Nonconjugated Linseed Vinyl Ether by Vinyl Transetherification. Preparation Procedure[1]

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An improved procedure is described for preparing nonconjugated linseed vinyl ether monomer by transetherification of linseed alcohol with ethyl vinyl ether. By use of a mercuric acetate-oxalic acid catalyst mixture, an excess of ethyl vinyl ether, a reaction temperature of 45°C., and an evaporation, water-extraction procedure for continuous removal of by-product ethanol as the reaction proceeds, 91% of the linseed alcohol was converted to the fatty vinyl ether in 6½ hrs. When mercuric acetate was used alone, more catalyst was required; at 90°C. and above, the over-all rate and yield were reduced by partial deactivation of the catalyst. This reduction was attributed to a side reaction wherein the mercuric salt was added to the fatty acid radical at points of unsaturation. All the various methods that were compared for purifying the linseed monomer produced a product of polymerization quality. While vacuum distillation, followed by an alumina adsorption treatment, gave a monomer of the highest purity, a monomer, vacuum-distilled only, should be of suitable polymerization quality for many purposes.

THE POLYMERS of fatty vinyl ethers obtained from linseed and soybean oils show promise as protective coatings because of their good alkali-resistance and adhesion to metal (4,5). Films prepared from the nonconjugated linseed vinyl ether polymer have pronounced air-drying properties whereas the baked films are somewhat harder and have greater alkali-resistance. This paper reports on an improved method for the preparation of nonconjugated fatty vinyl ethers without the direct use of acetylene. A transetherification procedure, using mercuric acetate as a catalyst for preparing these fatty vinyl ethers from fatty alcohol and ethyl vinyl ether, has been described (4). The improvements relate to a method for continuously removing by-product ethanol from the reaction mixture and to the use of a mercuric acetate-oxalic acid mixture to catalyze the vinyl transetherification. With these improvements the catalyst level is cut by 80%, and the reaction time is reduced from several days to six to seven hrs.

Teeter, Gast, and Cowan obtained excellent yields of nonconjugated fatty vinyl ethers by modifying Watanabe and Conlon's procedure (6,7) for transetherification according to the following equation

$$\underset{\text{Fatty alcohol}}{ROH} + \underset{\text{Ethyl vinyl ether}}{C_2H_5OCH{=}CH_2} \overset{Hg(OA_c)_2}{\underset{25^{\circ}C.}{\rightleftharpoons}} \underset{\text{Fatty vinyl ether}}{ROCH{=}CH_2} + \underset{\text{Ethyl alcohol}}{C_2H_5OH}$$

Using a 10-mole excess of ethyl vinyl ether (EVE) and 0.031 mole of mercuric acetate with this interchange reaction, Teeter *et al.* obtained 88 to 90% conversion in the first step. After the removal of unreacted EVE and by-product ethanol by evaporation, new EVE and an additional 0.006 mole of catalyst were added for a second transetherification step, which gave a final conversion of 97 to 98%. Several days were required to complete the two steps at room temperature. If the mixture was refluxed, the time was reduced about one-half (4).

Experimental Results and Discussion

Materials and Methods. The nonconjugated linseed alcohol used was supplied by the Archer-Daniels-Midland Company, and its composition was similar to that reported previously (4,5). Commercial EVE was distilled to remove any inhibitor which sometimes interfered with the titration end-point in the vinyl ether analysis. Solvent-free transetherification mixtures were analyzed iodometrically for their fatty vinyl ether content (3).

Vinyl Transetherification. The relationship between various molar excesses of EVE and fatty vinyl ether yield was studied. A large molar excess and a long reaction time were required to obtain more than 90% conversion (Figure 1). This series of studies was made at 25°C., using 0.0256 mole mercuric acetate per mole of the linseed alcohol (*i.e.*, about 3 wt. % of the alcohol). With either 0.050 or 0.075 mole of catalyst added to 10 moles of EVE and 1 mole of the linseed alcohol, the time required for 90% conversion was reduced from about 80 to 24 and 12 hrs., respectively. However, if the quantity of catalyst was reduced to 0.013 mole, 310 hrs. were required to reach 85% conversion and after 600 hrs. the conversion was only 86%.

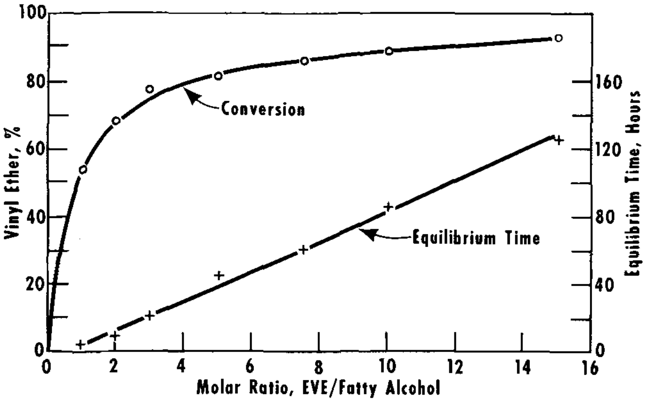

FIG. 1. Transetherification equilibrium values. Nonconjugated linseed alcohol was transetherified with ethyl vinyl ether at 25°C. with 0.025 moles of mercuric acetate used as the catalyst.

Continuous removal of by-product ethanol during the course of the reaction reduces the reaction time significantly. To accomplish this reduction a portion of the ethanol-EVE mixture was evaporated, condensed, and washed with water. The recycle EVE stream was either returned directly to the reactor or removed and dried for use in subsequent experiments. An apparatus for conducting the reaction in this manner at atmospheric pressure is illustrated in Figure 2. At higher temperatures the reaction was conducted under pressure in a 2,700-cc. cylindrical

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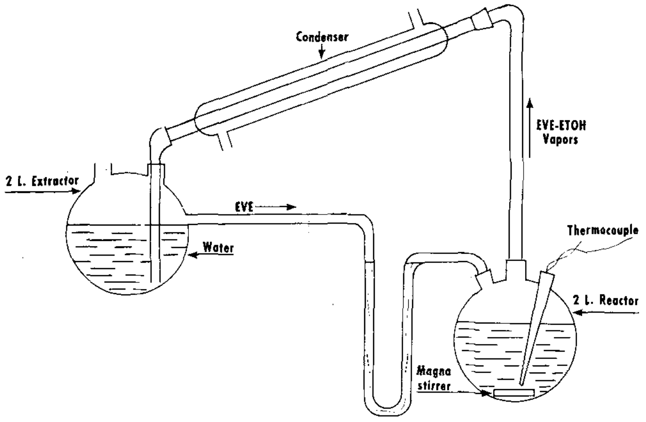

FIG. 2. *Vinyl transetherification apparatus.*

reactor, a condenser, a cylindrical washing chamber, and a settling chamber constructed of stainless steel or other metal. Conversions of 90% or better were obtained in both experimental units.

Transetherifications with continuous ethanol-removal were conducted at 45, 70, and 90°C., to determine if the reaction would proceed sufficiently rapidly at higher temperatures to permit the use of significantly smaller amounts of expensive mercuric acetate catalyst. Five moles EVE and 0.025 mole mercuric acetate were used per mole of linseed alcohol (Figure 3). To avoid the undesirable effect from possible water carry-over in this particular series of experiments the washed EVE was not returned directly to the reactor, but instead new EVE was added continuously to maintain the desired molar excess in the reaction mixture. In later experiments a direct EVE recycle reduced the final yield about 3%. Nitrogen was used to put the system under pressure and to raise the boiling point of the reaction mixture to the desired level, namely, about 20 to 40 p.s.i.g. for 70° and 90°C., respectively. As the reaction temperature increased, the initial transetherification rate increased; however, after 3 hrs. at 90°C., the over-all rate fell below that at 70°, and the final conversion was about 3% lower.

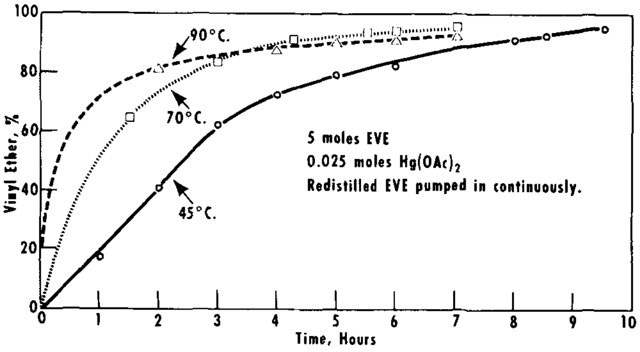

FIG. 3. Effect of temperature.

No acetals were found, but the presence of free mercury in the product indicated thermal degradation of the mercuric acetate at the 90°C. level.

Since the improvement obtained at higher temperatures was inadequate, the effects of modifying the mercuric acetate catalyst by adding oxalic, fumaric, and benzoic acids were investigated. Oxalic acid proved to be the most effective for reducing the mercuric acetate requirements. The reaction was conducted at 45°C. with 8 moles of EVE, and the washed ether was recycled directly. By incorporating anhydrous oxalic acid in the proper molar ratio, *i.e.*, about one mole per mole of mercuric acetate, the mercuric acetate level could be reduced to 0.0063 mole, or one-fifth the amount used initially with a 91% conversion obtained in 6½ hrs. Conversion curves for three reduced levels of catalyst are presented in Figure 4.

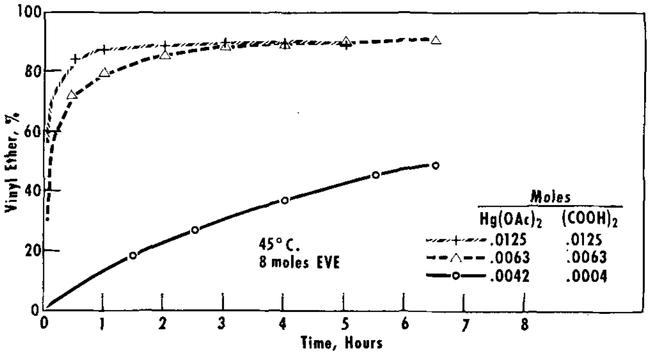

FIG. 4. Effect of mercuric acetate-oxalic acid catalyst level.

With 0.025 mole of oxalic acid and an equimolar quantity of mercuric acetate more than 86% conversion was obtained in the first hour. During the next 6 hrs. the fatty vinyl ether content progressively decreased (Figure 5), possibly because of hydrolysis, which is promoted by acidic conditions.

When fumaric acid was used in a 1/1 molar ratio, the initial conversion rate was lower than with oxalic, but the ultimate conversion was higher, almost 95% in 7 hrs. (Figure 5).

Benzoic acid in a 2/1 molar ratio and a reaction temperature of 45°C. gave only a slight increase in rate over mercuric acetate alone. In other transetherifications conducted at 65 and 97°C. with the benzoic-acid-modified catalyst at the 0.025-molar level, the over-all rate was lower at 97 than at 65°C. Since no free mercury was observed, the catalyst must have been partially deactivated by some mechanism other than thermal degradation. The reaction of mercuric salts with olefins to give addition compounds is well known; Ralston, Christensen, and Josh successfully added to methyl oleate equimolar quantities of mercuric acetate and methyl alcohol to prepare a weed killer (2). Chatt reviewed the preparation of addition compounds of olefins with mercuric salts but states that no satisfactory mechanism for the reaction has been advanced (1).

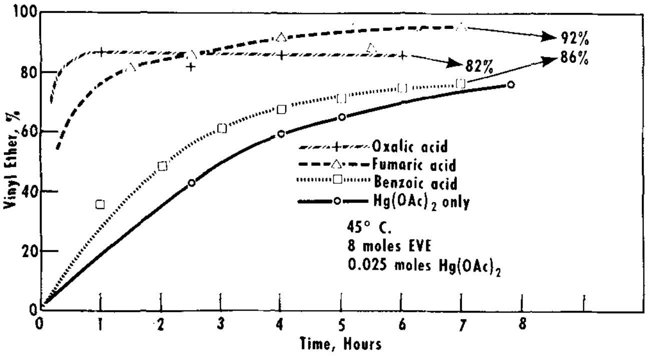

FIG. 5. Effect of catalyst modification, using one mole of added acid per mole of mercuric acetate. Numerical values given for oxalic, fumaric, and benzoic acids were obtained after reaction mixture stood over-night at room temperature.

The mercuric salts such as oxalate, benzoate, etc., were not tried. Neither were the higher homologs of oxalic acid, which are capable of forming cyclic mercuric salts with 6- and 7- rather than 5-membered rings.

Monomer Purfiication and Polymerization. EVE was removed from the transetherification mixture by evaporation at 100°C., first at atmospheric pressure and then under vacuum, and the stripped crude was distilled under vacuum. Products of equivalent purity were obtained with distillation pressures of 0.4 to 4 mm. A packed column gave distillates of the highest purity, usually 95 to 97%. A Vigreux column or a Claisen distilling head differed little in rectification ability and produced distillates of significantly lower purity. The Claisen head unit was much easier to operate. Fatty vinyl ether recovery approximated 85% with a packed column but was slightly higher with the Vigreux and Claisen head units.

The 23-mm. i.d. packed column contained 560 mm. of ⅛-in. ceramic Berl saddles while the Vigreux column was a typical 23-mm. i.d. unit with 17 sets of indentations spaced 25 mm. apart. The Claisen head had a 17-mm. i.d. x 200 mm. side arm tube. The three columns were operated at distillation rates of approximately 200, 115, and 230 g./hr., respectively, at about 2-mm. pressure and with a limited amount of reflux.

Various methods for purifying the linseed vinyl ether were compared because monomer purity directly influences the molecular weight and other characteristics of the polymer. The monomer was first purified by a single vacuum-distillation in a packed column containing 75 mm. of ⅛-in. Berl saddles, and the distillate was further purified by one of three methods. These were a second distillation in a Vigreux column, solvent extraction at 40°C. with an equal volume of anhydrous methanol, or an alumina adsorption treatment employing 1 g. of alumina per gram of monomer in a hexane solution. Polymers were prepared by the solvent polymerization technique, using a 6% solution of stannic chloride (6 ml. per 100 g. of fatty ether) as a catalyst (4). Monomer purities and molecular weights of the resultant polymers are given in Table I.

All monomers were of polymerization quality, and molecular weights of the polymers generally increased with the improvement in monomer purity. Although the molecular weight of the alumina-treated polymer was higher than normal, it illustrates the desirability of final monomer purification by alumina adsorption when the highest molecular weight is needed.

TABLE I
Influence of Monomer Purification Treatment upon Monomer Purity and Polymer Characteristics

Method of purification	Monomer purity	Polymer		
		Mol. wt.	Gardner viscosity	Gardner color
	%			
Single distillation	95.5	3700	X–Y	5–6
Redistillation of above	97.0	4650	W	1–2
Distillation and methanol extraction	97.7	3920[a]	X–Y	6
Distillation and alumina extraction	99.4	9350	Z_1–	2–3

[a] Molecular weight may have been reduced by a possible trace of methanol, which inhibits polymerization.

Subsequent exploratory studies indicated that polymerization conditions can be adjusted to produce polymers of higher molecular weight. By use of the best conditions, polymers that are satisfactory for a number of purposes should be producible from vacuum-distilled monomers.

Mercury Recovery. Free mercury was released from the linseed vinyl ether during the vacuum-distillation step and appeared in both the distillation flask and the product receiver. About 60% of the quantity used for the transetherification step at the 0.0250 molar level was recovered by a simple decantation.

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A Note on the Formation of 1,2-Diglycerides

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The reaction of glyceryl esters with fatty acids has been demonstrated to form an equilibrium mixture containing the 1,2-isomer as well as the 1,3-isomer previously reported (2). This procedure offers a method of synthesizing simple or mixed 1,2-diglycerides.

HERETOFORE the synthesis of 1,2-diglycerides has been feasible only through the use of special blocking techniques because of their tendency to isomerize to the 1,3-isomer by acyl migration (1). The work of Kester (2) describes the preparation of 1,3-diglycerides (simple and mixed) by the reaction of fatty acid with glycidyl ester. In our preparation of some pure 1,3-diglyceride compounds by Kester's procedure we also found appreciable quantities of the 1,2-isomer in the reaction mixture, indicating that an equilibrium mixture exists. Thus we have been able to prepare useful quantities of 1,2-distearin (26% yield) and 1,2-dipalmitin (23% yield) by this simple procedure.

These findings are in accord with the recent work of Crossley *et al.* (3), wherein equilibrium mixtures were produced by heat treatment of either of the two pure isomers.

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