

SYNTHESIS OF COPOLYMERS OF METHYL METHACRYLATE AND BUTYL VINYL ETHER IN THE PRESENCE OF THE SYSTEM TRIBUTYLBORON – 2,5-DI-*TERT*-BUTYL-*P*-BENZOQUINONE

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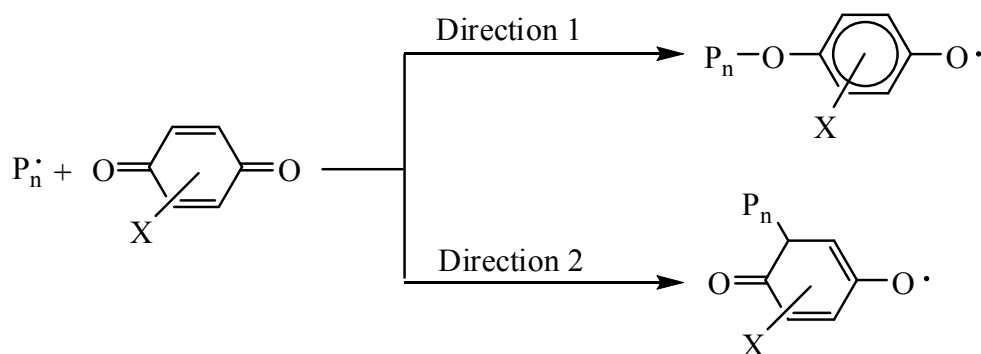
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The synthesis of copolymers of methyl methacrylate and butyl vinyl ether using the system tributylboron – 2,5-di-*tert*-butyl-*p*-benzoquinone has been carried out. This system does not influence the reactivity ratios of these monomers. Predominantly, the terminal unit of butyl vinyl ether reacts with *p*-quinone. Controlled radical polymerization is realized along with the conventional process.

Keywords: methyl methacrylate, butyl vinyl ether, azobisisobutyronitrile, tri-*n*-butylboron, 2,5-di-*tert*-butyl-*p*-benzoquinone, UV spectroscopy, controlled radical polymerization.

Introduction

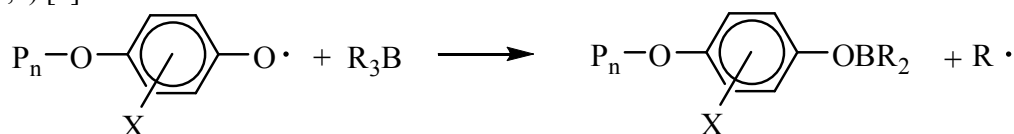
p-Quinones are inhibitors of radical polymerization. The inhibitory action is based upon acceptance of propagation radicals by the *p*-quinone molecule at C=O or C=C bonds, which leads to formation of stable radicals (Scheme 1) [1]:



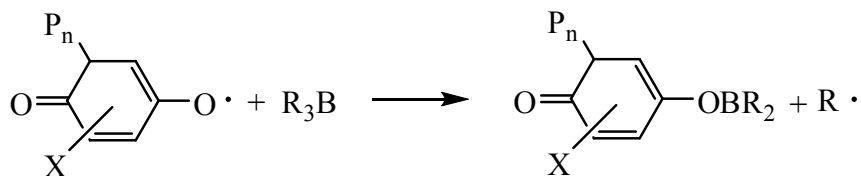
Scheme 1

The direction of reaction (1) is determined by the structure of a monomer and *p*-quinone [2–5]. Thus, polystyrene propagation radicals are added to the *p*-quinone molecule only at the C=O bond (Scheme 1, direction 1) [2], independently of its structure. Both directions (Scheme 1) are realized for methyl methacrylate (MMA), the ratio of the products is determined by electronic and steric characteristics of *p*-quinone substituents X [3, 6].

Introduction to the polymerization of styrene, MMA, vinyl acetate trialkyl boron in combination with *p*-quinone removes the inhibitory action of the latter, as oxygen-centered radicals (Scheme 1) enter S_R2 -substitution reaction at the boron atom of the trialkyl boron molecule with high rate constant (Scheme 2,3) [7]:

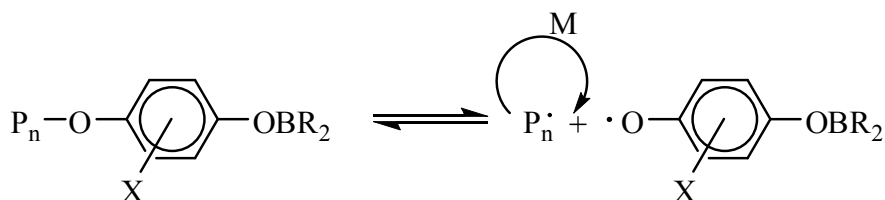


Scheme 2



Scheme 3

The macromolecules that are formed in compliance with Scheme 2, are macroinitiators, they are instrumental in re-initiation of the polymerization according to the reversible inhibition mechanism (Scheme 4) [4, 8]:



Scheme 4

Statistical and block copolymerization of (meth)acrylates and styrene [9, 10] in the presence of the system tributylboron – *p*-quinone is performed by the mechanism of "living" chains subject to the condition that the interaction of the propagation radical with *p*-quinone is carried out at the C=O bond (Scheme 1, direction 1).

The aim of the present study is the investigation of MMA copolymerization with butyl vinyl ether (BVE) in the presence of the system tributylboron (TBB) – 2,5-di-*tert*-butyl-*p*-benzoquinone (2,5-DTBBQ). The use of BVE as comonomer is caused by the fact that it does not form the homopolymer during radical polymerization, and its reactivity in copolymerization $r_{\text{BVE}} = 0$ [11]. Besides, the polymer products obtained on its basis are bio-compatible [12], which opens up strong possibilities for creation of materials with biomedical purpose.

Experimental

Organic solvents were purified by commonly accepted procedures [13]. MMA was washed free from the inhibitor by 10 % aqueous solution of alkali, then by distilled water until neutral pH of washings was reached; it was dried over sodium sulfate and distilled at reduced pressure; the fraction with boiling point 25 °C / 2.93 kPa was collected. BVE of the analytical grade was used without prerefining. Azobisisobutyronitrile (AIBN) was recrystallized from methyl *tert*-butyl ether and dried to constant weight. TBB was obtained by interaction of boron trifluoride etherate with *n*-butyl magnesium bromide in ether [14] and distilled at reduced pressure (90 °C/1.07 kPa). 2,5-DTBBQ was synthesized by oxidizing of the corresponding hydroquinone, then it was purified by recrystallization from light petroleum. Purity of the used substances was controlled by NMR spectroscopy.

For (co)polymerization of MMA and BVE the solution of AIBN and 2,5-DTBBQ in the monomer mixture was placed into an ampoule, degassed by triple freezing until residual pressure 0.13 Pa, then 0.8 % mol. of TBB was added by means of a dosing unit. The ampoule was unsealed and placed into a thermostat at temperature 60 °C. When the desired conversion was achieved, the ampoules were removed from the thermostat and cooled in liquid nitrogen. The obtained polymers were purified by double reprecipitation by isopropyl alcohol from the chloroform solution and dried under vacuum at room temperature until constant weight was reached. Monomer conversion was determined gravimetrically. To ensure post-polymerization the macroinitiator solution (5 % m/m) in the monomer was poured into the ampoule, degassed and kept at temperature 60 °C for the preset time interval.

Analysis of molecular weight characteristics of the polymers was performed by gel permeation chromatography in THF at 40 °C on the liquid chromatograph "Shimadzu" with the columns filled by polystyrene gel with pore size $1 \cdot 10^6$ and $1 \cdot 10^5$ Å. The differential refractometer was used for detection. The chromatograms were treated by the software routine "LCsolution". Narrow-disperse polymethyl methacrylate (PMMA) standards were used for calibration.

The UV spectra of the solutions of (co)polymers MMA and BVE in chloroform were registered on the spectrometer "Shimadzu UV-1800" at wavelengths from 190 to 900 nm.

The ^1H NMR spectra were registered on the spectrometer "Agilent DD2 400" in CDCl_3 at 400.13 MHz. Chemical shifts are presented in the delta scale (δ , ppm) in relation to Me_4Si . The content of poly(butyl vinyl ether) (PBVE) in its copolymer with PMMA was calculated according to the formula:

$$F_{\text{PVBE}} = \frac{I_{\text{CH}_2\text{-CH-O}}}{I_{\text{CH}_2\text{-CH-O}} + I_{\text{MeO}}},$$

where $I_{\text{CH}_2\text{-CH-O}}$ and I_{MeO} are peak areas of the $-\text{CH}_2\text{-CH-O}-$ group in PBVE and the methoxy group in PMMA, respectively.

Results and Discussion

Copolymerization of MMA and BVE has been studied at 60 °C, with AIBN as initiator, in the presence of TBB and 2,5-DTBBQ. On the strength of the experimental data the copolymer composition curve has been plotted (Fig. 1, curve 2), which is nearing the MMA and BVE copolymer composition curve, presented in paper [11] (Fig. 1, curve 1), therefore the introduction of TBB and 2,5-DTBBQ into copolymerization does not influence the reactivity constants of the given monomer pair.

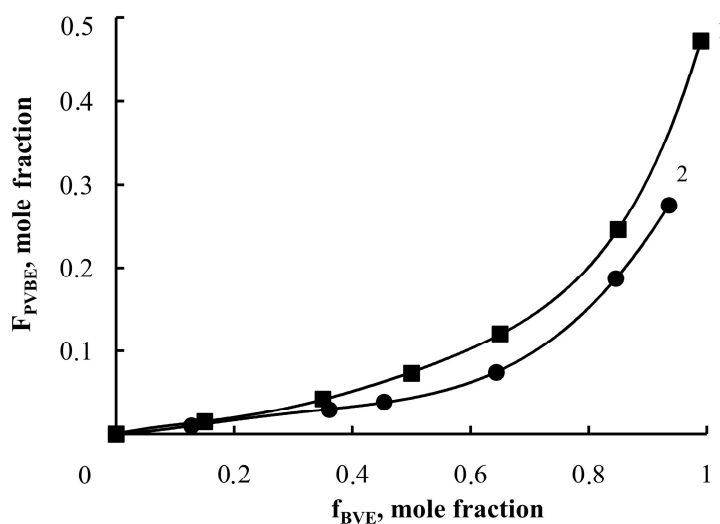


Fig. 1. The copolymer composition curve of PBVE – PMMA, synthesized in the presence of 0.6 % mol. AIBN [11] (1) and 0.1 % mol. AIBN, 0.8 % mol. TBB and 0.25 % mol. 2,5-DTBBQ (2)

Copolymerization of MMA and BVE in the presence of the system TBB – 2,5-DTBBQ is accompanied by decolorization of the polymerized mixture as early as the initial stages of the polymerization. The color change is related to the interaction of the propagation radical at the $\text{C}=\text{O}$ bond (Scheme 1, direction 1) and the following $\text{S}_{\text{R}2}$ substitution (Scheme 2), owing to it the quinoid structure is transformed into the aromatic one. The UV spectra of MMA and BVE copolymers are represented on Fig. 2. In the spectra of the copolymers there is the absorption band with the maximum at 292 nm (Fig. 2, curves 3 and 4), which can be related to the adjoint carbonyl group, distinct from the carbonyl group of 2,5-DTBBQ (Fig. 2, curve 1). The similar absorption band is present in the spectrum of PMMA homopolymer, synthesized under the same conditions (Fig. 2, curve 5). The absorption band shift suggests the rearrangement of the carbonyl group surroundings, which is possible if *p*-quinone is incorporated into the chain according to Scheme 1 (direction 2). The absence of the absorption band with the maximum at 292 nm in the BVE homopolymer spectrum (Fig. 2, curve 2) shows that the quinone incorporation into the polymer chains is carried out according to Scheme 1 (direction 1). When the BVE content in the polymerized mix increases, the absorption band (Fig. 2, curve 4), that is related to the incorporated quinoid structure, is transformed into a shoulder (Fig. 2, curve 3). Such a change in the spectrum is explained by the fact that basically the poly(butyl vinyl) macroradical reacts with *p*-quinone according to Scheme 1 (direction 1).

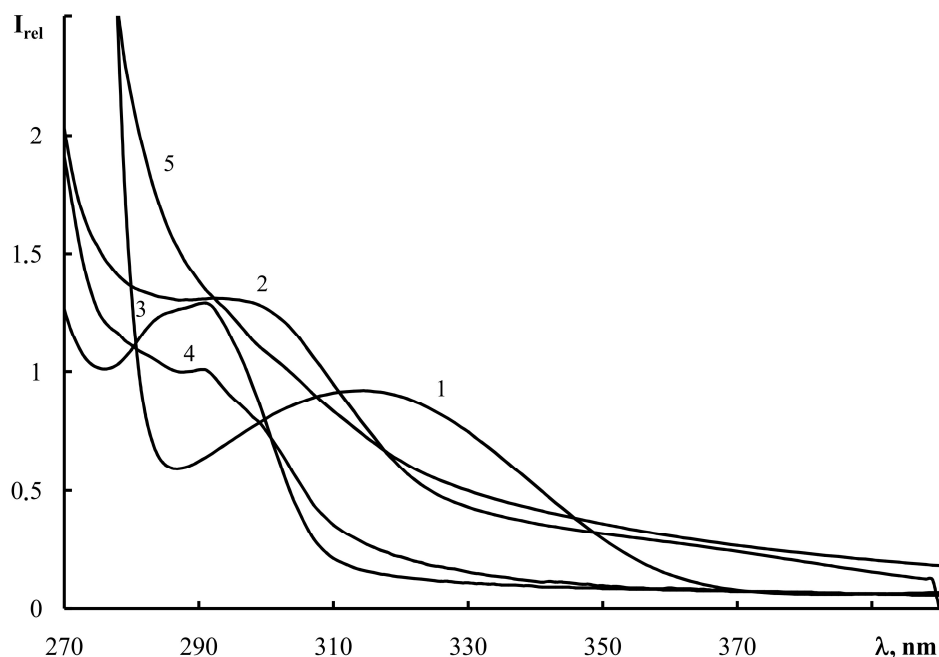


Fig. 2. UV spectra of chloroform solutions of 2,5-DTBBQ (1) and (co)polymers synthesized in the presence of 0.1% mol. AIBN, 0.8 % mol. TBB and 0.25 % mol. 2,5-DTBBQ: BVE homopolymer (2); the copolymer obtained from the monomer mixture 85 % mol. BVE and 15 % mol. MMA (3); the copolymer obtained from the monomer mixture 40 % mol. BVE and 60 % mol. MMA (4); MMA homopolymer (5)

As can be seen from Fig. 3, the BVE–MMA copolymerization rate (Fig. 3, curve 2) is significantly lower than the MMA homopolymerization (Fig. 3, curve 1) at the same conditions. The completion of copolymerization at 65 % conversion is due to the fact that BVE does not form the homopolymer in the radical way, and at this conversion practically entire MMA comes to an end. According to NMR spectroscopy data, the PBVE content in the copolymer equals 6.4 %. Appearance of gel effect is related to depletion of TBB and 2,5-DTBBQ, which furnish chain-transfer (Schemes 1–3), therefore, beginning from 20 % conversion, the indicators of the conventional radical polymerization appear, namely gel effect. The fraction of controlled radical polymerization is low, as the formation of the macroinitiator predominantly occurs if the BVE terminal unit participates. To prove the abovementioned suggestions the molecular weight characteristics of initial copolymerization and post-polymerization have been studied.

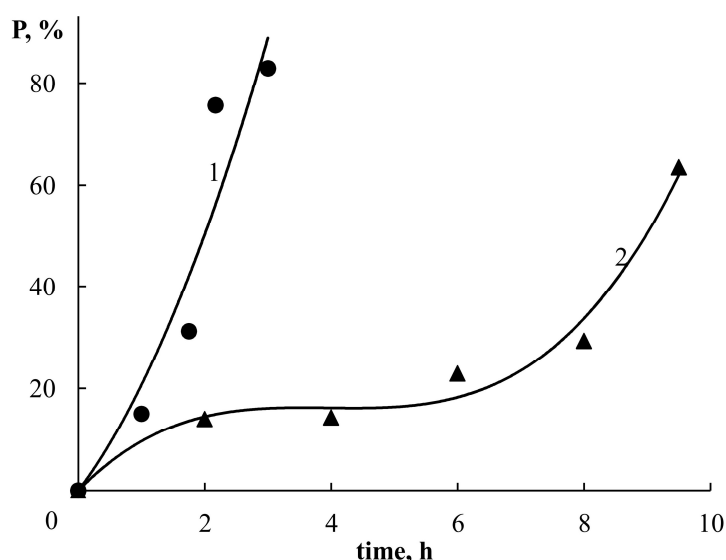


Fig. 3. Kinetic curves of MMA homopolymerization (1) and copolymerization of 40 % mol. BVE, 60 % mol. MMA (2) at 60 °C in the presence of 0.1 % mol. AIBN, 0.85 % mol. TBB, 0.25 % mol. 2,5-DTBBQ

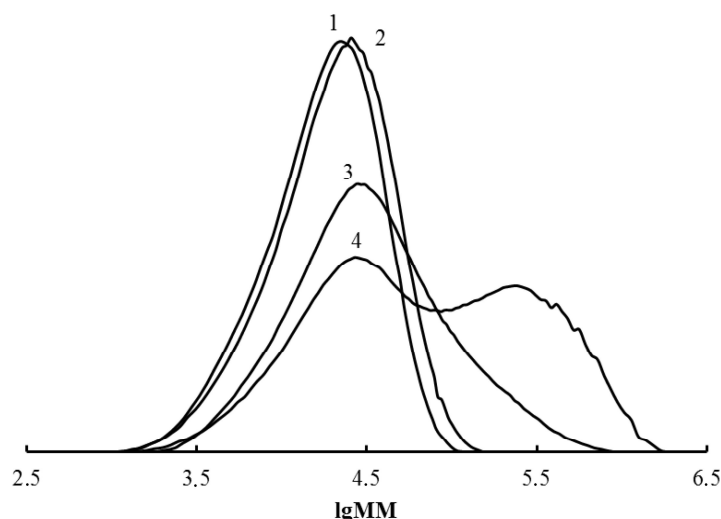


Fig. 4. The MWD curves of the copolymers obtained at 60 °C from the monomer mixture composed of 60 % mol. MMA, 40 % mol. BVE, in the presence of 0.1 % mol. AIBN, 0.8 % mol. TBB, 0.25 % mol. 2,5-DTBBQ at conversion level 14.0 % (1), 22.9 % (2), 29.3 % (3), 63.5 % (4)

Evolution of molecular weight distribution (MWD) of the copolymers with increasing conversion level is represented in Fig. 4. At the initial stages of the process the uniform displacement of MWD mode in the direction of greater molecular weights is observed (Fig. 4, curves 1, 2); beginning from 29.3 % (Fig. 4, curve 3) MWD broadens and the second mode appears (Fig. 4, curve 4). We believe that up to ~20 % conversion the macroinitiator is formed according to Schemes 1 and 2, then it becomes a source of radicals, favoring appearance of the additional mode. The similar dependence is revealed during the MMA homopolymerization in the presence of the studied system [15]. Concurrently, the copolymerization proceeds according to Scheme 1 (direction 2) and Scheme 3, as the result the macroinitiator is not formed, while the chain transfer occurs

through allyl radicals, which lead the polymer chain and promote the conventional radical polymerization. As is well known, the classic radical polymerization favors the characteristic gel effect and the sharp increase of molecular weight, observed in the present study (Fig. 3, curve 2 and Fig. 4, curve 4).

The MWD change in the process of BVE post-polymerization within 12 hours is moderate (Fig. 5, a), but is narrow, while M_n increases, as for conversion percent, it increases by the factor 1.2 only. The MMA post-polymerization in the presence of this macroinitiator (Fig. 5, b) proceeds at greater rate; it is characterized by significant MWD change: the second high molecular mode appears (Fig. 5, b, curve 2) related to PMMA obtained due to the spontaneous MMA polymerization (Fig. 5, b, curve 3). These results demonstrate weak initiating activity of the formed copolymers. We suppose that the preferential interaction of the poly(vinyl butyl ether) propagation radical with *p*-quinone causes fast release of the sufficiently reactive polymer radical, which hinders dissociation of the terminal fragment (Scheme 4).

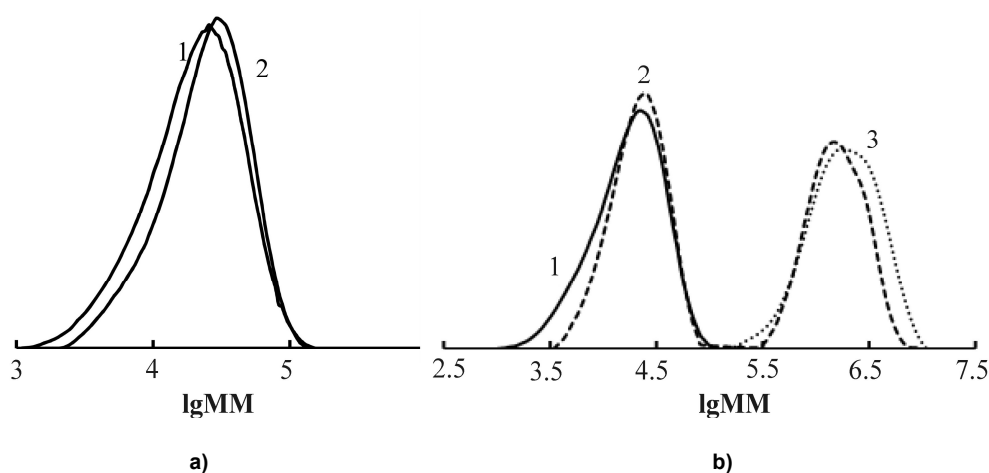


Fig. 5. The MWD curves: a) the macroinitiator synthesized from the monomer mixture of 60 % mol. MMA, 40 % mol. BVE, in the presence of 0.1 % mol. AIBN, 0.8 % mol. TBB, 0.25 % mol. 2,5-DTBBQ (1); the products of BVE post-polymerization (2); b) the macroinitiator synthesized from the monomer mixture of 60 % mol. MMA, 40 % mol. BVE, in the presence of 0.1 % mol. AIBN, 0.8 % mol. TBB, 0.25 % mol. 2,5-DTBBQ (1); the products of MMA post-polymerization (2); the MMA homopolymer obtained due to spontaneous polymerization at 60 °C (3). The macroinitiator concentration is 5 % m/m

Conclusion

Hence, the system TBB – 2,5-DTBBQ does not influence the MMA and BVE copolymerization constants. The process is carried out according to Schemes 1–4. At that *p*-quinone reacts basically with the terminal unit of BVE, which leads to synthesis of the macroinitiator, as the preferential direction of interaction for such macroradicals is at the C=O bond of quinone. However, such macroinitiator has low efficiency (Scheme 4) because of high reactivity of the corresponding propagation radicals. This results in the fact that the conventional radical polymerization with effective chain transfer according to Schemes 1–3 remains the main process.

Acknowledgements

The research was supported by the Ministry of Education and Science of the Russian Federation (assignment No. 2014/134, agreement dated 27 August 2013 No. 02.B.49.21.003 between the Ministry and NNSU).

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Received 7 November 2015

УДК 54.057+678.7-1

DOI: 10.14529/chem160104

СИНТЕЗ СОПОЛИМЕРОВ МЕТИЛМЕТАКРИЛАТА И ВИНИБУТИЛОВОГО ЭФИРА В ПРИСУТСТВИИ СИСТЕМЫ ТРИБУТИЛБОР – 2,5-ДИ-ТРЕТ-БУТИЛ-*p*-БЕНЗОХИНОН

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Осуществлен синтез сополимеров метилметакрилата и винилбутилового эфира с использованием системы трибутилбор – 2,5-дитретбутил-*p*-бензохинон. Данная система не оказывает влияние на константы сополимеризации указанных мономеров. С *p*-хиноном реагирует преимущественно концевое звено винилбутилового эфира. Наряду с традиционной реализуется контролируемая радикальная сополимеризация.

Ключевые слова: метилметакрилат, винилбутиловый эфир, динитрил азоизомасляной кислоты, три-*n*-бутилбор, 2,5-ди-трет-бутил-*p*-хинон, УФ-спектроскопия, контролируемая радикальная полимеризация.

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Поступила в редакцию 7 ноября 2015 г.

ОБРАЗЕЦ ЦИТИРОВАНИЯ

Kuznetsova, Yu.L. Synthesis of copolymers of methyl methacrylate and butyl vinyl ether in the presence of the system tributylboron – 2,5-di-*tert*-butyl-*p*-benzoquinone / Yu.L. Kuznetsova, N.A. Abramova, D.V. Ludin // Вестник ЮУрГУ. Серия «Химия». – 2016. – Т. 8, № 1. – С. 26–33. DOI: 10.14529/chem160104

FOR CITATION

Kuznetsova Yu.L., Abramova N.A., Ludin D.V. Synthesis of Copolymers of Methyl Methacrylate and Butyl Vinyl Ether in the Presence of the System Tributylboron – 2,5-di-*tert*-butyl-*p*-benzoquinone. *Bulletin of the South Ural State University. Ser. Chemistry.* 2016, vol. 8, no. 1, pp. 26–33. DOI: 10.14529/chem160104