Reactions of Unsaturated Fatty Alcohols. X. Preparation of Some Copolymers of Nonconjugated Linseed Vinyl Ether[1]

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PREVIOUS WORK at this laboratory showed that the unsaturated fatty alcohols obtained from the reduction of linseed and soybean oils may be converted to the corresponding vinyl ethers by vinylation at atmospheric pressure (7).

Later work was devoted to the study of the polymerization of these vinyl ethers with various cationic initiators and to the study of the properties of the films of these polymers (6). These vinyl ethers had a high degree of conjugated unsaturation because of the action of the alkaline catalysts used in the vinylation. Vinyl ethers having little conjugated unsaturation could be prepared from nonconjugated linseed and soybean alcohols by a modification (8) of the vinyl transetherification reaction described by Watanabe and Conlon (9). Gast and others have studied the copolymerization of nonconjugated linseed vinyl ether with a variety of lower alkyl vinyl ethers (3).

The purpose of the present investigation was to obtain further information on the behavior of nonconjugated linseed vinyl ether in copolymerization with other vinyl ethers, particularly cyclic and aromatic derivatives, and to evaluate the films prepared from these copolymers.

Preparation of Vinyl Ethers for Copolymerization Studies

Cyclohexyl vinyl ether was obtained from the Rohm and Haas Company and was purified before use by fractional distillation and chromatography on alumina.

1-Methoxy-1,3-butadiene was obtained from the Union Carbide Chemicals Company and was purified by fractionally distilling it twice through a 60-cm. Podbielniak concentric-tube column.

2-Phenylethyl, 3-phenylpropyl, 2-benzyloxyethyl, 2-(*para-tertiary*-butylphenoxy) ethyl, and tetrahydrofurfuryl vinyl ethers were prepared from the corresponding alcohols by an adaptation of the vinyl transetherification reaction (9). The alcohol to be transvinylated was mixed with ethyl vinyl ether, employing 3 to 8 moles of ethyl vinyl ether per mole of alcohol and from 2 to 5 g. of mercuric acetate per mole of alcohol. After dissolving the catalyst the solution was allowed to stand at room temperature for several days. The reaction was followed by removing a small sample of the reaction mixture and keeping the sample under water-aspirator vacuum for 5 min. to remove the ethyl vinyl ether and the ethanol. The vinyl ether content of the residue was then determined iodiometrically (8).

Often a further addition of mercuric acetate catalyst was beneficial. When the vinyl ether content of the samples failed to increase with time even upon further addition of catalyst, the reaction mixture was washed with water to remove ethanol; it was then dried and treated anew with mercuric acetate in the same proportion as before. Further progress of the reaction was followed as described. Again, when the reaction slowed or ceased, the reaction mixture was washed with water, dried, and distilled to remove ethyl vinyl ether. The crude vinyl ethers were then purified by fractional distillation and chromatography on alumina or by distillation from sodium.

2-Cyanoethyl vinyl ether was prepared by a modified vinyl transetherification reaction since 2-cyanoethanol was found to be immiscible with ethyl, isobutyl, butyl, and 2-ethylhexyl vinyl ethers. To overcome the solubility problem the following procedure was used. The 2-cyanoethanol was mixed with 3 moles of ethyl vinyl ether per mole of alcohol. Equal quantities of sodium acetate and mercuric acetate (approximately 2 g. of each per mole of alcohol) were dissolved in the mixture of cyanoethanol and ethyl vinyl ether, and the whole was heated at reflux for 16 hr. The upper layer was separated, washed with carbonate solution, dried, and distilled to remove ethyl vinyl ether. The lower layer was treated again with ethyl vinyl ether and mercuric acetate in the same proportion as before, and the mixture was refluxed for 6 hr. At that time only one liquid phase was present. The reaction mixture was washed with dilute carbonate solution, dried, and distilled to free it of ethyl vinyl ether. The residue was combined with the residue from the upper layer obtained previously and was purified by fractional distillation through the concentric-tube column.

2-Cyanoethyl vinyl ether was also prepared from the reaction of vinyl acetate and 2-cyanoethanol in the presence of mercuric sulfate according to the method of Guth and Schaefer (5). The yields were not as good as those obtained by the ethyl vinyl ether method.

Benzyl vinyl ether was made by refluxing benzyl alcohol, isobutyl vinyl ether (2 moles per mole of alcohol), and mercuric acetate for 7 hr. and then allowing the mixture to stand for 2 days. The crude vinyl ether was obtained by distillation from carbonate and was further purified by fractional distillation and distillation from sodium.

Phenyl vinyl ether was obtained by reacting vinyl acetate with phenol, employing 6 moles of the acetate per mole of phenol, in the presence of mercuric sulfate at −30°C., using Adelman's method (1). This vinyl ether was also prepared by heating 2-chloroethyl phenyl ether with powdered potassium hydroxide according to the method of Chalmers (2).

Data on the vinyl ethers used in preparing the copolymers with nonconjugated linseed vinyl ether are shown in Table I.

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Preparation of the Copolymers. Copolymers containing approximately 25-, 50-, and 75-mole percentage nonconjugated linseed vinyl ether were prepared by using stannic chloride as initiator. All the copolymers, except those made from cyclohexyl vinyl ether and from 1-methoxy-1,3-butadiene, were prepared by the following procedure.

The required amounts of the nonconjugated linseed vinyl ether, prepared as previously described (8), were weighed into an Erlenmeyer flask, and benzene was added to give a solution approximately 2 molar in vinyl ether groups. The flask was equipped with a thermocouple-recorder, stirrer, and nitrogen bubbler. The flask was swept with nitrogen for a minute to displace the air above the solution. The stirrer was started, and the recorder was turned on. Five milliliters of a 5% solution of stannic chloride in benzene were added. In most instances an exothermic polymerization occurred at once which carried the temperature of the solution upward as much as 73°C. When the maximum temperature had been reached, the polymerization was quenched by adding 25 ml. of 50% aqueous methanol. The polymer solution was then diluted with 100 ml. of benzene, washed with six 70-ml. portions of 50% aqueous methanol, dried over Drierite, and filtered. Benzene was removed by heating upon the steam bath under water-aspirator vacuum. The final stripping of benzene was carried out by heating the copolymer over a steam bath in a rotatory vacuum evaporator under a vacuum of less than 1.0 mm. Hg. for at least 1 hr.

After removing the last traces of benzene from the copolymer, its molecular weight was determined cryoscopically by using cyclohexane as a solvent (4). Gardner viscosities and Wijs iodine values were also determined. Determinations of the residual vinyl ether content of the copolymers showed that usually only 1 to 4% of vinyl ether remained in the copolymers. However with tetrahydrofurfuryl vinyl ether copolymers the residual vinyl ether contents were found to be as high as 24%. Some properties of the nonconjugated linseed vinyl ether copolymers are shown in Table II.

Some comonomers were much more reactive in the polymerizations than others. In the preparation of the copolymers of nonconjugated linseed vinyl ether with 1-methoxy-1,3-butadiene or with cyclohexyl vinyl ether, it was necessary to cool the monomer solutions prior to polymerization. If the reaction was attempted at room temperature, an almost explosive polymerization occurred with much loss of solution. Copolymers of tetrahydrofurfuryl vinyl ether formed more slowly than any of the other sets. 2-Cyanoethyl vinyl ether was also found to retard polymerization of nonconjugated linseed vinyl ether although not as extensively as did the copolymers of tetrahydrofurfuryl vinyl ether.

Phenyl vinyl ether behaved anomalously. The molecular weight of the nonvolatile material obtained from polymerizing phenyl vinyl ether with stannic chloride at room temperature corresponded to an intermediate between a dimer and a trimer whereas all the other vinyl ethers gave homopolymers with stannic chloride at molecular weights in excess of 1,000. Little heat was evolved during the reaction, which required 1 hr., nor did phenyl vinyl ether appreciably retard the polymerization of nonconjugated linseed vinyl ether. Judged by the iodine value and elemental analysis of the polymer, the incorporation of phenyl vinyl ether in a copolymer from a monomer mixture containing 50-mole percentage of linseed vinyl ether was almost negligible. No attempt was made to prepare other copolymers with phenyl vinyl ether.

All the copolymers reported were viscous liquids having Gardner viscosities ranging from N to much greater than Z-6. The copolymers ranged in color from Gardner 1 to 10. With most of the copolymers the observed iodine values were close to those calculated on the basis of the assumed composition of the copolymer, showing that the assumed compositions based on composition of monomer mixture were close to those actually obtained. Copolymers of tetrahydrofurfuryl and 2-cyanoethyl vinyl ether with nonconjugated linseed vinyl ether contained substantial amounts of residual vinyl ethers resulting in discrepancies between the calculated and observed iodine values. Observed iodine values of copolymers containing methoxybutadiene were less than those calculated, suggesting that some methoxybutadiene might have polymerized through both double bonds or that some might have been lost through volatilization.

Film Properties of Copolymers. Films on glass plates and on small glass test tubes were baked under three conditions and were tested for hardness and for alkali, acid, detergent, and solvent resistance as previously described (3).

Data on the hardness of films from one baking cycle are shown in Table II. In these tests many films were found to be softer than those from a nonconjugated linseed vinyl ether homopolymer (Table II). Other compositions in the series gave harder films than the nonconjugated linseed vinyl ether homopolymer, but none seemed to offer any outstanding advantage.

Baked films from all copolymers, except those containing the tetrahydrofurfuryl comonomer, were resistant to attack by 18% hydrochloric acid. Copolymer films containing tetrahydrofurfuryl vinyl ether were frosted and darkened by the acid solution within 24 hr.

TABLE I

Characterization of Vinyl Ether Comonomers

Vinyl ether	Boiling points °C. Found	Boiling points °C. Reported	Refractive indices Found	Refractive indices Reported	Purity,[e] %	Analyses Calculated C	Analyses Calculated H	Analyses Found C	Analyses Found H
Benzyl	81°/19 mm.	184° [a]	$n^{30/D}$ 1.5102	$n^{20/D}$ 1.5160 [a]	100.0	80.6	7.51	80.5	7.59
2-Phenylethyl	58°/2.4 mm.	97°/20 mm.[a]	$n^{30/D}$ 1.5035	....	98.0	81.0	8.16	81.0	8.30
3-Phenylpropyl	53°/0.5 mm.	....	$n^{26/D}$ 1.5086	....	98.8	81.5	8.70	81.5	8.78
2-Benzyloxyethyl	75°/0.75 mm.	....	$n^{30/D}$ 1.5033	....	98.7	74.1	7.92	73.9	7.91
2-(*Para-tertiary* butylphenoxy)-ethyl	m.p. 37–39°	....	....	....	98.2	76.3	9.15	76.2	9.19
Cyclohexyl	71–72°/47 mm.	82–83°/80 mm.	$n^{30/D}$ 1.4483	$n^{20/D}$ 1.4538	97.0	......	......	......	......
Tetrahydrofurfuryl	64°/21 mm.	60–64°/20 mm.[b]	$n^{25/D}$ 1.4463	$n^{20/D}$ 1.4335 [b]	98.4	65.6	9.42	65.2	9.44
2-Cyanoethyl	78–78.5°/47 mm.	79–80°/20 mm.[b]	$n^{30/D}$ 1.4292	$n^{20/D}$ 1.4335 [b]	98.0	......	......	......	......
1-Methoxy-1,3-butadiene	90°/749 mm.	91–92°/760 mm.[c]	$n^{28/D}$ 1.4588	....	95.6	......	......	......	......
Phenyl	151°/760 mm.	155° [d]	$n^{30/D}$ 1.5166	$n^{20/D}$ 1.5226 [d]	99.0	80.0	6.71	80.1	6.77

[a] Schildknecht, C. E., "Vinyl and Related Polymers," p. 621, New York, John Wiley and Sons, 1952. [b] Reference (9). [c] Meier, G., Ber. 77, 109 1944. [d] Reference (2). [e] Determined iodiometrically (7).

TABLE II

Properties of the Nonconjugated Linseed Vinyl Ether Copolymers

Comonomer ether	Mole percentage of comonomer	Molecular weight [a]	Gardner viscosity (color)	Iodine value [b]		Sward hardness of films [c]
				Observed	Calculated	
Benzyl vinyl	75	6,900	>Z-6 (5)	89.2	77.5	28
	50	10,000	>Z-6 (5)	127.3	126.5	32
	25	4,800	Z-1 (4)	150.9	159.9	16
2-Phenylethyl vinyl	75	4,800	>Z-6 (6)	82.5	73.2	8
	50	6,700	>Z-6 (4)	118.4	124.3	28
	25	6,300	Z-1 (6)	148.0	158.1	14
3-Phenylpropyl vinyl	75	4,600	Z-6 (7)	67.7	69.2	50
	50	4,700	Z-3 (2)	117.7	118.7	22
	25	5,600	Z-2 (4)	153.5	155.8	24
2-Benzyloxyethyl vinyl	75	3,000	Z-4 (3)	71.2	65.8	22
	50	4,300	Z-3 (2)	117.4	114.8	16
	25	5,800	Z-4 (4)	151.8	153.5	30
2-(*Para-tertiary*-butylphenoxy)-ethyl vinyl	75	4,400	>Z-6 (8)	84.0	56.9	14
	50	4,600	>Z-6 (6)	115.2	150.7	20
	25	4,500	>Z-6 (6)	160.8	147.3	24
Cyclohexyl vinyl	75	2,800	>Z-6 (2)	69.8	80.8	28
	50	5,900	>Z-6 (4)	133.6	128.7	20
	25	2,600	Z-4 (5)	195.4	161.1	24
Tetrahydrofurfuryl vinyl	75	980	N-M (9)	135.8	79.7	44
	50	1,300	V-W (6)	114.4	128.2	8
	25	5,000	Z-5 (6)	140.6	161.2	28
2-Cyanoethyl vinyl	75	784	Z to Z-1 (10)	152.0	92.2	20
	50	2,300	Z-4 (7)	150.0	138.6	26
	25	3,700	X (9)	174.0	166.6	36
Methyl-1-(1,3-butadienyl)	75	3,300	>Z-6 (6)	209.0	238.5	50
	50	3,800	Z-6 (6)	199.8	211.0	36
	25	10,000	Z-6 (4)	188.7	194.5	22
Phenyl vinyl	Calcd. 50 Found 0	2,700	T-U (5)	182.5	131.0	....
None	....	5,300	Z-1 (3-4)	184.5	184.0	32

[a] Cryoscopic measurement in cyclohexane. [b] Wijs. [c] Baked at 150° for 1 hr. with 0.1% Co drier.

The best alkali resistance was shown by films prepared from copolymers containing 2-(*para-tertiary*-butylphenoxy) ethyl vinyl ether. Films from a copolymer containing 75-mole percentage of this vinyl ether were completely unaffected by 5% sodium hydroxide solution after 24 hr., whereas a film similarly prepared from nonconjugated linseed homopolymer was swollen in 5 to 10 min. Alkali resistance of films from the other copolymer series was not significantly better than that of films from the homopolymer of linseed vinyl ether. The action of detergent solution appeared to be similar to, but considerably slower than, that of the alkali.

Solvents, such as chloroform and benzene, were found to swell many of the baked films, particularly those from copolymers containing a low percentage of nonconjugated linseed vinyl ether as comonomer. Films from copolymers rich in nonconjugated linseed vinyl ether were much more resistant to chloroform and benzene.

Summary

Vinyl ethers were prepared from benzyl, 2-phenylethyl, 3-phenylpropyl, 2-benzyloxyethyl, 2-(*para-tertiary*-butylphenoxy)-ethyl, tetrahydrofurfuryl, and 2-cyanoethyl alcohols. The vinyl ethers, as well as 1-methoxy-1,3-butadiene and cyclohexyl vinyl ether, when copolymerized with nonconjugated linseed vinyl ether produced viscous liquids that baked to films of moderate hardness and with fair resistance to alkali and acid. These copolymer films offered little improvement in hardness over similarly prepared films from nonconjugated linseed vinyl ether homopolymer. Baked films of nonconjugated linseed-2-(*para-tertiary*-butylphenoxy) ethyl vinyl ether copolymers had improved alkali resistance over the homopolymer baked films and were considered to be the best of the copolymer films studied.

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