

Copolymerizations of Esters and Glycerides of Unsaturated C₁₈ Fatty Acids with Ethyl Acrylate and Acrylonitrile

FRANK R. MAYO and CONSTANCE WILLARD GOULD,
Stanford Research Institute, Menlo Park, California

Abstract

This work was undertaken to assay the possibilities of making useful copolymers from linseed and similar oils. Methyl esters of linoleic, conjugated linoleic, linolenic, and alkali-cyclized linolenic acid have been copolymerized with ethyl acrylate at 60°C and monomer reactivity ratios have been determined. In comparison with benzene or methyl stearate as inert diluents, all of these esters and several glycerides with conjugated or unconjugated unsaturation, and also 3,5,7-decatriene as a model compound, retard the polymerization of ethyl acrylate. Methyl eleostearate and the decatriene are unusually strong retarders of polymerizations of styrene, acrylonitrile, and ethyl acrylate, increasing retardation in the order given. Several experiments on copolymerizations of acrylonitrile with linseed oil at 60–130°C show that the copolymerizations which incorporate much oil in the copolymer are slow but that the isolated copolymers have good drying and film-forming properties.

Introduction

THIS REPORT DESCRIBES work done under contract with the US Department of Agriculture and authorized by the Research and Marketing Act. The Contract was supervised by the Northern Utilization Research and Development Division of the Agricultural Research Service.

This work is a continuation of research previously reported (9) which described the copolymerization of styrene or acrylonitrile with the methyl esters of oleic, linoleic, conjugated linoleic, linolenic, and eleostearic acids with free radical initiators at 60–130°C. Acrylonitrile has considerably greater tendency than styrene to copolymerize, and conjugated methyl linoleate is more reactive than the unconjugated esters. Thus, copolymers are hardest to make with styrene and unconjugated esters, easiest with conjugated methyl linoleate and acrylonitrile. That work also brought out the surprising observation that methyl eleostearate, with three conjugated double bonds, inhibits the polymerization of both styrene and acrylonitrile. Since no precedent for this observation was known, and since conjugation of linseed oil acids (to enhance their tendency to copolymerize) would produce conjugated trienes (inhibitors) as well as dienes, it seemed desirable to investigate the inhibiting or retarding properties of another conjugated triene.

The present paper extends to ethyl acrylate our work on copolymerizations with C₁₈ esters; it shows that ethyl acrylate is intermediate between styrene and acrylonitrile in its ability to enter copolymers. This paper also shows that acrylonitrile can be copolymerized with linseed oil to give copolymers containing up to 87 wt% oil, some of which have good film-forming properties, but rates of conversion are rather low. All the unsaturated C₁₈ esters and

glycerides which we have tested are mild to strong retarders of polymerization of styrene, ethyl acrylate, and acrylonitrile. Their retarding properties are compared. 3,5,7-Decatriene has been prepared as a representative simple conjugated triene by Jorge Heller and C. B. Kingsley. Theodore Mill and Mrs. Madeline R. Rado have begun an investigation (to be reported later) of its inhibiting properties. Only those results which establish its unusually strong retarding properties are reported here.

Experimental

Materials

Ethyl acrylate was Eastman Yellow Label material, washed with dilute base and distilled immediately before use. Acrylonitrile was obtained from Matheson, Coleman, and Bell and was distilled immediately before use.

Linoleic acid, methyl linoleate, and methyl linolenate and methyl stearate (used as diluent), 99+% pure, were obtained from Calbiochem. Linoleic acid and its ester were prepared by physical means from safflower oil (urea complex formation, fractional crystallization at low temperatures). The methyl linolenate was prepared by chemical means (bromination-debromination). Conjugated methyl linoleate was prepared by conjugation of the linoleic acid according to a standard method (2) followed by esterification to conjugated methyl linolenate by the method of Clinton and Laskowski (3). Methyl eleostearate was prepared by the saponification of commercial tung oil, purification of the resulting eleostearic acid by recrystallization, and esterification of the acid (3). Distillation of the ester did not give methyl eleostearate of satisfactory purity, but recrystallization from methanol at -35°C gave a product which analyzed (7), for example, 104.0% methyl eleostearate, 101.0% *α*, and 0.25% *β*. Methyl oleate, used for standards, was 99.9+% pure material, previously obtained from Hormel Institute. It was redistilled before use.

3,5,7-Decatriene was prepared from acetylene and butyraldehyde essentially according to the procedure of Werner and Reynolds (10). Details of its preparation, purification, absorption spectra, and reactions with free radicals will be presented elsewhere. The NMR and UV spectra are the basis for the following tentative conclusions. The "mixed" product contained only about 50% of the expected 3,5,7-decatriene. The other 50% included some 2,4,6-decatriene and possibly some 5,6-diethyl-1,3-cyclohexadiene. A little of this material was "purified" by gas chromatography to give a sharp fraction which is thought to be about 75% 3,5,7- and 25% 2,4,6-isomer, not separated by the column.

Methyl esters of the following acids were supplied by the Northern Utilization Research and Development Division of the US Department of Agriculture: Fe(CO)₅-conjugated (6) safflower oil acids, Fe(CO)₅-conjugated (6) linseed oil acids, alkali-conjugated

(2) linseed oil acids, and monomeric unsaturated cyclic fatty acids. (The latter were prepared from alkali-cyclized linolenic acid and contain considerable conjugated diene and very little conjugated triene. The exact proportions of these polyenes are unknown because of a lack of suitable reference standards. The cyclic content was 85–87%.) The following glycerides came from the same source: "Superb" (unbodied) linseed oil, bodied G-Q linseed oil (256 cp at 25C), bodied S-70 linseed oil (4100 cp at 25C), and $\text{Fe}(\text{CO})_5$ -conjugated linseed oil (35% conjugated diene, 25% conjugated triene).

Procedure for Copolymerizations

The desired proportions of ethyl acrylate or acrylonitrile and C_{18} ester or derivative were weighed into small glass tubes with constricted stems and frozen, and the calculated amount of initiator [2,2'-azobis(2-methylpropionitrile), ABN] was added to make 0.01 or 0.1 M solutions. The tubes were then evacuated to 0.2 mm, sealed, and heated at 60C for 24 hr. Variations from this procedure are mentioned in the appropriate places.

Isolation of Copolymers with Ethyl Acrylate

Since the copolymers formed with ethyl acrylate are readily soluble in most solvents, the usual isolation by precipitation is unsatisfactory. Therefore the unreacted C_{18} esters were separated from copolymers by vacuum distillation followed by a near-molecular distillation. For the sake of economy with these esters, and because of low yields, charges were kept small and semimicro techniques were used. Any contact with steel or iron was avoided to prevent contamination that would affect the subsequent NMR analysis. The procedure for our reaction mixtures of 0.3 to 3 g was as follows: A partly copolymerized reaction mixture was transferred with benzene to a 10- or 20-ml flask lightly packed with glass wool (to increase liquid surface and prevent bumping). The benzene and unreacted ethyl acrylate were removed on a rotary evaporator, first with a water pump at room temperature, finally with a vacuum pump at 0.2 mm at 60C. The flask containing the nonvolatile product dispersed on the glass wool was then connected to a semimicro distillation head and receiver and heated in an oil bath at 200C and 0.2 mm to distill off monomeric C_{18} ester; this distillation was fairly complete in less than 10 min, although the glass wool slowed heat transfer. After cooling under vacuum, the residue in the flask was dissolved in benzene and transferred by capillary pipette to the carefully weighed outer flask of a semimicro sublimation apparatus. (This is a cylindrical, flat-bottomed flask ca 10×2.5 cm, with a ground-glass joint at the top and a side arm just below the joint; a flat-bottomed cold-finger reaching to within 1 cm of the bottom of the flask can be fitted into the joint.) The glass wool was rinsed 4 times with benzene; if a capillary pipette was used, the glass wool was easily sucked dry and transfer of the residue was quantitative.

The sublimation flask, with closed side arm, was connected to a rotary evaporator, and the benzene was removed with a water pump. The sides of the flask were rinsed down with a little benzene which was frozen and evaporated in vacuo, leaving a layer of polymer and any C_{18} ester not removed by the initial distillation on only the bottom of the flask. The cold finger was then inserted in the sublimation

flask, the flask connected to the vacuum, and dry ice-acetone put in the cold-finger to a depth of 3 or 4 cm. The flask was immersed in an oil bath at 200C to a depth of ca 1.5 cm and heated at 0.2 mm for 5-min intervals to constant weight. Usually two intervals were necessary. Not more than 0.1–0.2 g of polymer could be handled in the sublimation apparatus described; if more than ca 0.05 g C_{18} ester was still present, there was a tendency to spatter. Undecomposed initiator and initiator decomposition products were also removed during these distillations.

Tests of Isolation Method for Ethyl Acrylate. The following experiments show that ethyl acrylate copolymers are sufficiently stable under the conditions used above and that separations of unreacted initiator and C_{18} ester are complete. Because of the analytical method used, any changes in the copolymer which do not affect the ester groups may be unimportant.

In one experiment, 95 mg of solution-polymerized polyethyl acrylate was found to reach constant weight in 5 min and to be stable on further heating. After 15 min heating, 22.1 mg (24 wt%) of ABN was added and dissolved in the polymer with a little methylene chloride. 97% of this (all but 0.7 mg) decomposed or sublimed out of the polymer in 5 more minutes. Thus, polyethyl acrylate is stable, and removal of ABN is no problem.

In a second experiment, a copolymer of 64.4 mole % ethyl acrylate and 35.6 mole % methyl linolenate lost weight at the rate of about 0.4%/min for the first 40 min (mostly in the first 10 min), then more slowly (less than 0.1%/min). After 160 min heating, the ratio of ethoxy to methoxy groups in the copolymer was 0.706/0.294. This experiment shows that either the copolymers are sensitive to extended heating in vacuo at 200C or that they contain slowly volatile dimer.

In a third experiment, 93 mg of a homopolymer of methyl eleostearate, made in 8.5% yield by heating this ester with an equal volume of benzene and 0.1 M ABN for 24 hr at 60C, was heated as described above. It lost weight at the rate of 0.8%/min for the first 25 min, then more slowly, at about 0.2%/min. After 140 min of heating, 113 mg of methyl oleate was added to the remaining 52 mg of polymer. 97.6% of the added oleate was lost in the next 5 min of heating, all of it in the subsequent 5 min. This experiment shows that either this homopolymer is unstable or its dimer is volatile (or both) but removal of monomeric C_{18} ester from polymer, under our analytical conditions, is fast and complete.

Isolation of Copolymers of Linseed and Safflower Oils and Their Derivatives with Acrylonitrile

After the indicated reaction times, the products were dissolved in a minimum of benzene or N-dimethylformamide, then precipitated with 30–60C petroleum ether. This process was repeated about five times to remove unreacted monomers, and the product was freed from solvent by warming in vacuo to 100C at 0.2 mm. The soluble fraction was freed from acrylonitrile and solvent by heating at 0.2 mm, first at room temperature, finally at 100C.

Analyses of Copolymers

In previous copolymerizations of methyl esters with styrene or acrylonitrile, copolymers were analyzed by infrared absorptions of the carbonyl groups, an unattractive method when both monomers contain carbonyl groups. In the present work, with copolymers

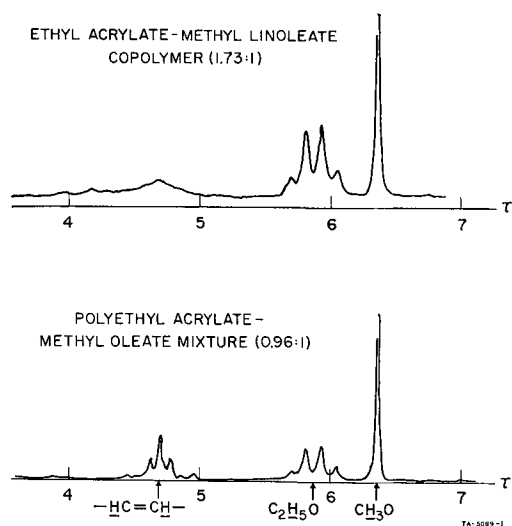


FIG. 1. NMR spectra of ethyl acrylate copolymer and mixture.

of ethyl acrylate and methyl esters of C_{18} acids, we determined the proportions of methoxy and ethoxy groups by nuclear magnetic resonance (NMR). Acrylonitrile copolymers were analyzed by nitrogen determinations.

Absorptions at τ 5.86 (CH_3CH_2O-) and τ 6.36 (CH_3O-) permit fairly clean measurements of relative concentrations of ethoxy and methoxy groups in the polymers if a clean separation of monomeric C_{18} ester from copolymer has been attained. To check the method, four standards were made up from pure methyl oleate and polyethyl acrylate and analyzed by NMR with the following results:

Composition	Mole Ratio, Ethyl/Methyl			
	I	II	III	IV
From weights of esters used	0.96	4.3	14.6	28.8
From NMR analysis	1.07	4.1	15.5	31.6

Spectra of a typical copolymer and of a standard mixture (Fig. 1) show that background is much higher when the C_{18} ester is bound in a polymer instead of mixed with it. Even the residual unsaturation does not show up clearly in the copolymer spectrum.

The shape of the ethoxy absorption band at τ 5.56 changes somewhat with changes in the composition and molecular weight of the copolymers; it is affected by the high background. These factors, and yields which are sometimes insufficient to permit optimum concentrations in analyses, affect the accuracy of our NMR results. Each analysis listed in Tables I and II is the result of four to six separate integrations made on the NMR sample. The precision is usually better than ± 3 mole % on the ethyl acrylate, less than 1 wt%. In a few samples, duplicate determinations have differed as much as 6 to 8 mole %, 2 to 2.5 wt%.

Copolymerization Experiments

Treatment of Data

Table I summarizes experimental data on copolymerizations of methyl esters of C_{18} unsaturated acids with ethyl acrylate. Data are arranged so that the necessary ratios can be easily inserted in the Fineman-Ross (5) equation for the calculation of monomer reactivity ratios:

$$(\rho - 1)/R = r_a - (\rho/R^2)r_e$$

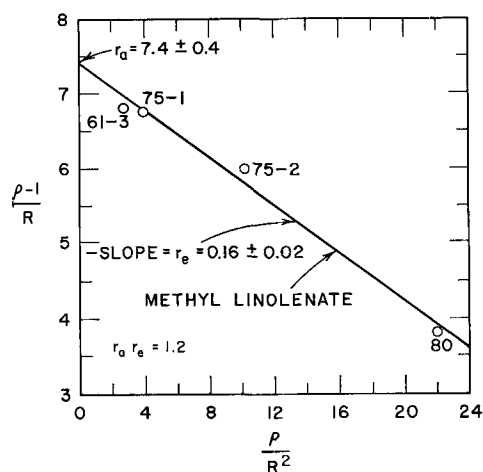


FIG. 2. Fineman-Ross plot for copolymerization of ethyl acrylate (a) with methyl linolenate (e) at 60C.

Here R is the average mole ratio of acrylate to C_{18} ester in the feed. ρ is the mole ratio of acrylate to C_{81} ester in the copolymer, r_a is the relative reactivity of acrylate and ester toward a polymer radical with a terminal acrylate group, and r_e is the relative reactivity of ester and acrylate toward a polymer radical ending in an ester group. When the experimental technique is satisfactory and the copolymerization equation applies perfectly, then a plot of $(\rho - 1)/R$ against ρ/R^2 gives a line with slope $-r_e$ and intercept r_a . The product $r_a r_e$ normally varies between zero (perfect alternation of monomers in the copolymer, each type of radical reacting only with the other type of monomer) and unity (perfectly random distribution of monomers in the copolymer, the relative reactivity of the monomers being the same toward each type of radical).

Copolymerizations of Ethyl Acrylate and C_{18} Methyl Esters

Fig. 2, 3, and 4 show how monomer reactivity ratios for several methyl esters were evaluated from Table I, and provide a measure of the consistency and probable accuracy of our results at 60C.

The copolymerizations in Table II were carried out to see if methyl linoleate would become much more reactive in copolymerizations with ethyl acrylate at 130C than at 60C. The effect of temperature appears to be about the same as with styrene, but other reactions of methyl linoleate complicate the results.

Although the first experiment in Table II indicates

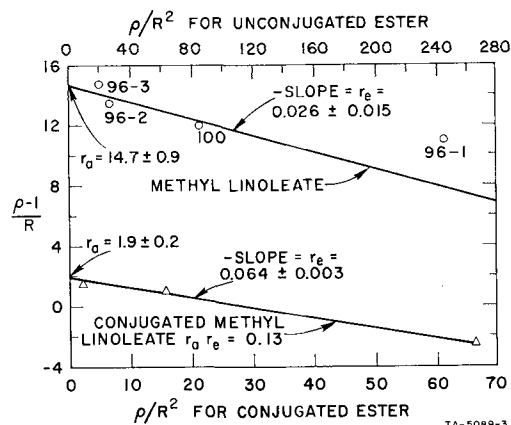


FIG. 3. Fineman-Ross plots for copolymerization of ethyl acrylate (a) with conjugated and non-conjugated methyl linoleate (e) at 60C.

TABLE I
Copolymerizations of Ethyl Acrylate (A) and C₁₈ Unsaturated Esters (E)
for 24 Hours at 60C with 0.1 M (or 0.01 M*) ABN

C ₁₈ Ester	Expt.	Millimoles (grams charged in parentheses)					$\left(\frac{A_{av}}{E_{av}}\right) = R$	$\left(\frac{\Delta A}{\Delta E}\right) = \rho$	Wt Polymer, %	Conversion, wt %	C ₁₈ in Polymer, wt %	
		A _o	−ΔA	A _{av}	E _o	−ΔE						E _{av}
Conjugated methyl linoleate	40-1*	1.117 (0.1118)	0.175	1.0295	1.023 (0.3014)	0.0695	0.9883	1.042	2.52	0.0380	9.2	53.9
	40-2*	1.208 (0.1209)	0.168	1.124	4.024 (1.1851)	0.126	3.861	0.2911	1.33	0.0540	4.1	68.9
	40-3*	1.010 (0.1011)	0.126	0.947	9.113 (2.6838)	0.172	9.027	0.1049	0.73	0.0633	2.3	80.1
Methyl linoleate	96-3	2.2375 (0.2240)	0.872	1.8015	2.377 (0.7000)	0.072	2.341	0.770	12.09	0.1085	11.7	19.6
	96-2	4.473 (0.4478)	1.761	3.593	6.600 (1.9436)	0.209	6.496	0.553	8.42	0.2379	9.95	25.9
	100	2.241 (0.2243)	0.670	1.906	9.556 (2.8141)	0.198	9.522	0.200	3.39	0.1253	4.1	46.5
	96-1	1.600 (0.1602)	0.605	1.298	14.461 (4.2585)	0.304	14.309	0.0907	1.99	0.1501	3.4	59.7
Methyl linolenate	10-1 ^a	15.17 (1.5170)	4.58	10.59	4.22 (1.2354)	0.440	3.78	2.80	22.8	0.587	21.3	11.7
	61-3*	7.641 (0.7649)	0.240	7.521	2.867 (0.8384)	0.017	2.859	2.63	18.8	0.0277	1.7	13.5
	75-1	7.734 (0.7742)	4.346 ^b	5.561	2.923 (0.8511)	0.084	2.965	1.88	13.7	0.1391	10.6	17.6
	75-2	3.144 (0.3147)	0.491	2.899	4.074 (1.1917)	0.093	4.028	0.720	5.3	0.0764	5.1	35.5
	80	3.494 (0.3498)	0.418	3.285	10.451 (3.0561)	0.189	10.357	0.317	2.21	0.0970	2.9	56.9
Methyl eleostearate	40-4*	0.981 (0.0982)	0	0.981	1.034 (0.3038)	0.021	1.024	0.958	0	0.0061	1.5	ca 100
	40-6*	3.550 (0.3554)	0.079	3.511	1.022 (0.2990)	0.203	0.921	3.819	0.39	0.0671	10.2	88.2
Methyl esters of alkali-cyclized linolenic acid	154-1	1.169 (0.1170)	0.270	1.034	1.112 (0.3252)	0.085	1.070	0.967	3.17	0.0518	11.7	48.0
	156-3	1.251 (0.1252)	0.271	1.116	4.066 (1.1893)	0.186	3.973	0.281	1.45	0.0816	6.2	66.8
	156-4	1.110 (0.1111)	0.236	0.992	10.332 (3.0220)	0.284	10.190	0.097	0.83	0.1066	3.4	77.9
	blank				(1.4065)					(0.0388)	2.8	100

* Imprecise result included for comparison with 40-6 (see text).

^b 3.205 millimoles of this was in polyethyl acrylate, polymerized from ethyl acrylate vapor into a lump of gel at the top of the reaction vessel, and not found in ΔA/ΔE by NMR.

that ethyl acrylate is about six times as reactive as methyl linoleate toward the acrylate radical ($r_a \cong 6$), the third experiment indicates that the nonvolatile product of this reaction contains more moles of linoleate than of acrylate—not a reasonable result for a free radical copolymerization in the light of our past experience. We therefore carried out the 1-hr (last) experiment in Table II to examine the reaction of methyl linoleate alone at 130C. This monomer formed 1.46% of nonvolatile material in the first hour at 130C, more than enough to account for all the linoleate found in the 24-hr experiment just above it. Since this monomer shows no tendency to polymerize by a free radical chain reaction at 60C,

the product in the last experiment is partly a dimer or other product formed by a nonradical mechanism to which the copolymerization equation would not apply. The complications in this system do not warrant further work unless the system assumes special importance.

Comparison of Copolymerizations at 60C

Table III summarizes all our work on the copolymerization of C₁₈ methyl esters with three vinyl monomers at 60C. It shows a consistent pattern: as judged by the monomer reactivity ratios, methyl linoleate is the least reactive ester; the conjugated ester is the most reactive; and the linolenic ester is intermediate, closer to the unconjugated linoleate. Styrene shows the most tendency to polymerize with itself and the least tendency to copolymerize with the esters. (A high value of r_a means that the radical ending in a vinyl monomer unit has a strong preference for reacting with the vinyl monomer rather than with the C₁₈ ester.) Hence, incorporation of much ester in a styrene copolymer is hardly practical; it would require constant slow addition of styrene to maintain a low proportion of this monomer in the feed. Such reactions are slow whenever the copolymer contains >20 wt% ester. Acrylonitrile shows the greatest tendency to copolymerize. The tendency toward copolymerization is very strong with the conjugated ester, great enough to be potentially useful with the unconjugated esters. Comparison of copolymerizations of ethyl acrylate or acrylonitrile with conjugated methyl linoleate shows that both vinyl monomers have a fairly strong alternating tendency, but that the growing ethyl acrylate radical has only $\frac{1}{6}$ as much tendency (relatively) as the acrylonitrile radical to react with conjugated linoleate.

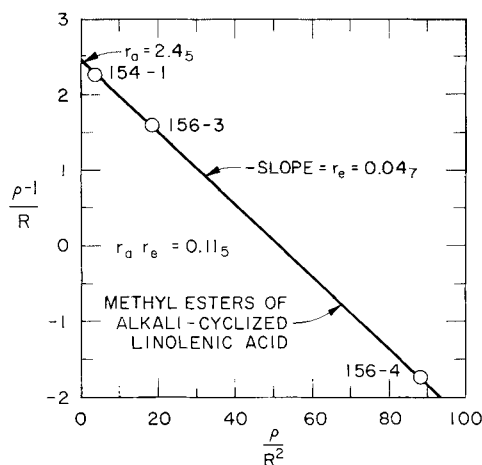


FIG. 4. Fineman-Ross plot for copolymerization of ethyl acrylate (a) with methyl esters of alkali-cyclized linolenic acid (e) at 60C.

TABLE II
 Copolymerizations of Methyl Linoleate (E) with Ethyl Acrylate (A)
 at 130C with Di-t-Butyl Peroxide

Initial conc. t-Bu ₂ O ₂ M	Millimoles								Wt polymer, g	Conver- sion, wt%	C ₁₈ in Polymer, wt%
	A ₀	ΔA	A _{av}	E ₀	ΔE	E _{av}	R = (A/E) _{av}	$\frac{\rho \Delta A}{\Delta E}$			
	24-hr reactions										
0.136	0.969	0.510	0.714	1.456	0.125	1.394	0.512	4.08	0.0880	16.7	41.9
0.137	1.004	0.494	0.757	4.346	0.454	4.119	0.184	1.09	0.1832	13.3	73.3
0.208	0.754	0.436	0.536	7.839	0.631	7.524	0.0712	0.69	0.2295	9.6	81.0
	1-hr reaction										
0.215	0			3.924					0.0142	1.46	

The difference between ethyl acrylate and acrylonitrile is smaller with the unconjugated esters. However, the indicated conversions with ethyl acrylate are only one third to one fourth of those with acrylonitrile at the same initiator concentration. The small positive r_e values with ethyl acrylate (rather than O) probably reflect a better analytical method than that used on the other monomers (9) rather than any fundamental difference in behavior. While further work might increase the accuracy of these results, the pattern and general conclusions would not be likely to change in any important respect.

In copolymerizations of the methyl ester of alkali-cyclized linolenic acid, the rather large blank in the last experiment in Table I, in comparison with the conversion in the last copolymerization, suggests that the stated r_e value may be too large. Comparison of the monomer reactivity ratios (Fig. 4) with those found for the other C₁₈ esters shows that the cyclized linolenic ester is fairly reactive in terms of the amount incorporated into copolymers with ethyl acrylate. Thus it closely resembles conjugated methyl linoleate and acts as if conjugation accompanied cyclization. Comparisons of yields of total copolymers at similar feeds show that the cyclized ester is about as reactive as unconjugated methyl linoleate, considerably more reactive than ordinary methyl linolenate, but considerably less reactive than conjugated methyl linoleate (the latter with one-tenth as much initiator).

These copolymerization results show that there is some latitude in choice of vinyl monomer for copolymerization with conjugated fatty acid residues, but for copolymerizations of unconjugated oils, acrylonitrile is the most promising monomer tested. The next section describes some experiments with Superb linseed oil.

Copolymerizations of Superb Linseed Oil with Acrylonitrile at 60C. The first three experiments in Table IV describe the copolymerization of an 18.1% acrylonitrile-linseed oil mixture for 24 hr at three different temperatures with appropriate initiators. Only the 60C run seemed to gel (between 13.5 and 16.5 hr) during 24-hr reaction, but all the isolated copolymers appeared to be homogeneous and soluble in benzene. The formation of petroleum ether-insoluble copolymer was accompanied by the formation of a petroleum ether-soluble low polymer which could not be separated from unreacted oil.

TABLE III
 Copolymerizations of C₁₈ Methyl Esters (r_e) with
 Vinyl Monomers (r_a) at 60C

Me ester	Styrene	Et acrylate	Acrylonitrile
Me linoleate	$r_a = 140$	$r_a = 14.7$	$r_a = 5$
	$r_e \sim 0$	$r_e = 0.026$	$r_e \sim 0$
Me linolenate	$r_a = 60$	$r_a = 7.2$	$r_a = 5$
	$r_e \sim 0$	$r_e = 0.16$	$r_e \sim 0$
Conj. Me linoleate	$r_a = 12$	$r_a = 1.9$	$r_a = 0.4$
	$r_e \sim 0$	$r_e = 0.064$	$r_e \sim 0$

Table IV shows also that as the reaction temperature increases, the total conversions of both acrylonitrile and oil increase regularly, but that the distinction between the "copolymer" and "oil" fractions tends to disappear. Since the 120C copolymer is the tackiest of the group and since the 120C oil contains 0.40 bound acrylonitrile unit per C₁₈ residue, it appears that the average molecular weight of the copolymer decreases with increasing temperature and that our separation of copolymer and recovered oil is arbitrary, depending on both molecular weight and nitrogen content.

As a result of the first three experiments in Table IV, two larger-scale experiments were carried out at 100C and 110C to obtain enough copolymer for preliminary evaluation. Smaller initial proportions of acrylonitrile were used to obtain higher proportions of linseed oil in the copolymer. The 100C experiment was carried out in sealed, air-free tubes. The 110C experiment was carried out under reflux in a nitrogen atmosphere; the bath temperature was gradually decreased from 116C to 112C to maintain reaction temperature at 110C during slow but decreasing rate of reflux. In both of these experiments, the initial products were analyzed; acrylonitrile and initiator were added to restore their original concentrations, and heating was resumed. This process was repeated several times to convert additional linseed oil. Only the results of the first treatment of the 100C experiment (comparable with the previous experiments) are reported in Table IV. Most of the results for the 110C experiment are for four treatments. Both experiments show that as the proportion of acrylonitrile in the feed is decreased, the conversion of acrylonitrile decreases (per half-life of the initiator (1), 18 hr at 100C, 6 hr at 110C) and the proportion of oil in the copolymer increases. (The irregularity in the 100C experiment is attributed to uneven distribution of acrylonitrile in the unstirred, gently refluxing mixture.) With (unreported) additional treatments, the proportion of copolymer which could be precipitated by petroleum ether increased steadily and the polymer became increasingly susceptible to gelation when isolated. The precipitable ("copolymer") fractions, with added drier, dried to clear films which attained tensile strengths of 1500-2000 psi in a few days and were resistant to water, 1% sulfuric acid, 2% sodium hydroxide, and gasoline. Neither the oils from which these copolymers were precipitated nor the whole unseparated fractions gave satisfactory films.

For making a practically useful linseed oil copolymer, the relative merits of a cheap but rather unreactive, unconjugated oil and of a more expensive but more reactive conjugated oil must be considered. The strong retarding properties of oils with three conjugated double bonds, discussed in the next sec-

TABLE IV
 Copolymerization of Superb Linseed Oil with Acrylonitrile (AN) at 60–120C

Temp., [Initiator] oil + AN, g	Conversions, wt %			Copolymer ^b				Oil Fraction			
	AN to copoly- mer	AN to oil	Oil to copoly- mer	Wt. g	N, % ^c	AN, wt %	Moles AN/C ₁₈	Wt. g	N, %	AN, wt %	Moles AN/C ₁₈
	1.22 moles AN per equiv. of C ₁₈ acid in feed (18.1 wt % AN); reaction time 24 hrs.										
60C, 0.1 M ABN, 0.8668 g	37.6	9.2	4.35	0.09	17.33	65.6	10.57 ^b	0.6914	0.55	2.09	0.118
100C, 0.088 M BzO ₂ t-Bu, 1.6303 g	45.2	19.7	13.2	0.3100	11.4	43.2	4.20 ^b	1.2317	1.25	4.9	0.275
120C, 0.1 M Cumyl ₂ O ₂ , ^c 0.6560 g	30.0	26.3	28.0	0.1865	5.1	19.3	1.32	0.4610	1.79	6.8	0.402
	0.99 mole AN per equiv. of C ₁₈ acid in feed (15.3 wt % AN); reaction time 18 hrs.										
100C, 0.100 M BzO ₂ t-Bu, 52.190 g	17.1	6.4	20.8	10.578	3.39	12.8	0.81	37.072	0.36	1.36	0.076
	0.67 moles AN per equiv. of C ₁₈ acid in feed (10.8 wt % AN); reaction time 6 hrs.										
110C, 0.049 M BzO ₂ t-Bu, 493.1 g ^a	33.3 (by GLC)			124.9 ^d	9.39 ^d	35.6 ^d	3.06 ^d	405.3 ^d	2.22 ^d	8.4 ^d	0.506 ^d

^a Wt of charge and % AN in charge do not include wt of initiator or, in 110C expt., the chlorobenzene added (to reduce viscosity) to make 10.2 wt % C₆H₅Cl in total reaction mixture.

^b The two highest AN copolymers were obtained as dry powders; others were initially tacky.

^c "Di-Cup," commercially recrystallized product, not further purified.

^d Conversion in 6 hr; product analyses are for 24-hr total reaction time, after three more treatments with original concentrations of AN and BzO₂t-Bu restored as described in text.

tion, present another problem in the utilization of conjugated oils.

Retardation Experiments

Retarding Properties of C₁₈ Esters and Oils

When we found that some of our C₁₈ methyl ester and unbodied glyceride samples retarded the polymerization of ethyl acrylate, we decided to compare the retarding properties of all of them. Mixtures were made which contained about 75% by volume of ethyl acrylate and 9–10 moles of ethyl acrylate per mole of C₁₈ residue in the methyl ester or glyceride being tested. The samples were heated for 24 hr at 60C in sealed, evacuated tubes with 0.01 M or 0.1 M ABN.

Because unreacted methyl esters can be distilled from the copolymers while glycerides cannot, the conversions are presented on different bases for the esters and glycerides. The conversions measure the retardation of polymerization of ethyl acrylate, not how much of these esters was incorporated into the copolymers. Results are summarized in Table V. The blanks in benzene and methyl stearate show that ethyl acrylate is nearly completely polymerized in these inert solvents under these conditions. All the other samples gave lower conversions. Comparison of conversions with 0.01 and with 0.1 M ABN show that *more* than three times (10^{1/2}) as much product is sometimes obtained with the higher concentration of ABN. Such results suggest that retarder is being removed during polymerization. The most retardation is found in the conjugated linseed oil derivatives which presumably contain the most triple conjugation (cf. following section). The conjugated esters from safflower oil (no trienes) give the most polymer, the unconjugated linseed oil (bodied, unbodied, or cyclized) the next most polymer. The heaviest-bodied linseed oils have the most tendency to gel at 60C, an effect which might be offset by higher reaction temperatures. The conjugated linseed oil and, to a lesser extent, the conjugated methyl esters of linseed oil, both formed by treatment with iron carbonyl, contained iron, and they left a residue on ignition. The effect of this contamination on copolymerization is unknown. Although Table V lacks experiments with conjugated and unconjugated methyl linoleate, and with methyl

linolenate, experiments with styrene and in Table I show qualitatively that their retarding properties increase in that order.

Although these data are suitable for comparing retarding properties of the esters and oils, retardation of ethyl acrylate polymerization is much greater with the lower proportions of ethyl acrylate used in making high-oil copolymers or in measuring monomer reactivity ratios. Two examples follow: (1) Mixtures of 0.24, 0.64, and 2.13 moles of ethyl acrylate (instead of 9–10 in Table V) per mole of methyl esters of acids from alkali-conjugated linseed oil were heated with 0.01 M ABN for 24 hr at 60C. The polymers formed amounted to only 1.2, 0.76, and 0.73 wt % of the charges, too little for analyses. (2) A mixture of 10.27 wt % of ethyl acrylate in unbodied Superb linseed oil (instead of 77 wt % as calculated for in Table V), 0.01 M in ABN, was made up and portions were heated in sealed evacuated tubes for 24, 50, 74, and 100 hr at 60C. The weight gains of the oil (note *e* in Table V) corresponded to only 2.6, 3.6,

 TABLE V
 Effect of C₁₈ Esters on Rate of Polymerization of Ethyl Acrylate for 24 Hours at 60C with 0.01 or 0.1 M ABN

[ABN] used, M Co-monomer or Diluent	Initial ratio Et acrylate/C ₁₈ ester				Conversion, ^b wt %	
	by moles ^a		by volume		0.01	0.1
	0.01	0.1	0.01	0.1		
Benzene	1.0	>94
Me stearate	9.3	3.0	>85
Me esters of conjugated linseed oil
Alkali- isomerized	10.0	9.2	3.3	3.0	4.1	32
Fe(CO) ₅ - isomerized	9.4	9.5	3.1	3.1	2.5	14
Me esters of alkali- cyclized linolenic acid	9.8	3.2	73 ^d
Me esters of conjugated safflower oil	9.4	9.5	3.1	3.1	42.4	85 ^e
Superb linseed oil	9.8	8.8	3.2	3.0	14	80
Conjugated linseed oil	10.0	9.6	3.3	3.3	3.1	13
Light-bodied linseed oil GQ	9.5	3.3	93 ^e
Heavy-bodied linseed oil S-70	9.5	3.2	53 ^f

^a One-third of molecular weight of glycerides used for calculation.
^b For methyl esters, % conversion = 100 × (wt of NV product) / (wt Et acrylate charged); for glycerides, % conversion of Et acrylate = 100 × (wt of final NVM - wt of oil charged) / (wt Et acrylate charged). The latter basis must give lower results than the former.
^c Mole ratio Et acrylate/Me ester = 15, corresponding to 71% conversion of Et acrylate, 45% of Me ester.
^{d,e,f} Gelation times more than 72^d, 20^e, or 2^f hr.

TABLE VI
Retardations of Polymerizations by Conjugated Trienes and Cyclopentadiene
(0.01 M ABN, 24 hr at 60C)

Conjugated triene or diene	Styrene			Ethyl acrylate			Acrylonitrile		
	Mole ^a ratio	Vol. ^a ratio	Yield ^b	Mole ^a ratio	Vol. ^a ratio	Yield ^b	Mole ^a ratio	Vol. ^a ratio	Yield ^b
Benzene (blanks)	3.9	50	3.8	94 gel	2.7	55 gel
Decatriene ^c	7.8	5.0	1.9	7.8	5.0	0.6	7.7	2.9	1.4
Methyl eleostearate, ^d 100.1%	8.0	2.6	9.8	8.1	2.5	3.4	8.0	1.5	6.7
Methyl eleostearate, ^d 95.1%	28.0	9.4	8.2	10.6	3.3	1.6	39.9	7.7	3.1
Methyl eleostearate, ^d 95.1%	20.0	6.3	1.3
Cyclopentadiene ^e	2.2	2.9	11.2
				7.9	10.0	gel			
				30.0	39.0				

^a Ratio of vinyl monomer to triene or diene in feed.

^b Yield of nonvolatile residue, as wt % of vinyl monomer.

^{c,d,e} Homopolymer from 1:1 (vol.) mixture with benzene, same conditions, 2.7 wt % of triene,^c 2.4 wt % of triene,^d or 1.1 wt % of diene.^e

6.6, and 10.1% of the ethyl acrylate charged. Since the ABN was being depleted rapidly (half-life is about 20 hr at 60C), the nearly steady rate of reaction of ethyl acrylate suggests steady depletion of the retarder and is consistent with the 14% conversion in Table V.

Retarding Properties of Trienes and of Cyclopentadiene

Table VI compares the retarding effects of methyl eleostearate and "mixed" 3,5,7-decatriene on three vinyl monomers. The benzene blanks contained about the same volume percents of vinyl monomer as were used in the retardation experiments in Table V. Methyl eleostearate which analyzed (8) 100.1% was used for the first set of experiments. After this sample had stood for 7 days under nitrogen at -15C, it analyzed only 95.1% eleostearate. The aged material was considerably better as an inhibitor (gave smaller yields of polymers); the reason is unknown.

The reduction in yield at the same level of inhibitor is least with styrene, greatest (nearly complete) with ethyl acrylate, and intermediate (closer to acrylate) with acrylonitrile. "Mixed" 3,5,7-decatriene is an even better inhibitor on a molar basis. The "purified" material seemed also to prevent polymerization of acrylonitrile. Cycloheptatriene and cyclooctatriene have recently been reported to inhibit the polymerization of acrylonitrile (4); and it has also been reported (7) that as little as 50 ppm of divinylacetylene (or other triply conjugated triene with one acetylene bond) retards the benzoyl peroxide-initiated polymerization of acrylonitrile. There is therefore no doubt that the inhibiting properties of eleostearate esters are real and due to the three con-

jugated double bonds. Further investigations with the decatriene, by Dr. T. Mill, are in progress.

Cyclopentadiene was tested as a retarder because abstraction of the very reactive allylic hydrogen atom would produce the same sort of conjugated cyclic radical which might form from the conjugated trienes. 31 mole % of cyclopentadiene retarded the polymerization of ethyl acrylate and reduced the molecular weight sufficiently to give a soluble polymer. Lower molar proportions of cyclopentadiene, which were very effective for the trienes, permitted formation of substantial (but not easily measured) yields of gelled polymer.

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