

## Functional Acetal Methacrylates: III.\* Electrophilic Addition of Diols to 2-(Vinyl-oxo)ethyl Methacrylate

O. V. Vysotskaya, L. A. Oparina, L. N. Parshina, N. K. Gusarova,  
and B. A. Trofimov

Faworsky Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, 664033 Russia

Received January 23, 2002

**Abstract**—Reactions of 2-(vinyl-oxo)ethyl methacrylate with diols [ethylene glycol, diethylene glycol, triethylene glycol, oligoethylene glycol-400, Z-2-butene-1,4-diol, 2-butyne-1,4-diol, 1,1,3,3-tetramethyl-1,3-bis(3-hydroxypropyl)disiloxane, 2,2-bis(4-hydroxyphenyl)propane] and polyols (glycerol, pentaerythritol) under electrophilic conditions (1 wt% of  $\text{CF}_3\text{COOH}$ , 20–60°C, 1–3 h) result in quantitative formation of functional acetal methacrylates.

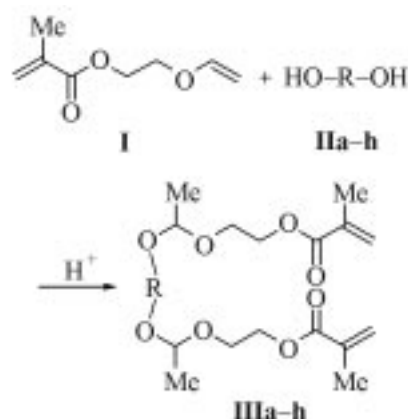
Oligomeric acrylates find wide application as adhesives, sealants, and binders [2, 3]. From copolymers of oligomeric methacrylates of various structures are prepared membranes permeable for urea and water [2, 4] or used for separation of cations [5], contact lenses and other materials for medicinal applications [6–11]. The most common procedure for preparation of acrylic esters is based on esterification of compounds containing two and more hydroxy groups with  $\alpha,\beta$ -unsaturated monocarboxylic acids or derivatives thereof [2].

Vinyl-oxoethyl methacrylates are highly reactive bifunctional monomers and semiproducts possessing both properties of vinyl ethers [12] and methacrylates [2, 4]. They are promising building blocks for creating new types of acrylate monomers.

Vinyl-oxoethyl methacrylates under mild conditions (1–2% of  $\text{CF}_3\text{COOH}$ , 20–40°C, 0.5–2 h) undergo addition of alcohols of various structures at the vinyl-oxo group giving rise to a new type of polyfunctional acetal methacrylate monomers [1] where the vinyl-oxo group plays the role of an “anchor” function. The specific role of trifluoroacetic acid in electrophilic addition to the vinyl-oxo group was first demonstrated by the example of alcohols reaction with functional vinyl ethers: 1-(vinyl-oxo)propylene-2,3-oxide, 3-(2-(vinyl-oxo)ethoxy)propylene 1,2-carbonate, 2-(vinyl-oxo)ethyl isothiocyanate. There-with acyloxy group is selectively substituted in the intermediately formed acylal [13–16].

In order to extend the synthetic potential of vinyl-oxoethyl methacrylates as “anchor” methacrylates and aiming at preparation of new bis- and polyacetal methacrylate monomers we investigated the reaction of an available 2-(vinyl-oxo)ethyl methacrylate [17–20] with various diols and polyols. We used here an approach developed earlier and systematically applied as an example to the new strategy of epoxy resins preparation by electrophilic addition of diols, polyols, di- and polycarboxylic acids and the other polyfunctional reagents to the “anchor” vinyl-oxoepoxides, for instance, to vinyl-oxoethoxymethyl-oxirane (“vinyl-oxo”) [21–24].

Scheme 1.



R =  $(\text{CH}_2)_2$  (**IIa**, **IIIa**);  $(\text{CH}_2)_2\text{O}(\text{CH}_2)_2$  (**IIb**, **IIIb**);  $(\text{CH}_2\text{CH}_2\text{O})_2(\text{CH}_2)_2$  (**IIc**, **IIIc**);  $(\text{CH}_2\text{CH}_2\text{O})_n(\text{CH}_2)_2$  ( $n \approx 7$ ) (**IId**, **IIId**); Z- $\text{CH}_2\text{CH}=\text{CHCH}_2$  (**IIe**, **IIIe**);  $\text{CH}_2\text{C}\equiv\text{CCH}_2$  (**IIf**, **IIIf**);  $[(\text{CH}_2)_3\text{SiMe}_2]_2\text{O}$  (**IIg**, **IIIg**);  $\text{Me}_2\text{C}(\text{C}_6\text{H}_4)_2$  (**IIh**, **IIIh**).

\* For communication II, see [1].

**Table 1.** Yield and characteristics of acetal methacrylates **IIIa-h**, **IVa, b**

Compd. no.	Yield, % <sup>a</sup>	$n_D^{20}$	Found, %		Formula	Calculated, %	
			C	H		C	H
<b>IIIa</b>	94	1.4552	57.38	8.13	C <sub>18</sub> H <sub>30</sub> O <sub>8</sub>	57.74	8.07
<b>IIIb</b>	96	1.4578	57.67	7.92	C <sub>20</sub> H <sub>34</sub> O <sub>9</sub>	57.40	8.18
<b>IIIc</b>	94	1.4574	57.41	8.28	C <sub>22</sub> H <sub>38</sub> O <sub>10</sub>	57.15	8.28
<b>III d</b>	98	1.4590	56.45	8.64	C <sub>32</sub> H <sub>58</sub> O <sub>15</sub>	56.29	8.56
<b>III e</b>	96	1.4620	59.59	8.42	C <sub>20</sub> H <sub>32</sub> O <sub>8</sub>	59.98	8.05
<b>III f</b>	94	1.4668	59.95	7.96	C <sub>20</sub> H <sub>30</sub> O <sub>8</sub>	60.29	7.59
<b>III g<sup>b</sup></b>	95	1.4478	55.62	9.26	C <sub>26</sub> H <sub>50</sub> O <sub>9</sub> Si <sub>2</sub>	55.48	8.95
<b>III h</b>	92	1.5152	68.54	7.09	C <sub>31</sub> H <sub>40</sub> O <sub>8</sub>	68.87	7.46
<b>IVa</b>	97	1.4532	58.65	8.10	C <sub>27</sub> H <sub>44</sub> O <sub>12</sub>	58.84	7.91
<b>IVb</b>	98	1.4644	58.61	8.01	C <sub>37</sub> H <sub>60</sub> O <sub>16</sub>	58.41	7.95

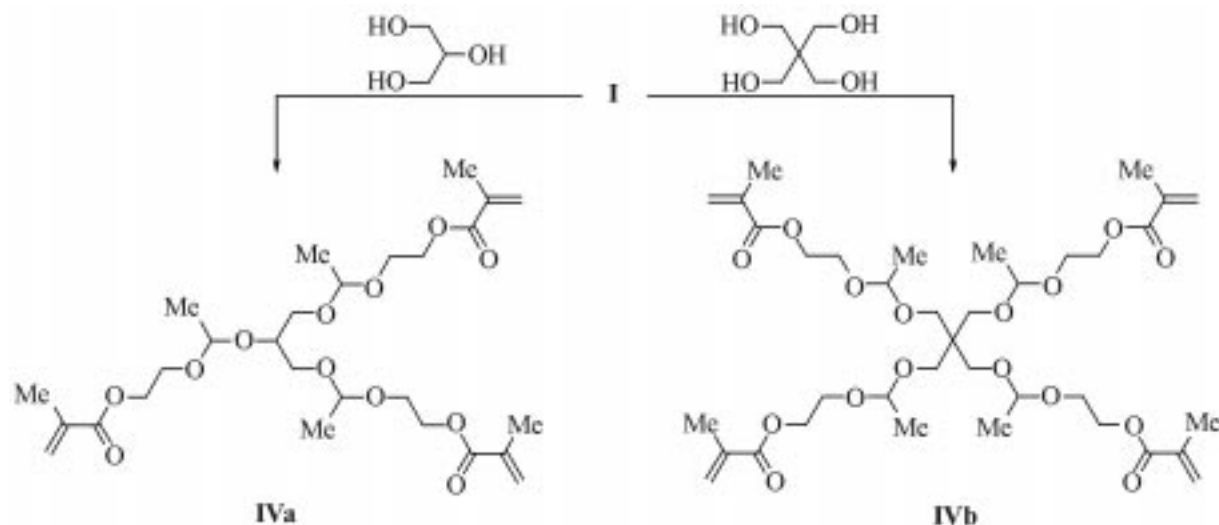
<sup>a</sup> Preparative yield is reported. <sup>b</sup> Found, %: Si 9.63. Calculated, %: Si 9.98.

Ethylene glycol, diethylene glycol, triethylene glycol, oligoethylene glycol of molecular weight 400, Z-2-butene-1,4-diol, 2-butyne-1,4-diol, 1,1,3,3-tetra-methyl-1,3-bis(3-hydroxypropyl)disiloxane, 2,2-bis-(4-hydroxyphenyl)propane] quantitatively, regio- and chemoselectively react with 2-(vinyloxy)ethyl methacrylate at molar ratio 1 : 2 under mild conditions (1 wt% of CF<sub>3</sub>COOH, 20–60°C, 1–3 h) furnishing the corresponding bisacetal methacrylates **IIIa-h** (Scheme 1, Table 1).

The monitoring of the reaction progress was performed by IR and <sup>1</sup>H NMR spectra of the reaction mixture. In the IR spectra gradually changed the pattern of the characteristic absorption bands of the vinyloxy group: the low- and high-frequency

components of the triplet band from the stretching vibrations of C=C bond (1620, 1645 cm<sup>-1</sup>), from =C–H bond (3046, 3080 cm<sup>-1</sup>) disappear, and the absorption bands in the region of the bending vibrations of =CH and =CH<sub>2</sub> bonds undergo considerable redistribution (815, 960, 1320 cm<sup>-1</sup>) [12, 25]. The intensity of the middle component of the triplet band at 1637 cm<sup>-1</sup> coinciding with the band of stretching vibrations of the C=C bond in the methacrylate group is somewhat reduced. In the region 1040–1170 cm<sup>-1</sup> appears a characteristic group of five bands belonging to acetals [26].

In the <sup>1</sup>H NMR spectra of reaction mixtures an only quartet of methine proton (δ 4.7–5.4 ppm) and an only doublet of the methyl group (δ 1.2–1.3 ppm)

**Scheme 2.**

**Table 2.** Spectral characteristics of adducts of diols and polyols with 2-(vinylxy)ethyl methacrylate **IIIa-h**, **IVa, b**

Compd. no.	IR spectrum, cm <sup>-1</sup>						
<b>IIIa</b>	519, 594, 655, 815, 858, 878, 944, 963, 1005, 1045, 1078, 1098, 1139, 1170, 1246, 1297, 1320, 1339, 1385, 1405, 1454, 1638, 1719, 2882, 2930, 2957, 2987, 3106						
<b>IIIb</b>	516, 598, 656, 815, 859, 944, 962, 1004, 1043, 1078, 1103, 1139, 1170, 1247, 1297, 1320, 1339, 1385, 1402, 1454, 1637, 1719, 2877, 2929, 2987, 3107						
<b>IIIc</b>	517, 537, 596, 654, 719, 815, 859, 941, 961, 1004, 1043, 1078, 1103, 1140, 1170, 1247, 1297, 1319, 1341, 1384, 1402, 1454, 1637, 1720, 2868, 2928, 2937, 3104						
<b>IIId</b>	520, 656, 718, 816, 857, 956, 1004, 1043, 1077 sh, 1106, 1138, 1166, 1248, 1297, 1320, 1348, 1384, 1405, 1453, 1637, 1718, 2875, 2984, 3100						
<b>IIIe</b>	518, 602, 655, 815, 881, 938, 960, 1041, 1080 sh, 1098, 1137, 1170, 1245, 1297, 1321, 1342, 1387, 1400 sh, 1453, 1638, 1720, 2882, 2929, 2988, 3105						
<b>IIIf</b>	517, 604, 655, 815, 864, 883, 936, 958, 1024, 1043, 1070 sh, 1094, 1138, 1170, 1246, 1297, 1320, 1339, 1388, 1402, 1453, 1638, 1720, 2882, 2928, 2988, 3105						
<b>IIIg</b>	518, 535, 658, 705, 796, 812, 840, 939, 958, 1048, 1073, 1099, 1137, 1169, 1254, 1297, 1320, 1340, 1387, 1403, 1453, 1638, 1721, 2874, 2932, 2955, 2987, 3107						
<b>IIIh</b>	555, 579, 602, 653, 737, 814, 835, 942, 1013, 1055, 1083, 1104, 1133, 1169, 1239, 1296, 1319, 1345, 1386, 1453, 1507, 1581, 1607, 1637, 1719, 2875, 2930, 2965, 3036, 3100						
<b>IVa</b>	517, 603, 654, 815, 865, 940, 961, 1006, 1043, 1076, 1097, 1118, 1140, 1170, 1245, 1297, 1319, 1339, 1385, 1405, 1453, 1638, 1719, 2879, 2930, 2957, 2988, 3105						
<b>IVb</b>	519, 595, 654, 815, 883, 940, 960, 1002, 1045, 1072 sh, 1097, 1139, 1169, 1246, 1297, 1319, 1342, 1382, 1402, 1453, 1504, 1638, 1720, 2885, 2930, 2957, 2987, 3105						
Compd. no.	<sup>1</sup> H NMR spectrum, CDCl <sub>3</sub> , δ, ppm ( <i>J</i> , Hz)						
	OCHO, q ( <sup>3</sup> <i>J</i> )	Me, d ( <sup>3</sup> <i>J</i> )	=CH <sub>2</sub>	Me-C=, br.s	CH <sub>2</sub> OC(O), m	CH <sub>2</sub> O, m	R
<b>IIIa</b>	4.79 (5.4)	1.30 (5.4)	5.55 d.q ( <i>trans</i> , <sup>2</sup> <i>J</i> , <sup>4</sup> <i>J</i> 1.6), 6.10 br.s ( <i>cis</i> )	1.93	4.26	3.71, 3.80 (1H each)	3.60 m, 3.69 m (1H each, OCH <sub>2</sub> )
<b>IIIb</b>	4.79 (5.4)	1.30 (5.4)	5.54 d.q ( <i>trans</i> , <sup>2</sup> <i>J</i> , <sup>4</sup> <i>J</i> 1.6), 6.09 br.s ( <i>cis</i> )	1.93	4.26	3.70, 3.77 (1H each)	3.58 m, 3.69 m (2H each, OCH <sub>2</sub> )
<b>IIIc</b>	4.78 (5.2)	1.30 (5.2)	5.55 d.q ( <i>trans</i> , <sup>2</sup> <i>J</i> , <sup>4</sup> <i>J</i> 1.6), 6.09 br.s ( <i>cis</i> )	1.93	4.26	3.69, 3.78 (1H each)	3.5 m, 3.69 m (3H each, OCH <sub>2</sub> )
<b>IIId</b>	4.78 (5.2)	1.30 (5.2)	5.55 br.s ( <i>trans</i> ), 6.10 br.s ( <i>cis</i> )	1.93	4.26	3.70, 3.80 (1H each)	3.65 m, 3.70 m (8H each, OCH <sub>2</sub> )
<b>IIIe</b>	4.80 (5.2)	1.32 (5.2)	5.57 br.s ( <i>trans</i> ), 6.12 br.s ( <i>cis</i> )	1.94	4.29	3.70, 3.79 (1H each)	4.13 d.t (2H, OCH <sub>2</sub> , <sup>3</sup> <i>J</i> 11.6, <sup>3</sup> <i>J</i> 3.9), 5.67 t (1H, CH=, <sup>3</sup> <i>J</i> 3.9)
<b>IIIf</b>	4.92 (5.4)	1.34 (5.4)	5.58 br.s ( <i>trans</i> ), 6.12 br.s ( <i>cis</i> )	1.95	4.29	3.78	4.25 m (2H, OCH <sub>2</sub> )
<b>IIIg</b>	4.74 (5.3)	1.30 (5.3)	5.56 br.s ( <i>trans</i> ), 6.12 br.s ( <i>cis</i> )	1.94	4.28	3.74, 3.81 (1H each)	0.05 m (6H, Me), 0.56 m (2H, CH <sub>2</sub> Si), 1.60 m (2H, CH <sub>2</sub> ), 3.40 m, 3.57 m (1H each)
<b>IIIh</b>	5.45 (5.2)	1.38 (5.2)	5.57 br.s ( <i>trans</i> ), 6.02 br.s ( <i>cis</i> )	1.90	4.20	3.72, 3.81 (1H each)	1.57 br.s (3H, Me), 6.88 d (2H, arom, <sup>3</sup> <i>J</i> 8.6), 7.09 d (2H, arom, <sup>3</sup> <i>J</i> 8.6)
<b>IVa</b>	4.81 (2H, 5.2), 5.01 (1H, 4.8)	1.30 (6H, 5.2), 1.36 (3H 4.8)	5.57 br.s ( <i>trans</i> ), 6.11 br.s ( <i>cis</i> )	1.93 (9H)	4.12–4.18 (1H each), 4.28 (4H)	3.73, 3.79, (3H each)	3.41–3.91 m (5H, OCH <sub>2</sub> , CHO)
<b>IVb</b>	4.68 (5.2)	1.25 (5.2)	5.56 br.s ( <i>trans</i> ), 6.10 br.s ( <i>cis</i> )	1.94	4.27	3.71, 3.80 (1H each)	3.53 m (2H, OCH <sub>2</sub> )

of the acetal fragment was observed indicating that dimethacrylates **IIIa-h** are the only products and form in the quantitative yield.

The rate of the electrophilic addition of alcohols to a definite vinyl ether depends on the inductive and steric effects of the substituent of the alcohol, and also on the characteristics of the medium (association of the alcohol, polarisability etc.) [27, 28]. In these reaction no significant influence of diol structure on the reaction duration was observed. Most of diols added to ether **I** within 1–1.5 h.

All other factors being equal the complete conversion of 2,2-bis(4-hydroxyphenyl)propane (**IIIh**) into bisacetal methacrylate was attained only in 3 h. It might however be caused by the fact that diol **IIIh** formed a suspension with ether **I**. Therefore the homogenization of the reaction mixture was attained by adding 1,2-dimethoxyethane as solvent. The same solvent was used with acetylene diol **IIe**.

Besides diols we involved into reaction with the vinyloxyethyl methacrylate also glycerol and pentaerythritol. The exhaustive electrophilic addition of these polyols to the vinyloxy group of ether **I** occurred in the presence of 1 wt% of  $\text{CF}_3\text{COOH}$  at the molar ratio ether **I**–glycerol 3:1 and ether **I**–pentaerythritol 4:1 (60°C, 1,2-dimethoxyethane) and completed in 3 h affording the corresponding methacrylates **IVa, b** in quantitative yield (Scheme 2).

Note that the disproportionation of target acetals observed at electrophilic addition of aliphatic alcohols to vinyloxyalkyl methacrylates [1] is not characteristic of acetals **IIIa-h, IVa, b**.

The acetal methacrylates synthesized **IIIa-h, IVa, b** are colorless moderately viscous fluids, well soluble in most organic solvents and insoluble in water. They are light-sensitive monomers and are capable of spontaneous polymerization yielding high-melting (>300°C) polymers. Therefore the storage of the acetals obtained is possible only with inhibitors (hydroquinone, ionol) preventing the spontaneous polymerization. The neutralization of the catalyst after completion of the synthesis was performed by addition to the reaction mixture of calcined  $\text{K}_2\text{CO}_3$ , and after standing for 1–2 h the mixture was filtered. The other way of catalyst neutralization consisted in passing the reaction mixture through a small bed of basic alumina using ethyl ether as eluent. The qualitative test of neutralization was disappearance in the IR spectrum of an absorption band at  $1780\text{ cm}^{-1}$  ( $\nu\text{ C=O}$  in  $\text{CF}_3\text{COOH}$ ).

The composition and structure of methacrylates synthesized are in agreement with the elemental analyses, IR and  $^1\text{H}$  NMR spectra (Tables 1, 2). In the IR spectra of acetals **IIIa-h, IVa, b** the absorption bands of the methacrylate groups are virtually independent of R structure (in the series of diols and polyols), and they appear at 859–883, 956–963, 1400–1405 ( $\delta\text{ CH}_2=$ ), 1637–1638 ( $\nu\text{ C=C}$ ), 1718–1721 ( $\nu\text{ C=O}$ ), 3000–3107 ( $\nu\text{ =CzH}_2$ )  $\text{cm}^{-1}$ . Similar conclusion follows from the analysis of  $^1\text{H}$  NMR spectra: The proton chemical shifts corresponding to the methacrylate groups in compounds **IIIa-h, IVa, b** are virtually constant and equal to 6.02–6.12 (*cis*-H), 5.51–5.58 (*trans*-H), 1.90–1.95 ppm (Me). The signals from groups OCHO and  $\text{CH}_3$  in acetals **IIIa-d** appear respectively at 4.78–4.79 and 1.30 ppm, whereas the quartet of the methine proton shifts downfield in acetal **IIIe** by  $\Delta\delta\text{H} \sim 0.13$  ppm, in acetal **IIIh** by 0.67 ppm, and in tetraakisacetal **IVb** the signal is displaced upfield by 0.1 ppm.

## EXPERIMENTAL

IR spectra were recorded on spectrometer Bruker JFS-25 from thin film.  $^1\text{H}$  NMR spectra were registered on spectrometer Bruker DPX-400 (400 MHz) in  $\text{CDCl}_3$  solutions, internal reference HMDS.

The initial diols and polyols were commercial products subjected to thorough drying before synthesis by known methods (distillation or recrystallization). Their physical constants were consistent with published data.

2-Vinyloxyethyl methacrylate (**I**) was prepared and purified as described in [19].

**Addition of diols to 2-(vinyloxy)ethyl methacrylate.** To a mixture of 1.56 g (0.01 mol) of vinyl ether **I** and 0.31 g (0.005 mol) of ethylene glycol was added 0.02 g (1 wt%) of trifluoroacetic acid. The mixture was stirred for 1.5 h till the absorption bands of vinyl ether **I** completely disappeared from the IR spectrum of the reaction mixture. The catalyst was neutralized by addition to the reaction mixture of 0.1 g of calcined  $\text{K}_2\text{CO}_3$ . The precipitate was filtered off after standing for 2 h. We obtained 1.75 g (94%) of bisacetal methacrylate **IIIa**.

Bisacetal methacrylates **IIIb-e, g** were obtained in the same way.

**Addition of 2-butyne-1,4-diol to 2-(vinyloxy)ethyl methacrylate.** To a solution of 0.43 g

(0.005 mol) of 2-butyne-1,4-diol in 2 ml of 1,2-dimethoxyethane was added 1.56 g (0.01 mol) of vinyl ether **I** and 0.02 g (1 wt% with respect to the reagents weight) of trifluoroacetic acid. The mixture was stirred for 1 h at room temperature till the absorption bands of vinyl ether **I** completely disappeared from the IR spectrum of the reaction mixture. The catalyst was neutralized with  $K_2CO_3$ . After the precipitate was filtered off and the solvent was removed in a vacuum we obtained 1.87 g (94%) of bisacetal methacrylate **III f**.

**Addition of 2,2-bis(4-hydroxyphenyl)propane to 2-(vinylloxy)ethyl methacrylate.** To a solution of 1.15 g (0.005 mol) of 2,2-bis(4-hydroxyphenyl)propane in 3 ml of 1,2-dimethoxyethane was added 1.56 g (0.01 mol) of vinyl ether **I** and 0.03 g (1 wt% with respect to the reagents weight) of trifluoroacetic acid. The mixture was stirred for 3 h at room temperature till the absorption bands of vinyl ether **I** completely disappeared from the IR spectrum of the reaction mixture. The catalyst was neutralized with  $K_2CO_3$ . After the precipitate was filtered off and the solvent was removed in a vacuum we obtained 2.5 g (92%) of bisacetal methacrylate **III h**.

**Addition of glycerol to 2-(vinylloxy)ethyl methacrylate.** To a solution of 0.28 g (0.0033 mol) of glycerol in 3 ml of 1,2-dimethoxyethane was added 1.56 g (0.01 mol) of vinyl ether **I** and 0.02 g (1 wt% with respect to the reagents weight) of trifluoroacetic acid. The mixture was stirred for 3 h at 60°C till the absorption bands of vinyl ether **I** completely disappeared from the IR spectrum of the reaction mixture. The catalyst was neutralized by passing the reaction mixture through a thin bed of basic  $Al_2O_3$  using ethyl ether as eluent. On removing the solvents in a vacuum we obtained 1.78 g (97%) of trisacetal methacrylate **IV a**.

Similarly from 0.3 g (0.0025 mol) of pentaerythritol in 3 ml of 1,2-dimethoxyethane and 1.56 g (0.01 mol) of vinyl ether **I** in the presence of 0.02 g (1 wt% with respect to the reagents weight) of trifluoroacetic acid we obtained 1.86 g (98%) of tetrakisacetal methacrylate **IV b**.

## REFERENCES

- Gorelova, O.V., Oparina, L.A., Parshina, L.N., Gusarova, N.K., and Trofimov, B.A., *Zh. Org. Khim.*, 2001, vol. 31, no. 12, pp. 1763–1768.
- Berlin, A.A., Korolev, G.V., Kefeli, T.Ya., and Sivergin, Yu.M., *Akrilovye oligomery i materialy na ikh osnove* (Acrylic Oligomers and Materials on Their
- Kikawa, H., Yamagishi, H., Suzuki, N., and Asao, Y., Japan Patent 0704701, 1995; *Chem. Abstr.*, 1997, vol. 124, 118275.
- Berlin, A.A. and Matveeva, N.G., *J. Pol. Science. Macromol. Rev.*, 1980, vol. 15, pp. 107–206.
- Aoyama, T., Hirai, O., Inoe, I., and Kumagai, H., Japan Patent 08081511, 1996; *Chem. Abstr.*, 1997, vol. 125, 35391.
- Masuhara, H., Masuhara, N., and Tarumi, J., Japan Patent 08119822, 1996; *Chem. Abstr.*, 1997, vol. 125, 123792.
- Kaetsu, I., Kumakura, M., Suyama, H., Kameda, N., and Kouyama, H., US Patent 4904708, 1988; *Ref. J. Khim.*, 1991, 5T434P.
- Bland, M.H. and Peppas, N.A., *Biomaterials*, 1996, vol. 17, no. 11, pp. 1109–1114; *Chem. Abstr.*, 1997, vol. 125, 67591.
- Pascual, B., Gurruchaga, M., Goni, I., Ginebra, M.P., Gil, F.J., Planell, J.A., Levenfeld, B., Vazquez, B., and San, R.J., *J. Mater. Sci.: Mater. Med.*, 1995, vol. 6, no. 12, pp. 793–798.
- Klee, J.F., Neidhart, F., Flammersheim, H.J., and Muelhapt, R., *Macromol. Chem. Phys.*, 1999, vol. 200, no. 3, pp. 517–523.
- Hirt, T., Baron, R.C., Lohmann, D., and Meier, W.P., *PCT Int. Appl. WO 9912059*, 1999; *Chem. Abstr.*, 1999, vol. 130, 227787.
- Trofimov, B.A., *Geteroatomnye proizvodnye atsetilena. Novye monomery, reagenty i poluprodukty* (Heteroatomic Acetylene Derivatives. New Monomers, Reagents and Semiproducts), Moscow: Nauka, 1981.
- Nedolya, N.A. and Trofimov, B.A., *Zh. Org. Khim.*, 1985, vol. 21, no. 2, pp. 271–275.
- Nedolya, N.A. and Trofimov, B.A., *Zh. Org. Khim.*, 1985, vol. 21, no. 4, pp. 705–755.
- Nedolya, N.A., Tatarova, T.F., and Trofimov, B.A., *Zh. Org. Khim.*, 1989, vol. 25, no. 4, pp. 721–724.
- Nedolya, N.A., Gerasimova, V.V., and Papsheva, N.P., *Zh. Org. Khim.*, 1989, vol. 25, no. 12, pp. 2501–2507.
- UK 976304, 1964; *Chem. Abstr.*, 1965, vol. 62, 11693.
- Trofimov, B.A., Lavrov, V.I., Alekankin, V.N., Stankevich, V.K., Maksimov, S.M., Grigorenko, V.I., Petrov, G.N., Rappoport, L.Ya., and Parshina, L.N., USSR Inventor's Certificate 771084, 1978; *SSSR Byull. Izobr.*, 1980, no. 38.
- Trofimov, B.A., Lavrov, V.I., Parshina, L.N., Alekankin V.N., Stankevich V.K., and Grigorenko V.I., *Zh. Org. Khim.*, 1982, vol. 18, no. 3,

- pp. 528–531.
20. Andrei, M., Marchese, L., Roggero, A., and Ferrari, M., US Patent 5264307, 1993; *Chem. Abstr.*, 1994, vol. 120, 147220b.
  21. Trofimov, B.A. and Nedolya, N.A., *Rev. Heteroatom Chem.*, 1993, no. 9, pp. 205–225.
  22. Nedolya, N.A., *Doctoral Sci. (Chem.) Dissertation*, Irkutsk, 1998.
  23. Trofimov, B.A., Nedolya, N.A., Khil'ko, M.Ya., Vyalykh, E.P., Mironov, G.S., and Moskvichev, Yu.A., USSR Inventor's Certificate 751811 1978; *SSSR Byull. Izobr.*, 1980, no. 28.
  24. Trofimov, B.A., Nedolya, N.A., Vyalykh, E.P., and Figovskii O.L., USSR Inventor's Certificate 761490 1978; *SSSR Byull. Izobr.*, 1980, no. 33.
  25. Trofimov, B.A., Shergina, N.I., Atavin, A.S., Kositsyna, E.I., Gusarov, A.V., and Gavrilova, G.M., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, no. 1, pp. 116–121.
  26. Nakanisi, K., *Infrakrasnye spektry i stroenie organicheskikh soedinenii* (IR Spectra and Structure of Organic Compounds), Moscow: Mir, 1965.
  27. Nedolya, N.A., Baranskii, V.A., and Trofimov, B.A., *Zh. Org. Khim.*, 1995, vol. 31, no. 3, pp. 321–324.
  28. Nedolya, N.A., Baranskii, V.A., Trofimov, B.A., *Zh. Org. Khim.*, 1995, vol. 31, no. 3, pp. 325–329.