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## MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

# A New Procedure for Preparing Butyl Acrylate–Vinyl *n*-Butyl Ether Copolymer as Effective Thickening Additive to Oils

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**Abstract**—The possibility of preparing copolymers by radical copolymerization on adding an active monomer, butyl acrylate, to refluxing inactive vinyl *n*-butyl ether was examined. The copolymer composition was studied by IR and NMR spectroscopy and by gravimetric analysis. The molecular weight and polydispersity coefficient of the copolymer were determined.

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Interest in copolymers as new polymeric materials, in particular, for use as additives to oils considerably increased in the past decades [1–5]. This is caused by new requirements to the quality and assortment of lubricating materials. In their production, synthetic primary materials find growing use along with mineral oils. Synthetic materials are more heat-resistant and ensure longer service life of the lubricating material. The most widely used are ester bases such as dioctyl sebacate (DOS) [1, 6] and oils based poly-α-olefins (PAO) [1, 7]. An urgent problem is ensuring compatibility of polymeric thickening additives with the basic materials.

It is known [1] that poly(meth)acrylate additives are better compatible with esters, whereas polymers based on vinyl butyl ether are better compatible with mineral oils. We have shown previously [8] that copolymers of butyl acrylate (BA) with vinyl n-butyl ether (VBE), prepared from the monomer mixture in evacuated ampules, in contrast to BA homopolymer, dissolve in DOS (homopolymerization of BA yields a cross-linked insoluble polymer [9, 10]) and can be used for thickening of DOS-based oils. Synthesis of the copolymer by adding acrylate into vinyl-*n*-butyl ether appeared to be considerably more feasible. The procedure allowed preparation of copolymers soluble both in synthetic oil bases (DOS, PAO) and in mineral oils, e.g., in AU [1, 11], AMG-10 [1, 12], I-20 [1, 13], and VMGZ [1, 14]. Copolymer concentrations as high as 10% can be attained. The copolymers can be used as effective thickening additives to mineral, synthetic, and semisynthetic oils. Furthermore, they exhibit high resistance to mechanical degradation in use [15].

Here we report the conditions for preparing a BA–VBE copolymer readily soluble in mineral and synthetic oils. We determined the copolymer composition by IR and NMR spectroscopy and by gravimetric analysis. We also evaluated the molecular-weight characteristics of the copolymer and its thickening ability.

## EXPERIMENTAL

In our study we used commercial VBE [16], BA [17], and azobis(isobutyronitrile) (AIBN) [18].

Polymerization was performed in a flask equipped with a reflux condenser. The copolymer was prepared

**Table 1.** Properties of BA–VBE copolymers prepared by adding BA to VBE, with AIBN initiator (0.15%)

| Sample no. | Initial weight ratio of monomers, BA/VBE | Time of adding acrylate, min | Content of acrylate units, mol %, determined by | | |
|---|---|---|---|---|---|
| | | | gravimetry | IR spectroscopy | NMR spectroscopy |
| 1 | 18/82 | 7 | 47 | 43 | 47 |
| 2 | 19/81 | 9 | 46 | 41 | – |
| 3 | 19/81 | 20 | 46 | 41 | – |
| 4 | 20/80 | 30 | 46 | – | – |

by two procedures: by the traditional procedure from the mixture of the monomers and AIBN initiator [10] at the boiling point of VBE until intense boiling of the ether ceased (~1 h, procedure 1) and by dropwise addition of a solution of AIBN in BA from a dropping funnel to refluxing VBE, followed by stirring for additional 20 min (procedure 2). After the polymerization completion, the liquid phase was distilled off. The resulting copolymer samples (viscous oil) were dried, weighed, and analyzed chromatographically for the BA content [19]. In all the cases, BA was quantitatively (to >99%) incorporated in the copolymer prepared by procedure 2. The conversion was estimated gravimetrically from the weight of the dry residue.

The composition of the copolymer prepared by procedure 2 was calculated from the results of gravimetric monitoring and from the IR and NMR data.

By IR spectroscopy, the composition of the VBE–BA copolymer was determined from the content of BA units. The spectra were taken with an Infrolyum-FI-801 spectrometer from chloroform solutions using KBr cells (layer thickness 0.51 mm). The BA content of the copolymer was calculated from the area of the characteristic vibration band of the carbonyl group (1727 $cm^{-1}$), using a calibration plot.

By NMR spectroscopy, the copolymer composition was calculated from the ratio of the integral intensities of the signals at $\delta$ = 3.31 and 4.02 ppm, belonging to $OCH_2$ protons in the butoxy groups of the ether and ester units, respectively. The spectra were taken with a Bruker DPX-200 spectrometer from $CDCl_3$ solutions.

The molecular-weight characteristics were determined by gel permeation chromatography (GPC) on a device equipped with a set of five Styrogel columns with the pore diameters of $10^5$, $3 \times 10^4$, $10^4$, $10^3$, and 250 Å (Waters, USA). An R-403 differential refracttometer (Waters) was used as detector. The eluent was tetrahydrofuran. Calibration was performed with close-cut polystyrene references [20]. Conversion of the molecular weights M from polystyrene references to BA–VBE copolymers was made by standard formulas using appropriate coefficients [20].

The kinematic viscosity of polymer solutions was determined with a VPZh-4 viscometer by the standard procedure [21]. The mechanical stability of the polymer was evaluated by monitoring changes in the viscosity of the oil base thickened by the polymer after ultrasonic treatment in accordance with GOST (State Standard) 6794–75 [12].

It is known [10] that the copolymer composition at radical initiation is determined by relative activities of the monomers. In each moment of the polymerization, the copolymer composition is determined by the running composition of the monomer mixture. When the relative activities of the monomers differ significantly, the copolymer is formed at a high rate in an excess of the active monomer, and it is enriched in the active monomer. The copolymer with a high content of inactive monomer fragments can be obtained in an excess of the inactive monomer. In this case, the copolymerization is slow, and the limiting conversion is low.

**Table 2.** Molecular-weight characteristics of BA–VBE copolymers

| Sample no. | $M_n \times 10^{-3}$ | $M_w \times 10^{-3}$ | $M_w/M_n$ |
|---|---|---|---|
| 1 | 18 | 55 | 3.1 |
| 2 | 17 | 47 | 2.8 |
| 3 | 16 | 46 | 2.9 |
| 4 | 18 | 50 | 2.8 |

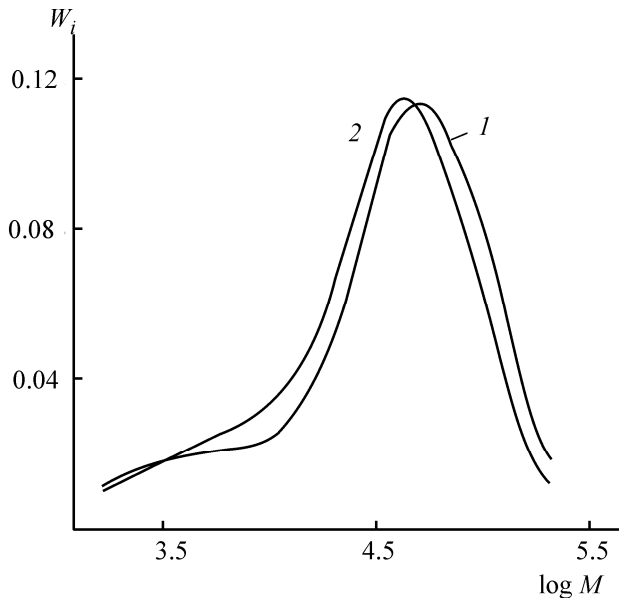
**Table 3.** Results of measuring the viscosity of DOS solutions with additives after ultrasonic treatment

| Run no. | Additive | | Viscosity at 100°C, cSt | | Degree of degradation, % |
|---|---|---|---|---|---|
| | composition | content, wt % | before treatment | after treatment | |
| 1 | BA–VBE copolymer[a] | 15 | 11.35 | 10.56 | 7 |
| 2 | BA–VBE copolymer[b] | 12 | 11.10 | 8.55 | 23 |
| | PMA V-2 | 7 | 12.41 | 4.84 | 61 |
| | Viscoplex 7-610 | 10 | 8.86 | 5.05 | 43 |
| | Vinipol VB-2 | 10 | 11.74 | 8.45 | 28 |
| | Izopol | 10 | 14.97 | 9.58 | 36 |

[a] Prepared by the newly developed procedure. [b] Prepared from the monomer mixture.

To prepare a BA–VBE copolymer with a high VBE content, we suggested to gradually add the active monomer, BA, to the inactive monomer, VBE, at the VBE boiling point (procedure 2). In this case, the acrylate at any moment of the process is in deficiency, i.e., conditions are provided for preparing a polymer with a high VBE content from the pair active monomer–inactive monomer.

This procedure allowed preparation within less than 1 h of compositionally uniform copolymers in a quantitative yield with respect to the active monomer (Table 1). This is indicated by the results of determination of the residual monomer, of gravimetric monitoring, and of IR and NMR determination of the copolymer composition (Table 1). The ratio of the ether and ester units in the copolymer is close to 50 : 50.




MWD curves for VBE–BA copolymer. ($W_i$) Fraction of polymer and ($M$) molecular weight. Curve nos. correspond to sample nos. in Table 1.

Analysis of the molecular-weight characteristics of the copolymers showed that, for the samples obtained, the molecular-weight distribution (MWD) curves are unimodal and differ from each other insignificantly. Therefore, in the figure we give only the curves for sample nos. 1 and 2 as examples. As can be seen, the curves have a low-molecular-weight shoulder, although the polydispersity coefficients $M_w/M_n$ (Table 2) in all the cases are lower than 3 ($M_w$ is weight-average, and $M_n$, number-average molecular weight). This fact indicates that the copolymers are uniform with respect to $M$. As seen from Table 2, BA–VBE copolymers have low $M$ values ($M_n$ = 16000–18000) compared to those of polyacrylates obtained at the same temperature ($M_n$ > 1000000) [10, 22]. This is one of the causes of good solubility of the copolymers in various materials for oil compounding. It should be noted that, in preparation of acrylate additives to oils, chain-transfer agents are added to the polymerizing mixture with the aim to decrease the molecular weight [1–5, 9]. In our case, this is unnecessary, which is a significant advantage of the procedure that we suggested for preparing the copolymer additive.

It should be noted in conclusion that the BA–VBE copolymer prepared by adding an unsaturated ester to an unsaturated ether is, as already noted, a copolymer with virtually equal content of the ether and ester units and, most probably, with alternating structure (according to [23], the VBE radical does not add to VBE, and its relative activity in the BA–VBE pair is close to zero). This is particularly important in the

context of using the copolymer as an additive to hydraulic oils based on mineral and synthetic oils, because alternation of the ether and ester groups in the polymer enhances the macromolecule stability. This is indicated by the results of testing the resistance of the copolymer to mechanical degradation.

As seen from Table 3, after ultrasonic treatment of a solution of the copolymer in DOS base, the sample prepared by adding the active monomer to the inactive monomer shows considerably smaller decrease in the kinematic viscosity, as compared to the sample prepared under the comparable conditions from a BA : VBE = 20 : 80 monomer mixture and having the structure of a gradient copolymer [1, 10], and also to commercial thickening additives [1] [polyalkyl acrylate PMA V-2, Viscoplex 7-610, poli(vinyl butyl ether) (Vinipol VB 2), and poly(vinyl isobityl ether) (Izopol)]. This fact, confirmed by a series of experiments, is of indubitable interest for the development of formulations of new thickened oils resistant to mechanical degradation.

## CONCLUSIONS

(1) Synthesis of a butyl acrylate–vinyl n-butyl ether copolymer by adding the acrylate to the ether occurs at a high rate.

(2) As shown by IR and NMR spectroscopy and by gravimetric analysis, the content of the ether and ester units in the copolymer is virtually equal.

(3) The number-average molecular weight of the synthesized butyl acrylate–vinyl *n*-butyl ether copolymer is about 16000–18000, and its molecular-weight distribution curves are unimodal.

(4) Butyl acrylate–vinyl *n*-butyl ether copolymers in dioctyl sebacate solutions show higher resistance to mechanical degradation than the known commercial thickening additives.

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