

# INFLUENCE OF SYNTHESIS CONDITIONS ON COMPOSITION OF ALKYL (METH)ACRYLATE – VINYL ALKYL ETHER COPOLIMERS

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Synthesis of methyl methacrylate copolymers with vinyl butyl ether has been carried out from the monomer mixture by compensate polymerization method. Analysis of their composition has shown that, respectively, either a conversion nonuniform copolymer is formed with methyl methacrylate units for the most part, or a copolymer nearing equimolar composition. By the example of monomer couple butyl acrylate–vinyl alkyl ether it has been shown that in order to get the structurally uniform copolymer, it is possible to use both classical radical initiators and binary alkylborane–oxygen initiators.

*Keywords: methyl methacrylate, butyl acrylate, vinyl butyl ether, vinyl isobutyl ether, radical initiation, azobisisobutyronitrile, amine complex, triethylborane, tri-n-butylborane, copolymer composition.*

## Introduction

Synthesis of new copolymers under radical initiation conditions is a promising direction in chemistry of high-molecular compounds. Modification of polymer properties using the development of copolymer synthesis without additives, with radical initiators of various types, is still an urgent problem [1, 2]. In particular, fractional introduction of one of the monomers into the reaction sphere makes it possible to obtain copolymers whose composition is unlike those from the monomer mixture, with correspondingly new properties. Thus, such a method, used for copolymerization of some alkyl (meth)acrylates (AMA) with vinyl alkyl ethers, leads to structurally uniform copolymers. The results have been obtained by the example of monomer couples, including butyl acrylate (BA), the mixtures of esters formed by methacrylic acid and higher alcohols of C<sub>8</sub>–C<sub>10</sub> fractions (CMA-1) and C<sub>12</sub>–C<sub>18</sub> fractions (CMA-2) with vinyl butyl ether (VBE), vinyl isobutyl ether (ViBE) [3-6].

The aim of the present study is the comparative analysis of the composition of methyl methacrylate (MMA) copolymers with vinyl alkyl ethers (VAE) in synthesis from monomer mixture by compensate polymerization method, as well as of various initiators used to obtain BA–VBE copolymers of equimolar composition.

## Experimental

Commercial reagents were used throughout.

In order to synthesize copolymers in ampoules the exact amounts of monomers and initiator were placed into glass ampoules, freed from oxygen by freezing the reaction mixture in liquid nitrogen and pumping out to residual pressure < 1.3 Pa. The ampoules were glass-sealed, then polymerization was carried out at strictly determined temperature. For that an ampoule was placed into a thermostat for pre-set time, after which the ampoule was taken out and frozen in liquid nitrogen to stop polymerization. The copolymer was isolated by recrystallization from solution [4]. Monomer conversion was gravimetrically determined.

The synthesis of copolymers by compensate polymerization method. The synthesis was performed in a four-necked flask with a reflux condenser, a paddle-type agitator, a thermocouple, and an outlet for reagent injection, placed in a thermostat. An exactly weighed sample of less reactive monomer was placed into the flask, the mixture was brought to boil while stirring. Through the outlet for reagent injection a solution of exactly weighed sample of azobisisobutyronitrile (BIN) was measured in doses with

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the use of a dropping funnel. After preset synthesis time the flask was cooled in water bath (40 °C). Unreacted monomers were pumped out at low pressure (to 0.5 mm of mercury). Under vacuumization conditions the polymer was dried in the flask to constant weight at  $T = 20\text{--}25\text{ }^{\circ}\text{C}$ .

In the case of using triethylborane- (TEB) or tri-*n*-butylborane (TNB) – oxygen, the commercial complex trialkylborane hexamethylenediamine was placed into the reactor, and organoelemental component was isolated by measuring in doses the equimolar amount of methacrylic acid together with the reactive monomer.

IR spectra of the synthesized copolymers were recorded on the Fourier-transform IR spectrometer Shimadzu FTIR-8400S in KBr cuvettes with pathlength 0.26 mm in chloroform solution. The range of wavenumbers was  $5500\text{--}550\text{ cm}^{-1}$ , determination error did not exceed  $\pm 0.05\text{ cm}^{-1}$ . The copolymer composition was determined with the use of calibrating curve by characteristic peak area. The analytical bands were the following: the band at  $1727\text{ cm}^{-1}$  for carbonyl group (acrylate fraction); the band at  $1100\text{ cm}^{-1}$  for C–O–C group of ether (VAE fraction).

$^1\text{H}$  NMR spectra were recorded on the Agilent DD2 400 spectrometer (solutions in  $\text{CDCl}_3$ ), at operating frequency 400 MHz. Chemical shifts are given in ppm in relation to the solvent residual signal (chloroform: 7.26 ppm). All spectra are recorded at temperature 25 °C.

### Results and Discussion

In accordance with the purpose in hand the samples of MMA and VBE copolymers were obtained from the monomer mixture (Table 1) and by compensate polymerization (Table 2), the composition analysis was performed by IR- and NMR-spectroscopy.

It can be seen from the data in Table 1 that the copolymer synthesis from the monomer mixture of the following composition: 60 mol % MMA and 40 mol % VBE leads to formation of samples composed by MMA units for the most part, their fraction insignificantly decreases with conversion. Similar results were previously obtained by the example of the monomer couple BA–ViBE. The obtained results are obviously explained by relative reactivities of comonomers, whose values equal  $r_{\text{MMA}} = 10\text{--}11$ ,  $r_{\text{VBE}} \sim 0$  [7, 8]: high reactivity of the growing MMA radical with respect to its monomer leads to formation of the macromolecule containing but small amount of VBE units. Though with conversion buildup the content of BVE fragments in the polymer insignificantly increases (rows 3, 4).

Table 1  
Characteristics of the copolymers obtained from the monomer mixture of the composition:  
60 mol % MMA, 40 mol % VBE, initiator BIN (0.1 mol %). Temperature 60 °C

No.	Time, h	Conversion, %	Content of MMA units, mol %, according to $^1\text{H}$ NMR data
1	2	15	98
2	4	27	96
3	6	57	–
4	8	55	94
5	10	62	94

Table 2  
Data on composition of MMA–VBE copolymers obtained by compensate polymerization method at general monomer ratio 1:4 in the presence of BIN (0.1 mol %) at boiling VBE

No.	MMA dosing time, min	Yield in reactive monomer, %	Content of MMA units, mol %, according to data	
			IR	$^1\text{H}$ NMR
1	20	44	58	56
2	40	51	53	53
3	53	62	56	57
4	80	78	59	57
5	180	92	54	53

The use of compensate copolymerization method (uniform dosing of MMA into VBE) makes it possible to obtain the copolymer with almost equimolar composition (Table 2). At that the calculation results of copolymer composition according to IR- and <sup>1</sup>H NMR-spectroscopy data are in close agreement. Similar results have been obtained by the example of monomer couples including BA, CMA-1 and C<sub>12</sub>–C<sub>18</sub> fractions (CMA-2) with VAE [4, 6].

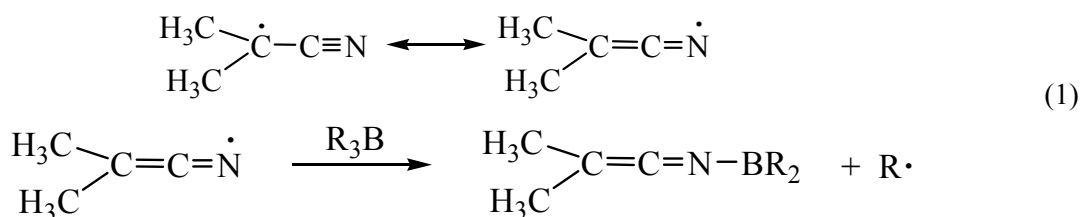
Among initiators of radical polymerization the initiating systems involving trialkylboranes are of great interest [9, 10]. In the present paper their initiation effect has been studied both during copolymerization from the monomer mixture by the example of the couple MMA–VBE at initiation by the system BIN-TNB (Table 3), and during compensate copolymerization of the comonomers BA and VAE (VBE and ViBE) in the presence of TEB and TNB (Table 4). In the latter case atmospheric oxygen acts as the co-initiator together with trialkylboranes, air is present in the reaction mixture at abovementioned process conditions in small proportion. For comparison, Table 4 shows data on the composition of copolymers BA-BAE, synthesized by compensate copolymerization in the presence of BIN.

Table 3

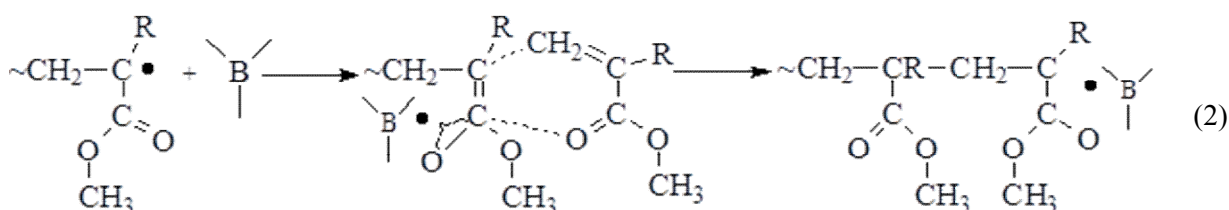
Characteristics of the copolymers obtained from the monomer mixture of the composition:  
60 mol % MMA, 40 mol % VBE, initiator BIN + TNB (0.1 + 0.8 mol %). Temperature 60 °C

No.	Time, h	Conversion, %	Content of MMA units, mol %, according to <sup>1</sup> H NMR data
1	2	22	98
2	4	33	96
3	6	50	94
4	8	59	93
5	10	60	93

At data correlation for Tables 1 and 3 it can be seen that during copolymerization from the monomer mixture the use of the initiating system BIN–TNB does not lead to significant changes in the copolymer MMA–VBE composition: the formed samples are composed by MMA units for the most part, their fraction insignificantly decreases with conversion. Previously it was observed [10] that at MMA polymerization initiated by BIN–TNB the rate of polymerization increased compared to that with azo-initiator, which increased if TNB concentration increased in its ratio to BIN. In this instance it is also possible to note somewhat greater conversion of the copolymers in the early stages. It is related to the fact, described in [10], that the radical system on the basis of TNB and BIN is appropriate for polymerization of methyl methacrylate in the absence of oxygen-containing oxidizing agents. Possibly, azo-initiator, coordinated by TNB through nitrile groups, dissociates homolytically to generate n-butyl radicals. Their formation proceeds according to S<sub>R</sub>2 reaction, in which the resonance forms of nitrogen-centered cyanoisopropyl radicals on the boron atom are substituted in compliance with scheme 1:



Besides, the increasing rate can be explained by coordination of the growth radical TNB and coordination radical polymerization in compliance with the following scheme [11]:



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Such coordination is possible for AMA and acrylonitrile [11]. As coordination proceeds on the basis of the growth radical, formed by the reactive monomer, consequently, copolymer composition should be determined only by the way of synthesis.

Table 4

Data on composition of the copolymers BA-VAE obtained by compensate polymerization method in a total proportion of the monomers 1:4 in the presence of trialkylboranes at reflux of VBE

No.	Initiator	VAE	BA dosing time, min	Yield in reactive monomer, %	Content of BA units, mol %, according to IR data
1	BIN*	VBE	20–30	~100	51–52
2	TEB			56–66	51–52
3	TNB			18–20	48–50
4	BIN	ViBE	40	~100	65–70
5	TEB			50–51	59–60
6	TNB			30	65–66

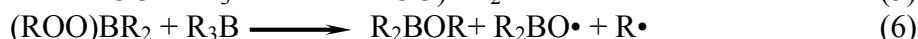
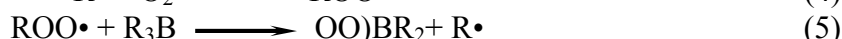
\* data [4].

Based upon the data in Table 4, the composition of the copolymer BA-VAE, obtained at initiation by BIN, compared to trialkylboranes TEB and TNB, which form initiating radicals after oxidizing by atmospheric oxygen [9], left in small proportion in boiling VAE, is almost the same. For the copolymer BA-ViBE, synthesized in the presence of trialkylboranes (rows 5, 6), the content of acrylate is somewhat less than for it at initiation by BIN (row 4). Note that the use of organoelemental initiator leads to decrease of the copolymer yield. This is obviously correlated to the characteristic features of polymerization initiation in the presence of trialkylboranes [9]: at introduction of trialkylborane the oxygen in the reaction mixture is rapidly consumed. Autooxidation begins with homolytic  $S_{R2}$  substitution by oxygen of an alkyl radical in trialkylborane (scheme (3)). The formed alkyl radical interacts with the next oxygen molecule, yielding peroxy radical (scheme (4)), which can further react with original trialkylborane (scheme (5)), continuing the chain reaction (6). Then monoalkylperoxyborane reacts with oxygen to produce dialkylperoxyborane (scheme (7)) or with original trialkylborane (scheme (8)). In the latter case the product is dialkylalkoxyborane (RO)BR<sub>2</sub>, capable of further reaction with oxygen, eventually forming trialkylborate B(OR)<sub>3</sub> (scheme (9)) [9]:

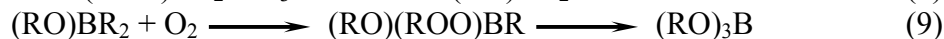
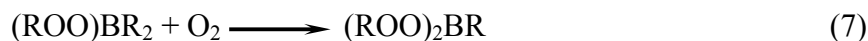
Initiation:



Chain growth:



Following reactions:



Except the abovementioned reactions, other processes are possible. Conversion level for autooxidation of trialkylboranes depends on the ratio of borane and oxygen. Apparently, under the conditions of compensate copolymerization, the results of which have been shown in Table 4, the specific features are such that it is impossible to obtain the copolymer with quantitative yield in acrylate. Though the copolymer composition stays almost equimolar, independently on the used initiator.

Thus, the investigation on the influence of the synthesis conditions for copolymers of AMA with VAE upon their composition, by the example of several monomer couples, has allowed detecting that the method of monomer introduction into the reaction mixture influences the process significantly, and that the nature of initiator causes but a slight change in the copolymer composition; the use of organoelemental initiator leads to decrease in copolymer yield.

### Conclusions

1. Copolymers of methyl methacrylate with vinyl butyl ether have been synthesized from the monomer mixture and by compensate polymerization method. The analysis of their composition has shown that in the first case the gradient copolymer is formed, nonuniform in conversion, with methyl methacrylate units for the most part; when acrylate is dosed uniformly, the copolymer of almost equimolar composition is obtained.

2. It has been shown that in order to obtain the structurally uniform copolymer from the monomer couple butyl acrylate–vinyl alkyl ether it is possible to use both classical radical initiators, e.g. BIN, and binary alkylborane–oxygen initiators. At that the copolymer conversion decreases if trialkylboranes are used for initiation.

### Acknowledgments

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**ВЛИЯНИЕ УСЛОВИЙ СИНТЕЗА НА СОСТАВ СОПОЛИМЕРОВ  
АЛКИЛ(МЕТ)АКРИЛАТ-ВИНИЛАЛКИЛОВЫЙ ЭФИР**

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Проведен синтез сополимеров метилметакрилата с винилбутиловым эфиром из мономерной смеси и компенсационным способом. Анализ их состава показал, что происходит образование, соответственно, неоднородного по конверсии сополимера с преимущественным содержанием звеньев метилметакрилата и сополимера близкого к эквимольному составу. На примере мономерной пары бутилакрилат-винилалкиловый эфир показано, что для получения композиционно однородного сополимера могут быть использованы как классические радикальные инициаторы, так и бинарные инициаторы боралкид-кислород.

*Ключевые слова: метилметакрилат, бутилакрилат, винилбутиловый эфир, винилизобутиловый эфир, радикальное иницирование, динитрил азоизомазляной кислоты, аминный комплекс, триэтилбор, три-н-бутилбор, состав сополимера.*

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**ОБРАЗЕЦ ЦИТИРОВАНИЯ**

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