SYNTHESIS OF BUTYL METHACRYLATE COPOLYMERs
WITH THE USE OF COMPENSATE POLYMERIZATION METHOD

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Butyl methacrylate copolymers with vinyl alkyl ethers and styrene have been obtained by compensate polymerization method. The properties of copolymers have been determined with the use of gel-penetration chromatography, IR- and 1H NMR-spectroscopy.

Keywords: butyl methacrylate, vinyl butyl ether, vinyl isobutyl ether, structurally uniform polymers, molecular weight characteristics.

Introduction
The most commonly encountered industrial method to obtain copolymers is by radical initiation. In spite of diversity of the modern molecular design methods, such as complex-radical processes, pseudo-living radical polymerization, etc. [1–3], the problem of characteristics modification for polymer materials using development of copolymer synthesis without additives, with classical radical initiators, is of as great importance as before. One of such methods is compensate copolymerization, which involves fractional introduction of one of the monomers into the reaction sphere. In this way it is possible to obtain copolymers differing in composition from the monomer mixture, therefore, possessing new characteristic features. In the series of papers [4–7] the results were presented, concerning application of the compensate copolymerization method to obtain structurally uniform copolymers of vinyl alkyl ethers (VAE) with alkyl(meth)acrylates (AMA). The advantages of the chosen method were shown compared to synthesis from a monomer mixture, enabling the synthesis of gradient copolymers. Butyl acrylate (BA) was mostly used as the model monomer couple in order to study the synthesis features.

The aim of the present paper is the investigation of compensate radical copolymerization of vinyl monomers demonstrated by the example of monomer couples including butyl methacrylate (BMA), specifically, BMA – vinyl butyl ether (VBE), BMA – vinyl isobutyl ether (ViBE), BMA – styrene.

Experimental
Commercial reagents were used throughout.

In order to determine relative reactivity of comonomers BMA–VBE and BMA–ViBE the synthesis of copolymers from a monomer mixture was performed in vacuumed ampoules. During the experiment monomer mixtures with various ratios were used: from 5 to 95 % (mol) VAE. The copolymers were isolated at 5–7 % conversion. Relative reactivities were calculated by Kelen-Tudos method [8].

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 preset 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 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 one monomer or its solution was 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 preset 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 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 one monomer or its solution 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 another monomer was measured in doses with the use of a dropping funnel. After preset synthesis time the flask was cooled in water bath (40 °C). (Unreacted mono-
mers 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 $T=20–25 \, ^\circ\mathrm{C}$.

Molar masses and molecular mass distribution of the copolymers were determined at the set of 5 styrogel columns with pore diameters $10^5$, $3 \cdot 10^4$, $10^4$, and $250 \, \text{Å}$ (Waters, USA). Detection was performed by differential refractometer R-403 and UV-detector UV-101 (Waters). Tetrahydrofuran was used as the eluent. Calibration was carried out with the use of narrow-dispersed polystyrene (PST) standards [9].

The calculation of molar masses for styrene copolymers was carried out in conformity with PST standards, while for AMA copolymers it was accomplished by the standard formula (1) using Kuhn–Mark–Houwink constants for AMA and styrene.

$$\log M(\text{copolymer}) = \frac{1 + \alpha(\text{PST})}{1 + \alpha(\text{PAMA})} \times \log M(\text{PST}) + \frac{1}{1 + \alpha(\text{PAMA})} \times \log K(\text{PST}) \times \frac{K(\text{PAMA})}{K(\text{PAMA})}.$$  

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 5500–550 cm$^{-1}$, determination error did not exceed ±0.05 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 cm$^{-1}$ for carbonyl group (acrylate fraction); the band at 1100 cm$^{-1}$ for C–O–C group of ether (VAE fraction); the band at 1600 cm$^{-1}$ for C=C vibrations of styrene aromatic ring (styrene fraction).

$^1$H NMR spectra were recorded on the Agilent DD2 400 spectrometer (solutions in 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 $^\circ\mathrm{C}$.

Results and Discussion

According to the radical copolymerization theory [10], the copolymer composition at radical initiation is determined by relative reactivity of monomers. In the case of greatly different relative reactivities— which is true in the case of AMA and VAE copolymerization— high rate of polymer formation from a monomer mixture is observed at the excess of the reactive monomer, and the formed copolymer is richer in the reactive monomer. The method using uniform introduction of the reactive monomer (compensate copolymerization) at any moment provides conditions of yielding a polymer with greater VAE content from the couple "reactive monomer – non-reactive monomer": due to its high reactivity the introduced AMA leaves the reaction sphere, forming copolymerization product, while VAE is in significant excess again. The formed copolymer, e.g. BA–VBE [4, 5, 7], has high degree of structural uniformity, which is ensured, among other things, by VAE inability for homopolymerization at the radical initiation conditions. It has been considered interesting to obtain copolymer of BMA and VAE at the similar conditions.

For monomer couples BMA–VBE and BMA–ViBE the values of relative reactivities are not described in the literature, it was necessary to find them experimentally. Table 1 shows the ratios of monomer mixtures BMA ($M_1$) with VBE and ViBE ($M_2$), as well as copolymers ($m$) obtained from the given monomer mixture at low conversion.

| $[M_2]$ | $[M_1]$ | $[m_2]$ | $[m_1]$ |
|---------|---------|---------|---------|
| 1       | 2       | 3       | 4       |
| ViBE–BMA |
| 5       | 95      | 0.9     | 99.1    |
| 20      | 80      | 2.2     | 97.8    |
| 35      | 65      | 5.1     | 94.9    |
| 50      | 50      | 11.4    | 88.6    |
| 60      | 40      | 14.2    | 85.8    |
The calculation has given values for comonomers BMA–ViBE $r_1 = 7.8$ and $r_2 \approx 0; \ BMA–VBE \ r_1 = 4.1$ and $r_2 \approx 0$. If the obtained values are compared to those for BA (BA–ViBE $r_1 = 5.2$ and $r_2 \approx 0; \ BA–VBE \ r_1 = 1.43$ and $r_2 \approx 0$), it is obvious that the tendency of BMA for addition of its monomer is much higher than such of BA. This difference cannot but be reflected in experimental data at copolymerization. Indeed, compensate copolymerization of BMA with VAE (at comparable conditions for BA) leads to lower conversion, and the formed copolymer is characterized by slightly higher acrylate content (Table 2, rows 1, 2 and 4, 5, respectively). Nevertheless, there are strong grounds for affirmation that – unlike the copolymerization from a monomer mixture, leading to structurally nonuniform gradient copolymer [10] – formation of predominantly structurally uniform copolymer, nearing equimolar composition, takes place.

### Table 2

| AMA | Second monomer | AMA dosing time, min | Copolymer yield in reactive monomer, % | Content of acrylate units, mol %, according to data |
|-----|----------------|----------------------|---------------------------------------|---------------------------------------------------|
|     |                |                      |                                       | gravimetry  | IR spectroscopy | $^1$H NMR spectroscopy |
| 1   | BMA            | VBE                  | 74                                    | 57         | 54              | 56                      |
| 2   |                | ViBE                 | 53                                    | 68         | 68              | 65                      |
| 3   |                | styrene              | ~50                                   | –          | 39              | 41                      |
| 4   | BA             | VBE*                 | ~100                                  | 52         | 52              | 51                      |
| 5   |                | ViBE                 | ~100                                  | 64         | 70              | 61                      |

* Data [4].

In the case of the couple BMA–styrene, as well as BA–styrene, as opposed to compositions BA–VAE, BMA–VAE, both monomers have similar relative reactivities: BMA–styrene 0.64–0.54 [10] and BA–styrene 0.20–0.88 [11]. At initial monomer mole ratio 1:1 the polymerization proceeds at high rate due to gel effect, at that the copolymer composition at deep conversion stages is practically the same as the initial one, and by the example of BA–styrene it has been shown that mostly the structurally uniform copolymer is formed [11]. In the present study compensate copolymerization method has been used in the first stage of BMA–styrene copolymerization (Table 2), lest the polymerized mixture would be intensively heated due to gel effect. Toluene has been chosen with the intent of dissolving the formed copolymer; heptane has been used in order to maintain the synthesis temperature close to the VBE boiling point, for the purpose of nearing the polymerization conditions to the previous studies, carried out at the VBE boiling point. (VBE $T_{bp}$ = 94 °C; heptane $T_{bp}$ = 94 °C; it does not form any azeotrope mixture with
toluene.) In the dosing time ~30 min the conversion amounts to ~8%, and after the following stirring during 2.5 h the copolymerization proceeds to conversion ~50%, at that the polymerization process runs smoothly without gel effect. It can be seen (Table 2, row 3) that the formed copolymer is near to equimolar composition.

Table 3

| No. | Monomer couple | Monomer in the reaction mixture | Monomer in the doser | Content of acrylate units, mol %, according to data | $M_n$, Da | $M_w$, Da | $M_w/M_n$ |
|-----|----------------|---------------------------------|----------------------|---------------------------------------------------|----------|----------|----------|
| 1   | BMA–VBE        | BA                              | Styrene              | 48                                                 | 15000    | 28300    | 1.9      |
| 2   | BMA–Vibe       | Styrene                        | BA                   | 53                                                 | 13400    | 29600    | 2.2      |
| 3   | BMA–styrene    | Styrene                        | BMA                  | 39                                                 | 21200    | 54400    | 2.6      |
| 4   | BA–VBE         | Styrene                        | EHA*                 | 35                                                 | 18100    | 37900    | 2.1      |

*The sample is shown for comparison, EHA – ethylhexyl acrylate.

The study of the molecular mass characteristics of the newly synthesized copolymers BMA–VAE and BMA-styrene has shown that curves of molecular mass distribution are unimodal for all samples. As in the case of BA–VAE copolymers, molar masses are greater for BMA–Vibe than for BMA–VBE (Table 3, rows 1, 2 and 4, 5, respectively).

Table 4

| No. | Monomer couple | $M_n$, kDa | $M_w$, kDa | $M_w/M_n$ |
|-----|----------------|------------|------------|-----------|
| 1   | BMA–VBE        | 35         | 77         | 2.2       |
| 2   | BMA–Vibe       | 38         | 130        | 2.8       |
| 3   | BMA–styrene    | 21         | 54         | 2.6       |
| 4   | BA–VBE         | 18         | 55         | 2.9       |
| 5   | BA–Vibe        | 21         | 93         | 4.3       |

Conclusions

Butyl methacrylate copolymers with vinyl alkyl ethers and styrene have been obtained by compensate polymerization method. The properties of copolymers have been characterized with the use of gel-penetration chromatography, IR- and $^1$H NMR-spectroscopy. The values of relative reactivity have been found for the couples BMA–VBE and BMA–Vibe.

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СИНТЕЗ СОПОЛИМЕРОВ БУТИЛМЕТАКРИЛАТА
С ИСПОЛЬЗОВАНИЕМ КОМПЕНСАЦИОННОГО СПОСОБА

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Сополимеры бутилметакрилата с винилалкиловыми эфирами и стиролом получены с использованием компенсационного способа. Свойства сополимеров определены с использованием методов ГПХ, ИК- и 1Н ЯМР-спектроскопии.

Ключевые слова: бутилметакрилат, винилбутиловый эфир, винилизобутиловый эфир, композиционно-однородные сополимеры, молекулярно-массовые характеристики.

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