

## Specific features of "compensating" copolymerization of butyl acrylate with vinyl butyl ether in the presence of triethylboron\*

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Copolymerization of butyl acrylate with a large excess of boiling vinyl butyl ether was carried out in the presence of triethylborane. The analysis of the composition of the obtained product demonstrated that an alternating low-molecular-weight copolymer was predominantly formed. The formation of macromolecules occurred by both conventional and controlled radical polymerization (CRP), as evidenced by a bimodal molecular weight distribution. As conversion increased, the mode corresponding to the CRP mechanism shifted toward larger molecular masses. The relative activities of comonomers for the process initiated by triethylborane were calculated.

**Key words:** butyl acrylate, vinyl butyl ether, compensating copolymerization, triethylborane, dissociation-combination.

The interest toward trialkylborane—oxidant systems as radical polymerization initiators is related to the recently discovered possibility of forming polymer chains by dissociation-combination (pseudo-living polymerization) due to boroxyl radicals formed during trialkylborane oxidation.<sup>1</sup> Thus, it was found that the characteristic features of pseudo-living radical polymerization are observed during the polymerization of alkyl methacrylates initiated by an organoborane—oxygen system. However, this process does not occur for alkyl acrylates under the same conditions, and a rapid increase in conversion to an almost complete consumption of the monomer takes place instead. The differences in question are a result of the different activities of the monomers and the propagating radicals of these compounds.<sup>1</sup> The copolymerization of vinyl monomers in the presence of the organoborane—oxygen initiating system has virtually not been studied.

The goal of this work is to study the parameters of the copolymerization of butyl acrylate (BA) with vinyl butyl ether (VBE) under conditions of "compensating" copolymerization in the presence of triethylborane (TEB), as well as to determine the structure of the obtained copolymer and its molecular weight characteristics.

\* Dedicated to Academician of the Russian Academy of Sciences G. A. Abakumov on the occasion of his 80th birthday.

### Results and Discussion

The works<sup>2–6</sup> report on the synthesis of some copolymers under conditions of "compensating" copolymerization in the presence of radical initiators. Thus, the copolymerization of alkyl(meth)acrylates (AMA) and styrene with a large excess of VBE and vinyl isobutyl ether (ViBE) under reflux of the reaction mixture was investigated. The analysis of the structure of the products demonstrated that the approach in question makes it possible to obtain an entire series of new copolymers uniform in composition and having a unimodal molecular weight distribution (MWD). A copolymer with an alternating structure was obtained when using AMA. It should be noted that in contrast to the usual copolymerization of AMA with VBE, which is characterized by a noticeable gel effect, the formation of the copolymer under the "compensating" copolymerization conditions is not accompanied by this effect, but is characterized by a uniform heat release, a sufficiently high rate, and the involvement of a low-active monomer in the polymerization. AIBN was used as the polymerization initiator.

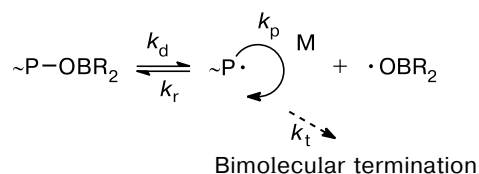
In this work, a "compensating" copolymerization of BA with a large excess of VBE was carried out in the presence of a TEB—oxygen system. A small amount of oxygen contained in the boiling ether was enough to oxidize the TEB. This method has several advantages. First, a process without evacuation simplifies polymer

preparation and is of considerable interest for practical application. Second, virtually only AMA<sup>3</sup> from the binary monomer mixture is involved in chain propagation at the initial copolymerization stage and a significant gel effect is observed for AMA—alkyl vinyl ether pairs in the usual process. This effect should be even more pronounced when using initiating systems containing triethylboranes, since their characteristic feature is a noticeably higher rate than, for example, in the case of AIBN.

To detect the changes in the molecular weight parameters which accompany the polymer chain growth under comparable conditions, the samples were collected by interrupting the process after the completion of BA dosing every 10 minutes during the first hour and then every hour. It was found that at the beginning of the process immediately after BA dosing, the copolymer MWD curve is bimodal (Fig. 1, curve 1). The first MWD mode corresponds to low molecular weight (MW) values ( $M_n = 900$ ,  $M_w = 1030$ ) and a polydispersity index of  $P = 1.1$ , characteristic of an oligomer. The second mode corresponds to the values  $M_n = (50-60) \cdot 10^3$ ,  $M_w = (90-100) \cdot 10^3$  and  $P \sim 2$ . Ten minutes after the completion of BA dosing, the bimodal distribution of MW for the BA-VBE copolymer is retained (see Fig. 1, curve 2). However, the oligomeric branch of the MWD curve is displaced relative to its counterpart in curve 1, and an increase in MW ( $M_n = 950$ ,  $M_w = 1090$ ) is observed with  $P = 1.1$  remaining the same, while the intensity and the position of the second mode remain unchanged. Beginning from the sample collected 40 min after the onset of synthesis, a merging of the MWD bands is observed and a large shoulder corresponding to the low-molecular-weight product appeared in the resultant curve. The formation of the oligomer along with the high-molecular-weight polymer can be explained by the fact that a polymer chain

propagation center is formed by the dissociation-combination mechanism due to the interaction of the boroxyl radical, which was previously registered during the oxidation of trialkylborane,<sup>1</sup> with the initiating or growing radical.<sup>7,8</sup> In the case of a stable boroxyl radical, chain propagation occurs according to Scheme 1. A clear proof of this is the polydispersity index close to  $P = 1$ .

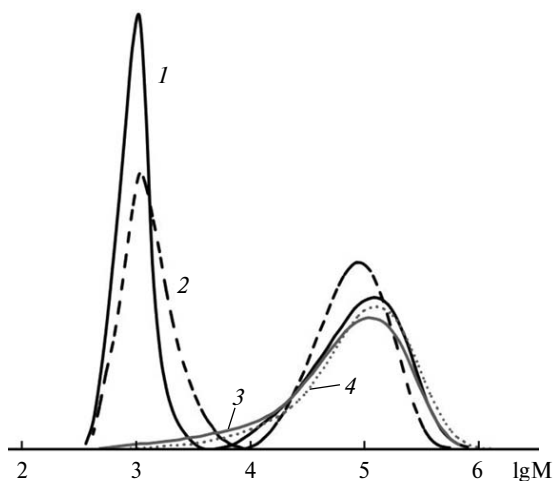
Scheme 1



*Legend:*  $\sim\text{P}$  is the propagating macroradical,  $k_d$  is the adduct dissociation rate constant,  $k_r$  is the recombination rate constant,  $k_p$  is the chain propagation rate constant,  $k_t$  is the termination reaction rate constant.

The second and considerably larger MWD mode (see Fig. 1, curve 1) belongs to the BA-VBE copolymer prepared by the process of macromolecule formation through normal bimolecular termination, *i.e.*, to the so-called "dead" copolymer. After the completion of dosing, the copolymer in question is no longer formed. This conclusion follows from previously obtained results on the polymerization of AMA in the presence of trialkylboranes: it was found that after all the dissolved oxygen is consumed, the polymerization proceeds under conditions in which new chains are practically no longer formed.<sup>1</sup> Further increase in conversion of monomers occurs through the dissociation-combination growth of the chains initiated at the beginning of the reaction. The increase in the MW of chains obtained by dissociation-combination leads to a shift of the MWD curve. Copolymers with a MW, which is equal to the MW of the "dead" copolymer, are formed. The processes in question lead to the emergence of a common MWD curve with a shoulder formed due the presence of low-molecular-weight products. The collapse of the modes prevents further control over the change in the low-molecular-weight mode. However, if we track the change of the low-molecular-weight mode of the copolymer of BA with VBE (Table 1), it can be seen that it increases during the process, indicating the growth of the MW of the copolymer, which is formed by dissociation-combination. This fact, as well as the continuing increase in the conversion of monomers, confirm further copolymer formation.

The  $M_n$  values, which should be considered starting from the 40 minute of the process for unimodal MWD, also increase with the increase in conversion. Moreover, the  $M_n$  dependence on conversion is linear (Fig. 2), which



**Fig. 1.** MWD curves for the BA-VBE copolymers obtained in the presence of TEB for a reaction duration of 20 (1), 30 (2), 40 min (3), and 4 h (4).

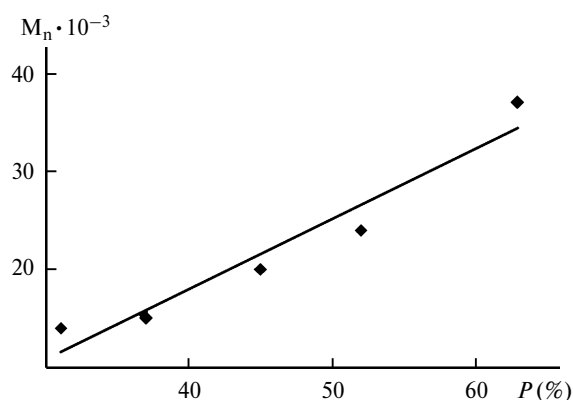
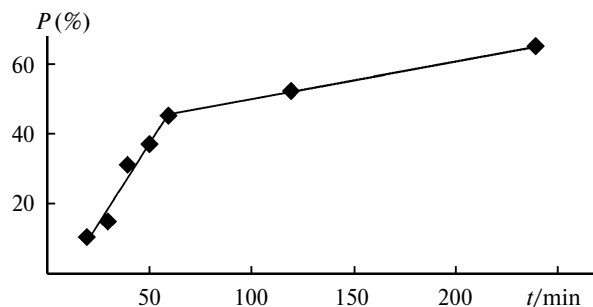
**Table 1.** Change in the conversion and the molecular weight characteristics of the copolymer during synthesis

Entry	$\tau^a$ /min	Yield <sup>b</sup> (%)	$M_{\min}$	$M_n \cdot 10^{-3}$
1	20	5–10	360	—
2	30	10–15	420	—
3	40	30–32	420	14
4	50	35–37	460	15
5	60	42–45	530	20
6	120	50–54	540	24
7	240	63–65	780	37

<sup>a</sup> Duration of the synthesis.<sup>b</sup> Yield on the active monomer.

is a characteristic feature of pseudo-living processes. Naturally, the curve of this dependence does not pass through zero, as is the case with "ideal" pseudo-living polymerization, as for styrene for example,<sup>7</sup> because the formation of the "dead" BA-VBE copolymer occurs before a conversion of ~40%. It should also be noted that the conversion of monomers increases during the first step of the synthesis (to 40–50 min) much more rapidly than during the subsequent time. This is related to the predominant formation of the "dead copolymer" while the system contains active radicals  $R^\cdot$  and  $RO^\cdot$ .<sup>1</sup> The graphical dependence of the conversion of monomers on the synthesis duration (Fig. 3) demonstrates that the curve has an inflection point at a conversion of ~40–45%. This fact, which indicates an increase in the copolymer mass along with an increase in the  $M_n$  values (see Fig. 2), confirms the transition to the formation of macromolecules mainly by the dissociation-combination mechanism, since the low polymer formation rates and the linear dependence of  $M_n$  on conversion are signs of pseudo-living polymerization.<sup>7,8</sup>

When investigating trialkylboranes as initiators of radical (co)polymerization, it was found<sup>9,10</sup> that for a number of monomer pairs (BA—methacrylic acid,

**Fig. 2.** Dependence of  $M_n$  on the conversion of monomers ( $P$ ) during the synthesis of the BA-VBE copolymers by the "compensating" method in the presence of TEB.**Fig. 3.** Dependence of the conversion of monomers ( $P$ ) on the duration of the BA-VBE copolymer synthesis obtained by the "compensating" method in the presence of TEB.

methyl methacrylate—allyl chloride, *etc.*) they are able to exert a noticeable effect on the relative activity of monomers, and, accordingly, on the composition of copolymers due to the participation of the boron atom in the coordination interactions with monomers and radicals. In particular, in the case of the pair BA—methacrylic acid, a copolymer with a uniform composition is observed on a large portion of the composition of monomers curve.<sup>10</sup> In this regard, it was necessary to determine the relative activities of BA and VBE monomers when initiating the process by systems containing TAB compared to those initiated by AIBN. The calculations using the Kelen—Tudos method were carried out based on the dependences of the composition of copolymers on the monomer mixture composition over a wide range of ratios. The relative activities of BA and VBE for copolymerization initiated by trialkylborane in the presence of small amounts of air oxygen under comparable conditions, calculated for the first time, were found to be similar to those for the process in the presence of AIBN: for VBE in all the cases they are close to 0, for BA they are  $1.45 \pm 0.07$  and  $1.50 \pm 0.08$  for TEB and AIBN, respectively (the published result for AIBN is  $1.40 \pm 0.05$ <sup>11</sup>). The obtained results indicate that there is no noticeable influence of the complexation of monomers and radicals with trialkylborane on copolymer composition under the conditions in question.

For all the samples of copolymers synthesized in the presence of TEB, the composition and the structure of the macromolecular chain were determined by IR and <sup>13</sup>C NMR spectroscopy, respectively. All the samples were found to have a virtually equimolar composition (the content of BA is 51–52% after the end of BA dosing and increases up to no more than 60% when the process is continued for 4 hours) and a copolymer structure similar to an alternating one. The <sup>13</sup>C NMR spectra of the BA-VBE copolymer synthesized in the presence of TEB are identical to those of the alternating BA-VBE copolymer obtained using AIBN as the initiator.<sup>1</sup> This is quite expected, since it is known<sup>8</sup> that the relative activities of monomers during copolymerization under conditions of a pseudo-living process do not differ from those of ordinary radical copolymerization.

In conclusion, it was established that the formation of macromolecules occurs along two paths during radical "compensating" copolymerization of butyl acrylate with refluxing vinyl butyl ether in the presence of triethylborane: according to the usual radical mechanism and by dissociation-combination. Moreover, the contribution of the second process increases with conversion, as evidenced by the shift of the MWD curve of the first mode toward the region of larger molecular masses and the increase in the copolymer weight. The calculated relative activities of butyl acrylate and vinyl butyl ether for copolymerization initiated by triethylborane in the presence of small amounts of air oxygen coincided with these values obtained in the presence of AIBN. This allowed us to conclude that complexation did not affect copolymer composition. Therefore, it is precisely the "compensating" copolymerization method that leads to a predominantly alternating structure of the synthesized copolymer of butyl acrylate with vinyl butyl ether.

### Experimental

Commercial VBE (Sigma-Aldrich, CAS N 111-34-2), BA (Sigma-Aldrich, CAS No. 141-32-2), TEB in complex with hexamethylene diamine (2TEB-GMDA) (Aviabor Ltd, lot No. 081301), methacrylic acid (MAA) (Sigma-Aldrich, CAS No. 79-41-4), and AIBN (Sigma-Aldrich, CAS No. 79-41-4) were used in the work. The copolymers were synthesized with boiling VBE (94 °C) in a four-neck flask placed in a thermostat and equipped with a reflux condenser, a paddle stirrer, a thermocouple, and a dropping funnel. The molar ratio BA : VBE was 1 : 4. The flask contained a solution of the 2TEB-GMDA complex in VBE, BA with a MAA additive, its molar amount proportional to the amount of amine, was dosed uniformly from the dropping funnel over 20 minutes. After the dosing, the stirring was continued over some time. After the completion of polymerization, the liquid fraction was distilled off. The obtained copolymer samples, which were a viscous mass, were dried, weighed, and the content of BA units was determined. Conversion was estimated gravimetrically using the dry residue.

To determine the relative activity of BA-VBE comonomers, they were synthesized from monomeric mixtures of various compositions in evacuated ampoules. In the case of TEB, the ampoules were filled following a certain sequence in order to prevent an uncontrolled proceeding of the process: the boramine complex, dissolved in one-half of the monomer mixture, was placed into an ampoule and frozen by being placed into a vessel with liquid nitrogen. Afterward, not allowing the contents to defreeze, the second half of the monomer mixture with MAA was added to the ampoule. Then, while preventing defreezing of the reaction mixture, the reagents were degassed to remove oxygen by evacuating the ampoules on a vacuum unit to a residual pressure of <1.3 Pa, following which the mixture was sealed. The synthesis was carried out to a conversion of 5–7% (at 20 °C). The process was terminated by refreezing the ampoule, then the ampoule was unsealed and, gradually heating, the excess of unreacted monomers was simultaneously pumped off. After drying, the conversion of monomers was

determined gravimetrically, and the polymer was recovered by dissolving in chloroform and transferring into a storage vial, followed by repeated drying in a vacuum oven.

When using AIBN as the initiator, the exact amounts of monomers and initiator were placed in glass ampoules, degassed to remove oxygen, freezing the reaction mixture in liquid nitrogen and evacuating to a residual pressure of <1.3 Pa on a vacuum unit. The ampoules were sealed and polymerization was carried out at an exactly set temperature. To accomplish this, the ampoule was placed in a thermostat for a predetermined period of time, after which it was removed and frozen in liquid nitrogen in order to terminate the polymerization. The synthesis was carried out to a conversion of 5–7% (at 60 °C). In order to purify the synthesized copolymers from the residue of monomers, the samples were transferred to pre-weighed beakers and dried under reduced pressure to a constant weight.

The relative activities were calculated using the Kelen–Tudos<sup>12</sup> method in accordance with the Eqs (1–5).

$$\frac{[m_1]}{[m_2]} = \frac{[M_1]}{[M_2]} \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]}, \quad (1)$$

where  $m_1$  and  $m_2$  are the content of monomers in copolymer, mol.%;  $M_1$  and  $M_2$  are the content of monomers in the mixture, mol.%.

$$\eta = r_1 \xi - \frac{r_2}{\alpha} (1 - \xi), \quad (2)$$

where

$$\eta = \frac{([M_1]/[M_2])\{([m_1]/[m_2]) - 1\}}{[m_1]/[m_2]} : \left( \alpha + \frac{([M_1]/[M_2])^2}{[m_1]/[m_2]} \right), \quad (3)$$

$$\xi = \frac{([M_1]/[M_2])^2}{[m_1]/[m_2]} : \left( \alpha + \frac{([M_1]/[M_2])^2}{[m_1]/[m_2]} \right), \quad (4)$$

$$\alpha = \sqrt{\frac{\{([M_1]/[M_2])^2\}_{\min}}{[m_1]/[m_2]} : \frac{\{([M_1]/[M_2])^2\}_{\max}}{[m_1]/[m_2]}}, \quad (5)$$

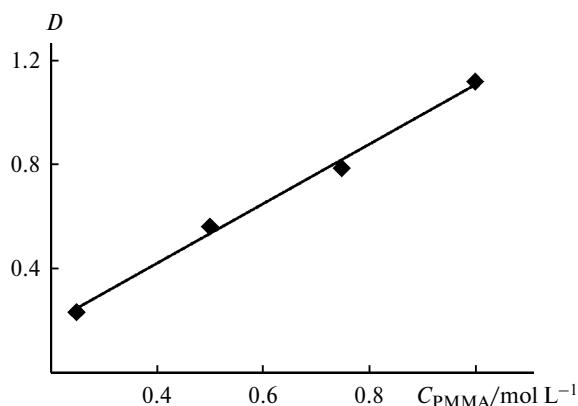


Fig. 4. Calibration graph for determining the composition of the alkyl (meth)acrylate copolymers by IR spectroscopy.

**Table 2.** Data for calculating relative activities using the Kelen—Tudos method

[M <sub>2</sub> ]	[M <sub>1</sub> ]	[m <sub>2</sub> ]	[m <sub>1</sub> ]	[M <sub>1</sub> ]/[M <sub>2</sub> ]	[m <sub>1</sub> ]/[m <sub>2</sub> ]	α	ξ	H
TEB + O <sub>2</sub>								
20	80	13.9	86.1	4.00	6.19	0.164	0.94	1.22
50	50	27.5	72.5	1.00	2.64	0.164	1.00	1.64
60	40	34.4	65.6	0.67	1.91	0.164	0.59	0.80
70	30	38.8	61.2	0.43	1.58	0.164	0.41	0.56
80	20	39.0	61.0	0.25	1.56	0.164	0.20	0.44
90	10	45.8	54.2	0.11	1.18	0.164	0.06	0.10
AIBN								
50	50	27.9	72.1	1.00	2.58	0.066	0.85	1.35
60	40	34.0	66.0	0.67	1.94	0.066	0.78	1.10
70	30	39.1	60.9	0.43	1.56	0.066	0.64	0.83
80	20	44.6	55.4	0.25	1.24	0.066	0.43	0.42
90	10	47.6	52.4	0.11	1.10	0.066	0.15	0.13

Notations: M<sub>1</sub> is BA, M<sub>2</sub> is VBE.

Different ratios of monomers in the initial mixture were used during the study (Table 2).

The composition of the BA-VBE copolymers was determined by the content of the BA units. IR spectra of the synthesized copolymers were recorded on a Shimadzu FTIR-8400S IR Fourier-transform spectrophotometer in 0.26-mm path-length cells (KBr) in chloroform solutions. The content of BA in copolymer was calculated according to the calibration curve (Fig. 4), taking into account the difference in the molecular masses of BA and methyl methacrylate, the optical density was calculated using the intensity of the carbonyl group vibration peak (1727 cm<sup>-1</sup>). The obtained results are presented in Table 2. Relative activities were calculated by linearizing the composition equation, while the α factor was used to account for the degree of scatter of the experimental data.

<sup>13</sup>C NMR spectra of copolymers dissolved in CDCl<sub>3</sub> were recorded on a Bruker DPX-200 instrument.

The molecular weight characteristics were determined by GPC on a setup with a set of five styrogel columns with pore diameters of 10<sup>5</sup>, 3·10<sup>4</sup>, 10<sup>4</sup>, 10<sup>3</sup>, and 250 Å (Waters, USA). An R-403 differential refractometer (Waters) was used as the detector. The eluent was tetrahydrofuran. Narrow-dispersed polystyrene standards were used for the calibration.<sup>13</sup> The recalculation of the MW values on the polystyrene samples to the copolymer of BA with VBE was carried out using the BA coefficients and the standard formulas.<sup>13</sup>

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## References

1. M. Yu. Zaremski, E. S. Garina, M. E. Gurskii, Yu. N. Bubnov, *Polym. Sci., Ser. B*, 2013, **55**, 304.
2. L. L. Semenycheva, V. V. Vins, E. I. Bogatova, E. V. Malysheva, G. V. Khoroshen'kov, E. A. Zav'yalova, A. S. Shavyrin, A. A. Moikin, *Russ. J. Appl. Chem.*, 2009, **82**, 1644.
3. E. V. Geras'kina, A. A. Moykin, L. L. Semenycheva, *Vestn. Kazansk. tekhnol. un-ta [Bull. Kazan Technol. Univ.]*, 2015, **18**, 28 (in Russian).
4. L. L. Semenycheva, E. V. Geras'kina, Yu. O. Matkivskaya, A. A. Moikin, Yu. A. Kurskii, *Russ. J. Appl. Chem.*, 2015, **88**, 1686.
5. L. L. Semenycheva, Yu. L. Kuznetsova, E. V. Geraskina, Yu. O. Matkivskaya, A. A. Moikin, *Bull. South Ural State University, Ser. Chem.*, 2015, **7**, 59.
6. Yu. O. Matkivskaya, E. P. Chukhmanov, T. I. Liogon'kaya, A. A. Moykin, L. L. Semenycheva, *Izv. VolgGTU [Bull. Volgograd State Technol. Univ.]*, 2015, **7**, 92 (in Russian).
7. G. V. Korolev, A. P. Marchenko, *Russ. Chem. Rev.*, 2000, **69**, 409.
8. M. Yu. Zaremski, V. B. Golubev, *Polym. Sci., Ser. C*, 2001, **43**, 81.
9. D. F. Grishin, L. L. Semenycheva, *Russ. Chem. Rev.*, 2001, **70**, 425.
10. D. F. Grishin, A. A. Moikin, *Polym. Sci., Ser. A*, 1997, **39**, 180.
11. B. A. Zhubanov, E. M. Shaykhutdinov, E. F. Osadchaya, *Prostyie vinilovyye efiry v radikal'noy polimerizatsii [Vinyl Ethers in Radical Polymerization]*, Nauka, Alma-Ata, 1985, 160 pp. (in Russian).
12. F. Tudos, T. Kelen, T. Foldes-Bereznykh, B. Turcsanyi, *React. Kinet. Catal. Lett.*, 1975, **2**, 439.
13. B. G. Belen'kiy, L. Z. Vilenchik, *Khromatografiya polimerov [Chromatography of Polymers]*, Khimiya, 1978, 344 pp. (in Russian).

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