SYNTHESIS AND TRANSFORMATIONS OF VINYL ETHERS OF ETHANOLAMINES

COMMUNICATION 15. POLYMERIZATION OF VINYL ETHERS OF ETHANOLAMINES

I. A. Chekulaeva, I. V. Lipovich, and M. F. Shostakovskii

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 3, pp. 535-540, March, 1963
Original article submitted June 6, 1962

In connection with the search for new monomers for application in the rapidly expanding field of polymeric materials it was of interest to study the reactivity in polymerization reactions of vinyl ethers of ethanolamines, $CH_2=CHOCH_2CH_2NR_2$, which are based on widely accessible raw materials, acetylene and ethanolamines. It is known [1] that alkyl vinyl ethers $CH_2=CHOAlk$ are extremely reactive and polymerize readily under the influence of ionogenic catalysts. The presence of both a double bond and an amine group in vinyl ethers of ethanolamines enables us to determine the effect of the nature of the amino group on the course of the reaction and on the properties of the polymers obtained. Study of the polymerization of vinyl ethers of ethanolamines in presence of catalytic amounts of ionogenic catalysts (concentrated hydrochloric acid, ferric chloride) showed that these ethers have low reactivity in ionic reactions in comparison with unsubstituted alkyl vinyl ethers. The tendency for ionic polymerization to occur is the less, the greater the basic character of the nitrogen atom, which in its turn depends on the character of the substituents on the nitrogen. For the 2-(vinyloxy)ethylamines $CH_2=CHOCH_2CH_2NH_2$, $CH_2=CHOCH_2CH_2NAlk_2$, $CH_2=CHOCH_2CH_2NAr_2$, and $CH_2=CHOCH_2CH_2NHCOCH_3$, heterolytic polymerization has been realized in practice only in the case of N,N-diphenyl-2-(vinyloxy)ethylamine, $CH_2=CHOCH_2CH_2N(C_6H_5)_2$, for which we succeeded in preparing a polymer of low molecular weight in 40% yield.

As regards the other vinyl ethers of ethanolamines of this series, their low tendency to undergo heterolytic polymerization may evidently be explained by the formation of stable complexes of the ammonium type with the catalyst, as a result of which the activating action of the latter is neutralized. However, these compounds may be polymerized if a quaternary ammonium salt is prepared, e.g., from 2,2',2''-trisvinyloxytriethylamine and methyl iodide. In the last case a cross-linked polymer containing quaternary ammonium groups is obtained in 54% yield. Analogous results of the polymerization of 2-diethylaminoethyl vinyl ether in presence of BF_3 etherate taken in rather more than the equimolecular amount are described in the British patent [2].

To determine the behavior of vinyl ethers of ethanolamines in free-radical polymerization, reaction in presence of azodiisobutyronitrile was studied, for we have used this successfully in the polymerization of 2,2',2''-trisvinyloxytriethylamine [3, 4]. Benzoyl peroxide does not initiate the polymerization of vinyl ethers of ethanolamines. It was shown that vinyl ethers of ethanolamines of the following structure $CH_2=CHOCH_2CH_2NR_2$ (R = hydrogen, alkyl, aryl, $-CH_2CH_2OCH=CH_2$; $-CH_2COOCH_3$, $-CH_2CH_2COOCH_3$, $-COCH_3$) are able to polymerize under the initiation of azodiisobutyronitrile, though with different degrees of ease (see table). The tendency to polymerize is determined by the structure of the vinyl ether. In their activity in polymerization in presence of azodiisobutyronitrile monovinyl ethers of ethanolamines differ little from unsubstituted alkyl vinyl ethers. The tendency for polymerization increases along the series:

$$CH_2=CHOCH_2CH_2NR_2 < (CH_2=CHOCH_2CH_2)_2NR <$$
$$(CH_2=CHOCH_2CH_2)_3N < CH_2=CHOCH_2CH_2NR'COCH_3$$

$$R = H,\ Alk,\ -CH_2CH_2OH;\ -CH_2COOCH_3,\ -CH_2CH_2COOCH_3$$
$$R' = H\ \&\ CH_2=CHOCH_2CH_2-$$

Under the given conditions (60° for 48 hours) high activity is shown by 2,2',2''-trisvinyloxytriethylamine $(CH_2=CHOCH_2CH_2)_3N$ and particularly by N-acetyl-2-(vinyloxy)ethylamine and N-acetyl-2,2'-bisvinyloxydiethylamine, $CH_2=CHOCH_2CH_2NHCOCH_3$ and $(CH_2=CHOCH_2CH_2)_2NCOCH_3$.

Polymerization of Vinyl Ethers of Ethanolamines in Presence of Azodiisobutyronitrile

Expt.	Vinyl ether	B.p., °C (p in mm)	n_D^{20}	Yield of polymer, %	Mol. wt. of polymer*	Characteristics of polymer
1	CH_2-$CHOCH_2CH_2NH_2$	115-116	1.4390	14-15	—	thick, yellow, soluble in water and alcohols
2	CH_2=$CHOCH(CH_3)CH_2NH_2$	127-128	1.4380	10-11	—	same
3	CH_2=$CHOCH_2CH_2N(C_2H_5)_2$	155-157	1.4328	7-8	435 451	thick, yellow, soluble in ether, benzene, acetone, methanol
4	CH_2-$CHOCH_2CH_2N(CH_3)_2$	123-124	1.4242	7-8	450 465	same
5	CH_2-$CHOCH_2CH_2N(C_6H_5)_2$	158-159 (3)	1.5980	10-11	475	thick, yellow, soluble in acetone and benzene
6	$(CH_2$-$CHOCH_2CH_2)_2NH$	80-81 (8)	1.4576	19-21	1490 1550	thick, dark-yellow, soluble in benzene, acetone, and alcohols
7	$(CH_2$=$CHOCH_2CH_2)_2NC_4H_9$	90-91 (4)	1.4536	18-40	—	same
8	$(CH_2$-$CHOCH_2CH_2)_2NCH_2COOCH_3$	126-127 (5)	1.4640	20-21	—	same
9	$(CH_2$-$CHOCH_2CH_2)_2NCH_2CH_2COOCH_3$	124-125 (5)	1.4652	20-22	—	same
10	CH_2=$CHOCH_2CH_2NHCH_2CH_2OH$	95-96 (1)	1.4687	5-7	—	thick, yellow, soluble in alcohols
11	CH_2-$CHOCH_2CH_2N(CH_2CH_2OH)_2$	141-142 (3, 5)	1.4805	6-7	—	thick, yellow, soluble in water and alcohols
12	$(CH_2$=$CHOCH_2CH_2)_2NCH_2CH_2OH$	125-126 (4, 5)	1.4725	19-20	—	solid, yellow, insoluble in the usual solvents, infusible
13	$(CH_2$=$CHOCH_2CH_2)_3N$	120-122 (5)	1.4678	38-40	—	same
14	CH_2=$CHOCH_2CH_2NHCOCH_3$	104-105 (3)	1.4671	68-70	—	colorless, resinlike, soluble in water and alcohols
15	$(CH_2$=$CHOCH_2CH_2)_2NCOCH_3$	120-121 (4)	1.4778	70-72	—	colorless, solid, insoluble in the usual solvents, infusible

*The molecular weight was determined cryoscopically in benzene.

The polymers prepared from the above-indicated vinyl ethers of ethanolamines are very varied in their properties. The polymers of the di- and tri-vinyl ethers of triethanolamine and of the divinyl ether of N-acetyldiethanolamine (N-acetyl-2,2'-bisvinyloxydiethylamine) have three-dimensional structures. The remaining polymers of linear structure dissolve in organic solvents or are soluble in water, this applies, for example, to the polymers prepared from 2-(vinyloxy)ethylamine and its N-acetyl derivative.

Of the monomers investigated, the following were synthesized for the first time N-butyl-2,2'-bisvinyloxydiethylamine, 2-(vinyloxy)propylamine, methyl [bis[2-(vinyloxy)ethyl]amino]acetate, and methyl 3-[bis[2-(vinyloxy)-ethyl]amino]propionate. The reactions were as follows

$$C_4H_9N(CH_2CH_2OH)_2 + 2HC\equiv CH \rightarrow C_4H_9N(CH_2CH_2OCH=CH_2)_2$$

$$H_2NCH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OH + HC\equiv CH \rightarrow H_2NCH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OCH=CH_2$$

$$(CH_2=CHOCH_2CH_2)_2NH + ClCH_2COOCH_3 \rightarrow (CH_2=CHOCH_2CH_2)_2NCH_2COOCH_3 + HCl$$

$$(CH_2=CHOCH_2CH_2)_2NH + CH_2=CHCOOCH_3 \rightarrow (CH_2=CHOCH_2CH_2)_2NCH_2CH_2COOCH_3$$

The other vinyl ethers of ethanolamine and their N-acetyl derivatives were prepared by methods developed earlier [5, 6].

EXPERIMENTAL

Vinyl ethers of ethanolamines CH_2-$CHOCH_2CH_2NR_2$, in which R = H, CH_3, C_2H_5, $CH_2CH_2OCH=CH_2$, were prepared by the vinylation of the corresponding amino alcohols [5] and were purified by distillation. N-Acetyl derivatives of the vinyl ethers of mono- and di-ethanolamines were synthesized by acylation of the vinyl ethers with vinyl acetate [6]. The constants of the compounds obtained are given in the table.

Synthesis of N-Butyl-2,2'-bisvinyloxydiethylamine. A two-liter flask was charged with 55 g of 2,2'-(butylamino)diethanol (n_D^{20} 1.4621), 6 g of its potassium derivative, and 100 ml of benzene. Acetylene was then passed in up to a pressure of 12-14 atm, and the autoclave was rotated and heated at 160° for 2-3 hours. The reaction mixture was washed with water, benzene was driven off, and the residue was vacuum-fractionated. We obtained 53.9 g (74%) of the vinyl ether, a colorless liquid with b.p. 90-91° (4 mm) and n_D^{20} 1.4536. Found C 67.91%, 67.93%, H 10.96%, 10.76%, N 6.73%, 6.72%. $C_{12}H_{23}O_2N$. Calculated C 67.60%, H 10.80%, N 6.57%.

Synthesis of 2-(Vinyloxy)propylamine. The vinyl ether was prepared in a two-liter autoclave, which was charged with 50 g of 1-amino-2-propanol [b.p.77° (25 mm), n_D^{20} 1.4472], 5 g of potassium hydroxide powder, and 100 ml of benzene, acetylene was passed in up to a pressure of 15 atm. Reaction was at 140-150° for 4-5 hours. From the reaction products we isolated 38 g (61%) of the vinyl ether by vacuum distillation. It was a colorless liquid, b.p.127-128°, n_D^{20} 1.4380, d_4^{20} 0.8850. Found C 59.10%, 58.97%, H 10.88%, 11.04%, N 14.26%, 14.50%, MR 29.99. $C_5H_{11}ON$. Calculated C 59.40%, H 10.96%, N 13.85%, MR 29.89.

Synthesis of Methyl 3-[bis[2-(vinyloxy)ethyl]amino]propionate. A glass ampoule was charged with 19.5 g of 2,2'-bisvinyloxydiethylamine [b.p. 80-81° (9 mm), n_D^{20} 1.4578] and 10.5 g of methyl acrylate [b.p. 22° (68 mm), n_D^{20} 1.3990]. The ampoule was heated in a boiling water bath for 12-15 hours, and its contents were then vacuum-distilled. We obtained 6 g of the desired product as a colorless liquid, b.p. 124-125° (5 mm), n_D^{20} 1.4652. Found C 59.28%, 59.51%, H 8.43%, 8.55%, N 6.26%, 6.18%. $C_{12}H_{21}O_4N$. Calculated C 59.23%, H 8.69%, N 5.75%.

Synthesis of Methyl [Bis[2-(vinyloxy)ethyl]amino]acetate. A mixture of 37.2 g of 2,2'-bisvinyloxydiethylamine [b.p. 80-81° (9 mm), n_D^{20} 1.4578] and 12.8 g of methyl chloroacetate (b.p 131.5°) was heated at 50° for four hours in a three-necked flask fitted with stirrer, thermometer, and condenser. 3-3.5 hours after the commencement of heating a precipitate began to form, and toward the end of the reaction the whole reaction mixture became solid. an aqueous solution of sodium hydroxide (8 g in 12 ml of water) was added quickly with stirring. Two layers were formed, and sodium chloride was precipitated. The latter was dissolved by the addition of 11 ml of water, then 25 ml of benzene was added, and the mixture was stirred and separated. The aqueous solution was extracted with benzene. The benzene solutions were combined, dried with potassium carbonate, and distilled. We obtained 13.8 g (51%) of product as a colorless liquid, b.p. 126-127° (5 mm), n_D^{20} 1.4640 d_4^{20} 1.040. Found C 58.0%, 57.90%, H 8.41%, 8.15%, N 6.03%, 6.10%, MR 60.80. $C_{11}H_{19}O_4N$. Calculated C 57.64%, H 8.35%, N 6.10%, MR 61.0.

Polymerization of Vinyl Ethers of Ethanolamines in Presence of Ionogenic Catalysts. The polymerization was carried out in a three-necked flask fitted with thermometer and reflux condenser. The vinyl ether (10 g) was boiled

under a vacuum of 4-5 mm, 2-3 drops of catalyst were added through a capillary, and the ether was kept at the boiling point for five hours. As catalyst we used concentrated hydrochloric acid or ferric chloride (as a 5% solution in butyl alcohol). From N,N-diphenyl-2-(vinyloxy)ethylamine we obtained a thick dark-bordeaux reaction product, which was dissolved in acetone. From the acetone solution the polymer was precipitated with methanol. It was purified by reprecipitation and vacuum-dried. Yield 3.8-4.3 g, mol. wt. 420-620. From the acetone-methanol solution by vacuum distillation we isolated unchanged vinyl ether and 2.2-2.3 g of polymer, mol.wt. 448-617, formed as a result of the further heating during distillation.

In the case of the remaining ethers (see table) the reaction products were vacuum-distilled and the original monomers were almost completely recovered unchanged.

Preparation of a Polymer from Quaternized 2,2',2"-Trisvinyloxytriethylamine. A mixture of 22.7 g of 2,2',2"-trisvinyloxytriethylamine [b.p. 120-122° (5 mm), n_D^{20} 1.4678] and 42.5 g of methyl iodide (b.p. 42°) was kept at 15-20° for 24 hours. The solid reaction product was washed with methanol and dried. We obtained 20 g of a yellow powder which was insoluble in the usual organic solvents and was infusible. Found C 37.92%, 37.63%, H 6.33%, 6.39%, I 37.84%, 37.18%, N 4.06%, 4.06%. $C_{13}H_{24}O_3NI$. Calculated C 42.28%, H 6.55%; I 34.37%, N 3.79%.

Polymerization of Vinyl Ethers of Ethanolamines in Presence of Azodiisobutyronitrile. The vinyl ether (5 g) was heated continuously for 48 hours with 0.1 g (2% on the weight of the ether) of initiator in a glass ampoule at 60°. The treatment of the reaction products was determined by the properties of the vinyl ethers and the polymers obtained. The results of the polymerization are given in the table. In Experiments 1-4 and 6-9 unchanged vinyl ether and polymer were separated by vacuum distillation. In Experiments 11-15 the polymer was precipitated from the reaction products with diethyl ether. The polymer from N,N-diphenyl-2-(vinyloxy)ethylamine (Expt. 5) was precipitated from acetone solution with methanol and purified by reprecipitation. The polymers were vacuum-dried.

SUMMARY

1. A study was made of the polymerization of some vinyl ethers of ethanolamines in presence of ionogenic and free-radical catalysts.

2. Vinyl ethers of ethanolamines are less reactive in ionic polymerization than unsubstituted alkyl vinyl ethers, and they tend to undergo radical polymerization under the initiation of azodiisobutyronitrile.

3. The relation of the structure of the ethanolamine vinyl ether to its tendency to polymerize was examined.

4. The introduction of an amide grouping into the β-position of the alkoxy group of an alkyl vinyl ether considerably increased its reactivity in radical polymerization.

5. From vinyl ethers of ethanolamines polymers containing amino groups were prepared both three-dimensional polymers, and linear polymers, some of which were water-soluble.

LITERATURE CITED

1. M. F. Shostakovskii, Vinyl Ethers [in Russian], Moscow (1942).
2. British Pat. 713487, Aug. 11, 1954.
3. M. F. Shostakovskii and I. A. Chekulaeva, Izv. AN SSSR, Otd. khim. n. (1959), 130.
4. M. F. Shostakovskii, B. N. Laskorin, G. N. Nikul'skaya, I. A. Chekulaeva, and P. G. Ioanisiani, Vysokomolek. soed., 131, 398 (1961).
5. M. F. Shostakovskii and I. A. Chekulaeva, Izv. AN SSSR, Otd. khim. n. (1951), 328, (1953), 368, (1954), 1111, (1955), 913; (1957), 75.
6. M. F. Shostakovskii, I. A. Chekulaeva, and I. V. Lipovich, Izv. AN SSSR, Otd. khim. n. (1963), 532.

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
