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Polymerization of Methyl Methacrylate in the Presence of *o*-Iminoquinones: Reversible and Irreversible Inhibition

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Abstract—New regulators of radical polymerization of methyl methacrylate based on *N*-(aryl)-*o*-iminoquinones of various structures are proposed. It is shown that samples of polymethylmethacrylate with the participation of *N*-(aryl)-*o*-iminobenzoquinones could be used as macroinitiators of polymerization. Optimal conditions to synthesize polymers in the presence of *o*-iminobenzoquinones are determined, which make it possible to obtain polymethylmethacrylate with a polydispersity coefficient of no more than 1.5 on deep conversions during bulk polymerization.

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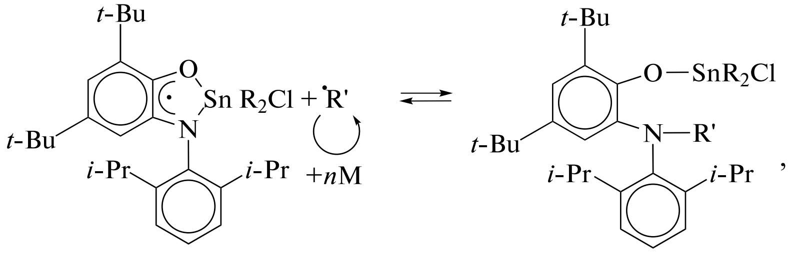
INTRODUCTION

Quinones, phenols, and their derivatives are widely used as substances capable of slowing or completely preventing radical polymerization [1–3]. This property makes it possible to use them as inhibitors in the storage and transportation of industrially significant vinyl monomers [1]. Some *o*-quinones [4] and binary systems of *o*-quinones in combination with complexes of transition metals [5, 6] are capable of regulating the molecular mass characteristics of polymers [7]. The use of nitrogen-containing structural analogs of *o*-quinones, *o*-iminobenzoquinones, and diimines for this purpose has scarcely been described [1, 8, 9]. However, it is known from the published data that the *o*-iminosemiquinolate tin(IV) complex with *tert*-butyl substituents is an iniferter in the polymerization of (meth)acrylates and styrene [10]. Similar paramagnetic tin(IV) complexes make it possible to obtain PMMA with a low polydispersity coefficient [10, 11]. According to quantum-chemical calculations and results of EPR studies, the “sleeping” form of the polymer radical is the organotin ether of *o*-aminophenol [11]

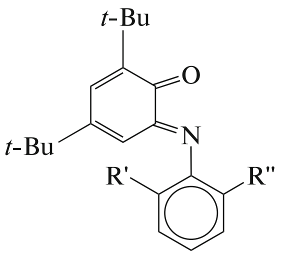


o-Iminosemiquinolate tin(IV) complex

o-Aminophenol ether

where R = Me, Et, *t*-Bu, Ph, or Cl, and R' is an initiating/oligomeric radical.

The purpose of this work is to study and compare the processes of radical polymerization of methyl methacrylate (MMA) with the participation of a number of *o*-iminoquinones in the individual state and the possibility to control the molecular mass characteristics of PMMA with their help. The subjects of the study were *N*-(aryl)-*o*-iminobenzoquinones



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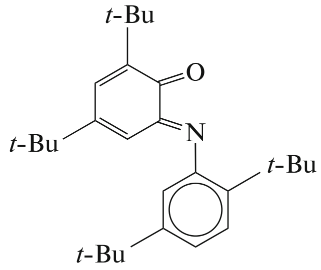

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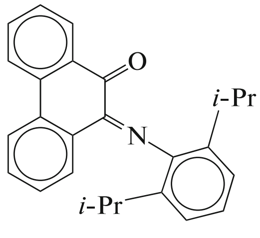
(R' = R'' = Me (**1a**); R' = Me, R'' = Et (**1b**); R' = R'' = Et (**1c**); R' = R'' = *i*-Pr (**1d**)), phenanthrene-*o*-iminoquinone



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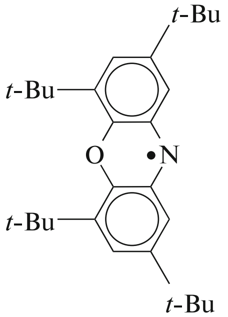
and the symmetric phenoxazinyl radical



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Compounds **1**–**3** are widely used as redox-active ligands in the chemistry of coordination and organometallic compounds [8], but there is practically no information on their effect on polymerization processes.

EXPERIMENTAL

The monomer, initiator, and solvents used were purified by traditional methods [12–14]. The *o*-iminoquinones were prepared according to the methods described in [15–17]. The physicochemical constants of all compounds used corresponded to the published data.

Samples for polymerization were prepared as follows: a monomer solution with the azobisisobutyronitrile (AIBN) initiator and *o*-iminoquinones in the selected ratio was placed in glass ampoules and degassed three times, freezing the ampoules in liquid nitrogen. The residual pressure was ~1.3 Pa. The ampoules were sealed and placed in a thermostat for a set time.

The monomer conversion was determined gravimetrically. To purify the polymer from the unreacted monomer, initiator, and *o*-iminoquinones, the samples were reprecipitated from the solution in methylene chloride and dried in vacuum to constant weight.

Samples of PMMA for further use as a macroinitiator were prepared at different *o*-iminobenzoquinone : AIBN : monomer ratios at 70°C. A sample of the doubly reprecipitated polymer was placed in an ampoule and the calculated amount of freshly distilled MMA was added. The concentration of the macroinitiator in the mixture for post-polymerization was 10–50 wt %. After homogenization of the system, the ampoule was degassed and sealed off. Post-polymerization was carried out at the temperature for the synthesis of the macroinitiator.

The molecular mass characteristics of PMMA were determined by gel permeation chromatography [18]. Polymer samples were analyzed using a Knauer installation with a linear column (Nucleogel, Germany) or a cascade of columns (10^3–10^5, Phenomenex, USA). The detector was a K-2301 RI detector and a K-2501 UV detector; the eluent was THF (25.0 ± 0.1°C). For calibration, narrowly dispersed PMMA standards were used.

The EPR spectra were recorded on a Bruker-EMX radio spectrometer (operating frequency 9.75 GHz). As a standard, diphenylpicrylhydrazyl (g = 2.0037) [19] was used to determine the *g*-factor of radical particles.

RESULTS AND DISCUSSION

Effect of Substituents on the Aryl Moiety of o-Iminoquinones

Table 1 presents the results of the study of the effect of *N*-(aryl)-*o*-iminobenzoquinones, differing in the composition of the aryl moiety, on the yield and molecular weight characteristics of PMMA. As can be seen, the introduction of *o*-iminobenzoquinones slows the MMA polymerization and leads to a decrease in the molecular weight of PMMA and the polydispersity coefficient (M_w/M_n). The more bulky the alkyl substituents are at the 2 and 6 positions of the aryl moiety of compounds **1a**–**1d**, the lower the yield of the polymer over the same period of time. The value of the polydispersity coefficient is less when using compounds **1b**–**1d** as compared to compound **1a** and even more so as compared to compound **2**, which contains the most voluminous *tert*-butyl substituents at positions 2 and 5.

Figure 1 shows the kinetic curves of the MMA polymerization under the action of *o*-iminobenzoquinones **1a**–**1d** at 50 and 70°C in semi-log coordinates. At 50°C, for the equimolar ratio of the initiator and *o*-iminobenzoquinone **1a**–**1c**, the gel effect is manifested later than in the polymerization only under the action of AIBN (Fig. 1a, curves *2*–*5*). A twofold

Table 1. Effect of the composition of the aryl moiety in *o*-iminobenzoquinones on the yield and molecular weight characteristics of PMMA (AIBN concentration 0.1 mol %)

o- Iminobenzoquinone	*T*, °C	Concentration of *o*-iminoquinone, mol %	Time, h	PMMA yield, %	$M_n \times 10^{-3}$	M_w/M_n
–	50	0	2	11	330	2.12
–	50	0	6	88	720	2.75
–	70	0	1	26	170	2.14
–	70	0	2	94	430	7.57
–	90	0	0.25	19	66	1.67
–	90	0	0.75	95	120	4.99
1a	50	0.1	10	27	270	2.89
	50	0.2	10	11	110	1.81
	70	0.1	4	89	260	4.59
	70	0.2	4	77	180	2.54
	90	0.1	1	76	76	1.89
	90	0.2	1	66	63	1.85
1b	50	0.1	10	6	75	1.52
	70	0.1	4	44	140	1.46
1c	50	0.1	10	3	46	1.36
	70	0.1	4	75	200	1.95
	70	0.2	4	33	83	1.44
	70	0.4	4	7	22	1.44
	90	0.1	1	82	110	1.92
	90	0.2	1	70	73	1.69
1d	50	0.1	30	3	16	1.43
	70	0.05	10	80	110	2.01
	70	0.1	10	61	71	1.45
	70	0.2	10	24	28	1.51
	70	0.4	12	7	10	1.56
	90	0.1	1	47	54	1.63
	90	0.2	1	34	30	1.59
	90	0.4	1	9	7	1.70
2	70	0.1	10	21	23	3.09
	70	0.2	10	4	5	1.82
	90	0.1	1	23	19	2.12
	90	0.2	1	8	7	2.10

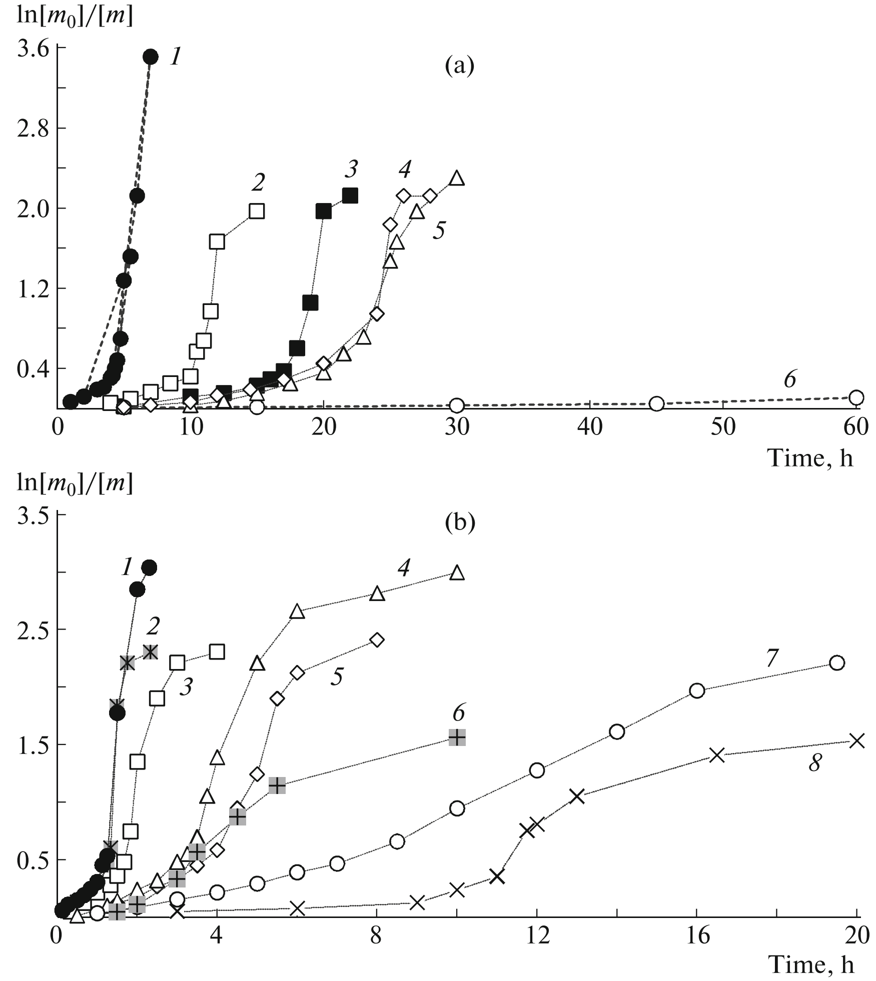


Fig. 1. Kinetic curves of MMA polymerization under the action of *o*-iminobenzoquinones at (a) 50 and (b) 70°C in semi-log coordinates initiated by 0.1 mol % of AIBN. *o*-Iminobenzoquinone: (a) **1a** (*2, 3*), **1b** (*4*), **1c** (*5*), **1d** (*6*); (b) **3** (*2*), **1a** (*3*), **1c** (*4*), **1b** (*5*), **4** (*6*), **1d** (*7*), **2** (*8*). Concentration: (a) 0 (*1*), 0.1 (*2, 4, 5*), 0.2 (*3*); (b) 0 (*1*), 0.1 mol % (*2–8*).

increase in the concentration of *o*-iminobenzoquinone does not have a noticeable effect on the autoacceleration of polymerization. On the contrary, *o*-iminobenzoquinone **1d** almost completely inhibits polymerization already at the equimolar ratio with the initiator (Fig. 1a, curve *6*).

With an increase in temperature to 70°C, the kinetics of the MMA polymerization under the action of compounds **1a** and **3** differs little from the kinetics of the polymerization initiated by AIBN (Fig. 1b, curves *1* and *3*). For *o*-iminobenzoquinones **1b** and **1c**, the gel effect on the kinetic curves appears later (curves *4*, *5*). The gel effect degenerates or is smoothed using compounds **1d**, **2**, and **4** (curves *6–8*). At 90°C, the kinetic regularities of the MMA polymerization described with inclusion of compounds **1–3** remain.

The molecular weight distribution (MWD) curves of PMMA samples obtained with the participation of *o*-iminobenzoquinones **1a–1d** are unimodal throughout the range of concentrations and monomer conversions studied, but they broaden with increasing monomer conversion during polymerization under the action of *o*-iminobenzoquinones **1a–1c**. This broadening is more noticeable when compound **1a** is used and is less evident for compounds **1b** and **1c**. In the case of *o*-iminobenzoquinones **1d**, the molecular weight distribution of the polymer is the narrowest, and the value of the polydispersity coefficient is 1.2–1.4 throughout the process. In this case, M_n of the polymers synthesized at 50°C is a linear function of conversion (Fig. 2a). In general, the value of the molecular weight of the polymer decreases with increasing size of alkyl substituents at positions 2 and 6 of the aryl moiety of *o*-iminobenzoquinone and increasing *o*-iminobenzoquinone : AIBN ratio.

When the temperature is raised to 70°C, the linear dependence of M_n of PMMA on conversion is observed only with an excess of *o*-iminobenzoquinone

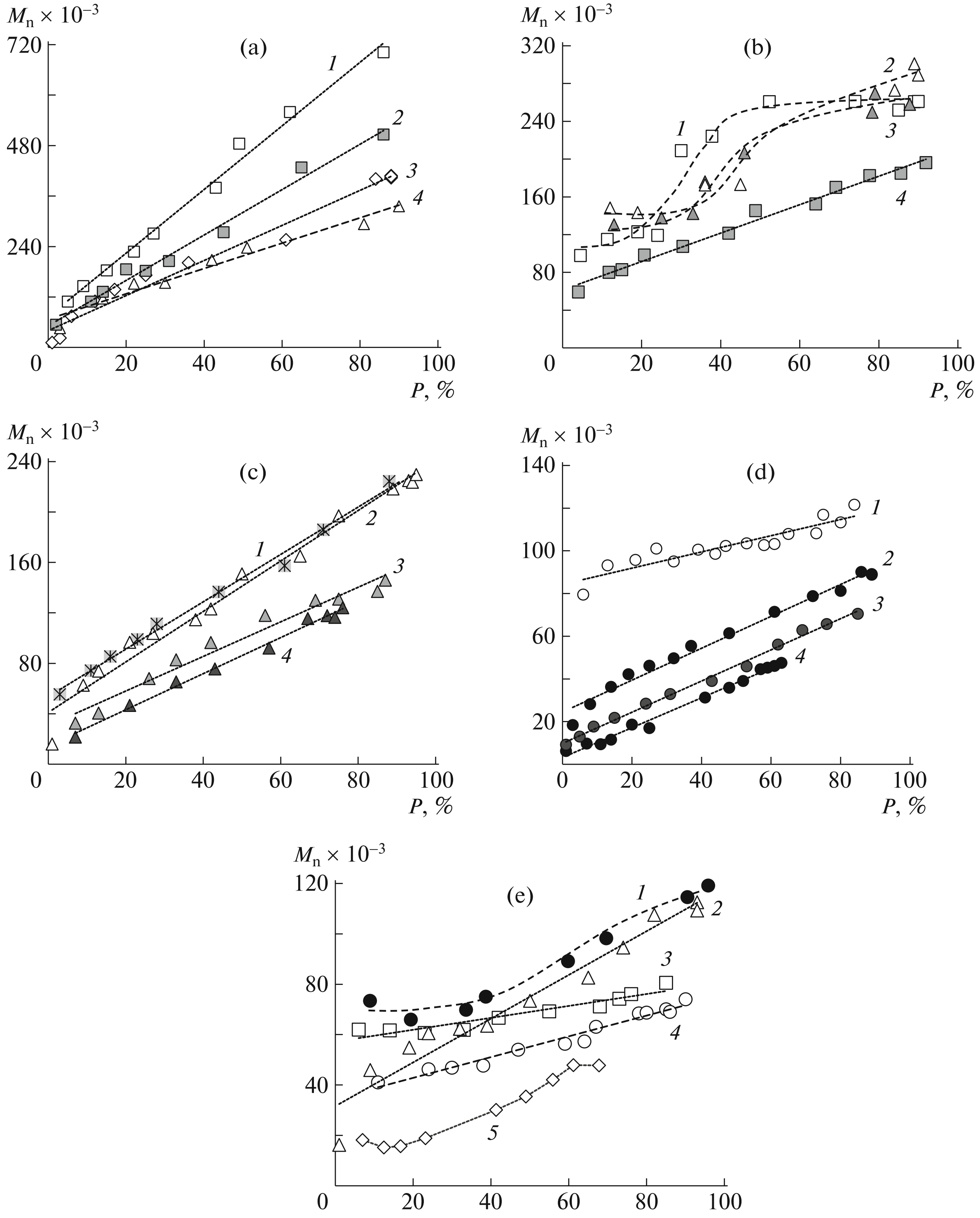


Fig. 2. Dependence of PMMA M_n on conversion of P obtained during the polymerization initiated by 0.1 mol % of AIBN in the presence of *o*-iminobenzoquinones. T = (a) 50, (b–d) 70, and (e) 90°C. *o*-Iminobenzoquinones: (a) **1a** (*1*, *2*), **1b** (*3*), and **1c** (*4*), concentration: 0.1 (*1*, *3*, *4*) and 0.2 mol % (*2*); (b) *o*-iminobenzoquinones: **1a** (*1*, *4*) and **3** (*2*, *3*), concentration 0.1 (*1*, *2*) and 0.2 mol % (*3*, *4*); (c) *o*-iminobenzoquinones: **1b** (*1*) and **1c** (*2–4*), concentration: 0.1 (*1*, *2*), 0.2 (*3*), and 0.4 mol % (*4*, *5*); (d) concentration of **1d**: 0.05 (*1*), 0.1 (*2*), 0.2 (*3*), and 0.4 mol % (*4*); (e) *o*-iminobenzoquinones: **1c** (*2*), **1a** (*3*), **1d** (*4*), and **2** (*5*), concentration: 0 (*1*) and 0.1 mol % (*2–5*).

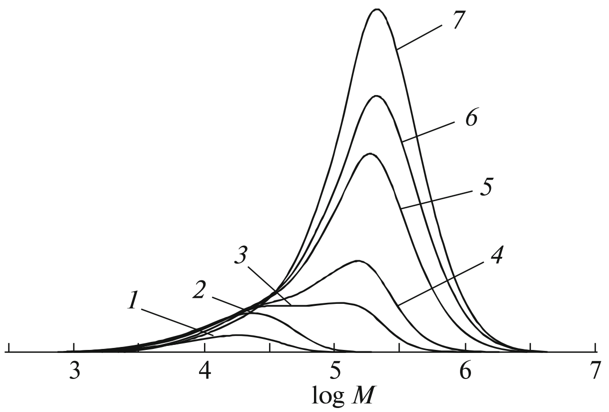


Fig. 3. Curves normalized to the monomer conversion of the MWD of the polymer obtained at 70°C using 0.1 mol % of AIBN and 0.1 mol % of compound **2**. Conversion: 5 (*1*), 12 (*2*), 21 (*3*), 30 (*4*), 54 (*5*), 65 (*6*), and 75 (*7*).

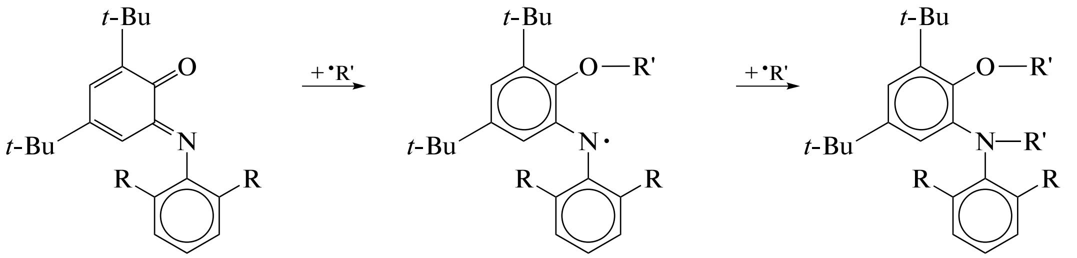
1a (Fig. 2b, curve *4*), but for all investigated concentrations of *o*-iminobenzoquinones **1b**—**1d** (Figs. 2c, 2d). In the latter case, the molecular weight of the polymers synthesized with one conversion in the presence of compounds **1b** and **1c** practically coincide. At 90°C, the linear dependence of M_n of PMMA on conversion remains for *o*-iminobenzoquinones **1a**—**1d** at their equimolar ratio for the initiator (Fig. 2e, curves *2*—*4*), and the value of the PMMA polydispersity coefficient is 1.7—2.0 regardless of the composition of *o*- iminobenzoquinones. The value of the molecular weight of the polymer decreases with increasing *o*-iminobenzoquinone : AIBN ratio (Figs. 2b—2d).

The regularities of the conversion changes in the molecular weight distribution of the polymer synthesized with the participation of compound **2** are close to those of the usual radical polymerization proceeding under the gel effect conditions (Fig. 3). At initial conversions, the MWD curves are unimodal, and when the gel effect occurs, the MWD broadens and becomes bimodal. An increase in the concentration of compound **2** or a change in temperature does not affect the character of the MWD in the course of the process. In this case, the dependence of M_n of PMMA on conversion is S-shaped, which is typical of classical radical polymerization of MMA in mass (Fig. 2e, curve *5*).

Thus, *o*-iminobenzoquinones affect the MMA polymerization differently as compared to *o*-benzoquinones, which as a rule are inhibitors of the process [1, 8]. However, the kinetics of MMA polymerization in the presence and absence of compound **3** is the same (Fig. 1b, curves *1*, *2*). The nature of the conversion change in MWD is also similar, and the dependence of M_n of PMMA on conversion is S-shaped (Fig. 2b, curves *2*, *3*). According to the results obtained, the role of phenanthrene-*o*-iminoquinone **3** in the MMA polymerization differs little from that of phenanthrenequinone-9,10 [1], and the *N*-aryl moiety modifies the properties of *o*-quinones without their pronounced changes.

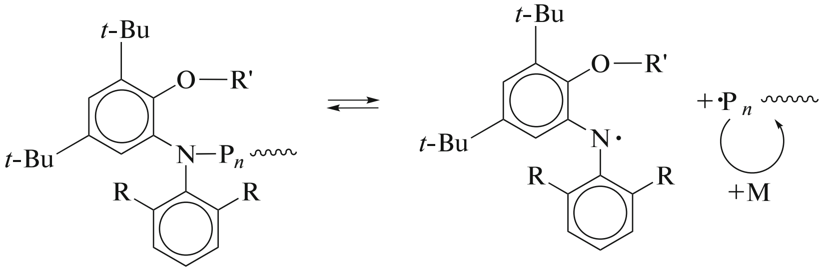
Mechanism of the Interaction between Growing Radicals and N-(Aryl)-o-iminobenzoquinones

The decrease in the total rate of the MMA polymerization when *o*-iminobenzoquinones **1a**—**1d** are added (Fig. 1) suggests the interaction between *o*-iminoquinones and initiator radicals or oligomeric radicals. *N*-(aryl)-*o*-iminobenzoquinones are structural analogs of sterically hindered *o*-benzoquinones; therefore, this reaction can be represented as a sequential accepting of the initiating or oligomeric radical ${}^\bullet$R' to form the ether of the corresponding *o*-aminophenol:



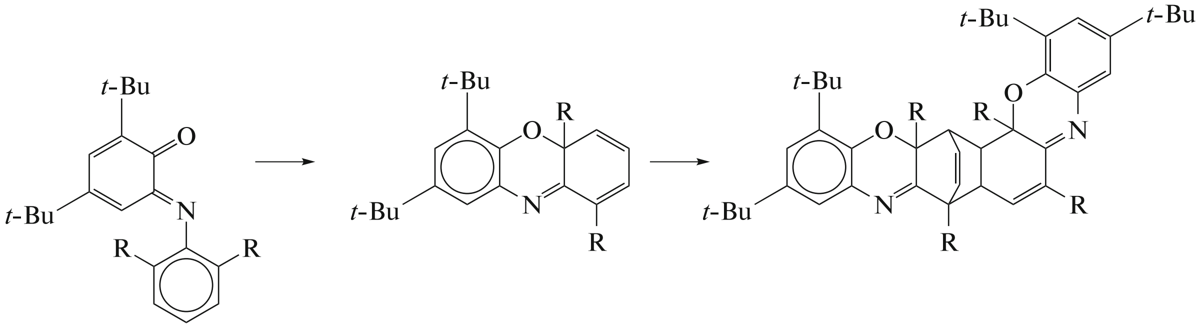
The aryl substituent at the nitrogen atom probably does not participate directly in the reaction with the radicals. This assumption is supported by the fact that the presence of the "*N*-aryl" fragment does not contribute to an increase in the inhibitory properties of phenanthrene-*o*-iminoquinone **3** [1].

The high yield of the polymer, the linear growth of M_n of the polymer with increasing conversion (Fig. 2) observed in a number of cases, and small values of the polydispersity coefficient allow one to assume the possibility of reversible interaction of *o*-iminobenzoquinones **1a**—**1d** with macroradicals according to the scheme



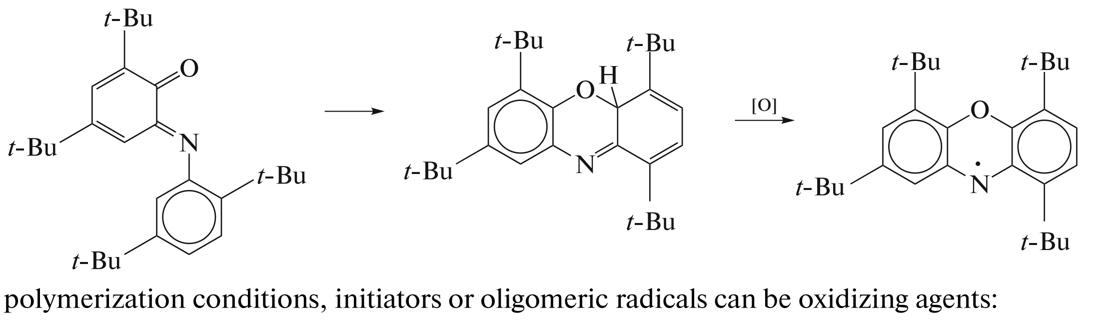
From the point of view of both the energies of the bonds being broken and steric factors, after the elimination, the formation of the N-centered radical derivative is more likely than the O-centered radical. This mechanism is confirmed by the EPR spectroscopy data for the example of reaction mixtures containing *o*-iminobenzoquinone **1d**. In the EPR spectrum, only one signal is recorded, a triplet (1 : 1 : 1) of doublets (1 : 1) (Fig. 4) corresponding to the interaction of an unpaired electron with magnetic nuclei of ^{14}N and ^{1}H ($a_i(^1H) = 0.38$ mT, $a_i(^{14}N) = 0.39$ mT, $g_i = 2.0039$). An analogous shape of the spectrum is characteristic of anion-radical forms of *o*-iminoquinone **1d** [20].

Significant differences in the effect of compounds **1a–1d** on the kinetic patterns of the MMA polymerization and the molecular weight characteristics of PMMA are apparently due to side reactions. In particular, *N*-(aryl)-*o*-iminobenzoquinones upon heating are capable of intramolecular cyclization followed by irreversible condensation [15]:



The probability of this reaction is affected by the structure and composition of *N*-(aryl)-*o*-iminobenzoquinones and temperature [15, 21, 22]. According to [21], the smaller the volume of alkyl substituents is at the 2 and 6 positions of the aryl moiety, the faster the cyclization and hence the subsequent condensation of *o*-iminobenzoquinones proceed. These regularities correlate with the results of studies of the MMA polymerization in the presence of compounds **1a–1d** at a different temperatures.

Differences in the kinetic regularities of the MMA polymerization and features of the change in the molecular weight characteristics of PMMA in the course of processes involving compounds **1a–1d** and **2** can also be associated with a side reaction of intramolecular cyclization. Particularly, phenoxazine **2** does not dimerize, but it is easily oxidized to a phenoxazinyl radical. When heated in polar media, compound **2** forms radical derivatives in a practically quantitative yield [22]:



Under polymerization conditions, initiators or oligomeric radicals can be oxidizing agents:

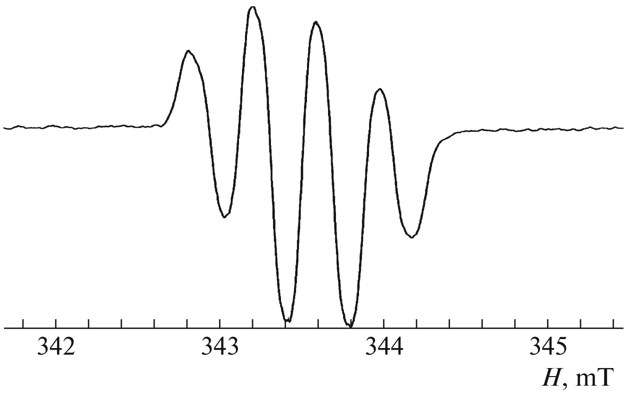


Fig. 4. EPR spectrum observed in the MMA polymerization in the presence of 0.05 mol % of AIBN and 0.05 mol % of compound **1d**. Reaction time is 20 min, $T = 70°C$.

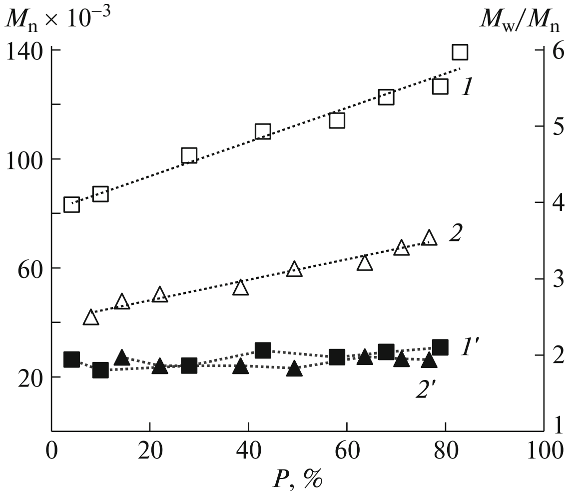
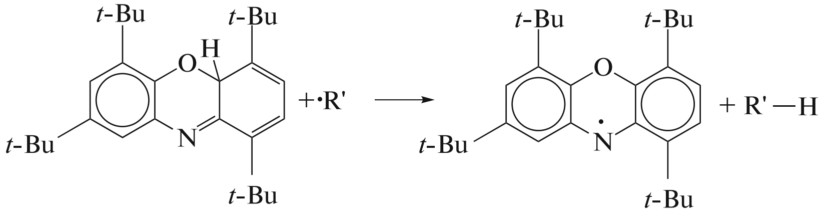
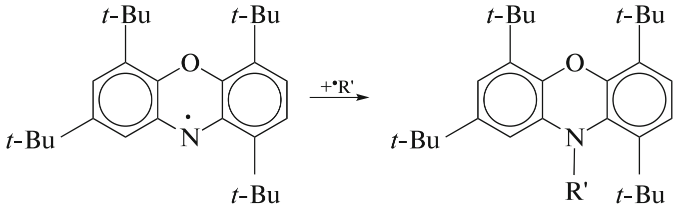


Fig. 5. M_n (*1*, *2*) and M_w/M_n of PMMA (*1'*, *2'*) as functions of conversion. $T = 70$ (*1*, *1'*) and 90°C (*2*, *2'*). Concentration of AIBN is 0.1 mol %; concentration of compound **4** is 0.1 mol %.



Thus, a long period of induction when using *o*-iminobenzoquinone **2** can be a consequence of both the breakage of the active radicals and the course of the cyclization side reaction. In the latter case, further interaction of polymer radicals with the resulting phenoxazinyl radical derivatives is possible, which leads to a decrease in the yield of PMMA and broadening of MWD:



The direct introduction of the phenoxazinyl radical (**4** as an example) into the reaction system favors reduction of the MMA polymerization rate in the temperature range of 70–90°C (Fig. 1, curve *4*). In this case, the molecular weight of the resulting PMMA decreases, the MWD curves are unimodal throughout the process, and the M_n dependence on the conversion becomes linear (Fig. 5). The value of the polydispersity coefficient is 1.7–2.0 at 70 and 90°C.

Methyl Methacrylate Post-polymerization

To confirm the assumption of the possibility of realizing the mechanism of reversible breakage in the MMA polymerization under the action of *o*-iminoquinones, a set of macroinitiators based on PMMA were synthesized, and they were tested in the post-polymerization (Table 2). It is shown that the yield of the polymer increases, and the MW of the reaction product, as a rule, decreases with an increase in the macroinitiator concentration. This suggests that the resumption of the MMA polymerization is due to the use of macroinitiators. Naturally, the ability of PMMA to reinitiate the polymerization is determined by the conditions for its preparation (MW, nature of *o*-iminobenzoquinone, ratio of *o*-iminobenzoquinone to AIBN, and synthesis time).

Table 2. Molecular weight characteristics of macroinitiators and MMA post-polymerization products ($T = 70°C$)

imQ	Characteristics of PMMA initiator					[Macroinitiator], wt %	Time, h	Characteristics of post-polymerization products		
	imQ/AIBN*	time, h	conversion, %	$M_n \times 10^{-3}$	M_w/M_n			conversion, %	$M_n \times 10^{-3}$	M_w/M_n
1c	1 : 1	3	38	124	1.49	10	5	15	330	3.25**
	2 : 1	4.5	38	75	1.42	10	5	27	360	3.10**
							10	36	630	5.38**
	4 : 1	8	43	76	1.48	10	5	17	270	3.11**
							10	31	410	5.23**
	4 : 1	13	73	124	1.44	10	5	15	265	3.06**
						20	5	44	350	2.82**
1d	1 : 1	6	20	43	1.32	20	2	24	99	1.29
	1 : 1	8.5	48	60	1.44	10	5	10	180	2.25**
						20	5	21	170	2.00**
	2 : 1	22	73	63	1.52	10	5	13	170	3.35**
							10	22	210	4.21**
	4 : 1	30	52	48	1.56	20	5	44	98	3.52**
	1 : 1	12	57	77	1.38	10	5	10	180	10.79**
						10	10	43	410	7.07**
						20	5	25	160	6.25**
						50	5	65	150	4.04**
	2 : 2	12	61	42	1.36	10	5	26	130	1.59
						20	5	30	100	1.41
						50	5	36	57	1.34
	4 : 4	12	65	29	1.38	10	5	25	110	1.55
						20	5	35	68	1.45
						50	5	43	34	1.37

* Concentration is a multiple of 0.1 mol %.

** Two modes.

The post-polymerization products synthesized using PMMA prepared with the participation of compound **1c** are characterized by a bimodal MWD (Fig. 6a, Table 2). The width of the MWD of the polymers formed by the action of macroinitiators obtained in the presence of compound **1d** depends on the MW of the macroinitiator (Table 2). With a low MW macroinitiator, a unimodal and relatively narrow MWD of the post-polymerization product is observed (Fig. 6b). With a high MW and a long polymerization time, the MWD curves of the polymers are bimodal regardless of the macroinitiator concentration. In this case, the low-molecular mode corresponds to the initial macroinitiator, and the high-molecular mode corresponds to the resulting polymer.

Thus, the effectiveness of the macroinitiator in the reinitiation of the process depends on the conditions for its preparation. As a rule, the higher the concentration of AIBN and *o*-iminobenzoquinone in the synthesis of the macroinitiator and the higher its concentration in post-polymerization, the narrower is the MWD of the reaction product.

CONCLUSIONS

Here, a new class of regulators of radical polymerization, namely, spatially hindered *o*-iminoquinones, was proposed. Their effectiveness depends on the structure of alkyl substituents in the aryl moiety of *o*-iminoquinone, which determines the tendency of the

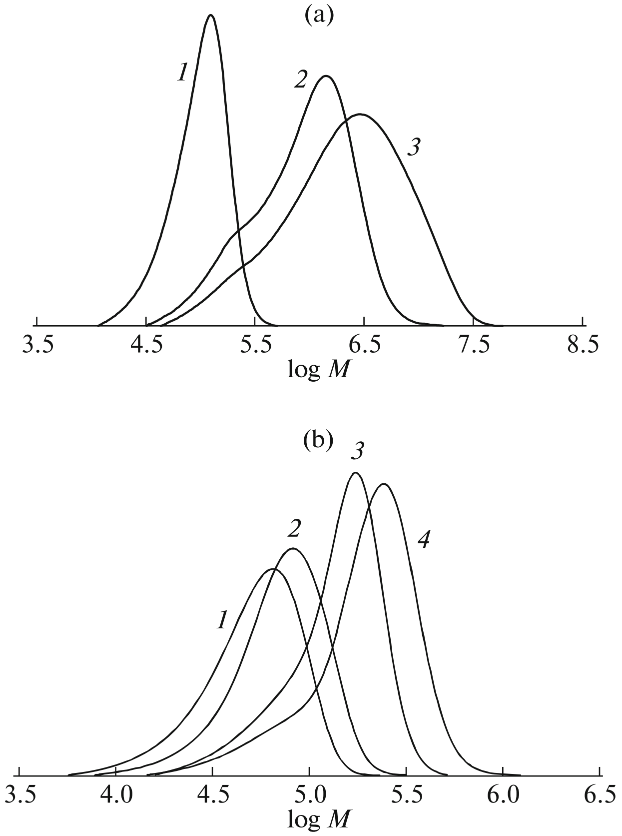


Fig. 6. MWD curves of post-polymerization products, $T = 70°C$. (a) Curve *1* is macroinitiator (prepared using compound **1c**, $M_n = 75.3 \times 10^3$, $M_w/M_n = 1.42$); curves *2* and *3* are post-polymerization products formed at the conversion of 27 (*2*) and 36% (*3*); (b) curve *1* is macroinitiator (prepared using compound **1d**, $M_n = 41.7 \times 10^3$, $M_w/M_n = 1.36$); curves *2*–*4* are post-polymerization products prepared at a concentration of the macroinitiator of 50 (*2*), 20 (*3*), and 10 wt % (*4*), conversion of 36 (*2*), 30 (*3*), and 26% (*4*).

compounds used to undergo side reactions when heated. It was shown that the use of 4,6-di-*tert*-butyl-*N*-(2-methyl-6-ethylphenyl)-*o*-iminobenzoquinone, 4,6-di-*tert*-butyl-*N*-(2,6-diethylphenyl)-*o*-iminobenzoquinone, and 4,6-di-*tert*-butyl-*N*-(2,6-diisopropylphenyl)-*o*-iminobenzoquinone and the traditional radical initiator makes it possible in some cases to polymerize MMA to deep conversions in the absence of the gel effect. In this case, a linear increase in the number-average molecular weight of the polymer is observed with an increase in the degree of monomer conversion, and the polydispersity coefficients remain in the range of 1.4–2.0.

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