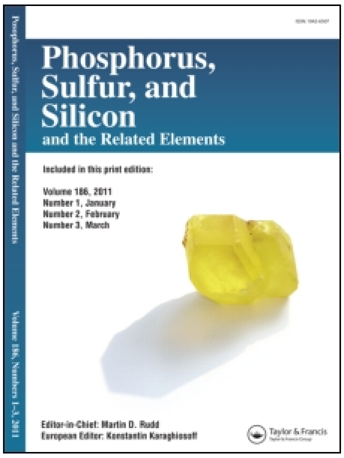

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Electrophilic and Nucleophilic Addition of Alkanethiols to 2-Vinyloxyethylmethacrylate

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ELECTROPHILIC AND NUCLEOPHILIC ADDITION OF ALKANETHIOLS TO 2-VINYLOXYETHYLMETHACRYLATE

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Under acid- or base-catalyzed conditions, thiols add regio- and chemoselectively either to vinyloxy or methacrylate group of vinyloxyalkylmethacrylates to give polyfunctional methacrylates or polyfunctional vinyl ethers, respectively.

Keywords: 2-Vinyloxyethylmethacrylate; alkanethiols; electrophilic; nucleophilic addition

Combination of two unsaturated bonds, possessing drastically different reactivity, in molecules of now available vinyloxyalkylmethacrylates[1–4] provides a virtually unlimited potential for application of these compounds in organic synthesis and chemistry of polymers. This is why the chemical properties of vinyloxyalkylmethacrylates and their potential as monomers are attracting attention. Thus, in the presence of trifluoroacetic acid, vinyloxyalkylmethacrylates add alcohols,[5] polyols,[6] and triazoles[7] regio- and chemoselectively (in the Markovnikoff fashion) to their vinyloxy group to give corresponding polyfunctional methacrylates in high yields. The vinyloxy group also takes part in the reaction with di(trifluoromethyl)ketone, which affords oxetanes[8] polymerizing to prospective flame-resistant liquids.

Vinyloxyalkylmethacrylates can be polymerized by involving either the acrylate function (under the action of anionic and radical initiators) or the vinyloxy group (by the cationic mechanism) to produce polymers possessing some special properties.[9,10] Presence of sulfur atoms in the

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acrylic monomers allows one to obtain transparent polymers, which may be used for preparation of optical lenses.[11]

To extend the stock of available sulfur-containing acrylates and to give more knowledge about competing reactivity of the vinyloxy and methacrylate groups, we have studied the reaction of 2-vinyloxy-ethylmethacrylate **1** with alkanethiols under acid- and base-catalyzed conditions. This article is a concise account of the study.

It is known that in the presence of acid catalysts, vinyl ethers add thiols to form not only the Markovnikoff adducts (through a cationic mechanism), but also the anti-Markovnikoff products (due to a spontaneous radical initiation).[12–19] Additionally, unlike simple alkyl vinyl ethers, those having a epoxy function show a higher tendency to homolytic thiylation, presumably, due to a trapping of acids by the oxirane group.[16,17]

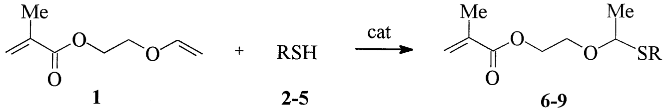
Addition of thiols to the double bond activated by electron-withdrawing substituents proceeds readily and follows the nucleophilic mechanism (base catalysis).[18,20–22] Under the action of radical initiators, thiols also add to vinyloxy[12,15] and acrylate groups[23] to afford corresponding β-adducts. Some examples of a facile non-catalyzed Michael addition of thiols to acrolein also were reported.[24,25]

Thus, the above brief analysis of the known data indicates that the interaction of vinyloxyalkylmethacrylates with alkanethiols may proceed differently and should be strongly dependent on the catalyst nature and reaction conditions.

RESULTS AND DISCUSSION

Electrophilic addition of alkanethiols to vinyl ether **1** was studied using cationic catalysts ($LiBF_4$, CF_3COOH, and a cation exchanger KU-2-15), possessing a mild selective catalytic effect in similar reactions.[12,26–28]

Under the action of the $LiBF_4$—1,2-dimethoxyethane catalytic complex, reaction of alkanethiols **2–5** with **1** proceeds regio- and chemoselectively to form the expected 2-[1-(alkylthio)ethoxy]ethylmethacrylates **6–9** (Scheme 1). A similar outcome is observed in the presence of catalytic amounts of CF_3COOH or KU-2-15, when radical inhibitors (hydroquinone, N-phenyl-2-naphthylamine) are used simultaneously.



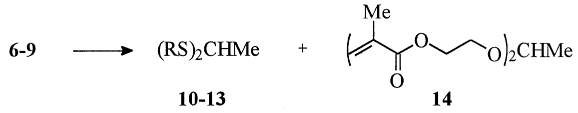
R = Et (**2**, **6**), *n*-Pr (3,7), *n*-Bu (**4**, **8**), *n*-$C_{12}H_{25}$ (**5**, **9**)
Cat: $LiBF_4$ — 1,2-dimethoxyethane, CF_3COOH - hydroquinone, KU-2-15 - N-phenyl-2-naphthylamine

SCHEME 1

In the presence of $LiBF_4$—1,2-dimethoxyethane complex or KU-2-15—N-phenyl-2-naphthylamine system (1 wt% each), the reaction completes quantitatively in 4 h at room temperature, whereas when CF_3COOH and hydroquinone (1 wt% each) are used, full conversion of vinyl ether **1** is achieved within 16–24 h.

Formation of methacrylates **6–9** is indicated in the ^1H NMR spectra (δ) by the appearance of peaks of the thiocetal moiety SCH(Me)O [4.7 qand 1.5 d, ppm] and simultaneous decrease of intensities of the vinyloxy- (6.46, 4.20, and 4.02 ppm) and thiol (1.37 ppm) signals, up to their complete disappearance. Simultaneously, in the IR spectra disappearance of the vinyloxy- (815, 960, 1200, 1323, 1612, 1638, 3080, 3104 cm^{-1}) and SH (2575 cm^{-1}) groups absorption is observed.

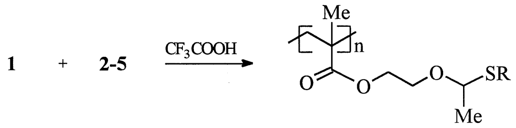
Individual thioacetalmethacrylates **6–9** were not isolated due to a fast symmetrization to 1,1-(dialkylthio)ethanes **10–13** and 1,1-[bis(2-methacryloylethyl)]ethane **14** (Scheme 2), which takes place under reaction conditions, as indicated by the ^1H NMR spectra in which the signal of the thioacetal SCH(Me)O proton (4.7 ppm) is replaced by two quartets of OCHO and SCHS protons (4.85 and 3.91 ppm, respectively).



R = Et (**10**), *n*-Pr (**11**), *n*-Bu (**12**), *n*-$C_{12}H_{25}$ (**13**)

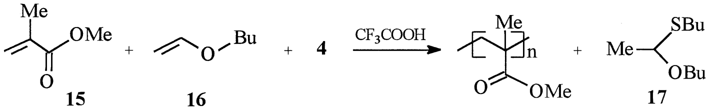
SCHEME 2

In the presence of CF_3COOH (but without radical inhibitors), electrophilic addition of alkanethiols **2–5** to **1** is accompanied by radical polymerization of the adducts **6–9** (Scheme 3), involving the methacrylate group due to a transfer of an electron from thiol (or its anion) to the intermediate carbocation as shown.[16,17]



SCHEME 3

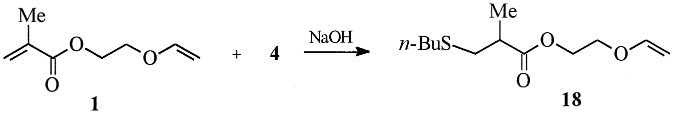
Actually, a model experiment with concurrent participation of equimolar amounts of methylmethacrylate **15**, thiol **4** and *n*-butyl vinyl ether **16** in the presence of trifluoroacetic acid showed that polymerization of the methylmethacrylate does occur, while butyl vinyl ether adds the thiol regioselectively to furnish the adduct **17** (Scheme 4).



SCHEME 4

Therefore, in the above reactions (Schemes 3 and 4), the methacrylate group acts as a "radical trap," and homolytic addition of alkanethiols to vinyl ethers (**1** and **16**) (with formation of anti-Markovnikoff adducts) does not occur.

Under base-catalyzed conditions (NaOH), 2-vinyloxyethylmethacrylate **1** reacts readily with thiol **4** at room temperature to give the Michael adduct **18** in high yield (Scheme 5).



SCHEME 5

Thus, the reaction of alkanethiols with vinyloxyalkylmethacrylate selectively can be directed either to the vinyloxy or methacrylate groups, under the action of acid or base catalysts, respectively.

EXPERIMENTAL

IR spectra were recorded on a Bruker IFS-25 spectrometer. ^1H NMR spectra were taken on a Bruker DPX-400 (400 MHz) instrument in $CDCl_3$ with HMDS as an internal standard. GLC analyses were performed on a LXM-80 machine, equipped with a heat conducting detector, 3000 × 3 mm column, liquid phase: Silicone DS-550, 5% on Chromaton N-AW-HMDS.

Thiols were dehydrated thoroughly and distilled prior to use. Their constants matched the literature ones. 2-Vinyloxyethylmethacrylate **1** was synthesized and purified according to Trofimov et al.[2,3]

Addition of Alkanethiols to 2-Vinyloxyethylmethacrylate (1) in the Presence of the $LiBF_4$-1,2-Dimethoxyethane Complex

A 10% solution of $LiBF_4$ in 1,2-dimethoxyethane was added to a mixture of **1** (1.09 g, 7 mmol) and RSH (7 mmol) [(R = Et (**2**), *n*-Pr (**3**), *n*-Bu (**4**) and *n*-$C_{12}H_{25}$ (**5**)]. The mixture was stirred for 4 h at room temperature until complete disappearance of absorption bands of vinyl ether **1** in the IR spectrum. ^{1}H NMR spectra taken during the synthesis demonstrated the formation of asymmetric thioacetals **6–9** and their subsequent symmetrization to dialkylthioacetals **10–13** and acetal **14**. After the synthesis, the catalyst was neutralized with 5% aqueous solution of $NaHCO_3$. Vacuum distillation gave symmetric 1,1-(dialkylthio)ethanes (**10–13**) (with admixture of a corresponding asymmetric 2-[1-(alkylthio)ethoxy]ethylmethacrylate **6–9**) and 1,1-[bis(2-methacryloylethyl)]ethane (**14**) (in 80–90% total yield), which were identified by ^{1}H NMR and GLC (comparison with an authentic sample). Constants of 1,1-(dialkylthio)ethanes **10–13** after an extra distillation corresponded to those described in the literature.[29]

The reaction in the presence of CF_3COOH—hydroquinone or the cation exchanger KU-2-15-N-phenyl-2-naphthylamine catalytic systems was performed analogously.

1,1[Bis(2-methacryloylethyl)]ethane (14)

B.p. 105–106°C (2 mm Hg), n_D^{20} 1.4560. IR (film, cm^{-1}): 652, 816, 878, 943, 960, 1003, 1043, 1087, 1100, 1137, 1171, 1246, 1298, 1320, 1340, 1384, 1402, 1454, 1637, 1718, 2881, 2926, 2957, 2988, 3101. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.12 dq, 5.59 dq (2H each, CH_2=, ^2J 1.6, ^4J 0.9, ^4J 1.6 Hz), 4.85 q (1H, OCHO, ^3J 5.4 Hz), 4.30 m (4H, OCH_2), 3.82 m, 3.73 m (2H each, OCH_2), 1.95 dd (6H, Me, ^4J 0.9, ^4J 1.6 Hz), 1.35 d (3H, Me, ^3J 5.4 Hz).

Addition of Alkanethiols to 2-Vinyloxyethylmethacrylate (1) in the Presence of CF_3COOH

Trifluoroacetic acid (1 wt%) was added to an equimolar mixture of 2-vinyloxyethylmethacrylate **1** and RSH (7 mmol) [(R = Et (**2**), *n*-Pr (**3**), *n*-Bu (**4**) and *n*-$C_{12}H_{25}$ (**5**)], and the mixture was allowed to stay at room temperature. Gradual increase of the reaction mixture viscosity and simultaneous loss of the solubility were observed, although during the first day they still were suitable to take ^{1}H NMR spectra. The spectra showed broadening and coupling of peaks (characteristic of the initial stages of the polymerization) of both starting vinyl ether **1** and formed asymmetric **6–9** and symmetric **10–14** products. IR spectra showed gradual decrease of the absorption bands intensity not only for the vinyloxy group (1620, 1637, 3160 cm^{-1}), but also for the methacrylate group (1637, 3107 cm^{-1}), up to their complete disappearance. As a result, the whole reaction mixture solidified and lost its solubility. Powdering and multiple washing of the obtained solid products with ether allowed one to reduce the content of sulfur in the polymers as compared with that calculated for asymmetric adducts **6–9**. This may be accounted for by washing out of symmetric thioacetals **10–13** formed simultaneously with the polymerization. Found for the polymer, prepared by addition of butane-1-thiol, %: C, 57.07; H, 8.88; S, 10.40. Calculated for the asymmetric acetal **8,** %: C, 58.50; H, 9.00; S, 13.02.

Concurrent Reactions of Methylmethacrylate and *n*-Butyl Vinyl Ether with Butane-1-thiol in the Presence of CF_3COOH

Trifluoroacetic acid (0.015 g, 1 wt%) was added to a mixture of methylmethacrylate **15** (0.50 g, 5 mmol), butyl vinyl ether **16** (0.50 g, 5 mmol), and *n*-BuSH (0.45 g, 5 mmol). The mixture was stirred for 5 h at room temperature and then analyzed by ^{1}H NMR. Conversion of butyl vinyl ether was 50%. Only peaks of the α-adduct **17** were observed in the spectrum. Vacuum distillation (2 mm Hg) of unreacted *n*-butyl vinyl ether and the α-adduct **17** gave a light-yellow syrup-like residue (0.23 g, 25% yield). IR and ^{1}H NMR spectra of the residue corresponded to polymethylmethacrylate containing terminal BuS-groups.

Addition of Butane-1-thiol to 2-vinyloxyethylmethacrylate (1) in the Presence of NaOH

To a mixture of **1** (1.56 g, 10 mmol) and *n*-BuSH (0.90 g, 10 mmol), NaOH (0.07 g, 3 wt%) was added, and the mixture was stirred for 2 h at room temperature. Removal of the solid precipitate and subsequent vacuum distillation gave 1.72 g (70% yield) of 2-(vinyloxy)ethyl-3-(butylsulfanyl)-2-(methylpropionate) **18**, b.p. 112°C (3 mm Hg), n_D^{20} 1.4634. IR (film, cm^{-1}): 607, 702, 743, 758, 821, 864, 964, 980, 1056, 1078, 1101, 1163, 1201, 1249, 1275, 1322, 1342, 1378, 1415, 1458, 1619, 1637, 1738, 2874, 2932, 2958, 3046, 3117. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.46 dd (1H, CH=), 4.32 t (2H, CH_2O, ^3J 4.8 Hz), 4.20 dd, 4.03 dd (1H each, CH_2=, $^3J_{trans}$ 14.3, $^3J_{cis}$ 6.8, ^2J 2.2 Hz), 3.88 t (2H, OCH_2 ^3J 4.8 Hz), 2.82 dd, 2.57 dd (1H each, CH_2S, ^3J 6.9, ^2J 7.1 Hz), 2.70 q (1H, CH, ^3J 6.9 Hz), 2.51 t (2H, CH_2S, ^3J 7.2 Hz), 1.54 m, 1.37 m (2H each, CH_2), 1.25 d (3H, Me, ^3J 6.9 Hz), 0.89 t (3H, Me, ^3J 7.3 Hz). Anal. Calcd for $C_{12}H_{22}O_3S$: C, 58.52; H, 9.00; S, 12.99; Found: 59.06; H, 8.82; S, 13.24.

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