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* Reactions of poly(methyl methacrylate) radicals with some *p*-quinones in the presence of tri-*n*-butylboron in methyl methacrylate polymerization

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The polymerization of methyl methacrylate initiated by dicyclohexyl peroxydicarbonate at 30 °C was studied in the presence of tri-*n*-butylboron and a series of quinones, namely, *p*-benzoquinone, chloranil, and 2,5-di-*tert*-butyl-*p*-benzoquinone, whose concentration changed from 0.25 to 2.00 mol.%. The initial polymerization rate and molecular weight of poly(methyl methacrylate) depend on the structure and concentration of quinone. The growth radicals react with *p*-benzoquinone and chloranil predominantly at the C=C bond, while they react at the C=O bond of 2,5-di-*tert*-butyl-*p*-benzoquinone. The terminal stable oxygen-centered radicals that formed react with alkylborane, terminating reaction chains and generating alkyl radicals into the bulk. The latter are involved in chain initiation.

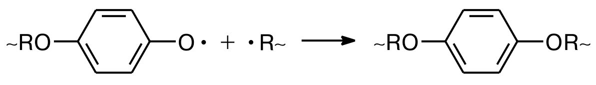
Key words: radical polymerization, methyl methacrylate, dicyclohexyl peroxydicarbonate, *p*-benzoquinone, chloranil, 2,5-di-*tert*-butyl-*p*-benzoquinone.

Quinones and especially *p*-benzoquinone (**1**) are efficient inhibitors of radical processes, including radical polymerization of vinyl monomers.[1,2]

For the development of a novel class of acrylate adhesive compositions,[3–5] which make it possible to adhere thermal plastics with a low surface energy, *e.g.*, polyethylene, polypropylene, and others, and for the solution of several other practical problems,[6] it is necessary to study methyl methacrylate (MMA) polymerization in the simultaneous presence of efficient inhibitors and trialkylboron in concentrations considerably exceeding the concentration of a radical initiator.

The interaction of quinones with radicals is determined by the structures of both the radical and quinone. Methyl radicals formed upon the decomposition of methylphenyltriazene in saturated hydrocarbon add to the C=C bond of quinone.[1] At the same time, π-e-conjugated cyanisopropyl radicals add predominantly at the C=O bond, because the corresponding mono- and diesters of hydroquinone were found in the reaction products of azoisobutyric acid dinitrile (AAD) with **1** in benzene.[1] As for the interaction of poly(methyl methacrylate) radicals at multiple C=C or C=O bonds, no answer to this question was found so far. However, on the one hand, it is known that one molecule of **1** is in the composition of a macromolecule formed by MMA polymerization in the presence of ^{14}C-labeled *p*-benzoquinone **1**. On the other hand, a rather unique fact was established for MMA polymerization initiated by ^{14}C-labeled AAD: each macromolecule contains two initiator moieties.[7] These data indicate unambiguously that the termination of reaction chains in radical polymerization in the presence of **1** occurs at terminal stable oxygen-centered radicals (Scheme 1).

Scheme 1



~R is growth radical.

It is known that **1** in ether reacts with trialkylboranes to form alkyl-substituted hydroquinones almost in ~100% yield.[8–10] The reaction involves free radicals and ceases within 1 h, and oxygen acts as an initiator (Scheme 2).

Alkyl radicals of alkylboron add at the multiple bond of the ring.

When trialkylboron and **1** are introduced in combination into the polymerizing mixture, **1** does not inhibit polymerization but behaves as a mediator of reaction chains.[11] Triisobutylboron (**2**) (0.4 mol.%) in combination with **1** (0.3 mol.%) are known[12] to initiate the poly-

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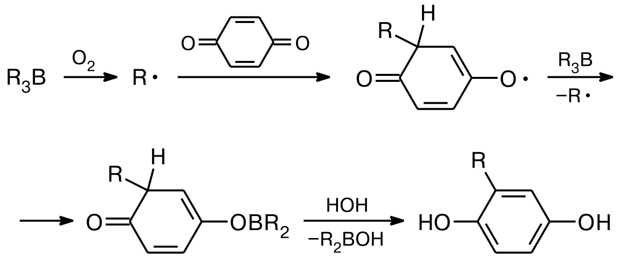
Scheme 2



merization of MMA at 30°C to produce poly(methyl methacrylate) (PMMA) in 28% yield.

The purpose of this work is to study reactions of poly(methyl methacrylate) radicals with *p*-quinones **1**, 2,5-di-*tert*-butylquinone (**3**), and chloranil (**4**) in the presence of tri-*n*-butylboron and to establish the direction of interactions of these radicals at both the C=C and C=O bonds under the conditions of MMA polymerization initiated by dicyclohexyl peroxydicarbonate (**5**) at 30 °C. When choosing quinones, we aimed at estimating the influence of electronic and especially steric factors of the compounds chosen on the direction of interaction of growth radicals resulting in the formation of both benzoquinoid and aromatic structures incorporated into a macromolecule.

Experimental

Organic solvents were purified by commonly accepted procedures.[13] Methyl methacrylate was distilled at 25 °C under reduced pressure (22 Torr). Compound **5** (industrial product) was recrystallized from an aqueous-methanol solution. Tri-*n*-butylboron (**6**) was synthesized by the reaction of $BF_3 \cdot Et_2O$ with BuMgBr[14] and distilled at 90 °C under reduced pressure (8 Torr). Compound **1** was synthesized by the oxidation of hydroquinone with potassium bichromate followed by recrystallization.[15] Compound **3** was synthesized as described previously.[16] Technical grade chloranil **4** was recrystallized from Et_2O. Before polymerization, required amounts of MMA, **5**, and *p*-quinone were placed in an ampule, the mixture was degassed by triple freezing—thawing *in vacuo*, and tri-*n*-butylboron in hexane was added. The ampule was sealed, the contents was thoroughly stirred, and the polymerization kinetics was studied by the dilatometric method.[17]

The resulting PMMA was doubly precipitated from chloroform into hexane and then from chloroform into non-dried Et_2O. PMMA samples were studied by UV spectroscopy on a Specord M40 spectrometer as chloroform solutions and by IR spectroscopy on a UR-20 spectrometer as thin films. Unreacted quinones were determined in solutions after polymers were precipitated. In all PMMA samples obtained with high conversion, the residual monomer was determined by the bromide-bromate method.[18] Molecular weights were determined by viscosimetry[18] in chloroform at 25 °C.

Results and Discussion

As already mentioned,[12] the yield of PMMA under the action of the triisobutylboron—benzoquinone system in the absence of peroxide did not exceed 28%. The polymerization of MMA initiated by **5** (0.17 mol.%) at 30 °C in the simultaneous presence of tri-*n*-butylboron (**6**) (0.80 mol.%) and chosen quinones **1**, **3**, and **4** (0.25 mol.%) occurs without an induction effect, and the initial rate exceeds that in the absence of *p*-quinones (Fig. 1). Therefore, radicals initiating the process are formed not only as a result of peroxide **5** decomposition but also under the action of butyl radicals. The latter are formed by the reactions of *p*-quinones with alkylborane (see Scheme 2)[8—10] and by accepting poly(methyl methacrylate) radicals, for instance, **1** (Scheme 3), followed by the S_R2 substitution of oxygen-centered radicals **7** and **8** on the boron atom of tri-*n*-butylboron at both the multiple C=O bonds and C=C bonds, respectively, to form aromatic (**9**) and benzoquinoid (**10**) terminal boron-containing fragments.

Scheme 3 does not contain the elementary step of interaction of the aryloxy radicals with the growth radicals, due to which incorporated aromatic and quinoid fragments are introduced into the macrochain.

It has previously[19] been found that alkylboranes do not catalyze the decomposition of peroxide **5** and do not accelerate MMA polymerization. According to Scheme 3, the initial polymerization rate depends substantially on the molar ratio [**6**] : [*p*-quinone] (Fig. 2).

The data presented (curves *1* and *2*) differ from each other and depend substantially on both the quinone structure and molar ratios [**6**] : [*p*-quinone]. No similar curve was obtained for chloranil because of its restricted solubility in MMA.

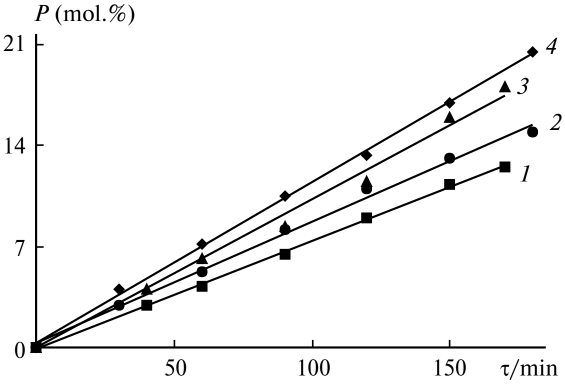
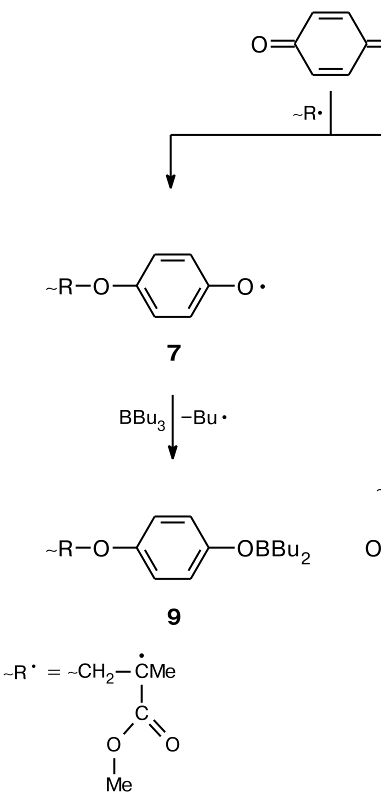


Fig. 1. Initial regions of the kinetic curves of MMA polymerization at 30 °C initiated by **5** (0.17 mol.%) in the presence of **6** (0.80 mol.%) in the absence (*1*) and presence of quinones (0.25 mol.%) **1** (*2*), **4** (*3*), and **3** (*4*). *P* is the amount of the polymer.

Scheme 3



In the presence of **1** (see Fig. 2, curve *1*), the initial polymerization rate increases to a maximum value at the molar ratio of components [**6**] : [**1**] = 1.6 : 1. Beginning from the molar ratio [**6**] : [**1**] = 1 : 1, the polymerization rate decreases sharply to a value close to zero due to the reactions shown in Scheme 3. Both **6** and *p*-quinone **1** are produced at this ratio. When the concentration of **1** increases to the molar ratio [**6**] : [**1**] = 1 : 1, the yield of the polymer and its molecular weight (M) decrease (Table 1). However, the polymerization continues very slowly and ceases at 92—97% conversion within 1 day at room temperature.

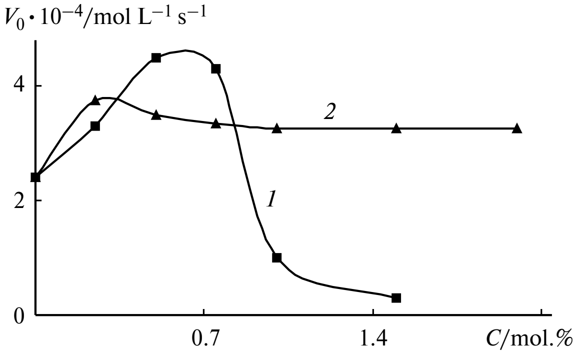
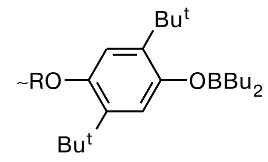


Fig. 2. Influence of the concentration (C) of quinones **1** (*1*) and **3** (*2*) on the initial rate of MMA polymerization (V_0) at 30 °C initiated by **5** (0.17 mol.%) in the presence of **6** (0.80 mol.%).

Table 1. Molecular weights of PMMA obtained by MMA polymerization at 30 °C in the presence of dicyclohexyl peroxydicarbonate, tri-*n*-butylboron, and some quinones

Quinone	C (mol.%)	τ/h	Conversion (%)	$M \cdot 10^{-3}$
1	0.25	4.5	32.8	73.3
	0.50	4.5	28.1	37.9
	0.75	6.0	14.6	17.0
	1.00	6.0	11.5	9.8
3	0.25	4.0	21.3	84.7
	1.00	4.0	21.6	74.6
4	0.25	4.5	7.8	15.3

In the case of compound **3** (Fig. 2, curve *2*), the rate increases insignificantly and reaches a maximum at the molar ratio [**6**] : [**3**] = 2.6 : 1, then somewhat decreases, and remains almost unchanged down to the ratio [**6**] : [**3**] = 1 : 2.5. The rate remains higher than the rate in the absence of **3**, and M remains virtually unchanged (see Table 1). To explain this experimental fact, we assume either MMA copolymerization with **3**, similar to the copolymerization of **1** with polystyrene radicals,[7] or the incorporation of **3** directly into a macromolecule or, which is most probable, as a terminal group.



Sterically hindered structures can act as macroinitiators of radical pseudo-living polymerization.[20]

Thus, the presented plots of the initial rates of MMA polymerization *vs.* concentration of *p*-quinones (see Fig. 2) and the data on molecular weights indicate that the reaction chains terminate predominantly on terminal aryloxy radicals **7** and **8**. The latter accept the growth radicals[7] or undergo S_R2 substitution on the boron atom of tri-*n*-butylboron with high rates (see Scheme 3) to form both aromatic and benzoquinoid structures and the corresponding boron-containing fragments **9** and **10** incorporated into the macrochain (see Scheme 3). We believe that the probability of decay of the poly(methyl methacrylate) radicals due to disproportionation and dimerization is low under the conditions studied.

According to the task stated, we studied the PMMA samples obtained with 8—30% (see Table 1) and 92—97% conversion, whose molecular weights are 200—490 thousands, by UV and IR spectroscopy.

The PMMA samples colored from yellow to light brown were doubly precipitated (see Experimental). In the case of **1** and **3**, no starting quinones were found in supernatants even at low conversions (see Table 1). This indicates that quinones react completely in the initial steps

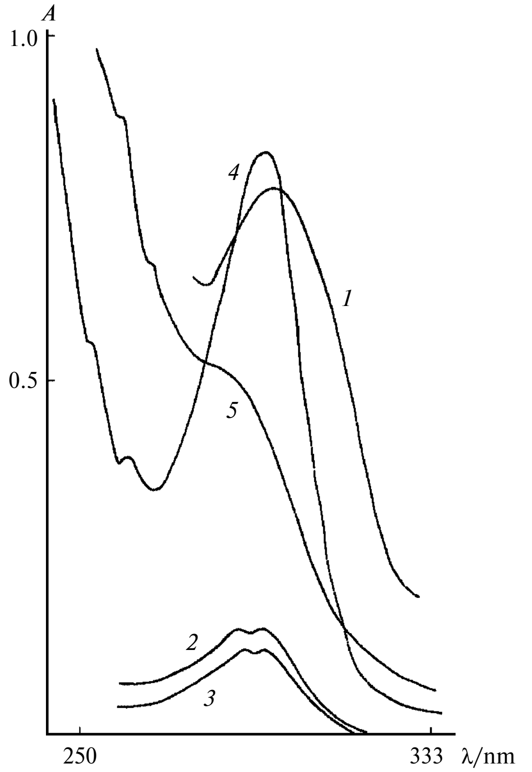


Fig. 3. UV spectra of solutions: **1** in chloroform ($5.0 \cdot 10^{-2}$ mol L^{-1}, *1*); PMMA samples, obtained in the presence of 0.25 mol.% **1**, in chloroform after single (*2*) and double (*3*) precipitation; washing solutions after the first (*4*) and second (*5*) precipitation of these samples.

of polymerization. The color of the polymers is caused by the presence of incorporated benzoquinoid structures formed due to the interaction of the growth radical with quinones at the multiple C=C bond (**8**, Scheme 3) and subsequent S_R2 substitution (**10**, see Scheme 3).

The UV spectra of solutions of the PMMA samples, obtained in the presence of **1** (0.25 mol.%), in chloroform contain an absorption band with maxima at 284 and 287 nm (Fig. 3, curves *2* and *3*). This band differs from the band of the starting compound **1** (300 nm, see Fig. 3, curve *1*).[21]

The hypsochromic shift of the absorption band maximum and its narrowing indicate that this quinone is inserted into the C=C bond (product **10**) according to Scheme 3. This is related to different changes in intensities of vibrational modes of an electron transition of the *n*-π-type in the free and incorporated chromophores. After precipitation, the UV spectrum of solvents contains, along with the absorption band of the incorporated quinoid structure, narrow absorption bands at 240—260 nm (see Fig. 3, curves *4* and *5*) characteristic of aromatic moieties. The latter are formed due to the hydrolysis of the oxygen—boron bond at the precipitation stage. The absorption band of the starting compound **1** is absent. The study of the PMMA samples obtained in the presence of 0.50, 0.75, and 1.00 mol.% **1** revealed no qualitative changes in the UV spectra, and only a change in the intensity of the absorption band of the incorporated quinoid structure was observed (see Table 2). The IR spectra of polymeric films of the doubly precipitated PMMA samples containing **1** exhibited a broad absorption band with a maximum at 3400 cm^{-1} characteristic of associated hydroxyl groups. The presence of aromatic moieties and hydroxyl groups indicates the hydrolysis of terminal structure **10** *via* a mechanism similar to Scheme 2.

Sterically hindered quinone **3** having two bulky *tert*-butyl groups differs substantially from **1** in reactivity toward growth radicals. The UV spectrum of a solution of PMMA obtained in the presence of **3** (0.25 mol.%) contains no absorption band of the quinoid structure but exhibits absorption bands at 240—260 nm (Fig. 4, curves *2* and *3*) characteristic of aromatic moieties. This indicates that **3** reacts with the growth radical at the C=O bond (see Scheme 3). The solvents were analyzed after precipitation and did not show the starting quinone, and a weakly resolved absorption band at 295 nm was observed along with those of aromatic moieties (see Fig. 4, curves *4* and *5*). This band can be attributed to quinoid structure **10**, which differs from the initial one (315 nm, see Fig. 4, curve *1*). The appearance of this structure in the low-molecular fraction of PMMA can be related to the reaction of **3** with **6** affording butyl radicals (see Scheme 2). The presence of an absorption band related to the hydroxyl groups in the IR spectra of the polymeric films indicates the hydrolysis of the oxygen—boron bond.

The UV spectra of solutions of PMMA obtained in the presence of **4** (0.25 mol.%) (Fig. 5, curves *2* and *3*) exhibit

Table 2. Absorbances (*A*) of the absorption bands with maxima at 284 and 287 nm for the PMMA samples obtained in the presence of *p*-benzoquinone (**1**)

Concentration of **1** in initial mixture (mol.%)	Conversion (%)	Absorbance after precipitation	
		single	double
0.25	32.8	0.29	0.23
0.50	28.1	0.61	0.41
0.75	14.6	1.16	0.76
1.00	11.5	1.42	0.81

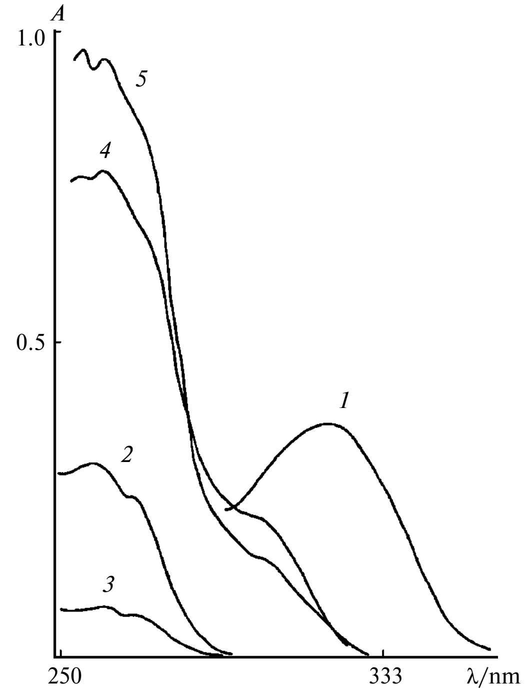


Fig. 4. UV spectra of solutions: **3** in chloroform ($5.0 \cdot 10^{-2}$ mol L^{-1}, *1*); PMMA samples, obtained in the presence of 0.25 mol.% **3**, in chloroform after single (*2*) and double (*3*) precipitation; washing solutions after the first (*4*) and second (*5*) precipitation of these samples.

an absorption maximum at 304 nm along with that characteristic of the starting quinone (see Fig. 5, curve *1*). The appearance of this maximum is related to the incorporation of **4** into the polymeric chain at the C=C bond similarly to **1**; however, the presence of several chlorine atoms in the conjugation chain results in the appearance of a long-wave absorption maximum. This maximum is pronounced in the spectrum of the sample after the second precipitation (see Fig. 5, curve *3*) and is present as a shoulder in the spectrum of the samples after the first precipitation (see Fig. 5, curve *2*), because single precipitation removes incompletely the starting chloranil **4** from the sample. The same is indicated by the UV spectra of the washing solutions (see Fig. 5, curves *4* and *5*). The absorption band of the washing solution after the second precipitation (see Fig. 5, curve *5*) has a maximum at 282 nm and shoulders at 294 and 304 nm, indicating that the solution contains hydrolysis products formed *via* Scheme 5.

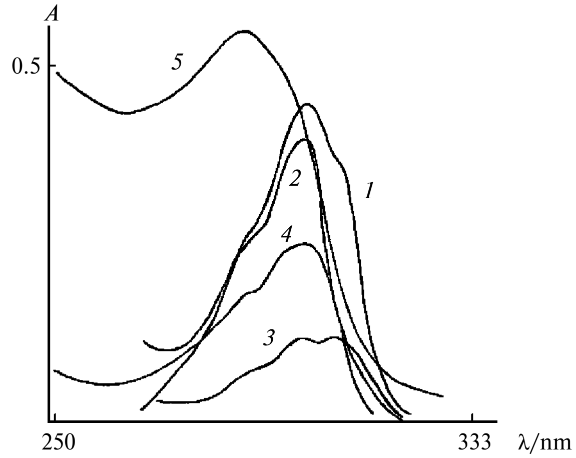
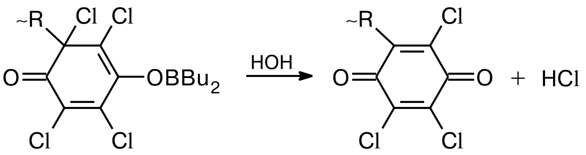


Fig. 5. UV spectra of solutions: **4** in chloroform (*1*); PMMA samples, obtained in the presence of 0.25 mol.% **4**, in chloroform after single (*2*) and double (*3*) precipitation; washing samples after the first (*4*) and second (*5*) precipitation of these samples.

Scheme 5



Evolved HCl was determined as a chloride anion in the solvents after precipitation using the known Volhard method.

The UV spectra of solutions of PMMA obtained with 92—97% conversion in the presence of the quinones chosen correspond to the spectra of solutions of PMMA with 8—30% conversion.

Thus, for MMA polymerization initiated by dicyclohexyl peroxydicarbonate, even in the presence of rather high concentrations of quinone, the introduction of alkylboranes eliminates the inhibition effect of the former. It was shown by the UV and IR methods that the poly(methyl methacrylate) radicals react with benzoquinone and chloranil predominantly at the C=C bond, while the reaction with 2,5-di-*tert*-butyl-*p*-benzoquinone occurs at the C=O bond. The formed terminal oxygen-centered aryloxy radicals react with tri-*n*-butylboron *via* the S_R2 mechanism to generate butyl radicals involved in the step of chain initiation.

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