

Copolymerization of Styrene with Methyl Methacrylate in the Presence of the System Tributylborane–*p*-Quinone¹

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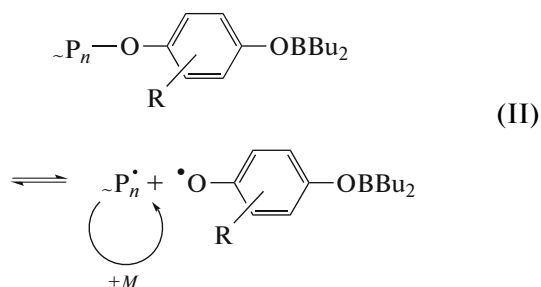
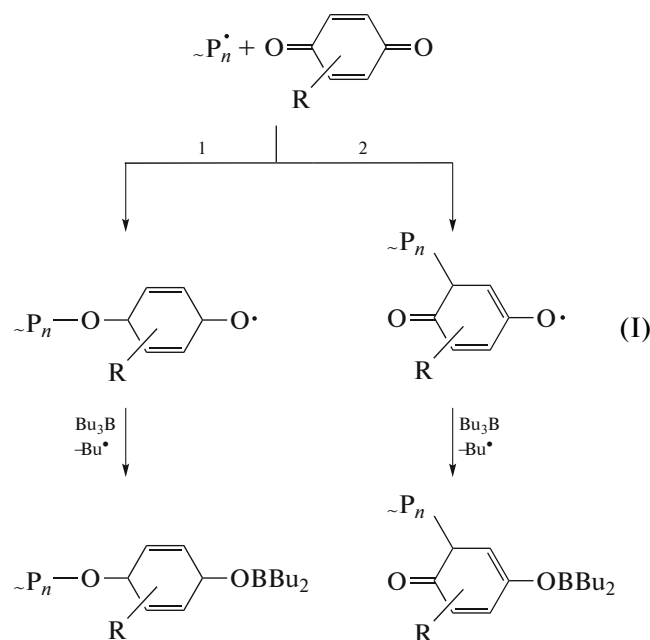
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Abstract—The copolymerization of styrene with methyl methacrylate at 80°C in the presence of catalytic system tributylborane–*p*-quinone (1,4-naphthoquinone, duroquinone) has been studied. The copolymerization proceeds via the mechanism of the reversible inhibition. The number-average molecular weights of the copolymers linearly increase with progress in monomer conversion. The contribution of the “living” mechanism in the total process depends on the structure of the quinone. Reactivity ratios of the monomers differ from the values known for conventional radical polymerization. The experimental data of triad concentration and average composition correlate with theoretical value.

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INTRODUCTION

It is known that homopolymerization of styrene and methyl methacrylate (MMA), initiated by radical initiator, 2,2'-azobis(isobutyronitrile) (AIBN) or dicyclohexyl peroxidicarbonate, in the presence of tributylborane (Bu₃B) and *p*-quinone, proceeds according to the mechanism [1–5].



Realization of directions 1 or 2 in reaction (I) will be determined by the chemical nature of quinone and monomer.

For example, in the polymerization of styrene the addition of the propagating radical to quinone leads to the formation of phenoxy radicals (reaction I, direction 1), which, with a subsequent radical substitution at the boron atom gives rise to the adduct capable of reversible homolytic dissociation via the C–O bond (reaction 2) [1]. In the polymerization of MMA, the macroradical can also add to the C=C bond of quinone with a formation of the quinoid structure (reaction I, direction 2) [2–5]. This product is undesirable, since it is incapable of reinitiating the process, i.e. this kind of macromolecules are “dead.”

The inhibiting ability of the quinone also determines the route of reaction (I). Thus, PMMA propagating radicals interact with duroquinone predominantly by C=O bond [2], while in the case of naphthoquinone both directions of reaction (I) are possible [4].

The aim of this work was to study the opportunity of the controlled synthesis of the copolymers of sty-

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rene and MMA under the influence of Bu_3B and quinones, possessing different inhibiting ability.

EXPERIMENTAL

Materials

MMA and styrene (Acros, 99%) as well as organic solvents were purified by generally accepted methods [6]. AIBN was recrystallized from methyl *tert*-butyl ether and dried to a constant weight. The purity of AIBN was checked by NMR-spectroscopy. Bu_3B was prepared by reaction of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ with *n*-butyl magnesium bromide in ether and purified by distillation under reduced pressure (90°C/1.07 kPa). Duroquinone (DQ) (“Aldrich”, 97%) was used as received; naphthoquinone (NQ) (“Reakhim”, 97%) was purified by recrystallization from petroleum ether.

Polymerization Procedure

The reaction mixtures were prepared by dissolving the necessary quantity of the initiator and *p*-quinone in the monomers feed directly in the ampoule. In another ampoule the necessary quantity of Bu_3B solution in hexane was added, and then the solvent was removed under reduced pressure. Both ampoules were first degassed by triple freezing in the vacuum and their content was thoroughly mixed in one ampoule, which was sealed. Copolymerization was performed at 80°C in bulk. The resulting copolymers were lyophilized from benzene solutions and precipitated into petroleum ether from ethyl acetate solutions. The conversion was determined gravimetrically.

Characterization

UV-spectroscopy (spectrometer Shimadzu UV-1650) was applied to study interaction between macroradicals and *p*-quinones in the presence of Bu_3B . UV-Vis spectra were measured in chloroform. The composition of copolymers was determined by ^1H NMR-spectroscopy, while the experimental triad composition [7] was determined by ^{13}C NMR-spectroscopy (Agilent DD2 400 at frequencies 400 MHz for ^1H and 101 MHz for ^{13}C). The molecular weight characteristics of the copolymers were analyzed via GPC in THF at 40°C on a Shimadzu LC-Prominence liquid chromatograph equipped with differential refractometer and columns packed with polystyrene gel having pore size of 1×10^5 and 1×10^4 Å. Chromatograms were processed using “LCsolution” software. Narrow disperse PS standards were used for calibration.

The triad composition of the copolymers was calculated using Alfrey/Mayo kinetics (first-order Markov statistics). Reactivity ratios of the monomers were determined by Fineman-Ross, Kelen-Tüdös methods and by the least-squares scheme. Co-

isotacticity parameter for copolymers was calculated using Ito-Yamashita equations [8].

RESULTS AND DISCUSSION

Earlier it was demonstrated that homopolymerization of both styrene and MMA in the presence of poor inhibitor DQ proceeds via the “living” radical mechanism, while addition of strong inhibitor NQ to MMA polymerization causes the formation of “dead” quinoid adducts [1, 2, 5]. Thus, the possibility of the realization of a “living” mechanism in the case of copolymerization in the presence of NQ will be determined by the nature of the terminal unit in the propagating radical. It is known that the kinetics of a radical copolymerization of styrene with MMA is described by the implicit penultimate model, while the composition of a copolymer complies with the terminal model [9].

At the first stage, we determined the composition of copolymers of styrene and MMA and estimated the reactivity ratios of the monomers. We expected that initiating system $\text{AIBN}-\text{Bu}_3\text{B}-p\text{-quinone}$ (NQ and DQ) may influence the reacting capacity of monomers and radicals. The chosen quinones are antipodes in terms of their inhibition ability (k_z) and by shielding the carbonyl group. The latter conclusion was illustrated by the values of Charton’s constants (ΣV). Table 1 shows that DQ, which is more sterically hindered, has lower values of the inhibition constant comparing to NQ.

As is seen from Table 2 and Fig. 1, the addition of Bu_3B and *p*-quinone in the reaction mixture leads to the change of the reactivity ratios of the monomers. Thus, in the copolymerization conducting in the presence of Bu_3B and NQ the significant shift of the azeotropic point is observed to the lower molar part of styrene in the monomer feed. Less effect is caused by the system $\text{Bu}_3\text{B}-\text{DQ}$. It may be proposed that coordination of growing PMMA macroradicals with

Table 1. Charton’s constants (ΣV) and inhibition constants (k_z) of *p*-quinones

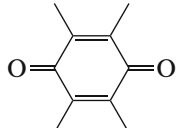
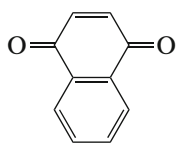
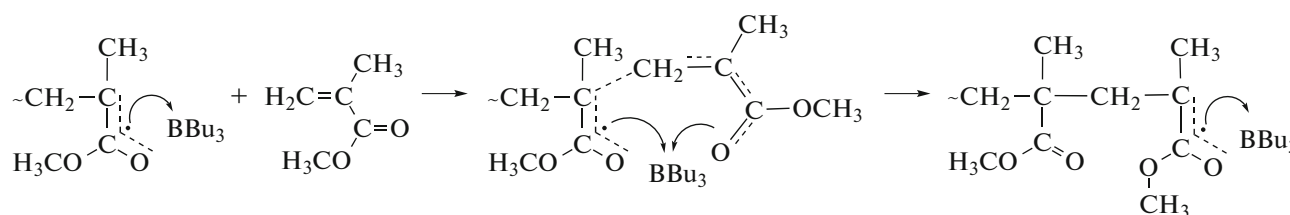
<i>p</i> -quinone	ΣV	$k_z \times 10^{-3}$, L/(mol s)	
		MMA	Styrene
 DQ	1.08	0.73	0.93
 NQ	0.52	1.05	10.5

Table 2. Relative activities for the copolymerization of MMA (M_1) with styrene (M_2) at $T = 80^\circ\text{C}$

<i>p</i> -Quinone	[<i>p</i> -quinone], mol %	[Bu ₃ B], mol %	[AIBN], mol %	r_1	r_2
—	—	—	0.10	0.42 ± 0.01	0.54 ± 0.02
—	—	0.80		0.50 ± 0.03	0.13 ± 0.04
NQ	0.25	0.80		0.62 ± 0.02	0.12 ± 0.04
DQ	0.25	0.80		0.62 ± 0.02	0.51 ± 0.03

Bu₃B molecule is responsible for the observed phenomenon. Similar effect was observed in the copolymerization in the presence of boron alkyls and het-

ero-organic peroxides [10]. The mechanism of coordination-radical polymerization was proposed by Grishin D. F. [10].



According to this scheme, the boron atom, holding the growing macroradical in its coordination sphere, attracts the electron density and, whereby, localizing carbon-carbon π -bond, contributes to the formation of energetically beneficial eight-membered reaction

complex. This facilitates the orientation of the reaction centers. By retaining its coordination sphere the growing macroradical, the atom of the boron orients the monomer molecule and creates conditions for chain propagation, which are most favorable from the energetic and steric standpoints. The above effects lead to the reduction of activity of PMMA propagating radicals, whereby, there is an increase of the fraction of units of this monomer in the copolymer.

For detailed study of quinone action, we have conducted a number of experiments of copolymerization of styrene with MMA in a wide range of monomer feed ratios.

Figure 2 shows that quinones have different effect on the kinetics of copolymerization. When using DQ, the copolymerization rate increases proportionally to the MMA content in the monomer mixture. In the case of NQ, this dependence is not so marked: the trend remains similar, however in the case of a six-fold excess of styrene the copolymerization rate also increases. We believe that this comes from the reaction ability of quinone with respect to the propagating radical. With such ratio of monomers in the mixture, the probability of coordinating the macroradical on Bu₃B reduces, which results in a faster chain transfer on Bu₃B. This assumption agrees with the change of molecular weight (MW) with the conversion.

Number-average molecular weight (M_n) of copolymers, obtained in the presence system Bu₃B – *p*-quinone increases linearly with conversion. Figure 3a shows that with the increase of MMA fraction in the monomer feed MW of copolymers grows, however, the slope ratio of the straight line remains the same. This proves the different efficiency of the catalyst sys-

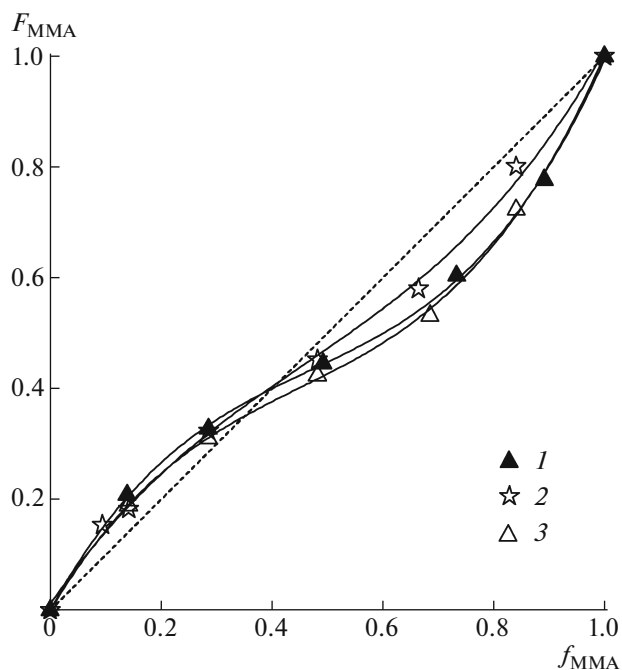


Fig. 1. Copolymer composition for styrene–MMA copolymerization in the presence of 0.10 mol % AIBN, (1) 0.80 mol % Bu₃B and 0.25 mol % (2) DQ or (3) NQ, $T = 80^\circ\text{C}$. F_{MMA} and f_{MMA} —molar fraction of MMA in the copolymer and in the monomer feed.

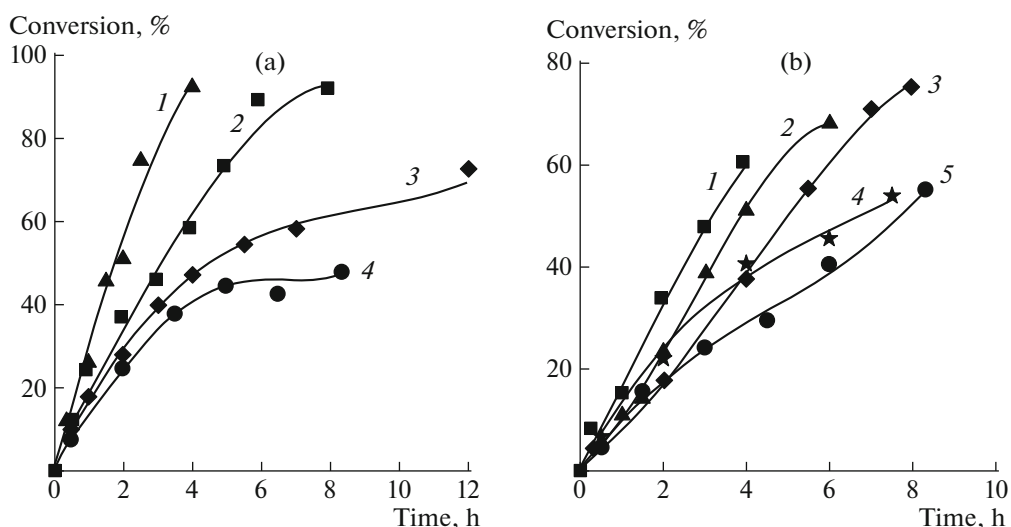


Fig. 2. Conversion as a function of time in copolymerization of styrene with MMA. Here and below (Figs. 3–6): in the presence of 0.25 mol % *p*-quinone, 0.10 mol % AIBN, 0.80 mol % Bu₃B, $T = 80^\circ\text{C}$. (a) DQ, $f_{\text{MMA}} = 0.84$ (1), 0.66 (2), 0.48 (3), 0.28 (4); (b) NQ, $f_{\text{MMA}} = 0.84$ (1), 0.68 (2), 0.48 (3), 0.28 (4), 0.14 (5).

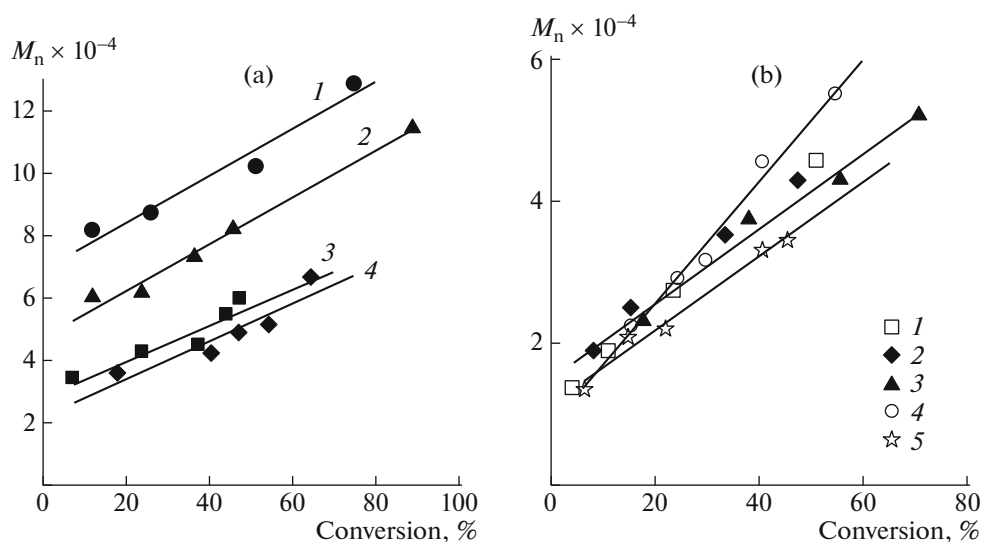


Fig. 3. Dependences of M_n vs. conversion for obtained copolymers. (a) DQ, $f_{\text{MMA}} = 0.84$ (1), 0.66 (2), 0.48 (3), 0.28 (4); (b) NQ, $f_{\text{MMA}} = 0.84$ (1), 0.68 (2), 0.48 (3), 0.28 (4), 0.14 (5).

tem on the base of DQ depending on the composition of the monomer mixture. When DQ is replaced by NQ the situation changes radically: MW of copolymers practically does not depend from the composition of the monomer mixture.

From the molecular weight distribution (MWD), shown in Figs. 4a and 4b, one can see that with the increase of the conversion the MWD becomes broader. Besides, copolymers synthesized in the presence of NQ initially have a broader MWD. The observed results can be explained by the following. DQ possessing poor inhibiting ability can hardly pro-

vide the controlled process. In the case of NQ, part of propagating radical with MMA terminal unit may react with quinone via C=C bond of quinone, thus leading to loose of polymerization control.

Additionally, the isolated copolymers were studied by UV-spectroscopy. This method was suggested previously to determine the route of the interaction of the PMMA radicals with quinones in the presence of Bu₃B [2].

The data given in Table 3 allow to concluding that with the growth of the monomer conversion the absorption at 308 nm, responding to the product of

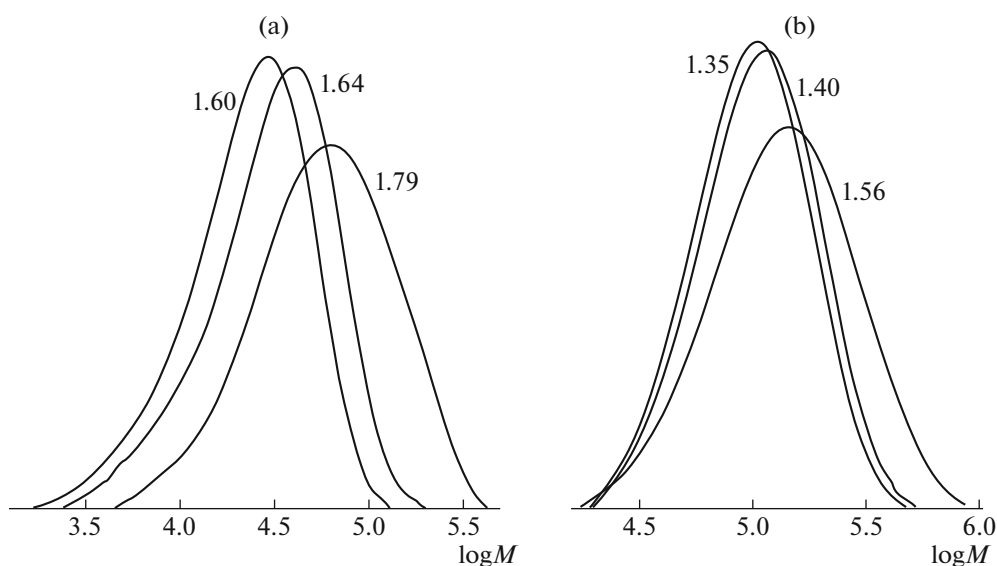


Fig. 4. GPC curves of copolymers obtained from the monomer mixture with $f_{\text{MMA}} = 0.84$. The numbers next to the curves correspond to polydispersity index values. (a) NQ, conversions from the left to the right 7.8, 15.0, and 47.4%; (b) DQ, conversions from the left to the right 7.8, 15.0, and 52.0%.

addition by C=C bond of NQ, increases. A sharp increase of the intensity of the absorption band takes place at the initial conversions. For instance, with the increase of conversion from 7.8 to 15.0% the intensity increases by 1.4 times. Simultaneously the rise of polydispersity index is observed. Due to a good inhibiting ability NQ, it is involved in the polymerization at the earliest conversions, when copolymers are enriched with a more active monomer (MMA). The higher concentration of the radical with terminal MMA unit provides the prevailed realization of direction 2 in reaction (I) and accumulation of dead chains. They are detected as low-molecular-weight “tail” on the MWD of the copolymers isolated at deep conversions (Fig. 4a). This is in accordance with the results of UV-spectroscopy.

Table 3. The characteristics of the copolymers obtained in the presence of 0.10 mol % AIBN, 0.80 mol % Bu_3B , 0.25 mol % NQ

f_{MMA}	F_{MMA}	$M_n \times 10^{-4}$	M_w/M_n	Conversion, %	A
0.84	0.81	1.90	1.60	7.8	0.523
	0.83	2.49	1.64	15.0	0.748
	0.83	3.52	1.70	33.3	0.827
	0.84	4.28	1.80	47.4	0.920
0.14	0.39	1.35	1.81	6.2	0.315
	0.38	2.08	2.26	14.5	0.405
	0.30	3.30	2.57	40.5	0.655

A is the absorption band intensity at 308 nm, f_{MMA} and F_{MMA} are the molar fraction of MMA in the feed and copolymer.

In order to validate the above reactivity ratios for copolymerization conducted to high conversions, the theoretical dependence of copolymer composition versus conversion was calculated. As is seen from the Figs. 5a and 5b, the good correlation is observed between the calculated and the experimental values obtained in the presence of both NQ and DQ. Keeping in mind the acquired data, one may come to the conclusion that the introduction of Bu_3B with *p*-quinone impacts the change of the copolymer composition only within the frames of classical concepts. In other words, the effect of the system components continues during the whole process of copolymerization.

As the introduction of the catalyst system Bu_3B –*p*-quinone affects the relative activities of the monomers, then the distribution of the monomer units in macromolecules is supposed to change. Proceeding from the selected copolymerization constants (Table 2) we have described the sequence distribution within the framework of the model of Mayo–Lewis. Comparing of the theoretical and experimental data of the triad composition of the copolymers gives the strict correspondence of the above values (Figs. 6a, 6b). Thus, no penultimate unit effect was found in the case of copolymerization of styrene and MMA in the presence of Bu_3B –NQ or Bu_3B –DQ. Hence, the components of the catalyst system influence the triad composition of the copolymers only within the frames of conventional beliefs. However, the introduction of Bu_3B and *p*-quinones may have a certain effect on the microstructure of the copolymers. It was found that the introduction of the catalyst system leads to a slight increase of the co-isotacticity parameter (σ_{SM}) (Table 4). Similar result was described for the com-

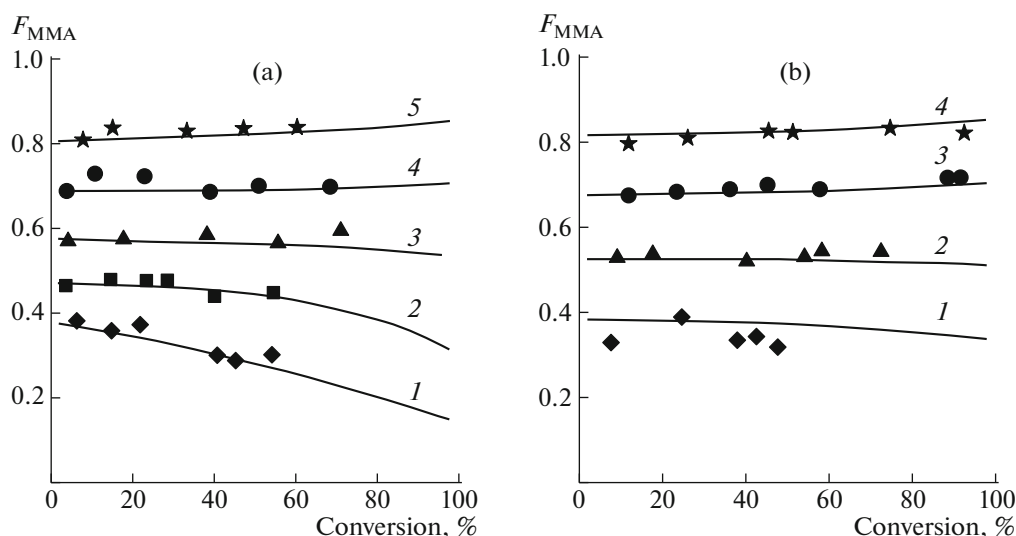


Fig. 5. Conversion dependences of the average compositions of the copolymers. The points are the experimental data, and the curves are the theoretical values. (a) NQ, $r_{\text{MMA}} = 0.62$, $r_{\text{S}} = 0.12$, $f_{\text{MMA}} = (1) 0.14$, (2) 0.28, (3) 0.48, (4) 0.68, (5) 0.84; (b) DQ, $r_{\text{MMA}} = 0.62$, $r_{\text{S}} = 0.51$, $f_{\text{MMA}} = (1) 0.28$, (2) 0.48, (3) 0.66, (4) 0.84.

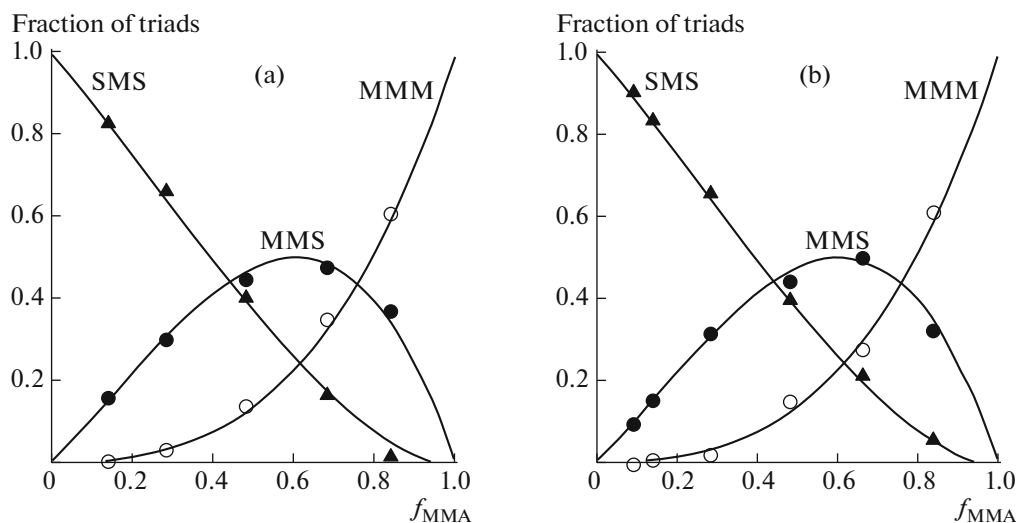


Fig. 6. Normalized statistical monomer sequence distribution triad concentrations vs. MMA mole fraction in the mixture: (a) NQ, (b) DQ. The points are the experimental data, and the curves are the theoretical values.

plex-radical mechanism of copolymerization: the introduction of Lewis acids (ZnCl_2 , EtBCl_2) leads to a significant increase of σ_{SM} [11]. Bu_3B , being a weak Lewis acid, has a slight effect on co-isotacticity.

Table 4. The effect of the system components on the co-isotacticity parameter (σ_{SM})

[AIBN]	[<i>p</i> -quinone], mol %	[Bu_3B], mol %	σ_{SM}
8 mmol/L	—	—	0.44 [12]
	—	0.80	0.53
0.10 mol %	DQ, 0.25	0.80	0.55
	NQ, 0.25	0.80	0.61

CONCLUSIONS

This research revealed that relative activities of the monomers change in the presence of the catalyst system Bu_3B -*p*-quinone. The probable reason for this phenomenon is coordination of the growth radical with a Bu_3B molecule. The work involved a detailed study of copolymerization of styrene with MMA in a wide range of compositions. It was established that in the presence of the poor inhibitor DQ, the rate of the process, as well as MW are directly proportional to the concentration of MMA in the monomer mixture. In the presence of the more active NQ, the MW of the copolymers does not depend on the composition of the initial mixture. The effect of the system Bu_3B -*p*-quinone on the composi-

tion of the copolymers, obtained at deep conversions, as well as on the triad composition of the copolymers is described well by the terminal model of copolymerization.

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