these may account for the sigmoid shape of the volume–temperature curves for copolymers. More important, they lead to the conclusion that the experimentally measured T_m will be low by an unspecified number of degrees. This error should be expected to increase as $1 - X_A$ is increased, hence a systematic error is introduced making the calculated h_u too small. The observed discrepancy between the heats of fusion evaluated by the two methods may arise from this source. However, it is not as great as was observed on comparison of the heats of fusion calculated for linear polyesters[5] on the basis of equations (1), (2) and (3), respectively. The T_m's for the polyesters and copolyesters were determined by the less accurate light depolarization method, which may have increased the discrepancy.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

Two Stage Polymerizations. II. Preparation and Polymerization of Vinyl Ethers of Unsaturated Alcohols[1]

BY GEORGE B. BUTLER AND JAMES L. NASH, JR.

Five new unsaturated ethers of ethylene glycol have been prepared and characterized. These compounds were prepared by reaction of the appropriate sodium alkenoxide with vinyl β-chloroethyl ether. It has been shown that those ethers containing two unsaturated radicals, only one of which is a vinyl radical, may be polymerized in presence of boron trifluoride at −70° to produce linear polymers containing residual unsaturation. These unsaturated polymers were cross-linked at elevated temperatures by peroxide catalysts to produce insoluble and infusible polymers. In addition, studies were made of the effect of several typical peroxide catalysts on several of these unsaturated ethers. In general, cross-linked polymers were obtained. Copolymerization of a typical ether of this type with a vinyl alkyl ether at −70° with BF_3 produced a linear polymer.

The first paper of this series[2] reported a study of the polymerization reactions of allyl ethers of allyl substituted phenols. It was shown that these ethers could be made to undergo a two-stage polymerization, the first stage resulting in the formation of unsaturated linear polymers as the result of polymerization of the allyloxy radical in presence of boron trifluoride, and the second stage resulting in the formation of cross-linked polymers by thermal polymerization of the allyl side chains.

The pronounced reactivity of vinyl ethers at low temperature in the presence of acid catalysts[3–5] prompted us to prepare and study vinyl ethers of other unsaturated alcohols as compounds which may lend themselves to a stepwise polymerization in which only the vinyl radical polymerized under a given set of conditions. This should result in an unsaturated linear polymer, which may later be cross-linked under a different set of conditions. It has previously been shown[6] that allyl ethers are copolymerized with other monomers in presence of peroxide catalysts at elevated temperatures. Those ethers containing two or more allyl groups serve as cross-linking agents for other monomers.[7,8] It has also been shown that divinyl ethers result in cross-linked polymers when subjected to polymerization in presence of acid catalysts.[3]

All of the compounds prepared and studied contained the vinyloxy radical. In the absence of other vinyloxy radicals, these compounds were found to produce only linear polymers at low temperatures in presence of boron trifluoride. These polymers were then subject to peroxide-catalyzed polymerization at elevated temperatures, resulting in cross-linked polymers. Polymerization of an ether which contained both the vinyloxy and furfuryloxy radicals resulted in a cross-linked polymer at −70° in presence of boron trifluoride. However, since the furfuryloxy radical is composed of both a vinyloxy and an allyloxy radical, this was not unexpected.

The potential usefulness of a compound capable of undergoing a two stage polymerization would be considerably enhanced if the degree of unsaturation in the first stage polymer could be varied over a wide range. Therefore, we considered it important to determine whether or not compounds of this type would copolymerize with a typical vinyl alkyl ether under similar conditions. Our experiments have shown that this can be done, resulting in a first stage polymer having a much lower degree of unsaturation than the homopolymer.

Although the chief purpose in preparation of these ethers was to determine whether or not the two-stage polymerization could be accomplished, studies were also made of the effect of several typical peroxide catalysts on several of these compounds. In general, reasonably large quantities of catalyst were required to initiate polymerization, but in most cases cross-linked polymers resulted. However, ethylene glycol vinyl furfuryl ether produced only linear polymers in presence of benzoyl peroxide.

Experimental

Materials.—Vinyl β-chloroethyl ether was obtained from Carbide and Carbon Chemical Corporation. The redistilled fraction boiling between 107–110° was recovered for use. Furfuryl alcohol was obtained from Quaker Oats Company and the fraction distilling between 68–70° (10

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[1] Abstracted from a thesis presented by James L. Nash, Jr., to the Graduate School of the University of Florida in partial fulfillment of the requirements for the degree of Master of Science.

[2] Butler and Ingley, THIS JOURNAL, **73**, 1512 (1951).

[3] I. G. Farbenindustrie, A. G., French Patent 734,129 (March 24, 1932).

[4] I. G. Farbenindustrie, A. G., British Patent 443,978 (March 11, 1936).

[5] I. G. Farbenindustrie, A. G., German Patent 634,408 (August 26, 1936).

[6] G. F. D'Alelio, U. S. Patent 2,332,900 (October 26, 1943).

[7] B. N. Rutovskii and K. S. Zabrodina, *Org. Chem. Ind.* (*U. S. S. R.*), **7**, 441 (1940).

[8] G. F. D'Alelio, U. S. Patent 2,340,111 (January 25, 1944).

TABLE I

Diether of ethylene glycol	Formula	$n^{25}D$	d^{25}_4	MR_D		B.p.,		Yield,	Analyses, %			
									Calcd.		Found	
				Calcd.	Found	°C.	Mm.	%	C	H	C	H
Vinyl furfuryl	$C_9H_{12}O_3$	1.0569	1.4739	45.09	44.72	76–77	1.5	37.1	64.27	7.19	64.23	7.44
Vinyl allyl	$C_7H_{12}O_2$	.8959	1.4315	36.88	37.06	150	760	42.3	65.60	9.44	65.33	9.76
Vinyl crotyl	$C_8H_{14}O_2$	.8918	1.4382	41.50	41.87	174–175	760	38.0	67.57	9.92	67.23	10.13
Vinyl methallyl	$C_8H_{14}O_2$	.8878	1.4328	41.50	41.61	77–78	32	13.8	67.57	9.92	67.47	10.29
Vinyl β-chloroallyl	$C_7H_{11}ClO_2$	1.0683	1.4553	41.75	41.32	76–80	10	9.2	Cl, 21.8		22.2	

TABLE II

Diether of ethylene glycol	Catalyst	Concn., %	Temp., °C.	Time, hr.	Nature of polymer
Vinyl furfuryl	Boron trifluoride	6	−70	1.5	Cross-linked, infusible
Vinyl furfuryl	Benzoyl peroxide	10	65	30	Linear, viscous
Vinyl furfuryl	Benzoyl peroxide	10	100	60	Linear, softens 35–54°
Vinyl furfuryl	*t*-Butyl hydroperoxide	6	100	26	Cross-linked, infusible
Vinyl furfuryl	Di-*t*-butyl peroxide	6	100	60	Cross-linked, sl. soluble
Vinyl allyl	Boron trifluoride	10	−70	3	Linear, very viscous
Vinyl allyl	Benzoyl peroxide	10	65	60	Cross-linked, infusible
Vinyl allyl	Benzoyl peroxide	10	100	21	Cross-linked, spongy, insoluble
Vinyl allyl	*t*-Butyl hydroperoxide	6	100	96	Cross-linked, infusible
Vinyl allyl	Di-*t*-butyl peroxide	10	100	90	Cross-linked, infusible, spongy
Vinyl crotyl	Boron trifluoride	10	−70	3	Linear, very viscous
Vinyl crotyl	Benzoyl peroxide	10	65	72	Cross-linked, infusible
Vinyl crotyl	Benzoyl peroxide	10	100	90	Cross-linked, softens, does not fuse
Vinyl crotyl	*t*-Butyl hydroperoxide	6	100	90	Linear, partially insoluble, softens at 60°
Vinyl crotyl	Di-*t*-butyl peroxide	10	100	90	Cross-linked, sl. soluble, softens at 48°

mm.) was used. Crotyl[9] and methallyl[10] alcohols were prepared in this Laboratory. Allyl alcohol was obtained from Shell Chemical Corporation and used without further purification. β-Chloroallyl alcohol was obtained through the courtesy of Shell Development Company and the fraction boiling between 136–140° was used. The benzoyl peroxide and *t*-butyl hydroperoxide were obtained through the courtesy of Lucidol Division, Novadel–Agene Corporation. Di-*t*-butyl peroxide was obtained through the courtesy of Shell Chemical Corporation. Boron trifluoride was obtained in the form of the diethyl ether complex through the courtesy of General Chemical Company.

Preparation of Unsaturated Ethers.—These ethers were prepared by the Williamson reaction of vinyl β-chloroethyl ether with the appropriate sodium alkenoxide. However, because of the unreactive nature of the chlorine atom in the above ether, a large excess of the appropriate alcohol was usually used. The following preparation of ethylene glycol vinyl allyl ether will serve to illustrate the general method: Five moles (290.3 g.) of allyl alcohol was placed in a three-necked, one-liter flask equipped with a condenser, stirrer and addition funnel. One mole (23 g.) of sodium was cut into small pieces and added slowly. After the sodium had dissolved, the flask was heated on a steam-bath while 110 g. of vinyl β-chloroethyl ether was added dropwise and for seven hours thereafter. The reaction mixture became cloudy and sodium chloride precipitated. Upon cooling, the liquid was filtered and distilled through an efficient column. The excess alcohol was removed and the fraction distilling at 146–150° was collected; yield 54.2 g.

The physical properties and analyses of these compounds are recorded in Table I.

Polymerization Studies.—The following experiments will illustrate the general procedures used:

Polymerization of Ethylene Glycol Vinyl Allyl Ether with BF_3.—Seventeen and one-half cc. of dry toluene and 4 cc. of $BF_3 \cdot O(C_2H_5)_2$ were placed in a three-necked, 200-cc. flask, equipped with a stirrer, drying tube filled with potassium carbonate, addition funnel and low temperature thermometer. The flask was immersed in a Dry Ice–acetone-bath until the temperature had dropped to −70°. Fifteen grams of ethylene glycol vinyl allyl ether was added dropwise over a period of one hour. There was no temperature rise noted during the addition; however, the material became very viscous. After addition was complete, the solution was stirred vigorously at this temperature for two hours, after which it was allowed to approach room temperature by removing the bath. When the temperature had reached −30°, 5 cc. of diethylaniline was added to inactivate the catalyst. When the temperature reached 0°, 25 cc. of water was added to ensure complete inactivation of the catalyst. Thirty cc. of 20% hydrochloric acid solution was added and the stirring continued for one-half hour. The toluene solution was separated, washed thoroughly with water, and the solvent removed under vacuum. The polymer was pale yellow in color and very viscous. It was soluble in acetone, benzene and toluene.

Polymerization of Ethylene Glycol Vinyl Allyl Ether with Benzoyl Peroxide.—One gram of the compound was placed in a 10-cc. beaker and 0.2 g. of benzoyl peroxide added. The peroxide was dissolved completely by stirring. The solution was placed in an oven set at 65° and allowed to remain for 60 hours. The polymer was found to be insoluble in acetone, benzene and toluene, and was infusible. The conditions and results of these experiments are recorded in Table II.

Copolymerization of Ethylene Glycol Vinyl Allyl Ether and Vinyl Isopropyl Ether with BF_3.—By a procedure similar to that described above for the polymerization of ethylene glycol vinyl allyl ether alone, a mixture of 5 g. of this ether with 15 g. of vinyl isopropyl ether was polymerized. The polymer was light brown in color, and had a softening point of 52°.

Conversion of Linear Polymers to Cross-Linked Polymers by Peroxide Catalyst.—Two grams of the linear polymer obtained by polymerization of ethylene glycol vinyl allyl ether with BF_3 was placed in a 10-cc. beaker and 0.4 g. of benzoyl peroxide added. After thorough mixing, the beaker was placed in an oven set at 65°. After twenty-four hours at this temperature, the polymer was solid. It was found to be insoluble in acetone, benzene and toluene. It was also found to be infusible.

The linear polymer of ethylene glycol vinyl crotyl ether was converted to an insoluble and infusible polymer by similar treatment.

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[9] Roger Adams, *et al.*, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 200.

[10] Tamele, Ott, Marple and Hearn, *Ind. Eng. Chem.*, **33**, 115 (1941).