Controlled radical polymerization of alkyl acrylates in the presence of the tri-*n*-butylborane—*p*-quinone system*

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The reactivities of different *p*-quinones in the radical polymerization of methyl and *tert*butyl acrylates were studied. The inhibitory effect of *p*-quinones decreases with an increase in the volume and number of substituents. The radical polymerization of alkyl acrylates in the presence of tri-*n*-butylborane and *p*-quinones proceeds without gel effect by the "living" polymerization mechanism. UV spectroscopy showed that the reaction between the growth radical and *p*-quinone proceeds with different regioselectivity and depends on the nature of the latter. The obtained polyacrylates possess the capability of reinitiating polymerization. The reinitiation mechanism was studied by mass spectrometry (MALDI-TOF) and ESR spectroscopy. Gel permeation chromatography showed that, depending on the nature of *p*-quinone, macroinitiator polymers exhibit different activity in post-polymerization.

Key words: tri-*n*-butylborane, *p*-quinone, radical polymerization, alkyl acrylate.

Experimental

In our previous works, 1-4 it was shown that homopolymerization of styrene and methyl methacrylate (MMA) in the presence of the catalytic system based on tri-nbutylborane (Bu₃B) and *p*-quinones proceeds as controlled radical polymerization by the mechanism of reversible inhibition.^{2–4} The resulting macroinitiator-type polymers possess the capability of reinitiating polymerization upon addition of a new monomer portion. For example, postpolymerization of MMA affording high-molecular-weight (MW) products⁵ and block copolymerization of styrene with MMA were carried out. The block copolymer obtained by the second method was characterized by high physical and mechanical properties.⁶ This catalytic system can be used also for the synthesis of a new class of polymer materials, viz., gradient copolymers. The possible synthesis of such copolymers was shown by the example of copolymerization of styrene and vinyl acetate.⁷ Compared to methacrylates and styrene, alkyl acrylates possess a higher activity in the radical polymerization. For this reason, the control of the process rate and the MWs of polyacrylates is a complex problem.

The aim of the present work was to study whether the controlled synthesis of polyacrylates in the presence of a Bu_3B —*p*-quinone catalytic system can be realized.

Organic solvents were purified according to known procedures.8 Methyl acrylate (MA, Reakhim, 98%) was dried over calcium hydride and distilled under atmospheric pressure (101.3 kPa, 80 °C). tert-Butyl acrylate (TBA, Acros, 99%) was distilled under reduced pressure (8.0 kPa, 61-63 °C). Azoisobutyronitrile (AIBN) was recrystallized from methyl tert-butyl ether and dried until constant weight; its purity was controlled by NMR spectroscopy. Dicyclohexyl peroxydicarbonate (DCPD) was obtained by the reaction of cyclohexyl chloroformate and sodium peroxide⁹ and recrystallized from methanol. Its purity was determined by iodometric titration. Tributylborane was prepared by the reaction between boron trifluoride etherate and n-butyl magnesium bromide in diethyl ether according to the earlier described procedure¹⁰ and distilled under reduced pressure (1.07 kPa, 90 °C). Phenyl N-tert-butylnitrone (Alfa-Aesar, 98%), duroquinone (DQ, Aldrich, 97%), and 2,5-di-tert-butylbenzoquinone (DTBQ, Aldrich, 99%) were used as received. Naphthoquinone (NQ, Reakhim, 97%) was purified by recrystallization from petroleum ether. Benzoquinone (BQ) was obtained by oxidation of hydroquinone in the presence of potassium bichromate and sulfuric acid followed by recrystallization from petroleum ether¹¹ (the yield was 86%). ¹H NMR (CDCl₃), δ: 6.78 (s, 4 H). Dimethylbenzoquinone (DMBQ) was synthesized from 2,3-dimethylhydroquinone (Aldrich, 97%) by oxidation in the presence of CrO₃ and acetic acid followed by recrystallization from petroleum ether¹¹ (the yield was 60%). ¹H NMR (CDCl₃), δ: 2.03 (s, 6 H); 6.71 (s, 2 H).

Polymerization mixture was prepared in an ampule dissolving the required amounts of the initiator and *p*-quinone in the

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monomer. The required amount of a solution of Bu₃B in hexane from a vacuum line-connected burette was added to another ampule. Hexane was removed from the solution by distillation under reduced pressure. Both ampules were degassed by six-fold freezing in vacuo. The contents of the ampules was mixed fast and frozen in liquid nitrogen. The ampules were sealed. Prior to polymerization, they were stored in liquid nitrogen. After defrost, the ampule was placed in a thermostat set to either 60 °C (for the AIBN-initiated polymerization) or 25 °C (for the DCPDinitiated polymerization). In a given time after initiation of polymerization, the ampules were removed from the thermostat and cooled with liquid nitrogen. The resulting polymers were isolated by rapid precipitation in petroleum ether (in the case of PMA) or ethanol-water (9:1) (in the case of PTBA). Polymerization kinetics was studied by gravimetry or dilatometry. To study the post-polymerization, a solution of the PMA macroinitiator (5 wt.%) in the monomer was prepared, placed in an ampule, degassed, and kept in a thermostat at 30 °C.

The dried polymer samples were dissolved in chloroform and studied by UV spectroscopy on a Shimadzu UV-1650 spectrometer. The MALDI-TOF analysis of polymers was performed under linear conditions on a Bruker Microflex LT instrument equipped with a nitrogen laser ($\lambda = 337.1$ nm). The spectrometer was calibrated by the peaks $[PMMA + Na]^+$ of narrow-disperse PMMA standards (Waters, $M_n = 2580$ and 8200). The calibration dependence was approximated by a third-power polynomial. The experimental data were processed by the Bruker flexControl and flexAnalysis software. The matrix was trans-2-[3-(4-tertbutylphenyl)-2-methyl-2-propenylidene]malonitrile. Test samples were prepared mixing a solution of polymer (10 mg mL⁻¹, 5 L), a solution of the matrix (20 mg mL⁻¹, 10 L), and sodium trifluoroacetate (5 mg mL⁻¹, 3 L) in THF. The resulting solution (2 L) was applied onto a stainless steel support and analyzed. ESR spectra were recorded on a Bruker EMX X-range spectrometer. The molecular weights of polyacrylates were calculated from the values of intrinsic viscosity:

 $[\eta] = K \cdot M_{\eta}^{a}.$

The measurement conditions and values of Mark—Kuhn— Houwink constants (K, a) are given in Table 1.

 Table 1. Mark—Kuhn—Houwink constants for PMA and PTBA¹²

Compound	Solvent	<i>T</i> /°C	$K \cdot 10^4 / dL g^{-1}$	а
PMA	Chloroform	30	3.22	0.678
PTBA	Acetone	25	4.70	0.750

The molecular weight characteristics of polymers were determined by GPC in THF at 40 °C (the flow rate of the eluent was 0.7 mL min⁻¹) on a Prominence LC-20VP liquid chromatograph (Shimadzu) using Tosoh Bioscience polystyrene gel-packed columns with a pore size of $1 \cdot 10^5$ and $1 \cdot 10^4$ Å. The detector was a differential refractometer. Chromatograms were processed using the LCsolution software. Calibration was performed using the PMMA narrow-disperse standards (MWs $1 \cdot 10^3 - 2.5 \cdot 10^6$).

Results and Discussion

p-Quinones-inhibited polymerization of acrylates. At the first stage, we studied the inhibiting ability of differentnature guinones in the radical polymerization of MA and TBA. There are few studies in this field.^{13,14} For example, the kinetic regularities of inhibited polymerization of MA and ethyl acrylate in the presence of BQ, its halogen derivatives, and DQ have been studied earlier. To estimate the reactivity of quinones with regard to acrylate growth radicals, we studied the initial rate of MA and TBA polymerization, as well as the molecular weight characteristics of polymers synthesized in the presence of different-structure quinones (Table 2). As is known, the increase in the inhibition constant (k_z) , which is the ratio of the inhibition rate constant to the chain propagation rate constant, results in a decrease in the initial polymerization rate (V)and a decrease in the MW. The above-mentioned effects depend on the presence and size of a substituent in the quinone molecule.¹⁵ The steric hindrance of p-quinones was estimated using the Charton steric constants (ΣV). It is seen from Table 2 that, with an increase in the number and volume of substituents, the inhibition constant decreases. For example, the highest rate of MA and TBA polymerization is observed in using DQ and the lowest rate and the lowest MW were observed when BO was added to the system. In general, *p*-quinones can be arranged by the reactivity with regard to the acrylate macroradicals in the following order: BQ > DMBQ > NQ > DQ. As expected, this order does not depend on the nature of growth radicals. According to expectations, this order does not depend on the nature of growth radicals. From the data on polymerization rate and MW, one can conclude that *p*-quinones more efficiently trap the MA macroradicals compared to the TBA ones.

Polymerization of alkyl acrylates in the presence of tri*n*-butylborane and *p*-quinones. Introduction of *p*-quinones together with Bu_3B into polymerization of alkyl acrylates results in an increase in its rate compared to the inhibited polymerization. From the data given in Table 3, it is seen that addition of Bu_3B increases the polymerization rate on the average two-fold. For TBA, the rate of the process was higher than that for MA.

The increase in the process rate upon addition of p-quinones is due to the increase in the amount of reaction centers formed by the active chain transfer to Bu₃B.¹ With an increase in the concentration of p-quinone in the

Monomer	Quinone	$k_z \cdot 10^{-3}$ /L mol ⁻¹ s ⁻¹ 15	ΣV	<i>V</i> •10 ³ (% s ⁻¹)	Time/h	Conversion (%)	$M_\eta \cdot 10^{-4}$
MA	DQ	0.92	1.08	10.5	0.5	22.0	102
TBA	DQ	0.92	1.08	17.7	0.3	24.0	147
MA	NQ	10.3	0.52	6.9	2.0	24.1	40.1
ТБА	NQ	10.3	0.52	9.5	2.1	29.5	96.0
MA	DMBQ	22.1	0.52	3.4	3.8	29.4	22.8
TBA	DMBQ	22.1	0.52	3.7	3.5	27.9	68.9
MA	BQ	108	0	1.4	4.6	23.7	15.9
TBA	BQ	108	0	1.3	4.5	25.4	14.3

Table 2. Data from polymerization of MA and TBA initiated by AIBN (0.10 mol.%) at 60 °C in the presence of p-quinones (0.25 mol.%)

Scheme 1



system, the initial polymerization rate of acrylates increases (see Table 3).

In Ref. 1, we found that the addition of MMA macroradicals to quinone can proceed by two pathways (Scheme 1). Pathway I results in the formation of adducts responsible for the "living" polymerization. The cumulative data obtained in the present work allow us to state that, as in the case of MMA, the reaction of the growth radicals with *p*-quinone can proceed by two pathways (see Scheme 1).

The addition of macroradical to the C=O bond of *p*-quinone results in the formation of the phenoxyl radical which reacts with Bu_3B to form terminal boraryloxy groups (1) (see Scheme 1). Similar adducts can reinitiate polymerization by the mechanism of reversible inhibition (Scheme 2).^{4–6} The addition of the macroradical to the C=C bond of *p*-quinone followed by the S_R2-substitution at the boron atom (see Scheme 1, pathway 2) results in the formation of "dead" quinoid derivatives 2 which cannot reinitiate polymerization. Their formation can widen the molecular weight distribution of the polymer.

Scheme 2



It is known that, upon polymerization of acrylates, there occurs a significant chain transfer onto the polymer, especially, upon a deep conversion, which results in the formation of branched and cross-linked structures. In addition, the conversion upon polymerization of acrylates corresponding to the beginning of self-acceleration is observed even at early stages. To avoid the above-mentioned adverse processes, we decided to decrease the synthesis temperature to 25 °C and to use the "low-temperature" initiator DCPD. The decrease in the synthesis temperature also resulted in a change in the ratio between the inhibition and chain propagation constants in favor of more efficient inhibition.

Figure 1 shows that polymerization of alkyl acrylates initiated by DCPD with addition of Bu_3B and *p*-quinones proceeds without self-acceleration. The kinetic regulari-

Table 3. Rates of MA and TBA polymerization initiated by AIBN (0.10 mol.%) at 60 °C in the presence of Bu_3B (0.80 mol.%) and different amounts of naphthoquinone

Monomer	[NQ] (mol.%)	$V \cdot 10^3 (\% \text{ s}^{-1})$		
MA	0.25	12.0		
	0.50	21.3		
	0.75	45.1		
TBA	0.25	18.5		
	0.50	36.0		
	0.75	75.0		



Fig. 1. Kinetic curves for polymerization of MA (*a*) and TBA (*b*) initiated by 0.10 mol.% of DCPD at 25 °C in the presence of 0.80 mol.% of Bu₃B and 0.25 mol.% of *p*-quinones: NQ (*1*); DMBQ (*2*); and BQ (*3*).

ties of MA polymerization in the presence of the Bu_3B *p*-quinone catalytic system are arranged in accordance with the reactivity of quinones (see Fig. 1, *a*). The highest polymerization rate is observed in using NQ (see Fig. 1, *a*, curve *I*) and the lowest rate is observed in using BQ (see Fig. 1, *a*, curve *3*). The analogous regularities take place upon polymerization of TBA; however, this effect is less pronounced. The kinetic curves of TBA polymerization in the presence of NQ (see Fig. 1, *b*, curve *I*) and DMBQ (see Fig. 1, *b*, curve *2*) virtually coincide. A similar effect was observed upon polymerization of styrene in the presence of the above-mentioned *p*-quinones.⁴ In our opinion, this can be due to the nature of the monomer, namely, due to steric hindrances during addition of the *tert*-butylacrylate radical to the quinone molecule and a lower polarity of TBA compared to MA. Polymerization of TBA in the presence of BQ tends to be retarded. This can be due to a decrease in the rate of dissociation of "living" adducts. As far as Bu₃B in the system becomes exhausted, polymerization kinetics starts to take the form of inhibited polymerization. In using *p*-quinones with a lower inhibiting ability (DQ, DTBQ), the gel effect cannot be suppressed (Table 4). Within 15 min, the degree of MA conversion reaches 60% and the weight-average MW (M_w) of PMA in using DQ reaches more than 500 kDa.

To obtain more detailed data on the mechanism of polymerization of alkyl acrylates in the presence of the p-quinone—Bu₃B system, we studied the molecular weight characteristics of resulting polymers. The number-average MW of polyacrylates (M_n) obtained using the Bu₃B*p*-quinone system increases linearly with an increase in the degree of conversion (Fig. 2). The pattern of the relationship between the MW and the degree of conversion is influenced by the portion of the "living" process and the addition of the growth radical to the C=C bond of quinone. The highest conribution of the "dead" polymer 2 to the MWD takes place when the strongest inhibitor, BQ, was used. On going to the weakest inhibitor (NQ), the slope of the linear relationship between the number-average MW and the degree of conversion increases. This is quite natural, since, when using NQ, the time to the inhibition act is longer and, correspondingly, higher MWs are achieved. In the case of BO, this can be due to the difficulty of "animation" of reversible inhibition adducts obtained using this *p*-quinone. Earlier, it was shown by the example of MMA that similar adducts virtually cannot dissociate.² The highest gain in the MW with conversion occurs in using DMBQ, despite its higher reactivity compared to NQ. In this system, reversible inhibition dominates over "usual" polymerization initiated by DCPD.

The polydispersity parameters of both PMA and PTBA obtained using different *p*-quinones tend to decrease during the process. Figure 3 shows the MWD curves for PMA isolated at different degrees of conversion. In general, PTBA is characterized by the analogous regularities (see Fig. 2, *b*). Also, the highest gain in the MW is achieved upon addition of DMBQ (see Fig. 2, *b*, curve *1*). When using NQ, uniform narrowing of the MWD modes for

Table 4. Data from polymerization of MA in the presence of Bu_3B (0.80 mol.%) and *p*-quinones (0.25 mol.%)

<i>p</i> -Quinone	Conversion (%)	Time/h	$M_\eta \cdot 10^{-4}$	$M_n \cdot 10^{-4}$	$M_w \cdot 10^{-4}$	M_w/M_n
DQ	56.7	0.25	35.0	15.6	61.2	3.92
DTBQ	63.4	0.25	11.6	7.69	13.8	1.79



Fig. 2. M_n as a function of the degree of conversion for PMA (*a*) and PTBA (*b*) obtained in the presence of 0.10 mol.% of DCPD, 0.80 mol.% of Bu₃B, and 0.25 mol.% of *p*-quinones: DMBQ (*1*); NQ (*2*); and BQ (*3*). T = 25 °C.

both PMA and PTBA (see Fig. 3) occurs with conversion. The analogous case is observed upon substitution of DMBQ for NQ. When a strong inhibitor (BQ) is used, only a slight increase in the MW with conversion upon polymerization of both MA and TBA is observed (Fig. 4), which can be due to the presence of a great amount of the "dead" polymer (2) and the difficulty of "animation" of the reversible inhibition adducts (1).

The addition products of growth radicals to p-quinones were analyzed by UV spectroscopy. The UV spectra of the PTBA samples synthesized in the presence of DMBQ and BQ (Fig. 5, curves 3 and 4, respectively) do not contain the absorption bands of the starting p-quinones (see Fig. 5, curves 1 and 2, respectively). In the case of DMBQ, the absorption bands of the aromatic fragments of poly-



Fig. 3. MWDs of the PMA samples obtained in the presence of 0.10 mol.% of DCPD, 0.80 mol.% of Bu_3B , and 0.25 mol.% of NQ at 25 °C. The degree of conversion and the polydispersity parameters are shown near the curves (in parentheses).



Fig. 4. MWDs of the PTBA samples obtained in the presence of 10 mol.% DCPD, 0.80 mol.% of Bu_3B , and 0.25 mol.% of BQ at 25 °C. The degree of conversion and the polydispersity parameters are shown near the curves (in parentheses).

mer 1 (242 nm) partially overlap with the weakly resolvable band corresponding to the quinoid structures 2 (see Fig. 5, curve 3), the absorption maxima of quinone and the "dead" polymer 2 are considerably remote from each other. In the case of BQ, the absorption bands of the starting quinone (283 nm) and "dead" polymer 2 (288 nm) differ only by 5 nm (see Fig. 5, curves 2 and 3). However, in both cases the polymer contains the aromatic structures 1 which correspond to the absorption maximum at 242 nm (see Fig. 5, curves 3 and 4). Adducts with this terminal



Fig. 5. UV spectra of solutions of DMBQ (1), BQ (2), and PTBA obtained using 0.10 mol.% of DCPD, 0.80 mol.% of Bu_3B , and 0.25 mol.% of DMBQ (3) or BQ (4) in chloroform.

group direct polymerization by the mechanism of reversible inhibition.

Thus, polymerization of MA and TBA in the presence of the Bu_3B-p -quinone catalytic system bears the signs of a "living" process. Quinones (NQ and DMBQ) act as the most effective mediators of chain propagation holding an intermediate position in the reactivity order. The use of weak inhibitors, DQ and DTBQ, does not result in the disappearance of the gel effect (see Table 4). Upon addition of the strong inhibitor, BQ, the progress of "living" polymerization is hindered due to the formation of a great amount of the "dead" polymer (2) and the difficulty of animation of the macroinitiator polymer (1).

Post-polymerization initiated by macroinitiators. One of the important properties of polymers obtained by the

"living" polymerization methods is the ability to restart the process upon addition of a new portion of monomer. Before starting this work, we have studied the structure of the macroinitiator polymers by MALDI-TOF. The spectrum shown in Fig. 6 display two types of "triads", polymer products differing in the type of terminal groups. These triads correspond to polymers obtained by the addition of the cyclohexyloxyl radical formed upon decomposition of DCPD or the butyl radical formed in the reaction of oxygen-centered radicals with Bu₃B. In both cases, there occurs chain termination on NQ followed by S_R2-substitution. Within each "triad", the peaks differ by 16 units, which corresponds to the oxygen atom being incorporated to the chain by oxidation of boron-carbon bonds inevitably occurring at the step of isolation (Scheme 3). The results of analysis of this spectrum are given in Table 5.

As Table 5 shows, the molecular structure of the macroinitiator contains both the boralkyl fragments and their oxidized forms. Earlier, it was shown by the example of polystyrene macroinitiators⁶ that oxidation of boron—carbon bonds adversely affects the initiating ability of the macroinitiator. Insertion of the oxygen atom at the B—C bond upon oxidation results in a decrease in the stability of the aryloxyl radical formed upon decomposition of macroinitiator 1 (see Scheme 2). Similar semi-oxidized and oxidized forms of the macroinitiator accumulate during air storage. For this reason, the contacts of macroinitiator and air oxygen should be minimized.

The polymers isolated after post-polymerization were analyzed by GPC. From the data given in Table 6, it follows that, within 1.5 h of the post-process, the MW of PMA increases and the MWD narrows. The highest increase in the MW (1.16-fold) is observed upon initiation



Fig. 6. Mass spectrum of PMA obtained using 0.10 mol.% of DCPD, 0.80 mol.% of Bu₃B, and 0.25 mol.% NQ at 25 °C. The degree of conversion was 20.9% and $M_n = 1.95 \cdot 10^4$.

Scheme 3



Table 5. Data from the mass-spectral analysis of the PMA samples obtained in the presence of DCPD (0.10 mol.%), Bu_3B (0.80 mol.%), and NQ (0.25 mol.%) at 25 °C

Polymer- structure	m/z	MW _{teor}		
1a	1702.7	1696.0		
1b	1718.2	1712.0		
1c	1733.5	1727.0		
2a	1743.9	1739.0		
2b	1759.9	1755.0		
2c	1775.9	1771.0		



1, 2: $R = OBBu_2$ (**a**), OB(OBu)Bu (**b**), $OB(OBu)_2$ (**c**)

of polymerization with the DMBQ-based macroinitiator. Approximately identical increase in the MW for the same time is observed when macroinitiators obtained involving BQ and NQ were used. The MWDs of post-polymerization products have different patterns (Fig. 7, a, b). The post-polymer obtained in the presence of the BQ-based macroinitiator is characterized by a bimodal MWD (see Fig. 7, a, curve 2). The appearance of the second mode suggests a considerable amount of the inactive polymer 2 formed due to the addition of the macroradical to the C=C bond of BQ. The high-molecular-weight mode corresponds to the polymer formed during post-polymerization due to dissociation of active adducts. These results allow assuming that the addition of the growth radicals to BQ is characterized by a low regioselectivity. When the NO-based macroinitiator was used, a regular shift in the MWD curves in favor of higher MWs accompanied by a decrease in the polydispersity parameter was observed. In this case, one can suggest the polymer chains to contain predominantly the boraryloxyl terminal groups formed upon the reaction between the macroradical and the carbonyl group of NQ. The analogous situation is observed also for macroinitiators obtained by polymerization in the presence of DMBO (see Fig. 7, b).

Since initiation proceeds involving the macroinitiator containing unoxidized boron-carbon bonds, to confirm the presumable mechanism of post-polymerization, one should exclude the possibility of reinitiation by means of residual air oxygen. To establish the mechanism of reiniti-



Fig. 7. MWDs of the PMA macroinitiators (*1*) obtained at 25 °C in the presence of 0.10 mol.% of DCPD, 0.80 mol.% of Bu_3B , and 0.25 mol.% of *p*-quinones: BQ (*a*) and DMBQ (*b*); as well as MWDs of the post-polymerization products (*2*).

Table 6. Characteristics of PMA macroinitiators and post-PMA obtained in the presence of macroinitiators (5 wt.%) within 1.5 h at 30 $^{\circ}$ C

<i>p</i> -Quinone	Macroinitiator		Post-polymer			
	$M_{n} \cdot 10^{-4}$	M _w /M _n	Conversion (%)	$M_n \cdot 10^{-4}$	M _w /M _n	
BQ	5.95	1.85	5.62	9.77, 6.16	1.80	
DMBQ	7.02	1.78	6.90	8.16	1.61	
NQ	7.52	1.53	5.91	8.50	1.53	



Fig. 8. ESR spectra of growth radicals formed upon decomposition of the PMA macroinitiator within 15 min (*a*) and 30 min (*b*). Parameters of spectrum *b*: $a_N = 1.432$ mT and $a_H = 0.325$ mT.

ation, we performed the ESR study in the presence of the spin trap, PBN. Earlier, ¹⁶ it was shown that alkyl and alkoxyl radicals are detected in the reaction between $Bu_{3}^{i}B$ and air oxygen in the MMA medium. During post-polymerization, the chain propagation radicals whose signal intensity increased over 30 min were detected only (Fig. 8).

Thus, reinitiation in post-polymerization is realized only through dissociation of aromatic fragments by the reaction shown in Scheme 2. The presence of such structures was proved by MALDI-TOF and UV spectroscopy. The PMA macroinitiators obtained involving DMBQ and NQ possess the highest activity. The post-polymers obtained on the macroinitiator using BQ are characterized by the bimodal MWD, which suggests the presence of a considerable portion of the "dead" polymer. This work was financially supported by the Ministry of Education and Science of the Russian Federation (State Task No. 4.1537.2014K).

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