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Uncontrolled pseudoliving free-radical polymerization of methyl methacrylate in the presence of butyl-*p*-benzoquinones

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Polymerization of methyl methacrylate initiated by dicyclohexyl peroxydicarbonate in the presence of tri-*n*-butylboron and butyl-*p*-benzoquinone or 2,5-di-*tert*-butyl-*p*-benzoquinone occurred with no induction period. The yields and molecular masses of the polymers linearly increased with an increase in the conversion degree, which suggests the free-radical mechanism of "living" chain polymerization. The poly(methyl methacrylate) macrochains of the prepolymers contained sterically hindered aromatic structures with labile C—O bonds. The latter underwent reversible homolytic dissociation to give a growth-inducing radical and sterically hindered aryloxyls. Pseudoliving free-radical polymerization in the presence of the prepolymer (macroinitiator) was studied at 45, 60, and 80 °C.

Key words: polymerization, methyl methacrylate, *p*-benzoquinone, 2-butyl-*p*-benzoquinone, 2,5-di-*tert*-butyl-*p*-benzoquinone, prepolymer, pseudoliving polymerization.

When studying the polymerization of methyl methacrylate (MMA) at 30 °C initiated by dicyclohexyl peroxydicarbonate (**1**) in the presence of tri-*n*-butylboron (**2**) and a number of quinones, we have obtained for the first time reliable data on the elementary steps of reactions of poly(methyl methacrylate) radicals with some quinones.[1] We have found that these growth-inducing radicals react with *p*-benzoquinone (**3**) mainly at the C=C bond to give quinonoid structures and with 2,5-di-*tert*-butyl-*p*-benzoquinone (**4**) at the C=O bonds resulting in the insertion of aromatic structures into the macrochain.

The polymerization of MMA has no induction period and its initial rate is higher than the rate of the polymerization initiated by organic peroxide **1**. The polymerization rate depends on the molar ratio of *p*-quinones to trialkylborane. For quinone **3**, the initial polymerization rate increases to a maximum value at a molar ratio of 1 : 1 and then drops virtually to zero. In the presence of quinone **4**, the rate increases only slightly and remains virtually unchanged at its high concentrations. To explain the observed fact, we have assumed that the sterically hindered aromatic fragments incorporated in the macrochain can act as macroinitiators inducing free-radical pseudoliving polymerization.[1]

With the foregoing in mind, here we studied the polymerization of MMA initiated by peroxide **1** in the presence of tributylboron (**2**), quinones **3**, **4**, and butyl-*p*-benzoquinone (**5**) to collect additional data and substantiate the peculiar features of the polymerization of MMA in the presence of *p*-quinone **4** and monosubstituted *p*-quinone **5**. We have shown[2] that the latter adds to poly(methyl methacrylate) radicals at both the C=O and C=C bond.

Experimental

Organic solvents were purified according to known procedures.[3] Methyl methacrylate was distilled under reduced pressure (22 Torr, 25 °C). Commercial peroxide **1** was recrystallized from aqueous methanol. Tri-*n*-butylboron (**2**) was prepared from $BF_3 \cdot Et_2O$ and *n*-butylmagnesium bromide in ether[4] and distilled under reduced pressure (8 Torr, 90 °C). Quinone **3** was synthesized by oxidation of hydroquinone with $K_2Cr_2O_7$ and recrystallized.[5] Quinones **4** and **5** were prepared by oxidation of 2,5-di-*tert*-butyl- and butylhydroquinone, respectively, with HNO_3 in acetic acid.[6]

A mixture of MMA, peroxide **1** (0.17 mol.%), and quinone **3**, **4**, or **5** (0.25 mol.%) was placed in a tube. After the tube was degassed by three sequential freezing—thawing cycles *in vacuo*, tri-*n*-butylboron (**2**) (0.80 mol.%) was added through a dosing device. The tube was then sealed and kept at 30 °C for a speci-

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† Deceased.

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fied period of time. The conversion degree (%) was determined by gravimetry.[7]

For post-polymerization, we prepared a prepolymer (macroinitiator). A two-neck flask containing MMA was charged with Bu_3B (0.80 mol.%) under argon. The resulting solution was transferred in portions (5 mL each) to tubes with *p*-quinone (0.25 mol.%). The tubes were kept in a thermostat without protection from air at 30 °C for 3 h. The prepolymer was reprecipitated with hexane from $CHCl_3$ and dried in a vacuum desiccator. The yields of the prepolymer were 13.3, 9.5, and 15.5% in the presence of quinones **3**—**5**, respectively.

The prepolymer (5 wt.%) was dissolved in MMA in a tube and the tube was degassed as described above and sealed off. Post-polymerization of MMA was carried out for 3 h at 45, 60, and 80 °C. The yield of the polymer was determined by gravimetry.[7]

The molecular masses [M] at 25 °C were calculated from the intrinsic viscosity [η] in chloroform[8]

$$[\eta] = 4.8 \cdot 10^{-5}[M]^{0.8}.$$

The molecular mass distribution (MMD) was determined by gel permeation chromatography (GPC) on a Waters setup (USA) consisting of five styrogel columns (pore diameters 10^5, $3 \cdot 10^4$, 10^4, 10^3, and 250 Å) and an R-403 differential refractometer (Waters) as a detector. Tetrahydrofuran was used as an eluent.

Solutions of poly(methyl methacrylate) (PMMA) samples in $CHCl_3$ were examined by UV spectroscopy on a Specord M40 instrument.

Results and Discussion

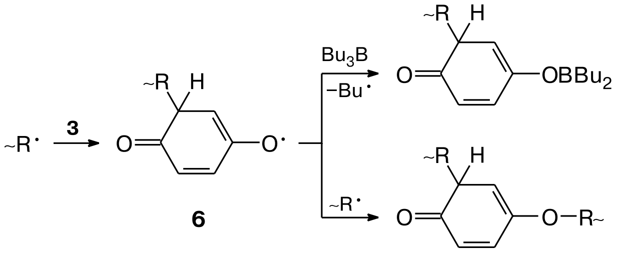
Earlier,[9—11] quinone **3** as an efficient inhibitor has been reported to react under polymerization conditions with the growth-inducing radical, depending on its reactivity. Using ^{14}C labeling, Bevington *et al.*[9,10] have shown that quinone **3** becomes a structural unit of the PMMA macromolecule and chain termination occurs on end aryloxyl radicals. In styrene polymerization,[11] isotope labeling has revealed 17 units of quinone **3** in the resulting macromolecule.

The polymerization of MMA initiated by peroxide **1** in the presence of Bu_3B (**2**) and *p*-benzoquinone (**3**) can follow two parallel free-radical pathways involving aryloxyls. The growing chain with the aryloxyl end group substitutes the butyl radical in Bu_3B according to the S_R2-reaction to produce a boron-containing end group with chain transfer or two growth-inducing radicals recombine (Scheme 1).

The rate constants of the S_R2-reaction at the B atom[12] and of the recombination of aryloxyls with the macroradical are of the order of 10^6—10^7 L mol^{-1} s^{-1}, which is much higher than the rate constant of the MMA macrochain growth ($2.50 \cdot 10^2$ L mol^{-1} s^{-1}).[13]

The initial rates of the MMA polymerization at 30 °C initiated by peroxide **1** in the presence of Bu_3B and quinones **3**—**5** differ insignificantly[1] and the process has no noticeable induction period (Fig. 1). The yields of the polymers in the presence of Bu_3B (**2**) and quinones **4** and **5** linearly increase with an increase in the reaction time. However, in the presence of quinone **3**, the yield of the polymer at the 25% conversion decreases and becomes virtually constant, showing a jump after 350 min. The gel effect may be attributed to the depletion of compounds **3** and **2**.

Scheme 1



~R• is the growth-inducing radical (~$CH_2C^{\bullet}(Me)CO_2Me$)

Variations in the molecular mass with the conversion degree are shown in Fig. 2. For systems containing butylboron **2** and quinone **4** or **5**, the molecular mass linearly increases with the conversion degree. Lines *2* and *3* (see Fig. 2) are virtually collinear. The results obtained suggest that the polymerization follows the living chain mechanism.[14]

At the same time, the yield (see Fig. 1, curve *1*) and molecular mass of the polymer (see Fig. 2, curve *1*) for the system with quinone **3** largely differ from analogous parameters for the two other systems studied. Thus, *p*-quinones **5** and especially **4** substantially change the mechanism of the low-temperature (30 °C) polymerization.

We synthesized some prepolymers and studied their post-homopolymerization to collect additional evidence for the living chain polymerization mechanism. The molecular mass distributions of the prepolymer and the

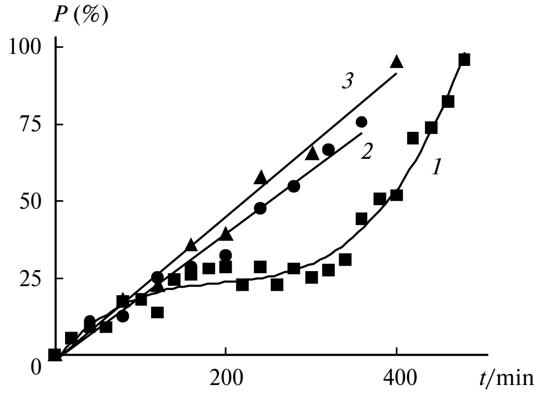


Fig. 1. Kinetic curves of the polymerization of MMA initiated by peroxide **1** (0.17 mol.%) at 30 °C in the presence of Bu_3B (**2**) (0.8 mol.%) and quinones **3** (*1*), **4** (*2*), and **5** (*3*) (0.25 mol.%); *P* is the conversion degree.

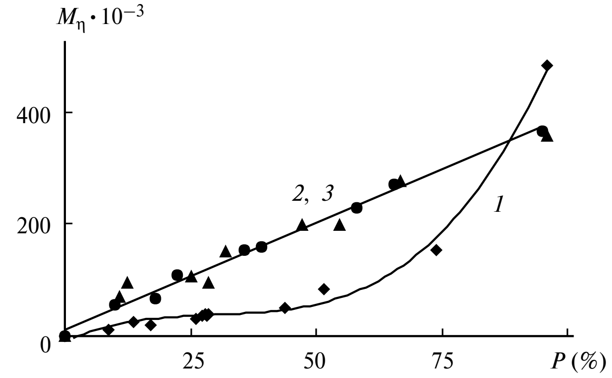
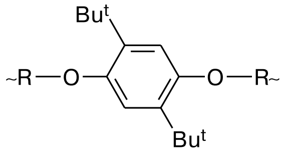


Fig. 2. Plots of the viscosity-average molecular mass M_η of the polymer *vs.* the conversion degree *P* for quinones **3** (*1*), **4** (*2*), and **5** (*3*).

PMMA postpolymers were examined by gel permeation chromatography.

In the polymerization in the presence of quinone **4**, two types of structures may be inserted into the PMMA macromolecule.



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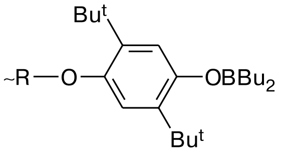

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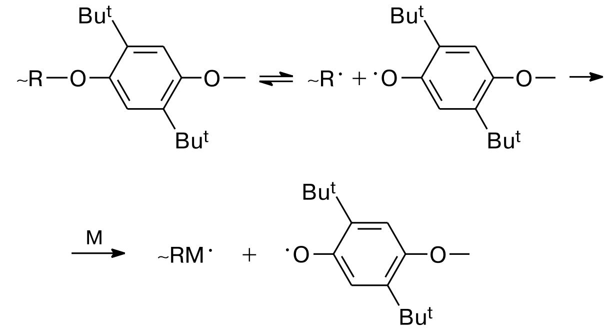
The prepolymer with sterically hindered aromatic structures contains a labile C—O bond, which may undergo homolytic dissociation of the reversible inhibition type under the polymerization conditions. As the result, the macrochain grows as in living polymerization.

This dissociation is thermodynamically allowed since it yields two π—e-conjugated radicals: poly(methyl methacrylate) and sterically hindered aryloxyls.[15] If the latter has the boron-containing end fragment, it can be additionally stabilized through the vacant p-orbital of the B atom.

GPC data for the starting prepolymers obtained in the presence of tri-*n*-butylboron (**2**) and quinone **3** or **4** are shown in Fig. 3. For instance, the MMD of a prepolymer synthesized in the presence of quinone **3** at a conversion up to 20% suggests conventional free-radical polymerization of MMA (see Fig. 3, curve *1*). Prepolymers synthesized under analogous conditions in the presence of quinone **4** at 20 and 57% conversions (see Fig. 3, curves *2*, *3*, respectively) show bimodal MMD. This experimental fact can be attributed to two ways in which the PMMA macrochain grows: conventional peroxide-initiated and pseudoliving free-radical polymerization (Scheme 2).

Scheme 2



M — $CH_2=C(Me)C(O)OMe$

It can be seen from Fig. 3 (curve *3*) that at 57% conversion of MMA, the area of the low-molecular-mass mode (low-molecular-mass fraction of PMMA) is reduced and the corresponding high-molecular-mass mode is shifted to the higher molecular masses.

To confirm the post-polymerization of MMA, we synthesized prepolymers (macroinitiators) in the absence of organic peroxide **1** but at the same concentrations of Bu_3B (**2**) (0.80 mol.%) and quinone **3** or **4** (0.25 mol.%) and the reaction conditions (30 °C, 3 h) without deoxygenation.

The prepolymer obtained in the presence of quinone **3** virtually did not change either the molecular mass or the conversion depth after 3 h at 45 °C. Under analogous conditions, the prepolymer obtained in the presence of quinone **4** acted as a macroinitiator, increasing the yield of the postpolymer 1.5-fold and its molecular mass 1.7-fold. The GPC data for the postpolymer obtained in 3 h at 45 °C are shown in Fig. 4. It can be seen that the

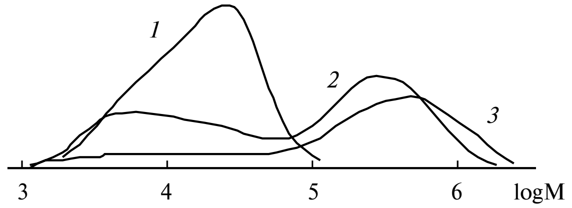


Fig. 3. GPC curves of the PMMA samples obtained in the presence of peroxide **1** (0.17 mol.%), tributylboron **2** (0.8 mol.%), and quinones **3** (*1*) and **4** (*2*, *3*) (0.25 mol.%). The conversion degree is ~20 (*1*, *2*) and ~57% (*3*).

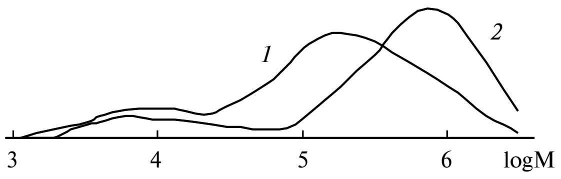


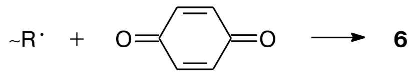
Fig. 4. GPC curves of the PMMA samples obtained in the presence of tributylboron **2** (0.8 mol.%) and quinone **4** (0.25 mol.%) under the following polymerization conditions: 30 °C, 3 h (*1*) and 45 °C, 3 h (post-polymerization) (*2*).

high-molecular-mass mode is appreciably shifted to the higher molecular masses and tends to be narrower.

With an increase in the post-polymerization temperature (60 °C), the yield and molecular mass of the polymer obtained from the above prepolymer increased 2.4- and 2.9-fold, respectively, in the same period of time. At 80 °C, these parameters increased 2.6- and 6-fold, respectively. The consumption of MMA in its thermal polymerization at 80 °C (control experiment) was no more than 1.9%.

To ascertain that homolytic dissociation of the C—O bond takes place in the prepolymer under examination with sterically hindered fragments, we carried out post-polymerization of MMA (80 °C, 4 h) in the presence of quinone **3** (0.25 mol.%). The yield of the polymer was only 1.1-fold higher and its molecular mass increased 2.4-fold. We assume that in the monomer cage, the resulting poly(methyl methacrylate) radical (~R$^\bullet$) mainly reacts with quinone **3** rather than with MMA since the rate constant of the reaction of the growth-inducing radical with quinone **3** ($2.58 \cdot 10^3$ L mol^{-1} s^{-1}) is an order of magnitude higher[13] than the rate constant of the macrochain growth (Scheme 3).

Scheme 3



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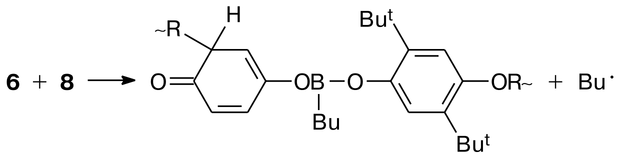
The resulting oxygen-centered radical **6** is probably stabilized in an S_R2-substitution reaction at the boron atom of, *e.g.*, a boron-containing end fragment (Scheme 4).

Scheme 4



It should also be noted that the UV spectrum of the postpolymer isolated from the reaction mixture shows an absorption peak at 287 nm assigned to the incorporated quinonoid structure.[1]

To sum up, the polymerization of MMA initiated by dicyclohexyl peroxydicarbonate in the presence of tri-*n*-butylboron and *p*-quinones (benzoquinone, butyl-*p*-benzoquinone, or 2,5-di-*tert*-butyl-*p*-benzoquinone) allows incorporation of the corresponding aryloxy structures into the PMMA macrochain. The prepolymers containing sterically hindered aromatic fragments incorporated in the macrochain act as peculiar kinds of initiators of the uncontrolled pseudoliving free-radical polymerization of MMA.

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