Reactions of Unsaturated Fatty Alcohols. VIII. Preparation and Properties of Some Copolymers of Nonconjugated Linseed Vinyl Ether and Lower Alkyl Vinyl Ethers[1]

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IN A PREVIOUS PUBLICATION (1) we described the preparation and properties of copolymers of conjugated fatty vinyl ethers with lower alkyl vinyl ethers. These copolymers were prepared in methylene chloride at −30°C. by using boron trifluoride etherate catalyst. Films prepared from these materials were hard, wrinkle-free, and resistant to most common solvents; also they had more alkali-resistance than the homopolymer films prepared from either conjugated linseed or soybean polymers.

Since drying and film properties of polyunsaturated vegetable oil derivatives are influenced by the presence of conjugation, it seemed desirable to compare the behavior of fatty vinyl ether polymers and copolymers derived from both conjugated and nonconjugated fatty alcohols.

The direct vinylation procedure (4) used for preparing conjugated fatty vinyl ethers could not be used for the preparation of nonconjugated materials because prolonged contact with the alkaline catalyst at 180°C. produced conjugated fatty vinyl ethers as products from nonconjugated alcohols. A modified transvinylation procedure (5), based on a method described by Watanabe (6), was worked out to produce nonconjugated fatty vinyl ethers of high purity and good yield. This paper reports on a method for preparing nonconjugated fatty vinyl ethers, their polymers and copolymers, and describes some of the preliminary evaluation tests performed on polymer and copolymer films.

Preparation and Properties of Polymers

Starting Materials. Nonconjugated linseed vinyl ether was prepared from nonconjugated linseed alcohol by transetherification reaction with ethyl vinyl ether (5). The product, fatty vinyl ether, was purified by distillation and by passing through a column of chromatographic grade alumina (1 g./g. of product). The over-all yield of water-white product was 80%. Vinyl ether content was 99–100%.

Isopropyl and 2,2-dimethylpentyl vinyl ethers were prepared by the transetherification technique from the corresponding alcohols, using *n*-butyl vinyl ether. Analytical data on the products were:

Vinyl ether	B.P./ 755 mm.	$n^{30/D}$	Carbon, %		Hydrogen, %	
			Calc.	Found	Calc.	Found
Isopropyl	53–4°C.	1.3739	69.72	69.95	11.71	11.36
2,2-dimethylpentyl	142–3°C.	1.4162	75.95	76.03	12.75	12.70

TABLE I

Copolymers of Nonconjugated Linseed and Lower Alkyl Vinyl Ethers

Comonomer	Mole % of comonomer	Molecular weight	Degree of polymerization [a]	Viscosity (Gardner-Holdt)
Ethyl	75	3640	28.7	Z1
	50	4700	25.9	Y
	25	5600	23.7	X–Y
Isopropyl	75	2380	17.3	Z5
	50	3500	18.6	Z1
	25	2680	11.2	X
n-Butyl	75	2170	14.7	W
	50	3660	18.7	W–X
	25	4450	18.3	X
Isobutyl	75	4590	31.1	Z6+
	50	6660	34.1	Z3
	25	6250	25.7	Z
2-Chloroethyl	75	1665	11.0	Z1–2
	50	2000	10.1	Y
	25	1990	8.2	W–X
2-Methoxyethyl	75	1130	7.6	T–U
	50	1575	8.1	U–V
	25	2300	9.4	W
2-Ethylhexyl	75	11,100	58.4	>Z6
	50	11,100	49.7	Z5–6
	25	4100	15.9	Z1
n-Octyl	75	7800	41.1	Z3
	50	5700	25.5	Z1
	25	6100	23.7	Z
2,2-Dimethylpentyl	75	3920	22.0	>Z6
	50	5520	25.4	Z5–6
	25	4080	16.1	Z1–2

[a] $\text{Degree of polymerization} = \dfrac{\text{Mol. wt. of copolymer}}{\text{Av. mol. wt. of repeating unit}}$

$\text{av. mol. wt. of repeating unit} = \dfrac{x\,M_1 + y\,M_2}{x + y}$

M_1 = Av. mol. wt. of fatty vinyl ether (approx. 292).
M_2 = Mol. wt. of comonomer.
x and y represent number of moles of reactants in the copolymer.

Preparation of Polymers and Copolymers. Polymers were prepared by polymerization at room temperature in benzene by using stannic chloride catalyst (Table I). All polymerizations were performed by dissolving the appropriate monomers in A.C.S. benzene (3 ml./g. of monomers) at 25°C. in a suitable flask fitted with a stirrer, recording thermocouple, and nitrogen-inlet tube. The reaction was initiated by adding a solution of 8% stannic chloride in benzene. The amount of catalyst necessary was approximately 0.06 ml./g. of monomers used. As the reaction proceeded, the temperature rose steadily to a maximum in about 5 to 30 sec., then slowly began to fall. At this point the reaction was terminated by adding 50% aqueous methanol solution. The rate of temperature rise and the maximum temperature reached were dependent on the comonomers used and the composition of the polymer prepared.

All copolymers prepared were viscous oils, varying in color from colorless to yellow-orange. The degree of polymerization (Table I) obtained with most copolymer series ranged from 10 to 25.

Iodine values on the copolymers were determined by the Wijs method. Since consistent iodine values cannot be obtained directly on vinyl ethers by this

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method, it was necessary to calculate the iodine value for these materials from the iodine value of the alcohol before vinylation. A comparison of the values obtained on the monomer and copolymer showed little or no change, which indicated that polymerization had occurred primarily through the vinyl groups.

The viscosity characteristics of these copolymers deserve some comment. In general, the copolymer groups containing straight-chain lower alkyl vinyl ether components (*e.g.*, ethyl, *n*-butyl, and *n*-octyl) have lower viscosities than the series in which the nonfatty monomer is branched. This effect is clearly shown in Table I. The *n*-butyl copolymers range in Gardner-Holdt viscosity from W to X, whereas the isobutyl series have viscosities up to Z6. The same trend was observed when the *n*-octyl and 2-ethylhexyl copolymers were compared. The substituting of both hydrogen atoms on the 2-carbon with methyl groups, as in the 2,2-dimethylpentyl copolymer, did not cause an appreciable increase in viscosity over the mono-substituted 2-ethylhexyl and 2-methylpropyl (isobutyl) copolymers. The substituting of methyl for hydrogen on the α-carbon (see isopropyl copolymers) appears to result in considerable increase in viscosity. Table I shows that the change in viscosity with composition in a given copolymer series was less in straight-chain copolymers than in materials with branching on either the α- or β-carbon in the lower alkyl vinyl ether. The introduction of a chlorine atom or methoxy group on the β-carbon of the lower vinyl ether appears to produce copolymers comparable in viscosity to the straight-chain materials. However the level of viscosity of the 2-chloroethyl and 2-methoxyethyl copolymers may be low relative to the other products because of low molecular weight.

Preparation and Properties of Nonconjugated Linseed Copolymer Films

Previous work on conjugated fatty vinyl ether polymers and copolymers demonstrated that these materials formed hard, tack-free films when baked at elevated temperature but gave soft, tacky films when air-dried. However nonconjugated linseed vinyl ether polymer and certain of its copolymers were found to produce moderately hard, almost colorless films when dried in air at ordinary temperatures. Properly formulated homopolymer films were tack-free in 1 hr. and considered dry in 3 or 4 hrs. Copolymers required correspondingly longer air-drying times, depending on the composition of the material tested. These polymers and copolymer films were also subjected to several baking cycles to form films varying in properties from moderately hard and flexible to hard and somewhat more brittle. Most films had excellent adhesion to substrates like glass, black iron, and aluminum.

Air-Dried Films. Solutions were prepared by dissolving 1 g. of polymer in 3 g. of toluene. Film formation was studied with and without cobalt drier (0.1% as cobalt metal was added). The films were cast on glass plates for hardness tests and dip-coated on small glass test-tubes for chemical-resistance tests. Table II shows the results of Sward hardness tests measured on air-dried films of nonconjugated linseed polymer and some typical copolymers. Cobalt drier at the concentration used in this study had little effect on the hardness of air-dried films, a result that was different from the behavior of baked films, as will be seen later. Copolymer films rich in lower alkyl vinyl ether were soft and tacky but increased in hardness as the content of fatty vinyl ether was increased. The hardest air-dried film in this series was obtained from nonconjugated linseed vinyl ether homopolymer. No significant differences in hardness were observed between copolymers containing branched lower vinyl ethers and those containing straight-chain components.

TABLE II

Hardness of Nonconjugated Linseed Copolymer Films Air-Dried 75 Hrs.

Comonomer	Mole % of comonomer	Hardness (Sward)	
		Cobalt drier	No drier
Isopropyl	75	T[a]	T
	50	6	4
	25	6	4
Isobutyl	75	4	T
	50	4	4
	25	6	6
n-Butyl	75	T	T
	50	2	2
	25	4	4
Ethyl	75	2	2
	50	4	4
	25	6	6
	0	8	8

[a] Tacky.

The copolymers listed in Table II were immersed in 18% hydrochloric acid for 24 hrs. Films had good resistance to acid but were swollen by alkali in several minutes to several hours. In general, the copolymers richest in fatty vinyl ether were more resistant to alkali than the other materials. All air-dried copolymer films were observed to swell within 24 hrs. in benzene, chloroform, acetone, 95% ethanol, and ethyl acetate. They were unaffected by white gasoline during this period.

Baked Films. Films evaluated in this study were prepared as described for the air-dry materials. Wrinkling or gas-checking observed with conjugated soybean homopolymer films (2) was not shown by nonconjugated linseed polymer or its copolymer films in any of the baking cycles studied. Since the properties of a copolymer film might be expected to vary with baking conditions, several baking cycles were selected for use in this study. Previous work (3) has shown that extensive degradation of conjugated homopolymer films was produced by baking for 1 hr. at 150°C. with cobalt drier and that small differences in film properties could be magnified under these conditions. Thus films from the 150°C.-baking cycle were evaluated along with films obtained from a 200°C., 10-min. cycle. Film hardness and alkali, acid, detergent, and solvent resistance of films were evaluated. Since nine copolymers in each of three compositions were studied under the conditions described, the data will not be presented in its entirety. Instead comparisons will be made between representative copolymers whenever differences seem to be significant.

Data on the hardness of copolymer films are shown in Table III. The values listed were obtained by averaging hardness of films from three baking cycles. These baking cycles were a) 1 hr. at 150°C. with 0.1% cobalt drier, b) 10 min. at 200°C. with 0.1% cobalt drier, and c) 10 min. at 200°C. with no drier added. As the composition of a copolymer was varied from 25- to 75-mole % of nonconjugated linseed vinyl ether, film hardness increased with most copolymers. Exceptions were the 2-chloroethyl and isopropyl materials. Among all the baked films the 2-chloroethyl

TABLE III
Average Hardness (Sward) of Baked Nonconjugated Linseed Copolymer Films

Comonomer	Mole % linseed[a]		
	25	50	75
2-Chloroethyl	22	17	24
2-Methoxyethyl	16	19	26
Ethyl	11	13	18
Isobutyl	7	13	18
n-Butyl	8	14	13
n-Octyl	7	11	13
Isopropyl	7	13	11
2,2-Dimethylpentyl	6	7	13
2-Ethylhexyl	7	7	11

[a] Nonconjugated linseed homopolymer had a Sward hardness of 13.

and 2-methoxyethyl copolymers were hardest. With the alkyl vinyl ether comonomers, the increasing of chain length produces softer films (see ethyl, *n*-butyl, and *n*-octyl series) as does the branching of the alkyl chain in the 2-position (see isobutyl, 2-ethylhexyl, and 2,2-dimethylpentyl products). Baking conditions used had considerable effect on the hardness of films. With added cobalt drier, films baked at 150°C. for 1 hr. had Sward rocker values two to three times greater than those baked for 10 min. at 200°C. However qualitative examination of the infrared spectra of films showed that films baked at 150°C. were more extensively oxidized than those baked at 200°C.

Stability to alkali varied considerably with components in the copolymers, type of baking cycle, and composition of a particular copolymer. Films baked for 1 hr. at 150°C. with cobalt drier showed the least stability to 5% sodium hydroxide although certain of these products are much more resistant than the corresponding conjugated soybean materials (1). Stability of the nonconjugated linseed copolymers to alkali was interpreted more from the tendency to dissolve in alkali than from swelling since the latter phenomenon does not appear to show a significant trend. As the composition of a copolymer is varied from 25- and 75-mole % fatty vinyl ether, better stability toward alkali is attained as shown in Table IV. This effect was not clearly shown with the conjugated soybean copolymers. Ease of oxidation of the side chain in nonconjugated linseed polymers (containing the 1,4-diene system) may serve to exert a protective influence over the ether linkage, thereby reducing degradation and increasing alkali stability of these polymers. A comparison of the infrared spectra of baked films of nonconjugated linseed copolymers with conjugated soybean copolymers appears to confirm this suggestion. The spectra of baked conjugated soybean copolymer films show considerable oxidative degradation about the ether linkage as evidenced by the appearance of a strong absorption at 1180 cm^{-1}. This band has been shown to be associated with the development of ester carbonyl in the polymer (3). Baked nonconjugated linseed copolymer films also develop the 1180 cm^{-1} band but to a smaller extent.

TABLE IV
Alkali Stability of Nonconjugated Linseed Copolymer Films Baked 1 Hr. at 150°C. with Cobalt Drier

Comonomer	Mole % of comonomer	Swelling	Dissolving
		hrs.	*hrs.*
Isobutyl	75	0.25	0.75
Isobutyl	50	0.25	5
Isobutyl	25	0.50	24
Ethyl	75	0	1
n-Butyl	75	1	2.5
n-Octyl	75	6	24
2-Ethylhexyl	75	6	24
2,2-Dimethylpentyl	75	....	None
....	0	0.5	22

With straight-chain and branched-chain vinyl ether copolymers, the increasing of the chain length of the lower alkyl vinyl ether increases stability to alkali. Substitution of both hydrogen atoms at the β-position in the lower vinyl ether with alkyl groups gave better alkali stability than the monosubstituted materials (compare 2-ethylhexyl and 2,2-dimethylpentyl copolymers).

In general, all nonconjugated linseed copolymers were stable to 18% hydrochloric acid when immersed for 24 hrs. Some films darkened or frosted slightly during this period. Immersion in a wide variety of solvents for 24 hrs., *e.g.*, 95% ethanol, butanol, diethyl ether, hexane, acetone, mineral oil, and kerosene, produced no effect on the baked films. Chloroform caused swelling of all films within 24 hrs. while benzene produced some swelling with the branched copolymers.

Summary

The preparation of nonconjugated fatty vinyl esters in high purity was accomplished by reacting unsaturated fatty alcohols with ethyl vinyl ether. The overall yield of vinyl ether ranged from 78–85%.

Polymers and copolymers of nonconjugated linseed vinyl ether were prepared in benzene by using stannic chloride catalyst. Polymerization was initiated at room temperature. Comonomers used with nonconjugated linseed vinyl ether were ethyl, isopropyl, *n*-butyl, isobutyl, *n*-octyl, 2-ethylhexyl, 2,2-dimethylpentyl, 2-chloroethyl, and 2-methoxyethyl vinyl ethers. Number average molecular weights of the products ranged from 1,500 to 11,000. All polymers and copolymers were liquids with Gardner-Holdt viscosities ranging from T to greater than Z6. Copolymers with straight-chain lower alkyl vinyl ethers had lower viscosities than copolymers containing branched chain molecules.

A nonconjugated linseed polymer and certain of its copolymers produced satisfactory films when dried in air at room temperature. Nonconjugated linseed homopolymer dried tack-free in less than 1 hr. and was considered dry in 3 to 4 hrs. Baked films of the nonconjugated linseed polymer and copolymers were wrinkle-free, moderately hard, and flexible, and they had excellent adhesion to substrates like glass, black iron, and aluminum. The films were unusually resistant to acids, alkali, and most organic solvents.

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REFERENCES

1. Gast, L. E., Schneider, W. J., O'Donnell, J. L., Cowan, J. C., and Teeter, H. M., J. Am. Oil Chemists' Soc., *35*, 347–350 (1958).
2. Rheineck, A. E., private communication (March 26, 1957).
3. Schneider, W. J., Gast, L. E., Melvin, E. H., Glass, C. A., and Teeter, H. M., J. Am. Oil Chemists' Soc., *34*, 244–247 (1957).
4. Teeter, H. M., Dufek, E. J., Coleman, C. B., Glass, C. A., Melvin, E. H., and Cowan, J. C., J. Am. Oil Chemists' Soc., *33*, 399–404 (1956).
5. Teeter, H. M., Gast, L. E., and Cowan, J. C., Ind. Eng. Chem., *50*, 1703–1704 (1958).
6. Watanabe, W. H., and Conlon, L. E. (Rohm and Haas Co.), U. S. 2,760,990 (1956).

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