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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 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 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=20–25 °C.

Molar masses and molecular mass distribution of the copolymers were determined at the set of 5 styrogel columns with pore diameters 10^5, $3\cdot10^4$, 10^4, 10^3, and 250 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.

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

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 °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.

Table 1

Data on copolymer composition in relation to monomer mixture composition for BMA–VBE and BMA-ViBE

$[M_2]$	$[M_1]$	$[m_2]$	$[m_1]$
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

Table 1 (end)

1	2	3	4
70	30	22.1	77.9
80	20	26.8	73.2
90	10	33.1	66.9
95	5	35.2	64.8
VBE–BMA			
5	95	1.1	98.9
20	80	5.7	94.3
35	65	12.0	88.0
50	50	14.7	85.3
60	40	22.3	77.7
70	30	27.4	72.6
80	20	35.2	64.8
90	10	40.6	59.4
95	5	42.7	57.3

The calculation has given values for comonomers BMA–ViBE r_1= 7.8 and r_2≈ 0; BMA–VBE r_1= 4.1 and r_2≈ 0. If the obtained values are compared to those for BA (BA–ViBE r_1= 5.2 and r_2≈ 0; BA–VBE r_1= 1.43 and r_2≈ 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 copolimerization. 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

Composition of copolymers synthesized by compensate polymerization

	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	20–30	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

Data on composition of acrylate and styrene copolymers and their molecular mass characteristics

No.	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
			IR	NMR			
1	BA	Styrene	48	47	15000	28300	1.9
2	Styrene	BA	53	54	13400	29600	2.2
3	Styrene	BMA	39	40	21200	54400	2.6
4	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

Molecular mass characteristics of the copolymers obtained by compensate polymerization method

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 ^{1}H ЯМР-спектроскопии.

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

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