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Part I

## Vinyl Monomers Derived from Fats and Oils

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### Abstract

Preparation, properties, and uses of monomers containing saturated or unsaturated C<sub>12-18</sub> fatty radicals derived from fats and oils and capable of polymerization or copolymerization by vinyl-type mechanisms are reviewed. Principal monomers discussed are vinyl esters and ethers, acrylic esters, allylic esters and ethers, and  $\alpha$ -olefins.

### Introduction

LONG CHAIN, vinyl monomers derived from fats and oils have both theoretical and practical significance. Study of these compounds not only has extended our knowledge of polymerization chemistry, but has broadened our understanding of the reactions of long chain fatty acids and of their versatility as intermediates in organic synthesis. A number of fatty vinyl monomers have achieved commercial importance both in the U. S. and abroad.

Although two reviews dealing with vinyl derivatives of fats appeared in 1960 (10,214), both are mainly concerned with vinyl esters and ethers and neither is in English nor readily available in the U. S. To make the extensive scientific and patent literature pertaining to the preparation, properties, and uses of vinyl monomers from fats and oils accessible, this comprehensive summary was undertaken.

In order to make the review as useful as possible while keeping it within reasonable bounds, certain criteria were observed in its preparation: 1.) Only monomers derived from saturated and unsaturated C<sub>12-18</sub> fatty materials are considered. 2.) Only monomers capable of vinyl polymerization are discussed, i.e., those containing the grouping CH<sub>2</sub>=CH-. 3.) Literature through 1960 has been covered if reported in *Chemical Abstracts*. However, not all references appearing in the scientific literature are cited. Instead, an effort has been made to select those that are leading references, that report research with well-characterized materials and methods, or that other-

wise contribute to a balanced presentation of the subject. A brief account of recent research at the Northern Division on vinyl ethers is included for completeness. 4.) Similarly, references to the patent literature are limited to those required to illustrate adequately the various possible industrial applications for each type of fatty vinyl monomer. 5.) Copolymers of one fatty vinyl monomer with another are discussed in connection with one monomer but not both.

### Discussion

#### Vinyl Esters

Much effort has been devoted to the development of a commercially useful synthesis for long chain vinyl esters. Reppe, who has summarized (165) his studies of acetylene chemistry, reported (167) preparing long chain vinyl esters as early as 1933 by reacting acetylene with fatty acids in presence of a catalyst. The reaction was conducted under pressure at 160-180°C with acetylene diluted with nitrogen to prevent explosions. Either the zinc or cadmium salt of the acid to be vinylated was used as catalyst. However, the possibilities for industrial exploitation of long chain vinyl esters were not at first appreciated. The extensive investigations of Swern and coworkers, which will be discussed more fully later in this section, resulted in development of a satisfactory process and in commercial production of vinyl stearate. Details of the process, including cost estimates, have been reported (43). The respective yields of crude, technical, and pure grades of vinyl stearate are about 94, 84, and 68%.

Several methods of synthesis that avoid use of acetylene under pressure are effective for laboratory

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TABLE I  
 Long Chain Vinyl Esters

Acid	Bp, C/mm Hg	$n_D^{20}$	$d_4^{20}$	Conversion to polymer, % <sup>a</sup>	Intrinsic viscosity <sup>b</sup>	Reference
Lauric.....	142/10	1.4368	0.8639	.....	.....	200
Myristic.....	147-8/4.8	1.4407	0.8617	.....	.....	200
Palmitic.....	168-9/4.5 <sup>c</sup>	1.4438	0.8602	.....	.....	200
Stearic.....	187-8/4.3 <sup>d</sup>	1.4423 <sup>e</sup>	0.8517 <sup>e</sup>	.....	.....	200
Oleic.....	178/2.8	1.4533	0.8691	.....	.....	198
Stearic.....	.....	1.4457	.....	85	0.166	88
Oleic.....	.....	1.4536	.....	57	0.119	88
Linoleic.....	148-50/0.75	1.4632	.....	9	0.033	88
10,12-Octadecadienoic.....	145-9/0.4	1.4750 <sup>f</sup>	.....	4	0.019	88
9,10-Epoxystearic.....	22.2-22.6 <sup>g</sup>	1.4529	0.9133	.....	.....	192
9,10-Epoxystearic.....	163-7/0.07	1.4539	.....	.....	.....	73
4-Ketostearic.....	53.6-54.2 <sup>g</sup>	1.4411 <sup>h</sup>	.....	.....	.....	31
12-Ketostearic.....	48.2-48.8 <sup>g</sup>	1.4457 <sup>i</sup>	.....	.....	.....	31

<sup>a</sup> Bulk polymerization; 2% benzoyl peroxide. <sup>b</sup> Benzene solution. <sup>c</sup> Mp 26.7-27.1C. <sup>d</sup> Mp 35-36C. <sup>e</sup> At 40C. <sup>f</sup> Sp.  $n_{221} = 98.5$ . <sup>g</sup> Melting point. <sup>h</sup> At 60C. <sup>i</sup> At 50C.

preparation of long chain vinyl esters. The best known is the vinyl interchange reaction between vinyl acetate and the fatty acid (1,211). Low temperatures are required for success of this reaction; at higher temperatures the mixed ethylidene ester is formed. Vinyl interchange is especially suitable for preparing vinyl esters from acids that are sensitive either to high temperatures or to alkaline conditions, e.g., linoleic acid. A procedure specifically designed for laboratory synthesis of long chain vinyl esters by vinyl interchange is available (201).

In 1954 Sladkov and Petrov (193) reported successful acylation of the enol form of acetaldehyde. For preparation of long chain vinyl ethers, the reaction is conducted at 60-80C in quinoline or pyridine solution. Vinyl laurate, myristate, palmitate, and stearate were obtained in yields of 79-88%, and vinyl oleate in yields of 68%.

An effective method for removing unreacted fatty acid from long chain vinyl ethers has been described (151,154). The crude ester is dissolved in acetone. Addition of sodium hydroxide precipitates the salt of the fatty acid which is removed by filtration. Urea complexes (203,204) may also be used for purifying long chain vinyl esters and ethers.

The properties of some long chain vinyl esters are summarized in Table I.

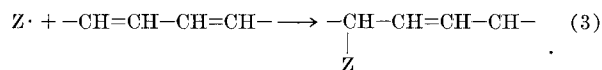
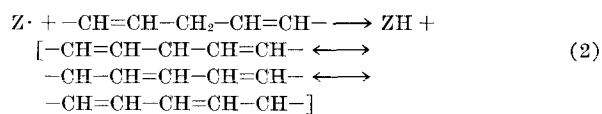
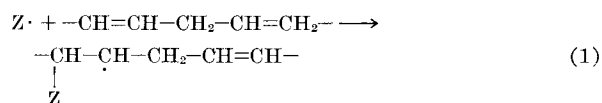
Vinyl esters of saturated long chain fatty acids readily respond to free-radical-induced polymerization. However, to achieve maximum conversions and molecular weights, these esters must be pure. In particular they must not be contaminated with esters of long chain unsaturated fatty acids, which are highly effective chain transfer agents. More than 5% of vinyl oleate in vinyl palmitate retards polymerization and sharply reduces conversion (151).

Harrison and Wheeler (88) conducted a comparative study of polymerization of several vinyl esters of C<sub>18</sub> acids containing different amounts and types of unsaturation (Table I). Both conversion to polymer and intrinsic viscosity of the products decreased as unsaturation increased and were lowest for vinyl 10,12-octadecadienoate in which the diene unsaturation is conjugated.

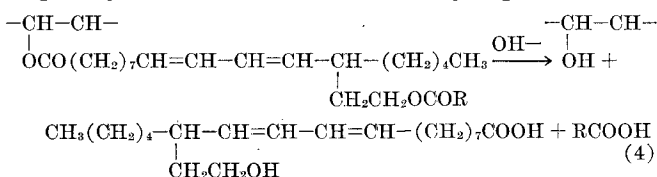
The result with the conjugated vinyl ester contrasts with observations made in a later study by Harrison and Tolberg (87) in which styrene was polymerized in the presence of methyl stearate, oleate, linoleate, linolenate and 10,12-octadecadienoate. As the amount of unsaturation increased, conversion fell from about 95 to 40% and the molecular weight of the polymer formed decreased from 39,000 to 13,400. Ester content of these polymers ranged from 0 to 1 molecule per 87 styrene molecules. The polymer formed in the presence of methyl 10,12-octa-

decadienoate, however, had a molecular weight of 40,000 and was obtained in 95% conversion. It contained about 1 molecule of ester per 25 styrene molecules and can be regarded as a copolymer. The ease of formation of this copolymer would not have been anticipated from the behavior of vinyl 10,12-octadecadienoate although, in retrospect, it suggests that the conjugated system should have participated to a considerable extent in the polymerization of this vinyl ester. It is possible that steric phenomena resulting from the presence of the vinyl and conjugated systems in the same molecule limit their interpolymerization in comparison with copolymerization of styrene and methyl 10,12-octadecadienoate.

Fatty acids obtained by saponifying polymers of unsaturated vinyl esters contained hydroxyl groups. Furthermore, poly(vinyl linoleate) contained diene conjugation, as well as polyunsaturation nonconjugatable with alkali; and poly(vinyl 10,12-octadecadienoate) retained about one-third of the diene conjugation originally present in the monomer. These results are convincing evidence for occurrence of reactions such as the following (Z· is an available free radical):



Radicals produced by these reactions do not participate effectively in chain propagation but undergo other reactions leading to chain termination and limiting conversion and molecular weight of the polymers. If Z· is derived from a vinyl ester, reactions 1 and 3 yield monomer units, such as the one shown in equation 4, from which hydroxyl-containing fatty acids would be obtained by saponification:



In their study of polymerization of highly purified, long chain vinyl esters, Port et al. (151) showed that polymers were readily obtained by bulk, dis-

persion (bead), solvent, or emulsion polymerization techniques. Molecular weights and conversions were influenced by the method of polymerization. Thus, the solution (in benzene) technique gave polymers from vinyl palmitate or laurate having molecular weights below 100,000, significantly lower than those obtained by the other methods. For example, polymers of these monomers, obtained by emulsion polymerization in conversions of 80–93%, had molecular weights (light scattering) of 270,000–685,000.

In general the degree of polymerization (DP) of polymers of long chain vinyl esters increased significantly when conversion exceeded 80%. DP's ranging from 2 (in presence of chain transfer agents) to 10,000 were observed. Polymers prepared in solution were unbranched, whereas those of high DP obtained by other procedures probably are branched.

Comparison of the behavior of vinyl acetate and vinyl stearate in copolymerization with isopropyl maleate, methyl acrylate, or acrylonitrile showed (228) that there was no essential difference that could be attributed to the length of the stearate chain. However for polymerizations in toluene, because the chain transfer constant increased with chain length (210), molecular weight obtainable for poly(vinyl stearate) was limited compared to poly(vinyl acetate).

In addition to these basic studies of the polymerization of long chain vinyl esters, Swern and coworkers investigated in detail copolymers of these esters with vinyl acetate, vinyl chloride, and vinyl alcohol. Vinyl acetate was copolymerized in various proportions with vinyl palmitate, stearate, and oleate (152). The reactions were conducted in benzene at 70–73°C and initiated with 0.5% benzoyl peroxide. True copolymerization took place with formation of copolymers having DP's of 400–500. Copolymerization with vinyl stearate and palmitate took place much more rapidly and in higher conversion than with vinyl oleate (7 hr vs. 36 hr and 55–65% vs. 21–58%).

Copolymerization with vinyl chloride was studied intensively with respect to both characteristics of the copolymerization reaction and properties of the copolymers (153). Copolymers were prepared by the suspension technique from vinyl chloride and up to 50 mole % of vinyl stearate or other long chain vinyl esters. Some typical results of the copolymerization experiments are given in Table II. Mechanical, thermal, viscous, and solubility properties of the products were determined in detail. Typically, values for properties such as flexural stiffness, tensile strength, brittle temperature, and modulus of elasticity decreased both with increasing chain length and with increasing content of the fatty comonomer. These results are similar to those observed in studies of plasticization of poly(vinyl chloride) with plasticizers like di-2-ethylhexyl phthalate or tri-cresyl phosphate. Copolymerization of vinyl chloride with long

TABLE II  
Copolymerization of Vinyl Esters of Long Chain Fatty Acids with Vinyl Chloride (153)

Ester	Amount in copolymer wt %	Tensile strength lb/in. <sup>2</sup>	Flexural stiffness (73°F) lb/in. <sup>2</sup>	Clash-Berg T <sub>r</sub> C	Milling temp F
Vinyl laurate	25.5	4840	177,000	.....	220
	34.8	2880	30,000	.....	150
Vinyl myristate	27.9	3160	141,000	.....	260
	29.8	2870	107,000	.....	240
Vinyl stearate	9.7	6000	226,000	41.7	265
	25.0	2800	103,000	19.4	275
	37.0	2160	.....	-11.8	180
Dioctyl phthalate	15.0	4820	214,000	28.9	340
	25.0	3720	11,000	1.0	340

TABLE III  
Reactivity Ratios in Copolymerization of Vinyl Stearate (M<sub>1</sub>) with Other Monomers

M <sub>2</sub>	r <sub>1</sub>	r <sub>2</sub>	Reference
Vinyl chloride.....	0.290±0.0028	0.745±0.025	127
Vinylidene chloride.....	0.075±0.025	3.80 ±0.05	127
Acrylonitrile.....	0.065±0.005	4.20 ±0.02	127
Acrylonitrile.....	0.03	4.3	228
Butadiene.....	0.034±0.034	34.5 ±6.6	127
Styrene.....	0.01 ±0.01	68 ±30	127
Vinyl acetate.....	0.78 ±0.01 <sup>a</sup>	1.15 ±0.13	152
Vinyl acetate.....	1.0 <sup>b</sup>	0.97	3
Methyl acrylate.....	0.03	5.8	228
Isopropyl maleate.....	0	0.0075	228

<sup>a</sup> For vinyl palmitate.

<sup>b</sup> For vinyl stearate containing 30% palmitate.

chain vinyl esters produces "internal" plasticization that is similar to "external" plasticization.

Copolymers containing less than 25 mole % of fatty comonomer were rigid and had good fabrication properties, such as low milling temperatures and viscosity-temperature coefficients. Those containing 30 and 50 mole % were permanently plasticized flexible products.

Copolymers of vinyl stearate and vinyl alcohol were prepared by selective hydrolysis of copolymers by vinyl stearate and vinyl formate (101). Water absorption of films of the copolymers was greatly reduced in comparison to films of poly(vinyl alcohol). As little as 1.5 mole % of vinyl stearate gave films insoluble in water at 98°C. The copolymers had high DP's and exhibited little branching. X-ray diffraction studies showed that the vinyl alcohol and vinyl stearate segments of the copolymers crystallized in separate lattices.

Reactivity ratios in copolymerization of vinyl stearate with a variety of other monomers are compiled in Table III.

In Japan, Asahara and coworkers (9,11) investigated the synthesis by vinyl interchange of saturated and unsaturated long chain vinyl esters and the copolymerization of acrylonitrile with vinyl esters of saturated fatty acids (9). Synthesis of vinyl laurate, stearate, oleate, and linoleate by reaction with acetylene under pressure has been reported by Otsuka et al. (143). Kimura and Yoshida (104) studied the copolymerization of vinyl chloride with several long chain vinyl esters. So far as can be determined from *Chemical Abstracts* references, the results of the Japanese workers are in agreement with those discussed.

In addition to the common free-radical sources, such as benzoyl peroxide or azobisisobutyronitrile, other agents can initiate polymerization of long chain vinyl esters. X-radiation has been reported (171) to induce polymerization of vinyl stearate in the solid state. Initiation with 1000 kv electrons yielded branched polymers (27). Irradiation of thin films with Co<sup>60</sup> γ-rays produced graft copolymers between vinyl stearate and polyethylene (15).

Long chain vinyl esters may also be polymerized thermally (146). Heating vinyl oleate at 230–250°C gave 38–44% free fatty acid plus a polymer approximating a trimer. Evidently thermal reversal of the original vinylation reaction occurred, for when an atmosphere of acetylene was provided and zinc oxide was added, heating gave a polymer having a molecular weight of 10,000. Amine oxides, e.g., trimethylamine oxide, are reported (55) to be suitable catalysts for polymerization of fatty vinyl esters at 50–250°C and 200–3,000 atmospheres.

Because vinyl esters of polyunsaturated fatty acids do not polymerize satisfactorily, products approxi-

mately equivalent to polymers of these vinyl esters have been prepared indirectly. Rheineck (172) described a procedure for direct esterification, in phenol solution, of polyvinyl alcohol with drying oil fatty acids. Eckey, Alderson, and Woestman (59) successfully prepared products equivalent to copolymers of vinyl acetate and polyunsaturated fatty vinyl esters by transesterification of polyvinyl acetate with fatty methyl esters in the presence of sodium tert-butoxide as catalyst. From 46 to 84% of the acetate groups were replaced by fatty acid groups, such as those from soybean methyl esters. Products prepared by either of these techniques showed promise as components of vehicles for protective coatings.

In addition to use of long chain vinyl esters as internal plasticizers for polyvinyl chloride, already discussed, other applications for these esters are numerous. Emulsion copolymers of vinyl acetate and vinyl stearate are excellent vehicles for water-thinned paints (155). A news report (7) indicated that one company undertook commercial production in anticipation of markets for vinyl stearate in this application, as well as in paper coatings for grease- and moisture-proof wrappings. Copolymers from vinyl acetate and 10–15% of vinyl stearate are fully plasticized and resist water and grease. Several reviews concern the use of vinyl stearate-acetate copolymers in emulsion paints (34,118,189).

Recently, however, production for the open market was stopped, presumably because the necessary selling price for vinyl stearate was too high to encourage development of large-volume outlets. It is believed that some captive production is maintained by at least one company for use in copolymerization with vinyl acetate to obtain a chewing gum base.

Possible use of poly(vinyl oleate) as a protective coating was revealed by Korshak et al. (110) who found that a polymer formed by heating vinyl oleate with benzoyl peroxide as catalyst for 104 hr gave films that would dry in 48 hr.

Copolymers of a variety of long chain vinyl esters with butadiene and terpolymers of these monomers with dimethylstyrene, styrene, and acrylonitrile have been evaluated as synthetic elastomers (158). Vinyl esters of stearic and oleic acids, as well as of linseed, cottonseed, or soybean fatty acids, were included in the study. Vulcanizates were somewhat softer than GR-S. Certain terpolymers, especially the terpolymer of butadiene, dimethylstyrene, and up to 10% of vinyl esters of linseed fatty acids have remarkable resistance to cut-growth.

Long chain vinyl esters have been proposed for use in a number of widely divergent applications. Polymers of vinyl esters of C<sub>14</sub>–C<sub>18</sub> acids (227); copolymers of these vinyl esters with vinyl chloride or maleic anhydride (157); and a terpolymer of vinyl stearate, maleic anhydride, and vinyl acetate (38) have been suggested as low-adhesion back coatings for pressure-sensitive tape.

Port et al. (156) investigated lubricant additives derived from polymers of fatty vinyl esters. The most promising materials for improvement of viscosity index and depression of pour point were poly(vinyl palmitate) and a vinyl palmitate-acetate copolymer containing 25 mole % of the palmitate. Products having similar uses are copolymers of long chain vinyl esters with fatty alcohol maleate esters (20) and copolymers of nitrogenous monomers such

as acrylonitrile with vinyl laurate or fatty alcohol fumarates (5).

Among other monomers, vinyl stearate has been suggested (195) for copolymerization with vinyl fluoride to obtain a binder for ultraviolet-absorbing coatings for polyethylene film. A copolymer of N-vinyl-2-pyrrolidone and vinyl laurate is reported to have surface-active properties (226). The iodine complex of a related copolymer prepared from vinyl stearate is stated (225) to be effective in nematode control.

#### Vinyl Ethers

General reviews of the preparation and properties of vinyl ethers are available (40,86,165,181,184). Because these reviews deal principally with synthesis of vinyl ethers by direct reaction of alcohols with acetylene and only to a limited extent with properties and polymerization of long chain vinyl ethers, emphasis will be placed specifically upon these long chain compounds.

The most satisfactory methods for synthesis of long chain vinyl ethers are very similar to those used for long chain vinyl esters: the alcohol plus acetylene in presence of a base and at 80 to 250°C; or the alcohol plus vinyl acetate in presence of mercurous acetate to give the interchange reaction. The first reaction, discovered by Reppe (166), was first reported in 1931. Acetylene, diluted with nitrogen to avoid explosion, may be employed at pressures up to 50 atmospheres and temperatures of 120–180°C or, for alcohols boiling at 180°C and above, acetylene at atmospheric pressure may be intimately contacted with the alcohol-catalyst mixture. Strong bases, such as potassium and sodium hydroxides, are preferred as catalysts although certain salts, e.g., zinc caproate, are reported (168) to be effective in the pressure reaction. Yields of vinyl ether obtained by the pressure reaction range from 80 to 95% based on alcohol for all primary alcohols from methyl through octadecyl (86).

The second reaction, which was studied by Watanabe (221,222), is convenient because it avoids use of acetylene and is effective for conversion of alcohols containing groups sensitive to heat or alkali. This reaction is however an equilibrium, and yields were reported (221) to be low (20–40%) if product vinyl ethers were not volatile enough to allow continuous removal during the reaction. Such removal is desirable because it drives the equilibrium to the right and also prevents a side reaction in which acetals are formed by addition of alcohol to vinyl ether. Modifications to overcome these difficulties will be discussed later.

Beginning about 1938, long chain vinyl ethers, especially stearyl and oleyl vinyl ethers and their polymers, were made and sold commercially in Germany (181). Although short chain vinyl ethers are available on the U. S. market, long chain vinyl ethers have not been produced industrially. However details, including cost estimates, of their production by pressure reaction with acetylene have been published (43).

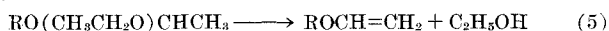
To facilitate laboratory-scale preparation of long chain vinyl ethers, Teeter and coworkers (207) studied in detail the reaction of acetylene at atmospheric pressure with fatty alcohols. Conditions and procedures were developed that gave excellent conversions in short times; e.g., conversion of stearyl alcohol to vinyl ether reached 85–88% in 1.5 hr at 180°C or

0.5 hr at 200C. Subsequently Mustakas and coworkers (137) modified the conditions and devised small pilot-plant-scale equipment whereby vinyl ethers of soybean fatty alcohols were obtained in purity of 98–99% and average yields of about 80% based on alcohol. Reaction time was less than 1 hr.

Principal modifications of the laboratory procedure that led to these excellent results were use of high acetylene flow rates (typically 2.4 l/min/kg charge), special precautions to insure very effective dispersal of acetylene in the reaction mixture, and heat treatment of the potassium hydroxide-alcohol mixture to convert hydroxide to alkoxide. A remarkable feature of this atmospheric pressure reaction is the efficient utilization of acetylene. Even though acetylene was passed through the reaction mixture at high rates, estimates indicate that up to 61% of the acetylene was absorbed and reacted.

When vinylation under alkaline conditions is applied to polyunsaturated fatty alcohols, such as soybean and linseed alcohols, the vinyl ethers produced, as expected, contain conjugation (e.g., soybean vinyl ether, 44% conjugation). The transesterification reaction was therefore investigated as a means of providing nonconjugated, polyunsaturated, fatty vinyl ethers. By using a 10-mole excess of ethyl vinyl ether as the transesterifying agent and providing for a second period of equilibration after removal of byproduct ethanol and addition of fresh catalyst and ethyl vinyl ether, conversions of 97–98% and 80% yields of purified vinyl ethers were obtained (78,208). Several days at room temperature were required to complete the two steps. Refluxing reduced the time about one-half. Under the conditions described no acetals were formed. Subsequently Brekke and Kirk (25) found that by use of a mercuric acetate-oxalic acid catalyst mixture, a reaction temperature of 45C, and an evaporation-water extraction procedure for continuous removal of byproduct ethanol, 91% conversions could be obtained in 6.5 hr. Required catalyst level was reduced by 80%.

Since these nonconjugated fatty vinyl ethers were needed to study coating films formed from them by baking, the presence of volatile mercury compounds in these products might be hazardous. Although sensitive tests failed to disclose the presence of mercury in purified products, an alternate method for their synthesis, dealcoholization of acetals (216), was investigated by DeJarlais (47). Deschamps et al (49) observed that preferential cleavage of the shorter chain alcohol occurred when lower molecular weight unsymmetrical acetals were dealcoholized by passage of their vapors over kaolin; consequently the following reaction should occur:



The required unsymmetrical acetals were readily obtained in yields up to 82% by addition of fatty alcohol to ethyl vinyl ether with *p*-toluene sulfonic acid as catalyst. When these acetals were heated at about 160C with either aniline sulfate or sulfanilic acid, the desired nonconjugated long chain vinyl ethers were obtained in yields of about 50%. Yields were limited by several side reactions including formation of ethyl vinyl ether and disproportionation yielding diethyl acetal.

Properties of some long chain vinyl ethers are given in Table IV.

Unlike vinyl esters, vinyl ethers yield only low molecular weight homopolymers when polymerization is initiated by free-radical catalysts. However poly-

TABLE IV  
Vinyl Ethers of Long Chain Alcohols

Alcohol	BP, C/mm Hg	$n_D^{20}$	Reference
<i>n</i> -Dodecanol.....	120/4	.....	166
<i>n</i> -Tetradecanol.....	140–5/4	.....	166
<i>n</i> -Hexadecanol.....	160–5/4	.....	166
<i>n</i> -Octadecanol.....	164/0.4 <sup>a</sup>	1.4451	207
<i>cis</i> -9-Octadecenol-1.....	165/1.25	1.4529	207
<i>trans</i> -9-Octadecenol-1.....	135–8/0.25	1.4530	207
<i>trans,trans</i> -9,11-Octadecadienol-1.....	160–2/0.6	1.4736	207
1,12-Octadecandiol (Divinyl ether).....	166/0.25	1.4524	207
(1-Monovinyl ether).....	135–80/2.0 <sup>b</sup>	.....	207

<sup>a</sup> Mp, 31C.

<sup>b</sup> Mp, 50.5–51.5C.

merization is readily initiated with ionic catalysts, such as sulfur dioxide, boron trifluoride, iodine, and metal halides like stannic chloride, ferric chloride, zinc chloride, and aluminum chloride. Catalysts, such as hydrosilicates, carbon, kieselguhr, and various metals precipitated on asbestos or silica gel, have been claimed to have catalytic activity (96). Recently it has been reported that short chain vinyl ethers are readily polymerized by Ziegler catalysts, such as vanadium trichloride-tri-*isobutyl* aluminum (89) or titanium tetrachloride-trialkyl aluminum (114), and by Grignard reagents (112).

Studies on polymerization of vinyl ethers have emphasized short chain materials as is evident from several reviews (60,184). Certain aspects of these studies deserve mention here because they are indicative of unrealized possibilities in polymerization of long chain vinyl ethers. If *isobutyl* vinyl ether is "flash" polymerized at –60 to –70C with boron trifluoride as catalyst, an adhesive, rubberlike polymer is obtained. However if boron trifluoride etherate is used as catalyst at about the same temperature, polymerization is slow and a nontacky polymer is obtained that, when stretched, yields a crystalline-type X-ray diffraction pattern (183). The crystalline polymer is the isotactic isomer (138). The polymer of *isobutyl* vinyl ether obtained at –78C by use of Ziegler catalysts likewise appears to be the isotactic isomer (114).

Except for octadecyl vinyl ether, no reports describing detailed studies of the polymerization of long chain saturated alkyl vinyl ethers and the properties of their polymers have been published. Teeter et al. (207) investigated the polymerization (benzene solutions at 30C to reflux temperature) of octadecyl vinyl ether with boron trifluoride and several metallic halides. The product with highest melting point (49C) had a number-average molecular weight of 4900 and was obtained by use of ferric chloride hexahydrate as catalyst. However poly(octadecyl vinyl ether) having a melting point of 55C is mentioned by Reppe and Schlichting (169). It was prepared by polymerization of molten octadecyl vinyl ether at 50–60C with the addition product of boron trifluoride and di-*n*-butyl ether as catalyst. Polymerization of octadecyl vinyl ether at 0C in a variety of solvents with boron trifluoride as catalyst was examined by Schneider et al. (186). Molecular weights varied from 1300 to 14,000 depending on the solvent. Solvents, arranged in order of increasing molecular weight of the polymer prepared therein, were chloroform, pentane-hexane, methyl chloride, carbon tetrachloride, and carbon disulfide. The polymer with the highest melting point (50–52C) had a molecular weight of 11,000. The polymer having a molecular weight of 14,000 melted at 48C, perhaps because of residual traces of solvent or other impurity.

TABLE V  
Viscosity-Molecular Weight Relationship for  
Long Chain Vinyl Ether Polymers  
Intrinsic viscosity =  $K'M^a$

Polymer series	$K' \times 10^3$	a
Octadecyl.....	1.7	0.47
.....	2.2 <sup>a</sup>	0.25
Soybean.....	5.1	0.34
Linseed.....	11.5	0.25

<sup>a</sup> See reference 71.

In a subsequent study Gast, Schneider, and Teeter (79) investigated the relationships between viscosity and molecular weight for polymers of octadecyl, soybean, and linseed vinyl ethers. Data fit the Mark-Houwink relationship: Intrinsic viscosity =  $K'M^a$ . Values obtained for  $K'$  and  $a$  are given in Table V. The value of  $a$  for poly(octadecyl vinyl ether) is near that usually obtained for linear vinyl polymers. Because the values for the soybean and linseed series are considerably lower, branching and crosslinking may have taken place via participation of the polyunsaturated fatty radicals in the polymerization. A similar study was made by Fee, Port, and Witnauer (71) on octadecyl vinyl ether polymers obtained by  $\gamma$ -irradiation.

Other basic studies of octadecyl vinyl ether include determination by Dunphy and Marvel (54) of the reactivity ratios in its copolymerization with vinyl 2-chloroethyl ether (monomer 2). Values obtained were  $r_1 = 2.67 \pm 0.06$  and  $r_2 = 0.21 \pm 0.06$ . These workers also prepared copolymers from octadecyl vinyl ether and 0 to 50 mole % of vinyl isobutyl ether (53). Melting points of the products decreased from 49 to 34C as the amount of short chain monomer was increased. In the same publication they note that a copolymer of octadecyl vinyl ether and vinyl 2-chloroethyl ether can be dehydrochlorinated to yield a product containing divinyl ether units and therefore pendant vinyloxyethyl groups. This product was easily crosslinked with acid catalysts.

Extensive studies still in progress by Teeter and coworkers on polymers of conjugated and nonconjugated linseed and soybean vinyl ethers and their copolymers with a variety of other monomers seek a product having satisfactory properties as a protective coating, especially for metal. Variables affecting polymerization of conjugated soybean vinyl ether, such as temperature, concentration, moisture content, and solvent ratio, were examined in detail (51). This work developed a highly reliable procedure for preparing polymers having molecular weights in the range of 4000-6000. With toluene as solvent and stannic chloride as catalyst, polymerization was initiated at room temperature and could be conducted successfully with up to 1 kg of monomer per batch. Further improvements in techniques for deactivating and separating the catalyst after polymerization and for reducing color were made by Mustakas, Raether, and Griffin (136), who successfully adapted the process to small (10-lb batches) pilot-plant production.

Study of formation of protective coating films (41, 209) from polyunsaturated fatty vinyl ether polymers and copolymers soon showed that these products had several unexpected properties. First, it was observed that despite their presumed high functionality to oxygen [DP's of the order of 15-20 and little or no loss of unsaturation during polymerization, especially for copolymers (77)], reaction with oxygen to give films was slow at room temperature. The films had to be baked to obtain good properties.

Secondly, if baking was conducted improperly, the films lost their initial high resistance to alkali and became easily soluble. This change was accompanied by appearance in the infrared spectrum of bands characteristic of ester group linkages (186).

Two basic investigations were conducted to obtain information on the possible causes for these two unexpected properties of the polymers. In one study (76), oxidative degradation of lauryl isopropyl ether was examined. This compound was selected as a simple analog of a unit in a vinyl ether polymer. In the presence of catalytic amounts of cobalt naphthenate, degradation of lauryl isopropyl ether produced lauric acid, acetone, isopropyl laurate, lower fatty acids from C<sub>2</sub> to C<sub>11</sub> and their esters, carbon dioxide, isopropyl alcohol, and polymeric acidic products. Obviously, if appreciable amounts of analogous products were formed in a fatty vinyl ether film, its resistance to alkali would be adversely affected.

In the second basic investigation (206), the molecular weight distribution was determined for several conjugated soybean vinyl ether homopolymers. A typical polymer having a molecular weight of 4800 showed a differential distribution curve closely approximating that expected for polymers obtained by simple difunctional polymerization. This curve showed that the species of the polymer present in largest amount had a DP of about 22. From the integral distribution curve, it was evident that half of this polymer consisted of species having molecular weights exceeding 7000.

While these studies were in progress, a large number of polymers, copolymers, and terpolymers were prepared in an effort to obtain desired film properties. Table VI itemizes the various materials that had been studied by the end of 1960. Space does not permit detailed discussion of the film properties of these products. However, considerably improved films were achieved. For example, certain allyl-conjugated linseed copolymers gave films when baked on steel for 30 min at 200C that were hard (Sward hardness 34), resisted 5% alkali for 24 hr, and displayed excellent flexibility and resistance to reverse impact (over 60 in.-lb). These properties contrast sharply with those of films obtained in the early phases of the

TABLE VI  
Copolymers of Polyunsaturated Fatty Vinyl Ethers

Comonomeric vinyl ether <sup>a</sup>	Fatty vinyl ether <sup>b</sup>		
	CS	CL	NCL
Ethyl.....	77 <sup>c</sup>	....	78
Isopropyl.....	....	....	78
n-Butyl.....	77	77	78
Isobutyl.....	77	....	78
2-Ethylhexyl.....	77	....	78
2-Chloroethyl.....	77	77	78
2-Methoxyethyl.....	77	....	78
Allyl.....	81	81	81
Vinyloxyethyl methacrylate.....	81	81	....
Divinyloxyethane.....	....	81	....
n-Octyl.....	....	....	78
2,2-Dimethylpentyl.....	....	....	78
Benzyl.....	....	....	48
2-Phenylethyl.....	....	....	48
2-Phenylpropyl.....	....	....	48
2-(p-tert-butylphenoxy)-ethyl.....	....	....	48
Cyclohexyl.....	....	....	48
Tetrahydrofurfuryl.....	....	....	48
2-Cyanoethyl.....	....	....	48
Methyl-1-(1,3-butadienyl).....	....	....	48
Phenyl.....	....	....	48
2-Benzyloxyethyl.....	....	....	48
Allyl + ethyl <sup>d</sup> .....	81	81	....
Allyl + isobutyl <sup>d</sup> .....	81	81	....
Allyl + 2-ethylhexyl <sup>d</sup> .....	....	81	....

<sup>a</sup> In nearly all examples several copolymers were prepared with varying amounts of comonomer.

<sup>b</sup> S = soybean; L = linseed; C = conjugated; NC = nonconjugated.

<sup>c</sup> Reference number inserted to indicate products prepared.

<sup>d</sup> Terpolymer.

work which at best resisted alkali for only about 2 hr.

The current status of research on vinyl ether films at the Northern Laboratory since 1960 deserves brief mention. From trends observed in study of the products shown in Table VI and from information obtained in the two basic investigations discussed, it was concluded that steric inhibition might be causing the difficulties encountered in realizing in full the anticipated potentialities of vinyl ether films. Even though a vinyl ether polymer chain contained many polyunsaturated units, their close proximity might lead to excessive intramolecular crosslinking instead of the intermolecular crosslinking needed for optimum film formation. Since proper curing of films greatly increased their alkali resistance, an adequate three-dimensional film structure might offer protection to sensitive ether linkages by minimizing access to oxygen. Therefore, bulky comonomers might possibly result in a disposition of polyunsaturated side chains that would favor intermolecular crosslinking.

To test these ideas, a number of copolymers of conjugated linseed vinyl ether with large cyclic comonomers, such as cyclopentadiene, 5-norbornene-2-methyl vinyl ether, dihydrocyclopentadienyl vinyl ether, and abietyl vinyl ether (52), were prepared. Results confirmed expectations since films from these copolymers showed greatly increased hardness and alkali-resistance. A typical product had a Sward hardness of 52 and resisted 5% alkali for 168 hr. Others resisted alkali for 288 hr.

An extension of this approach involved styrenation of these and other unsaturated vinyl ether copolymers (80,187). Again, properties were improved. A typical product containing 67% styrene had a Sward hardness of 60 and resisted alkali for over 65 days. Styrenation might be expected to lead to reduced intramolecular crosslinking although the large styrene content of the films would, in itself, contribute significantly to improved alkali resistance. Further studies of styrenated copolymers are in progress.

Studies on preparation and polymerization of saturated (108) and unsaturated (107) fatty vinyl ethers have been conducted in Japan by Komori and co-workers. Films from linseed, soybean, and cottonseed vinyl ethers and their copolymers with butyl and lauryl vinyl ethers were examined. Drying times of 4 to 6 hr were observed. Alkali resistance of homopolymers was reported as satisfactory while that for the copolymers ranged from fair to poor. Hardness of films was increased by baking, but no specific properties of the baked film were reported.

Polymers of vinyl ethers of saturated long chain alcohols were used in Germany as impregnating agents for leather and as synthetic waxes for floors and furniture. Also in Germany, low polymers of oleyl vinyl ether (188) were recommended as pour-point depressing agents in lubricating oils (see references 40, pp. 52-55, and 181, pp. 601-602, for discussion of utilization of long chain vinyl ethers in Germany).

Butler (30) has recommended poly(tetradecyl vinyl ether) as a pour-point depressant for lubricating oils. Chlorinated poly(oleyl vinyl ether) has also been suggested for this application (24).

Poly(C<sub>18</sub>-alkyl vinyl ethers) have been proposed as components of coatings for regenerated cellulose sheets (220) and as stabilizing agents for hydrogenation catalysts (94). Long chain vinyl esters and acrylate esters of long chain alcohols are also mentioned for this last application.

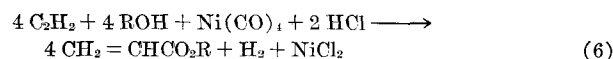
Although homopolymerization of vinyl ethers is ineffective if initiated by free radicals, this technique readily yields copolymers with other vinyl monomers. Copolymers of long chain vinyl ethers and maleic anhydride (141) or maleic esters (217) have been prepared as textile waterproofing agents. Copolymers of basic monomers, such as diethyl amino acrylate with vinyl dodecyl ether, dodecyl styrene, or dodecyl methacrylate, have been proposed as water-repellent compositions for textiles (133).

#### Acrylic Esters

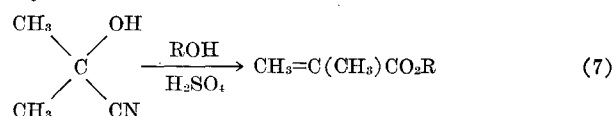
Acrylic esters include esters of long chain alcohols with acrylic acid as well as acids of similar or related structure, such as methacrylic, maleic, and itaconic acids. This group of monomers is important in lubricant additives, especially compounds like dodecyl and octadecyl methacrylates, which are available commercially.

Comprehensive reviews of methods of synthesis of acrylate (36a) and methacrylate (36b) esters are available; therefore, it will suffice to note here that, for long chain esters, a very convenient laboratory procedure is alcoholysis of methyl acrylate or methacrylate in the presence of an acidic catalyst and a polymerization inhibitor (164). Direct esterification is appropriate for preparation of maleates, fumarates, and other esters where the acids or anhydrides are readily available.

Acrylate esters are produced commercially (173) by the following reaction:



Methacrylates result from alcoholysis of acetone cyanohydrin:



In Table VII properties are given for a number of long chain acrylic esters. The patent literature is virtually the only source of reference for a variety of additional esters, such as dodecyl and octadecyl itaconates and hydrogen maleates, dedecyl maleate and fumarate, and oleyl itaconate. Information on their properties could not be found.

Acrylate and methacrylate esters, including the long chain members of the series, have been carefully characterized in great detail (163,164). Reference 163 presents equations useful for calculating boiling point, refractive index, molecular refraction, and density from the number of carbon atoms in any *n*-alkyl acrylate or methacrylate. Boiling points for

TABLE VII  
Long Chain Acrylic Esters

Acid	Alcohol	Bp, C/mm Hg	$n_D^{20}$	$d_4^{20}$	Brittle temp of polymer C	Reference
Acrylic	<i>n</i> -Dodecyl	120/0.8	1.4440	0.8727	-1	164
	<i>n</i> -Tetradecyl	138/0.4	1.4468	0.8700	23	164
	<i>n</i> -Hexadecyl <sup>a</sup>	148/0.04	1.4470 <sup>b</sup>	0.8628	35	164
	<i>n</i> -Octadecyl	31-32 <sup>c</sup>	1.4458	.....	42 <sup>d</sup>	102
Methacrylic	<i>n</i> -Dodecyl	167/10 <sup>e</sup>	1.4452	0.8755	-34	163
	<i>n</i> -Tetradecyl	191/10	1.4480	0.8710	-5	163
	<i>n</i> -Hexadecyl	213/10	1.4515	0.8695	15	163
	<i>n</i> -Octadecyl	235/10 <sup>f</sup>	1.4399 <sup>g</sup>	.....	34	85
Maleic Itaconic	<i>n</i> -Hexadecyl <sup>h</sup>	70-71.5 <sup>c</sup>	.....	.....	.....	92
	<i>n</i> -Hexadecyl <sup>h</sup>	76-76.5 <sup>c</sup>	.....	.....	.....	92

<sup>a</sup> Mp 24C. <sup>b</sup> At 30C. <sup>c</sup> Melting point. <sup>d</sup> Reference 85. <sup>e</sup> Boiling points for methacrylates are calculated values. <sup>f</sup> Mp 17C (71). <sup>g</sup> At 50C (71). <sup>h</sup> Monoesters.



TABLE VIII  
Reactivity Ratios in Copolymerization of Long Chain  
Acrylic Monomers

M <sub>1</sub>	M <sub>2</sub>	r <sub>1</sub>	r <sub>2</sub>	Reference
<i>n</i> -Dodecyl acrylate	Acrylonitrile	1.3±0.1	3.2±0.5	205
<i>n</i> -Octadecyl acrylate	Acrylonitrile	0.68±0.18	1.74±0.04	99
<i>n</i> -Octadecyl acrylate	Acrylonitrile	1.2±0.1	4.1±0.8	205
<i>n</i> -Octadecyl acrylate	Vinylidene chloride	1.01±0.01	0.91±0.05	205
<i>n</i> -Hexadecyl methacrylate	Vinyl acetate	68.3±3.2	0.135±0.055	134

methacrylate esters in Table VII were calculated by using the appropriate equation since experimental boiling points were presented graphically by Rehberg and Fisher (163) and could not be easily read. Table VII also shows brittle points of homopolymers obtained by free-radical polymerization. When brittle points are plotted against chain length for C<sub>1</sub> to C<sub>16</sub> acrylates and methacrylates, minimum brittle points are observed for *n*-octyl acrylate (-65C) and *n*-dodecyl methacrylate (-34C).

Polymerization of long chain acrylates and methacrylates is readily initiated by free radicals and yields solid, waxy polymers. Greenberg and Alfrey (58) investigated side chain crystallinity in such polymers. Side chain crystallinity is possible when a polymer contains long side chains; it is to be distinguished from second order transition phenomena and from crystallinity of segments of the backbone of the polymer. Melting ranges, changes in specific volume, and X-ray diffraction data show that side chain crystallinity is indeed present in these polymers. When the number of carbon atoms in the alkyl groups of polymers of alkyl acrylates and methacrylates is increased, beginning with methyl, mobility is increased and brittle point is reduced. This effect continues until chain length of the alkyl groups reaches 8 (acrylates) or 12 (methacrylates). At these points side chain crystallinity appears and causes reduced mobility and increased brittle points.

Study of copolymers of vinylidene chloride (102, 103) and acrylonitrile (100) with long chain acrylates has thrown new light on the phenomenon of internal plasticization. Butyl, octyl, and octadecyl acrylates were used as comonomers in these studies. In general, internal plasticization of poly(vinylidene chloride) gave compositions that showed improvement in properties, especially resilience, where deficiency had been observed in copolymers of vinyl chloride

and long chain vinyl esters. With the latter materials, the relatively small inherent crystallinity of poly(vinyl chloride) was considered to have been either decreased or destroyed by random distribution in the chain of units of the fatty comonomer. In externally plasticized poly(vinyl chloride), the plasticizer presumably solvates preferentially amorphous regions of the polymer. Poly(vinylidene chloride) is more highly crystalline than poly(vinyl chloride); therefore in copolymers with fatty monomers, sufficient crystallinity is retained to produce relatively better properties.

When acrylonitrile, whose homopolymers contain few crosslinks due to crystallinity, was copolymerized with the acrylate monomers, tensile strength and Clash-Berg temperatures varied inversely with weight percent of comonomer, regardless of its chain length. Orientation increased threefold the tensile strength of the copolymers. Both backbone and side chain crystallinity were detected in oriented copolymers of *n*-octadecyl acrylate.

Reactivity ratios for several long chain acrylic monomers have been determined (Table VIII).

Constants for the Mark-Houwink equation relating molecular weight and intrinsic viscosity have been determined (71) for *n*-octadecyl methacrylate:

$$a = 0.75; K' = 0.25 \times 10^{-4}$$

The most important application for long chain acrylic monomers is in the preparation of various types of lubricant additives. Table IX summarizes representative patents selected from the large number covering the various ways in which these monomers have been used in lubricant additives. A variety of other proposed uses for these monomers are summarized in the following paragraphs.

**Acrylates.** Products useful as textile fillers, adhesives, coatings, and wetting agents have been prepared (35) by polymerizing acrylic esters of castor oil and a variety of other hydroxylated fatty compounds. These esters were prepared by the nickel carbonyl reaction mentioned in this section. Mattil (130) suggests use of poly(C<sub>12</sub>-C<sub>18</sub> acrylates or methacrylates) to facilitate winterization of glyceride oils. Polyamides suitable for fungicides, bactericides, flocculants, and detergents have been prepared by aminolysis of a copolymer of methyl and dodecyl acrylates with 3-(isopropyl-amino)-propyl amine (132).

Copolymers of acrylonitrile with dodecyl and octadecyl acrylates and methacrylates were evaluated as

TABLE IX  
Use of Long Chain Acrylic Monomers in Polymeric Lubricant Additives

Monomers <sup>a</sup>	Function of polymer					References
	Viscosity index improver	Pour point depressant	Reduce wear and engine deposits	Reduce sludge	Detergent	
Dodecyl acrylate, methyl acrylate.....	X					150
Dodecyl methacrylate.....	X <sup>b</sup>	X <sup>b</sup>			X <sup>b</sup>	39
Dodecyl methacrylate, maleic anhydride.....			X			196
Dodecyl methacrylate, 2,3-dimethyl butadiene.....	X					84
Dodecyl methacrylate, acrylamide.....					X	4
Dodecyl methacrylate, <i>N</i> -dodecylacrylamide.....	X					32
Dodecyl methacrylate, <i>p</i> -aminostyrene.....	X				X	33
Dodecyl methacrylate, 2-methyl-5-vinyl pyridine.....	X	X	X		X	17
Dodecyl, octadecyl and methyl methacrylates.....	X	X				124
Dodecyl and octadecyl methacrylates, 2-methyl-5-vinyl pyridine.....		X				123
Cocoon alcohol fumarate, methyl methacrylate, vinyl acetate.....	X	X				65
Tallow alcohol fumarate, vinyl acetate, <i>N</i> -vinyl pyrrolidone.....				X <sup>c</sup>		63
Cetostearyl and octyl fumarates, vinyl acetate, <i>N</i> -vinyl pyrrolidone.....				X		64
Oleyl fumarate <sup>d</sup> .....				X		62
Oleyl fumarate, vinyl acetate.....					X <sup>e</sup>	66
Octadecyl itaconate, hexadecyl acrylate.....		X				215
Oleyl itaconate.....			X <sup>e</sup>			19

<sup>a</sup> When two or more monomers are mentioned together, they were copolymerized.

<sup>b</sup> Used as salt of sulfonated polymer.

<sup>c</sup> Polymer reacted with *t*-octylamine.

<sup>d</sup> Part of complex copolymer.

<sup>e</sup> Polymer reacted with P<sub>2</sub>S<sub>5</sub>.



wire insulation (176), but their properties were unsatisfactory. A terpolymer of acrylonitrile, dodecyl acrylate, and butyl methacrylate has been claimed as a sizing agent for synthetic fibers (175).

Terpolymers prepared from cyclohexyl acrylate or methacrylate; dodecyl or octadecyl acrylate or methacrylate; and a vinyl monomer, such as vinyl acetate, vinyl chloride, and styrene, are reported to have value in films and textile impregnating agents (67). These terpolymers can be crosslinked by heating at 100C with trishydroxymethyl propane.

**Methacrylates.** Long chain methacrylate homopolymers have been recommended as sizing materials for textiles (135). A copolymer of hexadecyl and octadecyl methacrylates can be used to make leather water-resistant (194). Adhesives have been obtained by copolymerizing dodecyl and hexyl methacrylates (115). On the other hand, copolymers of vinylidene chloride and octadecyl methacrylate have been claimed (106) as nonadhesive coatings for cellulose sheets. Alfrey (6) proposes copolymers of methyl methacrylate and long chain methacrylates of acrylates as chewing gum bases. Coatings with good adhesive strength, elasticity, and stability to light have been obtained (68) by copolymerizing styrene with a mixture of methyl and dodecyl methacrylates. Feldon et al. (72) studied elastomeric properties of copolymers of butadiene and octadecyl methacrylate, but their low-temperature flexibility was unsatisfactory.

**Other Acrylic Monomers.** Copolymers of mono-octadecyl maleate, dodecyl methacrylate, and styrene (18); of mono-octadecyl maleate, didodecyl maleate, butadiene, and styrene (70); and of (di-?) dodecyl maleate and styrene (37) have been suggested as textile sizes. Didodecyl maleate has been used for internal plasticization of vinyl chloride polymers (213). Copolymers of mono-octadecyl maleate and vinyl acetate serve as release agents for pressure-sensitive adhesives (105). Elastomers have been obtained by copolymerizing various mixtures of monomers containing butadiene and monododecyl maleate (69). Long chain monoesters of maleic acid have been used as intermediates in preparing copolymers that would be difficult to obtain directly. A copolymer of monohexadecyl maleate and styrene can be decarboxylated by heating 24 hr at 230C to obtain the corresponding acrylate copolymer (91).

#### Allylic Esters and Ethers

Long chain fatty acid esters of allyl and related alcohols can be prepared readily either by direct esterification with an acid catalyst and azeotropic removal of water or by alcoholysis of a fatty ester

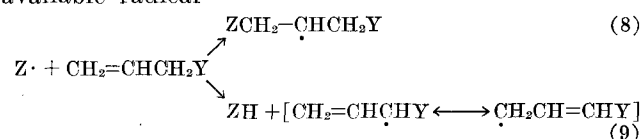
with the sodium alkoxide derived from the esterifying alcohol as catalyst. When appropriate, direct esterification usually produces much higher yields than does alcoholysis (198).

Swern, Billen, and Knight (198) investigated esters of oleic acid with allyl, 2-chloroallyl, methallyl, crotyl, 1-buten-3-yl, and furfuryl alcohols. The first two esters were prepared by direct esterification, the others by alcoholysis. Pertinent data are given in Table X, which also includes vinyl oleate for comparison.

Both homopolymerization of these esters and their copolymerization in amounts up to 40% with vinyl acetate were studied. Polymerizations were conducted in bulk at 100C with benzoyl peroxide as catalyst. As shown in Table X, 2-chloroallyl and furfuryl oleates polymerized most rapidly. These two esters are similar in that each contains an electronegative substituent on the  $\beta$ -carbon atom of the alcohol moiety. Copolymerizations with vinyl acetate proceed smoothly to yield products ranging from hard solids through tough elastic gels to soft masses or liquids. The occurrence of gelation is significant, because crosslinking could take place only by participation of the unsaturation in the oleic acid radical.

In a subsequent study, Swern and Jordan (200) extended this work to include esters of the same group of allylic alcohols with  $C_6$  through  $C_{18}$  saturated fatty acids. Data for the higher members of each series are collected in Table XI. Homopolymerization of the 2-chloroallyl, methallyl, and allyl esters was investigated. The 2-chloroallyl esters yielded brown viscous oils, whereas the allyl and methallyl esters showed little tendency to polymerize. Copolymers were prepared from vinyl acetate and the chloroallyl esters and from diallyl phthalate and the allyl esters. Products having a wide range of properties can be obtained.

In allylic polymerization there is competition in the formation of two types of radicals; if  $Z\cdot$  is an available radical



The radical formed by reaction 9 (degradative chain transfer) is stabilized by resonance, is less reactive, and is less effective in carrying on the chain than is the radical formed by reaction 8 (effective chain transfer). Presence of these unreactive radicals results in polymers having low DP's. In polymerization of allyl acetate, from 75 to 80% of chain trans-

TABLE X  
Allylic Esters of Unsaturated Fatty Acids

Alcohol	Acid	Yield, %	Bp, C/mm Hg	$n_D^{20}$	$d_4^{20}$	Relative rate of polymerization <sup>a</sup>	Conversion to polymer, % <sup>b</sup>	Intrinsic viscosity <sup>c</sup>	Reference
Allyl.....	Oleic	92	199-200/5	1.4539	0.8696	5	.....	.....	198
2-Chloroallyl.....	Oleic	80	216/5	1.4627	0.9318	1	.....	.....	198
Methallyl.....	Oleic	75	203-5/4.3	1.4546	0.8679	4	.....	.....	198
Crotyl.....	Oleic	79	203/3.5	1.4556	0.8693	6	.....	.....	198
1-Buten-3-yl.....	Oleic	68	193-4/3.5	1.4504	0.8628	7	.....	.....	198
Furfuryl.....	Oleic	80	195/0.1	1.4681	0.9295	2	.....	.....	198
(Vinyl).....	Oleic	(64)	(178/2.8)	(1.4533)	(0.8691)	(3)	.....	.....	198
Allyl.....	Stearic	.....	.....	1.4457	.....	.....	52	0.063	88
Allyl.....	Oleic <sup>d</sup>	.....	.....	1.4536	.....	.....	19	0.058	88
Allyl.....	Linoleic <sup>e</sup>	.....	148-50/0.1	1.4626	.....	.....	5	0.041	88
Allyl.....	10,12-Octadecadienoic	.....	154/0.08	1.4731 <sup>f</sup>	.....	.....	3	0.040	88
Allyl.....	Elaidic	.....	174-5/1.5	1.4528	.....	.....	.....	.....	212
2-Chloroallyl.....	Linoleic	73-84	184-9/1.9	1.4725 <sup>g</sup>	0.9455 <sup>g</sup>	.....	.....	.....	57

<sup>a</sup> Bulk polymerization; 1% benzoyl peroxide.

<sup>b</sup> Bulk polymerization; 2% benzoyl peroxide.

<sup>c</sup> Benzene solution.

<sup>d</sup> Epoxy derivative: bp 180-195C/0.5-1.0 mm (73).

<sup>e</sup> Diepoxy derivative: bp 210C/1 mm (73).

<sup>f</sup> Sp.  $\alpha_{332} = 95.2$ .

<sup>g</sup> At 25C.

TABLE XI  
Allylic Esters of Saturated Fatty Acids  
 $\text{RO}_2\text{C}_n\text{H}_{2n-1}$

R	n	Yield, %	Bp, C/mm Hg	$n_D^{20}$	$n_D^{30}$
Allyl <sup>a</sup>	12	90	136/4.5	1.4370	0.8648
	14	90	157/4.3	1.4404	0.8627
	16	85	25.3-25.5 <sup>b</sup>	1.4431	0.8609
	18	85	37.1-37.3 <sup>b</sup>	1.4420 <sup>c</sup>	0.8524 <sup>c</sup>
2-Chloroallyl <sup>a</sup>	12	80	151-2/4.2	1.4484	0.9493
	14	75	173/4.0	1.4505	0.9377
	16	60	28-29 <sup>b</sup>	1.4524	0.9291
	18	85	36-37 <sup>b</sup>	1.4497 <sup>c</sup>	0.9149 <sup>c</sup>
Methallyl <sup>d</sup>	12	40	165/1.0	1.4392	0.8638
	14	35	164-5/4	1.4423	0.8617
	16	35	186/4	1.4450	0.8604
	18	40	30.5-31 <sup>b</sup>	1.4471	0.8593
Crotyl <sup>d</sup>	12	65	167-8/10	1.4411	0.8656
	14	50	170/4.3	1.4442	0.8632
	16	70	188-9/3.8	1.4466	0.8616
	18	35 (85 <sup>a</sup> )	30.5-31 <sup>b</sup>	1.4467 <sup>c</sup>	0.8566 <sup>c</sup>
1-Buten-3-yl	12	80	156-7/10	1.4350	0.8567
	14	70	180/10	1.4384	0.8556
	16	70	180/4.3	1.4413	0.8546
	18	65	199/4.2	1.4440	0.8538
Furfuryl <sup>d</sup>	12	35	167-8/3.8	1.4578	0.9462
	14	40	187-8/3.9	1.4588	0.9352
	16	30	205-6/3.8	1.4580 <sup>e</sup>	0.9226 <sup>c</sup>
	18	35	40.7-41.4 <sup>b</sup>	1.4549 <sup>f</sup>	0.9086 <sup>f</sup>

<sup>a</sup> Prepared by direct esterification.

<sup>b</sup> Mp, C.

<sup>c</sup> At 40C.

<sup>d</sup> Prepared by alcoholysis.

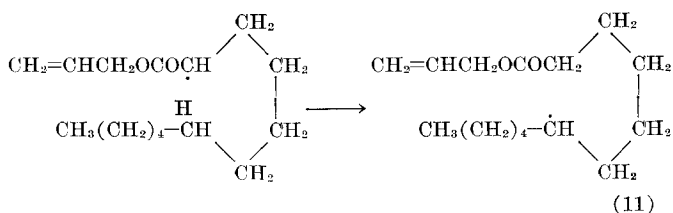
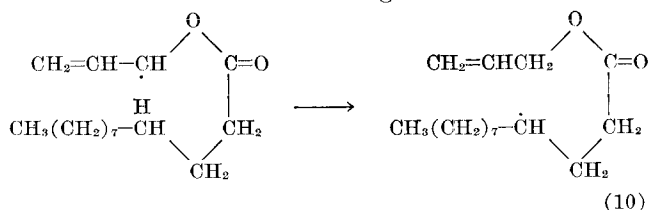
<sup>e</sup> At 35C.

<sup>f</sup> At 45C.

fers are degradative and DP's range from about 12 to 14.

Comparatively little is known about the kinetics and mechanism of polymerization of the long chain allylic esters. Sakurada and Takahashi (179) investigated the polymerization of allyl laurate and its copolymerization with vinyl acetate. If vinyl acetate is regarded as the "first" monomer in the copolymerization, reactivity ratios are  $r_1 = 0.71$  and  $r_2 = 0.8$ . For copolymerization of vinyl acetate and vinyl laurate,  $r_1 = 1.4$  and  $r_2 = 0.7$ . They found (178) that in homopolymerization allyl laurate showed effective chain transfer predominantly.

Gaylord (82), relying on the data of Sakurada and Takahashi (178), has noted that at 80C in the peroxide-catalyzed polymerization of allyl laurate, DP is approximately 7 but degradative transfer is only about 25%. He explains the low DP on the basis that allyl laurate contains many hydrogen atoms which can be abstracted by radical chains and thus stop their further growth. The low value for degradative transfer is considered to result from reactions such as the following:



Because allyl ethyl carbonate could undergo reaction 10 but apparently does not, Gaylord regards reaction 11 (which involves a different type of resonance-stabilized radical that can contribute to degradative chain transfer in allylic polymerization) as probably the more important reaction contributing to effective chain transfer in homopolymerization of allyl laurate. If this conclusion is correct, one would

expect effective chain transfer to become significant for allyl hexanoate or heptanoate because the chain length of the acid radicals in these esters is the minimum required to form a 5- or 6-membered ring of the type indicated for reaction 11. Allyl propionate exhibits about 57% of degradative chain transfer in its polymerization.

Still further complications of the allylic polymerization reaction are encountered with the isologous series of  $\text{C}_{18}$  allyl esters examined by Harrison and Wheeler (88). As indicated by the data of Table X, low molecular weight polymers were obtained as expected, however, conversions of allyl linoleate and 10,12-octadecadienoate to polymer were extremely low. As observed for the corresponding series of vinyl esters, fatty acids recovered by saponification of the polymers contained hydroxy groups. Allyl linoleate polymers contained both diene conjugation developed during polymerization and polyunsaturation nonconjugatable with alkali. Allyl 10,12-octadecadienoate polymers retained only about one-third of the diene conjugation originally present in the monomer. These results can be attributed to reaction of radicals with the fatty olefinic unsaturation, to abstraction of hydrogen from the 11-methylene group of linoleate, and to polymerization across the conjugated diene system of the 10,12-octadecadienoate.

Dyer and Meisenhelder (57) investigated polymerization of 2-chloroallyl linoleate and its copolymerization with styrene. Alone, this ester did not polymerize during 40 hr heating at 80C with benzoyl peroxide. With styrene, however, copolymerization took place readily. As the proportion of ester in the copolymer was increased to about 1 ester molecule per 9 styrene molecules, the softening point and intrinsic viscosity of the copolymers decreased. With greater proportions of ester, copolymers became infusible and largely insoluble. In these copolymerizations about 83% of the polymerization took place through the unsaturation of the chloroallyl group and the remainder through linoleate unsaturation.

A general review of allylic polymerization has been made by Laible (113).

Because direct polymerization of allyl esters of polyunsaturated fatty acids gives poor results, polymers of these esters are more conveniently prepared by esterification of poly(allyl alcohol). Polymers of allyl esters of linseed and soybean fatty acids have been prepared (2,42) by this procedure. Pollack (149) reported polymerization of allyl esters of linseed and soybean fatty acids by heating at 300C. The products presumably result from vinyl polymerization of the allyl groups and thermal polymerization of the fatty unsaturation.

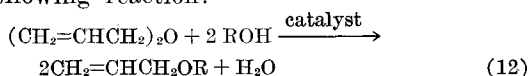
A wide variety of polymers and copolymers of fatty allyl esters have been proposed as viscosity index improvers, as pour-point depressants in lubricating oils, and as components of greases. To illustrate the scope of these uses, the following products may be listed: poly(allyl laurate) (116); poly(allyl myristate) (28); poly(allyl palmitate) (29); copolymers of allyl laurate, palmitate, and stearate with diallyl or divinyl phthalate (117), didodecyl itaconate (22a), vinyl laurate (22b), acrylate (22c,d) or methacrylate (22e) esters of fatty alcohols, 2-ethyl hexyl methacrylate (22f), and diodecyl maleate or fumarate (22g). In the last reference the use of methallyl stearate is also described. Allyl laurate may also be polymerized with maleic anhydride followed by esterification with mixed  $\text{C}_8\text{-C}_{18}$  alcohols (83a).

To obtain gelling agents for grease compositions, copolymers of allyl stearate and maleic anhydride have been converted to salts of metals, such as lithium, aluminum, and calcium (83b,c).

Jones (98) proposes copolymers of allyl esters with maleic anhydride as coatings and impregnating agents. After esterification with alcohols, these copolymers yield films by baking. He notes that while the copolymer with allyl caproate is a hard, colorless, fusible resin, copolymers with higher esters, such as allyl stearate, are elastic, soft, and waxy. Allyl, methallyl, and 2-chloroallyl esters of C<sub>6</sub>-C<sub>18</sub> acids yield copolymers with diallyl phthalate that are useful in coatings and adhesives (202). Use of allyl, methallyl, 2-chloroallyl, crotyl, 1-buten-3-yl, and furfuryl oleates as comonomers with vinyl chloride to produce internally plasticized copolymers has been described (199).

Monomeric allyl esters of long chain unsaturated acids, such as oleic, elaidic, linoleic, and linolenic acids and mixtures thereof, can be converted by epoxidation to products suitable for use as plasticizers, stabilizers, and crosslinking agents (73,148,212).

Very little information is available on allyl ethers of long chain fatty alcohols. Kornblum and Holmes (109) report synthesis of allyl octadecyl ether by reaction of octadecyl iodide and sodium alloxide. A more convenient method of synthesis, and one that might be attractive for commercial use, is described by Watanabe, Conlon, and Hwa (95,224). It is based on the following reaction:



Another procedure reported by these workers (233, 224) involves the reaction of allyl alcohol with fatty alcohols in presence of suitable catalyst. A suitable catalyst for either of these reactions is the equimolar complex of mercuric acetate and boron trifluoride. The first reaction gives considerably higher yields of long chain ethers than does the latter (71 and 47%, respectively, for allyl octadecyl ether). Properties of some long chain allyl ethers are given in Table XII.

Polymerization of allyl ethyl, butyl, and *n*-dodecyl ethers and their copolymerization with vinyl acetate have been studied by Sakurada and Takahashi (177). These monomers were less reactive in homopolymerization than were allyl esters, and lower DP's were observed. Degradative chain transfer amounted to 70% of the total transfer reaction. Copolymerization with vinyl acetate took place smoothly.

Allyl octadecyl ether has been suggested (161) as a component of a complex, hydrophobic, film-forming interpolymer for use as a carrier for silver halide in photography. Other components of the interpolymer include vinyl alcohol, *N*-allyl-palmitamide, and *N*-octadecyl-crotonamide.

#### $\alpha$ -Olefins

Long chain  $\alpha$ -olefins are perhaps the oldest fatty vinyl monomers known. Because preparation of these materials without isomerization of the  $\alpha$ -unsaturation to other positions in the chain is a problem, it is interesting that a method later found to be one of the best for avoiding isomerization was used by Kraft, who in 1883 reported (111) the preparation of very pure C<sub>12-18</sub>  $\alpha$ -olefins by pyrolysis of the corresponding long chain alkyl stearates and palmittates. Other esters have since been used in the same way; e.g., butyrate and laurate (129), phthalate

TABLE XII  
Allyl Ethers of Fatty Alcohols

Alcohol	Bp, C/mm Hg	Mp, C	n <sub>D</sub> <sup>20</sup>	Reference
Dodecyl.....	100/1	.....	.....	95
Hexadecyl.....	105-176/7	25	.....	95
	165-176/7	25	.....	46
Octadecyl.....	146-152/0.3	26-27	.....	224, 95
Octadecyl.....	150-52/2	28.5-29	1.4441	109
9-Octadecenyl.....	205-215/15	.....	.....	95

(218), and acetate (128,129). Asinger and Eckholdt (14) report a 60% yield of 95% 1-hexadecene by pyrolysis of octadecyl stearate at 360C.

Dehydration of fatty alcohols over acidic catalysts yields mixtures of isomeric long chain olefins. Asinger (13) has shown that dehydration of dodecanol over alumina yields all 6 isomeric olefins; the total of 1- and 2-isomers amounted to 40%. Asahara (8) dehydrated dodecanol with an alumina-phosphoric acid catalyst. The principal products were 2- and 3-dodecene with only minor amounts of the 1-isomer. Mixed isomers were also obtained when long chain primary alcohols were dehydrated at 330-370C with colophony as a catalyst (56). Walker (219) reported that dehydration in the vapor phase over alumina gave 90% conversion to a mixture of dodecene (60%) of unspecified isomeric purity and didodecyl ether (40%).

Pure  $\alpha$ -olefins are also formed by dehydrobromination of long chain alkyl bromides. Thus 98% yields of 99% 1-dodecene were obtained (93) by heating *n*-dodecyl bromide with dicyclohexylethyl amine. Somewhat lower yields were obtained when either silver stearate (12) or anion exchange resins (230) were used to effect removal of hydrogen bromide.

Olefins of unspecified isomeric purity have been obtained by deamination of long chain *n*-alkyl amines (as hydrochlorides or hypophosphates) (26) and by polymerization of ethylene with a trialkyl aluminum catalyst followed by treatment with nickel (231). The latter method produces a mixture of olefins containing 4 through 18 carbon atoms.

It has been reported that 50% yields of 1-dodecene were obtained by heating *n*-decanol with malonic acid in quinoline solution, adding anhydrous copper sulfate, and then distilling the mixture (147).

To obtain  $\alpha$ -olefins from unsaturated fatty acids, Marvel and Rogers (128) pyrolyzed oleyl acetate, elaidyl acetate, and *N,N*-dimethyl linoleyl amine oxide. Yields were 71%, 56%, and 42%, respectively.

Properties of long chain  $\alpha$ -olefins are given in Table XIII.

$\alpha$ -Olefins may be polymerized by heat or by catalysts of either free radical or cationic type (metal halides, hydrogen fluoride, and Ziegler catalysts). There are a number of references (e.g., 97,180,185, 197) to liquid polymerization products of  $\alpha$ -olefins and their use as lubricating oils. Dimerization of 1-dodecene and 1-octadecene by heating at 80-250C under pressure with aluminum or beryllium alkyls has been reported (232). However there is little information on the preparation and properties of solid polymers of high molecular weight.

Ziegler catalysts (e.g., triethyl aluminum-titanium tetrachloride) have been used to prepare copolymers of long chain  $\alpha$ -olefins having molecular weights of 100,000-1,000,000 (90). However physical properties of these products have not been described. By unspecified means Reding (162) prepared poly(1-dodecene) and poly(1-octadecene) that melted at 45 and 70C, respectively. He reported a first order crys-

TABLE XIII  
 Long Chain  $\alpha$ -Olefins and Related Compounds

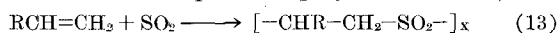
Olefin	Bp, C/mm Hg	Mp, C	$n_D^{20}$	$d_4^{20}$	Reference
<i>n</i> -Dodecene	89/10	-35.2	1.4256	0.7511	50
<i>n</i> -Tetradecene	119/10	-12.8	1.4320	0.7641	50
<i>n</i> -Hexadecene	147/10	4.1	1.4369	0.7741	50
<i>n</i> -Octadecene	172/10	17.6	1.4408	0.7818	50
1- <i>cis</i> -9-Octadecadiene	89/0.01	.....	1.4516 <sup>a</sup>	0.7932 <sup>b</sup>	128
1- <i>trans</i> -9-Octadecadiene	84/0.06	.....	1.4505 <sup>a</sup>	0.7852 <sup>b</sup>	128
1- <i>cis</i> -9- <i>cis</i> -12-Octadecatriene	69/0.015	.....	1.4610 <sup>a</sup>	0.7984 <sup>c</sup>	128

<sup>a</sup> At 25C. <sup>b</sup> At 26C. <sup>c</sup> At 22C.

tal-crystal transition at -25C for poly(1-dodecene). Marvel and Rogers (128) polymerized 1-dodecene and 1-octadecene with a Ziegler catalyst and obtained products having intrinsic viscosities of 2.98 (conversion, 97%; softening point 45-50C) and 1.52 (conversion, 83%; mp 73.5-78.0C). The last product had a molecular weight of 7850. Natta et al. (139) give the following second order transition temperatures for polymers of  $\alpha$ -olefins having the number of carbon atoms indicated: 12, -36C; 14, -32C; and 16, -27C. The minimum temperature is observed for poly(pentene-1) (-53C). Above this chain length, side chains become increasingly more important to the structure of the polymer than the backbone chain.

According to Marvel and Rogers (128), polymerization of 1-*cis*-9-octadecadiene and 1-*trans*-9-octadecadiene with a Ziegler catalyst gave products having intrinsic viscosities of 1.25 (conversion, 49%) and 1.35 (conversion, 72%), respectively. Softening points from 42 to 66C were observed for certain of the products prepared. 1-*cis*-9-*cis*-12-Octadecatriene yielded crosslinked polymers.

As do their short chain homologs, long chain  $\alpha$ -olefins readily react in the presence of peroxide catalysts with sulfur dioxide to produce polysulfones (44):



The most extensive field of application for long chain  $\alpha$ -olefins is in the preparation of various types of additives for lubricants and fuel oils. Typical of this use are copolymers with short chain olefins such as propylene (61), isobutene (75,229), or butadiene (74). The butadiene copolymer is condensed with a long chain mercaptan to obtain the desired lubricant additive. Additives are also derived from copolymers of long chain  $\alpha$ -olefins and vinyl acetate or other short chain vinyl ester. These copolymers may be used without further modification (23) after hydrolysis (142) or other hydrolysis and subsequent reaction with boric acid (190) or alkyl isocyanates (16). Similarly, ester groups of copolymers of  $\alpha$ -olefins and methyl methacrylate have been converted to amides (140). Additives have also been obtained by esterifying (with a long chain alcohol) copolymers of  $\alpha$ -olefins with maleic anhydride (121) or terpolymers with maleic anhydride and vinyl ethers (119). Copolymers of long chain  $\alpha$ -olefins with itaconic acid may be utilized as extreme pressure additives (120).

For other types of application, hard brittle resins have been obtained (160) by copolymerizing 1-hexadecene and maleic anhydride, and novel polyalcohols have been obtained (191) by hydrogenation of copolymers of 1-octadecene and acrolein. Copolymers of long chain  $\alpha$ -olefins and vinyl acetate have been proposed as subcoatings to minimize crater formation in epoxy coatings (45). Hydrolysis of similar copolymers containing up to 10% of  $\alpha$ -olefin yields high-vis-

cosity polyvinyl alcohol suitable for paper coatings and adhesives (26).

Esterifying copolymers of long chain  $\alpha$ -olefins and maleic anhydride with long chain alcohols yields products that increase the tensile strength of wax and facilitate its rapid application to paper (122). Pritchard (159) has proposed solid copolymers of 1-hexadecene and divinyl sulfide as oil-resistant gasketing material and liquid copolymers as rubber softeners.

#### Miscellaneous Fatty Vinyl Monomers

A number of additional vinyl monomers derived from fats are listed in Table XIV. Vinyloxyethyl esters of long fatty acids were prepared by alcoholysis of methyl esters with vinyloxyethanol (21). Peroxide-catalyzed polymerization of the saturated fatty acid esters yielded thermoplastic polymers (174). Polymerization of the linoleate was catalyzed by boron trifluoride etherate. The polymer produced a tough film when air-dried 2 days (cobalt drier) or baked 15 min at 150C (benzoyl peroxide as catalyst) (21). *N*-Vinyloxyethyl amides were prepared by reaction of acid chlorides with vinyloxyethyl amine (131). The products were polymerized (40% conversion) with azobisisobutyronitrile in dimethyl formamide. Related products were prepared from acid chlorides and 3-(vinyloxy)-*n*-propyl amine and its *N*-methyl derivative. With styrene 3-butene-1,2-diol dilinoleate yields clear, hard crosslinked copolymers that can be used as coating compositions or binders for floor coverings (58).

*p*-(*n*-Alkyl) styrenes in which the alkyl groups contain 2 through 18 carbon atoms have been studied by Overberger and coworkers (145).

The lower members of the series were polymerized at 70C with 0.1% of benzoyl peroxide as catalyst. The higher members (C<sub>12</sub>-C<sub>18</sub> alkyl groups) were polymerized by the combined catalytic action of benzoyl peroxide and ultraviolet light. Purification of polymers was effected by repeated solution in benzene and precipitation with methanol. The polymers were presumably liquid at room temperature except for the octadecyl derivative, which had a softening point at 32C. Determination of the relationship between chain length of the alkyl substituents and the second-order transition temperatures of the polymers showed that a minimum (-65C) occurred for poly(*p*-decylstyrene).

Polymers of long chain *p*-alkyl styrenes can be

 TABLE XIV  
 Miscellaneous Fatty Vinyl Monomers

Compound	Mp, C	Bp, C/mm Hg	Reference
Vinyloxyethyl laurate.....	.....	150/4	174
Vinyloxyethyl stearate.....	.....	195/1	174
Vinyloxyethyl linoleate.....	.....	188-205/1	21
<i>N</i> -Vinyloxyethyl lauramide.....	74-75	74-75	131
<i>N</i> -Vinyloxyethyl stearamide.....	86.5-88.0	86.5-88.0	131
3-Butene-1,2-diol dilinoleate.....	.....	.....	58
<i>p</i> - <i>n</i> -Dodecyl styrene.....	.....	158-163/1.2-1.4 <sup>a</sup>	145
<i>p</i> - <i>n</i> -Tetradecyl styrene.....	26-27	.....	145
<i>p</i> - <i>n</i> -Hexadecyl styrene.....	30.8-31.4	.....	145
<i>p</i> - <i>n</i> -Octadecyl styrene.....	38.3-39.0	.....	145
2-( <i>p</i> - <i>n</i> -Dodecylphenoxy) ethyl vinyl ether.....	.....	195-8/4	165
2-( <i>p</i> - <i>n</i> -Octadecylphenoxy) ethyl vinyl ether.....	.....	208-12/0.6	165
<i>p</i> - <i>n</i> -Dodecylcyclohexyl vinyl ether.....	.....	164-7/1.5	165
<i>n</i> -Dodecylphenyl vinyl ether.....	.....	.....	166
<i>n</i> -Octadecylphenyl vinyl ether.....	70/2 <sup>b</sup>	.....	166
<i>n</i> -Dodecyl vinyl thioether.....	.....	128-30/3 <sup>c</sup>	165
<i>n</i> -Octadecyl vinyl thioether.....	.....	183-5/2 <sup>d</sup>	165

<sup>a</sup>  $n_D^{25}$ , 1.5011.

<sup>b</sup> See text.

<sup>c</sup> Sulfoxide, mp 43-45C.

<sup>d</sup> Mp 33-34C; sulfoxide, mp 59C; sulfone, mp 57-59C.

used as coatings, adhesives, or chewing gum bases (144). Copolymers of hexadecyl styrene and methacrylic acids have been proposed (125) as detergents and antiwear additives for lubricating oils.

The remainder of the monomers listed in Table XIV were prepared by direct vinylation of the corresponding alcohol or mercaptan. No information on the physical properties of *n*-dodecylphenyl vinyl ether could be located. The boiling point indicated for *n*-octadecylphenyl vinyl ether is lower than would be anticipated in view of the boiling point of *p*-*n*-dodecylcyclohexyl vinyl ether and may be incorrect. No information on the polymerization of most of this last group of monomers could be located. *n*-Octadecyl vinyl thioether is reported to yield wax-like polymers if a solution in liquid sulfur dioxide is stirred for 12 hr at -10°C or if the monomer is heated for 24 hr at 50°C with iodine as a catalyst (170,182).

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