184	10.79*	2 modes
6	"	"	"	"	"	"	"	"	10	43	414	7.07*	2 modes
7	"	"	0.2	14	43	37.8	1.45	10	5	15	101	2.52*	2 modes
8	"	"	0.4	30	52	48.0	1.56	10	5	11	116	3.93*	2 modes
9	"	0.2	0.2	12	51	41.7	1.36	10	5	26	132	1.59	1 mode
10	"	"	"	"	"	"	"	"	10	35	199	1.96	1 mode
11	"	"	"	"	"	"	"	20	5	30	103	1.41	1 mode
12	"	"	"	"	"	"	"	"	10	40	140	1.56	1 mode
13	"	"	"	"	"	"	"	50	5	30	57.0	1.34	1 mode
14	"	"	"	"	"	"	"	"	10	67	63.8	1.34	1 mode

* Calculated from both modes.

This spectral shape is typical for the radical anion forms of *o*-iminoquinone **3** [4, 7].

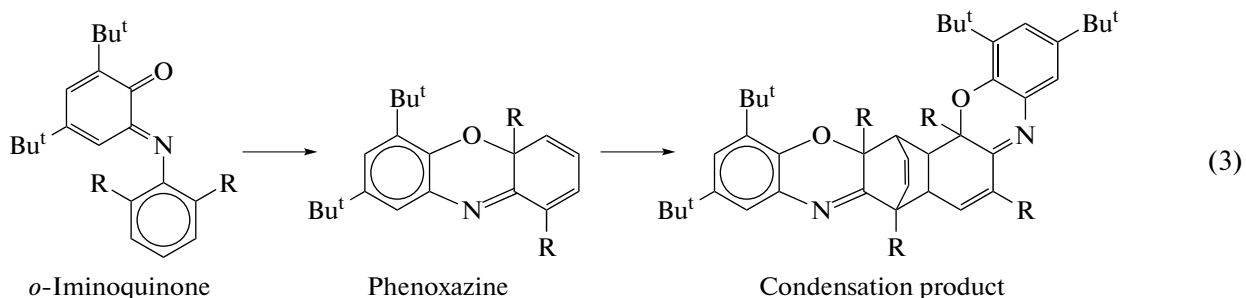
These data indicate that *o*-iminoquinones **1–3** react with the radicals formed in the system:



where R = Me (**1**), Et (**2**), Prⁱ (**3**); R' is an initiating or oligomeric radical.

The difference in the effect of compounds **1–3** on the kinetic features of polymerization and molecular-

weight characteristics of PMMA seems to be due to side reactions under these conditions. In particular, *o*-iminoquinones are apt to intramolecular cyclization on heating to form phenoxazines, which undergo subsequent irreversible condensation [4, 8]:



According to kinetic studies [8], the rate of cyclization for compound **1** is higher than for compound **3** due to steric factors. Thus, *o*-iminoquinone **1** is elim-

inated from reaction medium faster than compounds **2** and **3** on account of side reactions. These features agree well with the results obtained in the study of MMA polymerization with participation of *o*-iminoquinones **1–3** at different temperatures (Figs. 1, 2; Table 1).

The high yields of the polymer, linear increase in MW of macromolecules with conversion, and relatively low polydispersity indices (Table 1, Fig. 2) indicate the reversible character for the reactions of compounds **2** and **3** with growing radicals in an MMA medium.

To confirm the reversibility of reaction of growing radicals with the *o*-iminoquinones, PMMA prepared in their presence was used as a macroinitiator (MI) in the post-polymerization of MMA (Table 2). It was found that PMMA synthesized with the use of compounds **2** or **3** can re-initiate polymerization on addition of a new portion of the monomer. The shape of the molecular-weight distribution curves for the products of post-polymerization depends on the *o*-iminoquinone : AIBN ratio in the synthesis of macroinitiator and on the MW of the PMMA initiator and its concentration in the monomer (C_{MI}) during post-polymerization (Table 2).

In all cases when the post-polymerization products show bimodal MWD curves (samples 1–8, Table 2), the mode with the lower MW strictly corresponds to

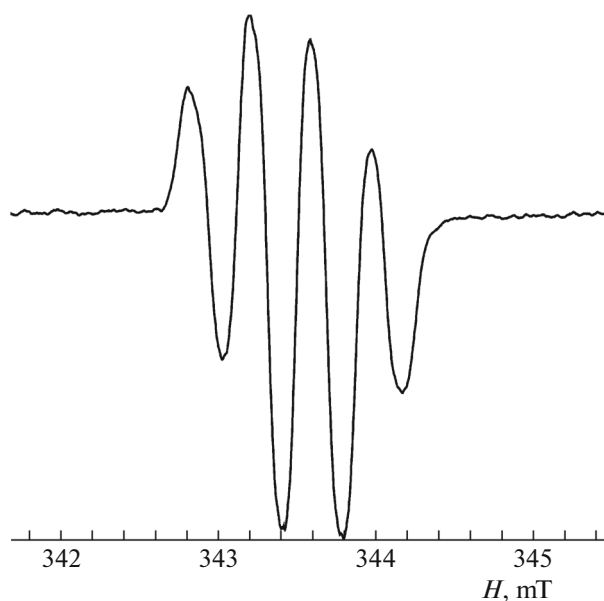
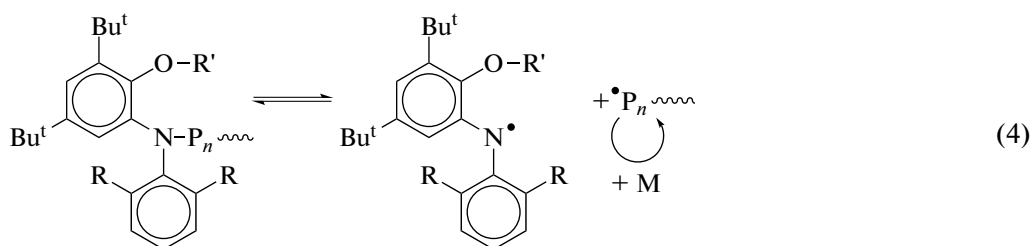


Fig. 3. EPR spectrum observed upon MMA polymerization in the presence of 0.05 mol % of AIBN and 0.05 mol % of *o*-iminoquinone **3**. $T = 70^\circ\text{C}$. Reaction time is 20 min.

the PMMA initiator. The emergence of the mode with the larger MW indicates the linear elongation of a portion of initial MI macromolecules. An increase in post-polymerization time enhances the conversion of the added monomer and shifts the resulting mode toward larger MW values (Table 2). Hence, a portion of PMMA macromolecules used as a macroinitiator is activated upon the addition of a new monomer portion and can propagate the process. The presence of the mode corresponding to the initial PMMA in the post-polymerization product indicates the formation of a “dead” polymer at the stage of the macroinitiator preparation and subsequent post-polymerization.



where R' is initiating or oligomeric radical, R = Et (**2**), *i*Pr (**3**)

The formation of the nitrogen-centered rather than oxygen-centered radical is more probable from the viewpoint of both energy of scissile bonds and steric factors.

Thus, N-aryl-*o*-iminoquinones, in contrast to *o*-quinones, can provide radical polymerization of methyl methacrylate in the reversible inhibition mode. The efficiency of regulation for the molecular-weight characteristics of the polymer depends on the size of the substituents in the aryl moiety and temperature. The use of 4,6-di-*tert*-butyl-*N*-(2,6-diethylphenyl)-*o*-iminobenzoquinone and 4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzoquinone for the polymerization of MMA leads to deep conversions even under radical initiation conditions. A fragmentary growth of number-average MW of the polymer is observed with an increase in conversion, while polydispersity indices remains in the range 1.4–2.0.

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The MWD curves for samples 9–14 (Table 2) are unimodal and are shifted in time toward larger MWs relative to the initial macroinitiator. The retention of low polydispersity indices indicates the high efficiency of used samples in the re-initiation of the process. Thus, the higher the concentration of *o*-iminoquinone in the synthesis of macroinitiator, the lower the MW of the PMMA initiator, and the higher the initiator concentration in the monomer, the better the homogeneity of the post-polymerization product.

The results of our study indicate that aminophenol ethers (the products of reaction 2) can reversibly eliminate accepted radical:

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