

Polymerization Studies with Vinyl Esters of Acids Derived from Agricultural Products

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This paper is a review describing the results of previously reported experimental work on vinyl esters derived from agricultural products. In particular, the reactivity ratios of a wide variety of vinyl esters with other vinyl monomers are reviewed. Also, the properties of a variety of vinyl ester-vinyl chloride copolymers are surveyed.

FOR the past eight years a research group has been working on the preparation of polymers from monomers obtained from various agricultural products. The work, initiated at the University of Illinois and continued at the University of Arizona, has dealt with a wide variety of monomers derived from cereal grains, oil seeds, animal fats, sugar cane, and naval stores. For this review, the topic is the polymerization of vinyl esters which have been synthesized from these various source materials.

Reactivity Ratios

One of the first projects undertaken was a study of the reactivity ratios of the vinyl esters of a wide variety of acids with various other polymerizable monomers (9) to learn something about the composition of the products which might be readily prepared and what charging ratios would lead to the most homogeneous products. Previous work had given values for vinyl acetate, vinyl formate, vinyl palmitate, vinyl stearate, and vinyl trifluoroacetate with such monomers as vinyl chloride, vinylidene chloride, acrylonitrile, styrene, methyl acrylate, and vinyl acetate. These values are collected in Table I.

The reactivity ratios of vinyl levulinate, vinyl pelargonate, vinyl pinonate, vinyl undecylenate, and vinyl stearate with representative monomers such as vinyl chloride, vinylidene chloride, acrylonitrile, butadiene, styrene, and methyl acrylate were determined for radical-initiated systems. The varied nature of the structures of these esters is illustrated by the formulas in Table II. The values of the reactivity ratios obtained are given in Table III.

In Table III note the narrow range of r_1 and r_2 values for the reactivity ratios of vinyl esters of widely different structures with vinyl chloride. The values obtained for these vinyl esters are also close to the r_1 and r_2 values for vinyl

Table I. Literature Values for Vinyl Ester Reactivity Ratios

M_1	M_2	r_1	r_2	Ref.
Vinyl acetate	Vinyl chloride	0.23 ± 0.02	1.68 ± 0.08	(14)
	Vinylidene chloride	0.0 ± 0.03	3.6 ± 0.5	(3)
	Acrylonitrile	0.061 ± 0.013	4.05 ± 0.3	(14)
Vinyl formate	Acrylonitrile	0.02 ± 0.02	6 ± 2	(4)
	Acrylonitrile	0.04 ± 0.005	3 ± 0.6	(2)
Vinyl stearate	Acrylonitrile	0.03	4.3	(22)
Vinyl acetate	Styrene	0.01 ± 0.01	55 ± 10	(14)
	Methyl acrylate	0.1 ± 0.1	9 ± 2.5	(14)
Vinyl stearate	Methyl acrylate	0.03	5.8	(22)
	Vinyl trifluoroacetate	Vinyl acetate	0.32	0.6
Vinyl palmitate	Vinyl acetate	0.78 ± 0.10	1.15 ± 0.13	(16)
Vinyl palmitate/stearate (30:70)	Vinyl acetate	1.00	0.97	(7)

Table II. Vinyl Esters Used in Reactivity Ratio Studies

Vinyl Ester	Formula
Vinyl levulinate (sugar)	$\text{CH}_3\text{CO}(\text{CH}_2)_2\text{COOCH}=\text{CH}_2$
Vinyl pelargonate (olive oil)	$\text{CH}_3(\text{CH}_2)_7\text{COOCH}=\text{CH}_2$
	$\text{CH}_2-\text{CH}(\text{CH}_2)_7\text{COOCH}=\text{CH}_2$
Vinyl pinonate (pinene)	$\text{CH}_2-\text{CO}-\text{CH}(\text{C}(\text{CH}_3)_2)$
Vinyl undecylenate (castor oil)	$\text{CH}_2=\text{CH}(\text{CH}_2)_9\text{COOCH}=\text{CH}_2$
Vinyl stearate (animal fat)	$\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}=\text{CH}_2$

Table III. Reactivity Ratios of Some Vinyl Esters

M_1	M_2	r_1	r_2
Vinyl levulinate	Vinyl chloride	0.419 ± 0.002	1.40 ± 0.004
	Vinyl chloride	0.282 ± 0.035	1.16 ± 0.06
Vinyl pelargonate	Vinyl chloride	0.446 ± 0.028	1.458 ± 0.04
Vinyl pinonate	Vinyl chloride	0.338 ± 0.065	1.06 ± 0.05
Vinyl undecylenate	Vinyl chloride	0.290 ± 0.025	0.745 ± 0.025
Vinyl stearate	Vinyl chloride	0.0 ± 0.01	4.08 ± 0.20
Vinyl pelargonate	Vinylidene chloride	0.03 ± 0.028	3.02 ± 0.18
Vinyl pinonate	Vinylidene chloride	0.054 ± 0.03	2.58 ± 0.09
Vinyl undecylenate	Vinylidene chloride	0.075 ± 0.025	3.80 ± 0.05
Vinyl stearate	Vinylidene chloride	0.059 ± 0.095	3.57 ± 0.16
Vinyl pelargonate	Acrylonitrile	0.143 ± 0.046	3.40 ± 0.04
Vinyl pinonate	Acrylonitrile	0.0 ± 0.01	1.82 ± 0.04
Vinyl undecylenate	Acrylonitrile	0.064 ± 0.005	4.2 ± 0.02
Vinyl stearate	Acrylonitrile	0.02 ± 0.02	26.3 ± 10
Vinyl pelargonate	Butadiene	0.015 ± 0.15	37.8 ± 6.5
Vinyl pinonate	Butadiene	0.015 ± 0.015	37.9 ± 4
Vinyl undecylenate	Butadiene	0.034 ± 0.034	34.5 ± 6.6
Vinyl stearate	Butadiene	0.01 ± 0.01	49.5 ± 15
Vinyl pelargonate	Styrene	0.01 ± 0.01	65 ± 17
Vinyl pinonate	Styrene	0.02 ± 0.02	29 ± 9
Vinyl undecylenate	Styrene	0.01 ± 0.01	68 ± 30
Vinyl stearate	Styrene	0.01 ± 0.01	68 ± 30

acetate and vinyl chloride. The r_1 values vary less than 0.1 from the average and the r_2 values vary less than 0.4 from the average.

The r_1 and r_2 values for the various vinyl esters with vinylidene chloride fall in a very close range. There is a slightly greater divergence in the r_1 and r_2 values of the various esters with acrylonitrile. The r_1 values for the butadiene and styrene copolymerizations were determined by assuming the maximum values of $r_1 = 1/r_2$; the minimum value was 0, and hence they were equal to $1/2 r_2 \pm 1/2 r_2$.

Vinyl undecylenate with methyl acrylate gave $r_1 = 0.031 \pm 0.026$ and $r_2 = 369.0 \pm 0.12$. This r_1 value is close to the values determined for vinyl stearate and vinyl acetate with methyl acrylate (22). Thus, the nature of the aliphatic acid moiety of a vinyl ester seems to have very little influence on its reactivity ratios with other vinyl monomers.

Levulinic acid is made from sugar by acid treatment; pelargonic acid is derived from oleic acid by oxidation; pinonic acid is obtained by oxidation of pinene; undecylenic acid is obtained by the pyrolysis of ricinoleic acid; and stearic acid is a constituent of most, if not all, natural fats.

Copolymer Studies

Another series of vinyl ester copolymerizations dealt with attempts to find a comonomer to use with vinyl chloride which might serve as a permanent plasticizer for the copolymer. Some experiments reported by Port and coworkers (77) had indicated that vinyl stearate copolymerized with vinyl chloride showed some internal plasticization, and it was felt that some other vinyl monomers with ester, keto, and halogenated and cyclic ring structures might serve this purpose better.

Preliminary experiments indicated that the level of vinyl ester incorporated in a vinyl chloride copolymer could not exceed 30% by weight without causing considerable depression in the tensile strength of the final product.

The esters which have been studied are listed in Table IV.

Vinyl pinonate (I) copolymerized readily with vinyl chloride to give polymers which milled readily at 120° to 150° C. and had a tensile strength and a rupture strength of about 8500 to 10,000 p.s.i. The best combination of properties came in the polymers containing about 20% of the vinyl ester. This composition had an elongation of 123%. The flex temperature determined by the Clash-Berg torsional stiffness method in ASTM D 1043-51 was 65° C. (73).

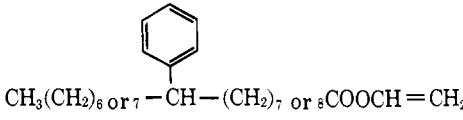
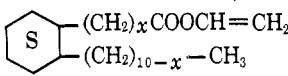
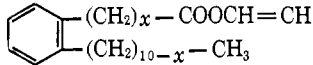
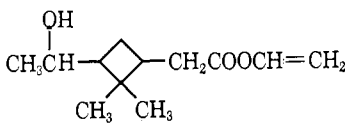
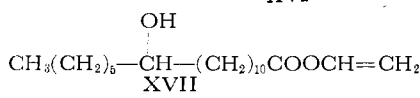
Pinic acid, like pinonic acid, is obtained by oxidation of pinene and the

Table IV. Some Vinyl Esters

Structure of Vinyl Ester	Agricultural Source	Ref.
From Pinonic Acid		
$\begin{array}{c} \text{CH}_3\text{CO} \diagdown \quad \diagup \text{CH}_2\text{CO}_2\text{CH}=\text{CH}_2 \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$ <p style="text-align: center;">I</p>	Pinene	(13)
From Pinic Acid		
$\begin{array}{c} \text{ROOC} \diagdown \quad \diagup \text{CH}_2\text{CO}_2\text{CH}=\text{CH}_2 \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$ <p style="text-align: center;">II</p> <p style="text-align: center;">R = C₂H₅—, n—C₄H₉—, and CH₃(CH₂)₃CH—CH₂— C₂H₅</p>	Pinene	(12)
$\begin{array}{c} \text{CH}_2=\text{CHOOC} \diagdown \quad \diagup \text{CH}_2\text{—CO}_2\text{R} \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$ <p style="text-align: center;">III</p> <p style="text-align: center;">R = C₂H₅—, n—C₄H₉—, CH₃(CH₂)₃CH—CH₂—, and $\begin{array}{c} \text{CH}_2\text{CH}_2\text{—} \\ \\ \text{C}_6\text{H}_5 \end{array}$</p>	Pinene	(12)
From Pinonic Acid		
$\begin{array}{c} \text{OCOCH}_3 \\ \\ \text{CH}_3\text{CH} \diagdown \quad \diagup \text{COOCH}=\text{CH}_2 \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$ <p style="text-align: center;">IV</p>	Pinene	(12)
$\begin{array}{c} \text{OC—O—C} \\ \quad \\ \text{CH}_2\text{—CH—(CH}_2\text{)}_3\text{COOCH}=\text{CH}_2 \\ \quad \quad \quad \\ \quad \quad \quad \text{CH}_3 \end{array}$ <p style="text-align: center;">V</p>	Pinene	(12)
From Ketostearic Acids		
$\text{CH}_3(\text{CH}_2)_{13}\text{CO}(\text{CH}_2)_2\text{—COOCH}=\text{CH}_2$ <p style="text-align: center;">VI</p>	Oiticia oil	(10)
$\text{CH}_3(\text{CH}_2)_{17} \text{ or }_{15} \text{CO}(\text{CH}_2)_8 \text{ or }_7\text{—COOCH}=\text{CH}_2$ <p style="text-align: center;">VII</p>	Vegetable oils	(10)
$\text{CH}_3(\text{CH}_2)_3\text{CO}(\text{CH}_2)_{10}\text{COOCH}=\text{CH}_2$ <p style="text-align: center;">VIII</p>	Castor oil	(10)
From Vegetable Oils		
$\text{CH}_3(\text{CH}_2)_7\text{CHClCHCl}(\text{CH}_2)_7\text{COOCH}=\text{CH}_2$ <p style="text-align: center;">IX</p>	Vegetable oils	(11)
$\text{CH}_3(\text{CH}_2)_4\text{CHClCHCl}(\text{CH}_2)_7\text{CHClCHCl}(\text{CH}_2)_7\text{—COOCH}=\text{CH}_2$ <p style="text-align: center;">X</p>	Vegetable oils	(11)
$\text{CH}_3(\text{CH}_2)_7\text{CHClCHCl}(\text{CH}_2)_{11}\text{COOCH}=\text{CH}_2$ <p style="text-align: center;">XI</p>	Vegetable oils	(11)
$\text{CH}_3(\text{CH}_2)_{14-20}\text{COOCH}=\text{CH}_2$ <p style="text-align: center;">(mixed C₁₆ to C₂₂ acid)</p> <p style="text-align: center;">XII</p>	Vegetable oils	(11)

(Continued on next page)

Table IV (continued)

Structure of Vinyl Ester From Vegetable Oils	Agricultural Source	Ref.
	Vegetable oils	(11)
<p>XIII</p> <p>From a Cyclic Acid and Hydroxy Acids</p> 	Vegetable oils	(11)
<p>XIV</p> 		
<p>XV</p> 	Pinene	(8)
<p>XVI</p> 	Castor oil	(18)
<p>XVII</p>		

isomeric vinyl esters (II and III) can be prepared selectively (6, 15). The isomeric vinyl esters (II and III) do not show any marked differences in copolymerization behavior with vinyl chloride, even though one has the vinyl ester carboxy group attached directly to the ring and the other has the vinyl ester carboxy group one carbon removed from the ring.

When the R group in the isomeric esters (II and III) was butyl, octyl, or hydrononyl, the rate of polymerization was slower than that observed when R was ethyl. The vinyl chloride copolymers containing 24 to 26% of vinyl ester component were tested as rigid plastics by the general procedure in ASTM Test 638-52T. None showed internal plasticization to an effective degree. The flex temperatures were in the range of 42° to 59° C., elongations were 20 to 140%, and tensile strength at the break point ranged from 7000 to 12,000 p.s.i. The hydrononyl moiety was less effective as a plasticizer than were the alkyl groups (12).

Vinyl pinolate acetate (IV) was obtained by acylation of the product obtained by catalytic reduction of pinonic acid followed by ester interchange with vinyl acetate. The lactone (V) was obtained by a Willgerodt reaction on homoterpenyl methyl ketone followed by ester interchange with vinyl acetate (6, 15). The test results on the vinyl pinolate acetate (IV)-vinyl chloride and the vinyl lactone (V)-vinyl chloride copolymers were very similar to those reported for vinyl pinolate (XVI) (12).

The ketostearic acids (VI, VII, and VIII) were obtained by oxidation of the corresponding hydroxy acids. The vinyl ketostearate-vinyl chloride copolymers showed interesting differences in properties depending on the position of the carbonyl group in the stearate chain. Vinyl-4-ketostearate (VI) at a 20% level gave copolymers with vinyl chloride which were too brittle to test. The mixed vinyl 9(10)-ketostearate (VII) and the vinyl 12-ketostearate (VIII) copolymers with vinyl chloride in the 20 to 25% ester composition range had tensile strengths somewhat higher than a vinyl stearate-vinyl chloride control copolymer and better elongation (150 to 200%) compared to a 65% elongation for the vinyl stearate control copolymer. The flex temperatures were in the range of 27 to 36° C. (10).

The chlorosubstituted vinyl esters (IX, X, and XI) were obtained by low temperature chlorine addition to the corresponding unsaturated acids (7, 20) followed by ester interchange with vinyl acetate. The 9(10)-phenylstearate (XIII) was obtained by the addition of benzene to oleic acid (27).

Vinyl 9,10-dichlorostearate (IX)-vinyl chloride copolymers containing about 26 to 27% of the vinyl ester had tensile strengths in the 3200-p.s.i. range, elongations of about 65% with some indication of necking down, and brittle temperatures of 16° C. which is only 10° higher than for a similar vinyl stearate-vinyl chloride copolymer. The vinyl tetrachlorostearate (X)-vinyl chloride copolymers had a lower tensile strength

and had a higher brittle temperature (47° C.). Vinyl dichlorobehenate (XI) at the 30% level gave a copolymer with vinyl chloride with good tensile strength (2600 p.s.i.), fair elongation (25%), and a brittle temperature of -2° C. The vinyl ester of technical behenic acid (XII) and the vinyl 9(10)-phenylstearate (XIII) copolymers with vinyl chloride were not promising (17).

The carbon skeleton of cyclic esters XIV and XV shown in Table IV is obtained by base-catalyzed cyclization of the linolenic acid (18). Small samples of the cyclized acid were readily hydrogenated; however, hydrogenation of larger samples proceeded slowly. A disproportionation or aromatization reaction competed with the hydrogenation reaction. The cyclic ester used in this polymerization series contained 60% of the aromatic ester (XV) and 40% of the saturated ester (XIV). The vinyl ester was obtained by addition of the free acid to acetylene under pressure (18).

The mixed cyclic fatty acid vinyl esters (40% XIV:60% XV) imparted a slight plasticization to vinyl chloride copolymers with brittle temperatures of 25° to 54° C. The 12% ester level gave the highest tensile strength (7100 p.s.i.), the highest elongation (30%), and the highest brittle temperature (54° C.) (17). It is believed that the saturated moiety (XIV) will give a fair degree of plasticization and work is currently directed toward its study.

The vinyl pinolate (XVI)-vinyl chloride copolymers were rigid plastics, but when plasticized with dioctyl phthalate, they resembled plasticized vinyl chloride-vinyl acetate copolymers. The vinyl pinolate-vinyl chloride copolymer and a vinyl pinolate-vinyl acetate copolymer were tested as glycols for the formation of foamed polyurethans and these show promise in the preliminary stage (8).

Vinyl 12-hydroxystearate (XVIII) copolymerizes smoothly with vinyl chloride, vinyl acetate, and vinyl stearate (19). No unusual properties were noted but all of these polymers have possibilities in polyurethan formation.

At present, the study of other vinyl esters derived from hydroxy- and chloro-eicosanoic and stearic acids, the completely saturated cyclic acids from linoleic acid, and some mixed ester amides in the pinic acid series is continuing but results are not yet complete enough to justify discussion.

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WORLD-WIDE RESEARCH

Fine Structure of the Cytoplasm in Relation to the Plant Cell Wall

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Our present knowledge of the disposition of microtubules in the cytoplasm of plant cells is summarized. The reports to date indicate that the orientation of the microtubules of the cell cortex mirrors that of the cellulose microfibrils in the adjacent wall, and it is suggested that the tubules in some way dictate the orientation of the microfibrils. An examination of the fine structure of the microtubule reveals that its wall is made of elements which are aligned in 13 files parallel to the long axis of the tubule. This structure is compared to that reported for the tubular component of sperm tails from animals.

MANY characteristics of plant products—such as fruit texture, fiber strength in cotton, structural properties of wood—are related to chemical make-up and architecture of the plant cell wall. The means by which the protoplast of the cell may determine its wall morphology is of interest to agronomists as well as students of cell differentiation.

Over a century ago Crüger (3) described a curious relationship of the cytoplasm to the deposition of patterned wall thickenings. He examined the behavior of certain cells which develop spiral thickenings and saw, prior to any detectable secondary wall growth, bars of streaming cytoplasm under which the wall thickenings subsequently appear. In a contemporary study of the physical make-up of the cell wall, Nägeli used polarized light to demonstrate its crys-

talline nature, a fact which eventually led to the discovery that the long cellulose molecules of the wall are grouped together into microfibrils.

During some 80 years which followed Crüger's work, similar observations were made by others; and the hypothesis gained acceptance that secondary thickenings and the orientation of cellulose microfibrils in the wall are determined by streaming patterns of the cytoplasm. The discovery of some exceptions led van Iterson in 1942 (6) to the postulate that anisotropy of some component of the ectoplasm (or the cortex of the protoplast) is in some way responsible for the orientation of cellulose micelles.

A recent study (8) of the fine structure of the cortex of plant cells actively engaged in wall synthesis revealed an array of units which renders the cortex anisotropic. The elements are tubular in form, of minute dimensions, and abundant in the interphase cell cortex

and in the mitotic spindle. These microtubules from plant cell cortices have been characterized in some structural detail (9). The report which follows summarizes our knowledge of the relationship of these cytoplasmic elements to orientation of the cellulose microfibrils in the cell wall and the structural similarity of the plant microtubules to similar elements found in certain animal cells.

Materials and Methods

There is reason to believe that the basic mechanisms of cell wall formation are essentially similar in various species of higher plants and even in diverse cell types. This permits us a wide choice of materials for investigation.

For this study we examined the cell cortices in root tips of *Phleum pratense* L. and *Juniperus chinensis* L., and the nectaries of *Euphorbia Mili*, Ch. de Moulins. These tissues were fixed in glutaraldehyde, a preservative which has proved

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