Crosslinkable Emulsion Polymers by Autoxidation. I. Reactivity Ratios

FUNG-BOR CHEN* and B. GEORGE BUFKIN,† *Polymer Science Department, University of Southern Mississippi, Hattiesburg, Mississippi 39401*

Synopsis

Lauryl acrylate (LA), oleyl acrylate (OA), linoleyl acrylate (LA2), and linolenyl acrylate (LA3) were prepared by reaction of acryloyl chloride with alcohols having zero, one, two, and three double bonds in the chain. The reactivity ratios of comonomers of ethyl acrylate (EA) or methyl methacrylate (MMA) with LA3, LA2, or OA were studied by the Kelen–Tüdös and the integrated transformation methods. With all of the comonomer pairs, the reactivity ratio data indicated that EA and MMA showed a tendency to form homopolymers while LA3, LA2, and OA tended to form alternating copolymers. The difference between the values of the reactivity ratios derived from the two methods was small.

INTRODUCTION

Polymers of saturated long chain fatty acrylates and their copolymers with styrene, methyl methacrylate, and other vinyl monomers have shown considerable promise as plasticizers, adhesives, chewing-gum bases, and lubricating oil additives.[1] However, only a few attempts have been made to polymerize unsaturated fatty acrylates and methacrylates, because unsaturation in the fatty chain adversely affects the polymerization of these monomers. As seen in the results of Harrison and Wheeler's[2] studies on the polymerization of vinyl and ally esters of fatty acids, the conversion of polymers decreases as the degree of unsaturation in the fatty vinyl monomers increases. In emulsion polymerization using linoleate and linolenate soaps as surfactants,[3,4] the isolated double bonds in the fatty chain retard the reaction. This is caused by the susceptibility of the allylic methylene hydrogen to abstraction by a growing free radical, together with the stabilization of the resulting soap by resonance as follows:

$$- CH = CH - \dot{C}H - CH = CH -$$

$$- CH = CH - CH = CH - \dot{C}H - \quad - \dot{C}H - CH = CH - CH = CH -$$
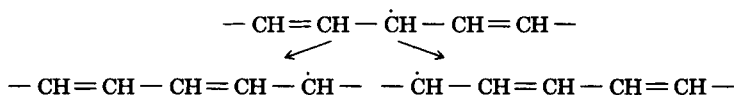
The linolenate soap interferes with the vinyl polymerization more than the linoleate soap. Port et al.[5] further confirmed that even 5% vinyl oleate in vinyl palmitate retards the polymerization rate of the latter considerably.

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* Present address: Deseret Medical, Inc., 9450 South State, Sandy, UT 84070.
† Present address: Sherwin-Williams Co., P. O. Box 6027, Cleveland, OH 44101.

Joshi and Chatterjee[6] determined that emulsion polymerization of fatty acrylates is preferred to solution polymerization in order to obtain polymers with reasonably good coating characteristics.

The primary goal of this research is to obtain high-conversion ($>98\%$) emulsion polymers containing unsaturation-modified monomers, which have various unsaturated moieties present in the 0–8 wt% range, and to investigate their essential physical and chemical properties.

In this paper the purity of monomers prepared will be discussed and the reactivity ratios of EA or MMA with LA3, LA2, or OA studied.

EXPERIMENTAL

Synthesis of Fatty Acrylates

The four acrylic esters of fatty alcohols were prepared by means of the following sample procedure.

Linolenyl Acrylate

Fatty acids (80%, linolenic acid) were reacted with bromine to obtain the pure hexabromostearic acid.[7] The hexabromide melting at 181–181.5°C (lit.[7] mp 181.5–181.9°C) was reduced to linolenic acid by zinc dust.[8] A yellow linolenyl alcohol was produced, after the linolenic acid was added into an anhydrous ether suspending with lithium aluminum hydride.[9] The alcohol was distilled at 0.7 mm Hg through a 3-in. column packed with glass beads. The alcohol distilled was reacted with acrylol chloride to obtain linolenyl acrylate as follows:

Triethylamine (6.0 g, 0.059 mol) and linolenyl alcohol (12 g, 0.045 mol) were placed in a three-neck flask containing 300 mL dry ether with an outside ice bath. Acryloyl chloride (5.0 g, 0.055 mol) in 100 mL dry ether was continuously dropped in for a time period (about 1 h) to keep the reaction temperature below 10°C. At the end of addition, the ice bath was removed. The solution was kept at room temperature for 2 h at which time the triethyl amine salt was removed. The filtrate was washed with distilled water and dried over anhydrous magnesium sulfate. A slightly yellow ester (65% yield) was obtained. The product was distilled at bp 201–203°C/4–5 mm Hg.

ANAL. Calcd for $C_{21}H_{34}O_2$: C, 79.19%; H, 10.76%; O, 10.05%. Found: C, 78.89%; H, 10.79%; O, 10.32%.

Linoleyl Acrylate

Linoleyl Alcohol. The purified linoleic acid was used as a raw material. The procedure of reduction of linoleic acid is similar to the previous method in the preparation of linolenyl alcohol.

Linoleyl Acrylate. The procedure used in the preparation of linolenyl acrylate was followed for the preparation of linoleyl acrylate. The product was distilled at bp 163–165°C/0.3–0.4 mm Hg. (lit[10,11] bp 190–192°C/2.5 mm Hg).

Oleyl Acrylate

Oleyl acrylate was obtained by the reaction of acrylol chloride with pure oleyl alcohol, following the procedure used in preparing linoleyl acrylate. The product was distilled at bp 170–175°C/1.0–1.5 mm Hg (lit[12,13] bp 185–195°C/5 mm Hg).

ANAL. Calcd for $C_{21}H_{38}O_2$: C, 78.20%; H, 11.88%; O, 9.92%. Found: C, 77.85%; H, 11.77%; O, 10.38%.

Lauryl Acrylate

Lauryl acrylate was obtained by alcoholysis of acrylol chloride with pure lauryl alcohol following the procedure used in preparing linolenyl acrylate. The product was distilled at 182–183°C/4–5 mm Hg (lit[14] bp 119–121°C/0.8 mm Hg).

Characterization of Monomers and Polymers

Preparation of Trifluoroacetate (TFA) Derivatives of Fatty Alcohols for Gas Liquid Chromatography (GLC)

The TFA derivatives were prepared quantitatively at room temperature according to Wood's trifluoroacetylation procedure.[15]

The TFA derivatives were prepared by placing 1 mg of the fatty alcohol in a 20-mL disposable vial, followed by the addition of 1 mL of trifluoroacetic anhydride and allowed to stand at room temperature for 15 min. The excess trifluoroacetic anhydride and the trifluoroacetic acid formed during the reaction were evaporated under a stream of dry nitrogen. Samples were diluted with hexane for GLC analysis.

Determination of the Purity of Fatty Alcohols

The chromatograms were obtained using a Hewlett-Packard 5710 gas chromatography instrumented with a 0.125 in. × 6 ft column of 10% polar liquid phase (DEGS-PS). The conditions of the instrument for analysis were: carrier gas flow rate 20 mL/min; hydrogen flow rate 30 mL/min; air flow rate 240 mL/min; detector temperature 300°C; injector temperature 250°C; oven temperature 200°C.

Determination of Unreacted Monomers of Copolymerization

A Hewlett-Packard 5710 gas chromatography instrumented with a 0.125 × 12 in. column of 5% UCW polar liquid phase was used to determine unreacted monomer concentrations. The conditions for analysis were the same as above except that the oven temperature was 230°C.

NMR Determination

The NMR determinations were conducted with a Varian A-60D Spectrometer.

Infrared Determinations

The infrared determinations were conducted with a Perkin-Elmer 567 and 283B spectrophotometers using NaCl cells 22 mm in diameter and 4 mm in thickness.

Copolymerization Studies

The copolymerization of ethyl acrylate (or methyl methacrylate)–fatty acrylate mixtures, initially containing 10, 50, and 90 mol% ethyl acrylate (or methyl methacrylate) and 1.0% AIBN by weight, was investigated. The polymerization was conducted at $60.0\pm0.1°C$, and the mixture was analyzed for unreacted monomers at regular intervals. Before injecting in the GLC, the samples (0.02 g) were diluted into 10 mL chloroform.

RESULTS AND DISCUSSION

Synthesis of Fatty Acrylates

The purity of fatty alcohols from which the four fatty acrylates were prepared was checked by gas liquid chromatography (GLC) using a 10% polar liquid phase (DEGS–PS) column and the trifluoroacetate (TFA) derivatives. Figure 1 is a typical chromatogram demonstrating fatty alcohol separation.

The results in Table I include the percent composition values based on the triangular area under the curves of chromatograms for the known wt% mixture of TFA derivative. Correction factors (F) are defined by the area ratio of palmityl alcohol derivative to the same amount of fatty alcohol derivatives.

The wt % composition of fatty alcohol j is calculated using the following equation[16]:

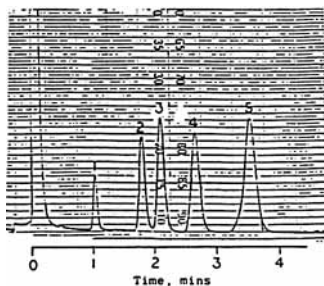$$\text{wt \% of } j = \frac{A_j F_j}{\sum\limits_{i=1}^{n} A_i / F_i} \tag{1}$$

Fig. 1.   Chromatogram of mixture analyzed as trifluroacetate derivatives on a 10% DEGS-PS column at 200°C. The numbered alcohol peaks are (1) palmityl (5.0% by wt); (2) stearyl (15.0% by wt); (3) oleyl (20.0% by wt); (4) linoleyl (25.0% by wt); (5) linolenyl (35.0% by wt).

TABLE I
Analysis of Gas Liquid Chromatographic Reference Fatty Alcohols[a]

TFA derivative of fatty alcohols	Mixture A			Mixture B			Mixture C			Average F
	Wt %	Area (%)	F	Wt %	Area (%)	F	Wt %	Area (%)	F	
C 16:0[b]	20.0	24.33	1	5.0	6.7	1	35.0	40.36	1	1
C 18:0	20.0	23.33	0.96	15.0	18.48	0.92	25.0	24.98	0.87	0.92±0.05
C 18:1	20.0	21.42	0.88	20.0	22.17	0.83	20.0	18.29	0.79	0.83±0.04
C 18:2	20.0	17.28	0.71	25.0	24.24	0.72	15.0	12.41	0.72	0.72±0.01
C 18:3	20.0	13.64	0.56	35.0	28.31	0.60	5.0	3.95	0.68	0.62±0.06

[a] Purchased from Nu Chek Prep Co.
[b] Shorthand system of nomenclature: the first number separated by a colon represents the number of carbon atoms in the hydrocarbon chain, and the second number represents the number of double bonds in the chain. F is the correction factor.

where A_i is the area of the fatty alcohol derivative i obtained from the GLC chromatogram. The components of fatty alcohols used in this research were determined using eq. (1) and are included in Table II.

The alcohols listed in Table II were reacted with acryloyl chloride to obtain fatty acrylates. Their physical and spectrometric characteristics are listed in Table III. Because the esterification of fatty alcohols with acryloyl chloride is one of the most rapid reactions to form esters,[17] the ratio of components of fatty acrylates are roughly equal to the same composition as originally present in the alcoholic state.

Reactivity Ratios

The integrated Transformation method[18,19] and the Kelen–Tüdös method were used to estimate the values of the reactivity ratios.

The Integrated Transformation Method[18,19]

The integration of the copolymerization equation[19] has been transformed into an expression for r_2:

$$r_2 = \frac{\log \dfrac{[M_2]_0}{[M_2]} - \dfrac{1}{p} \log \dfrac{1 - p[M_1]/[M_2]}{1 - p[M_1]_0/[M_2]_0}}{\left(\log \dfrac{[M_1]_0}{[M_1]} + \log \dfrac{1 - p[M_1]/[M_2]}{1 - p[M_1]_0/[M_2]_0} \right)} \tag{2}$$

The parameters r_1 and r_2 are defined by $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_2$, and k_{11} is the rate constant for a propagating chain ending in M_1 adding to monomer M_1, and so on. 0 indicates initial concentrations, and p is an integration constant defined by

$$p = \frac{1 - r_1}{1 - r_2}$$

TABLE II
Purity[a] of Alcohols Used in This Research

Components	Lauryl alcohol[a]	Oleyl alcohol	Linoleyl alcohol	Linolenyl alcohol
C:12:0[b]	99.0	x	x	x
C 16:0	x	x	x	0.3
C 18:0	x	0.4	x	0.95
C 18:1	x	99.6	x	0.67
C 18.2	x	x	99.6	0.66
C 18.3	x	x	0.4	97.42

[a] By wt %.

[b] Determined by Sigma Chemical Co.

[c] Shorthand system of nomenclature: the first number separated by a colon represents the number of carbon atoms in the hydrocarbon chain, and the second number represents the number of double bonds in the chain.

Calculation of monomer reactivity ratios from eq. (2) can be performed by separately determining the almost straight lines in an $r_1 - r_2$ diagram for each experiment. Next, the center of gravity of the intersection points of all these lines can be calculated and used to estimate values of r_1 and r_2.

The Kelen–Tüdös Method

Kelen and Tüdös[20,21] proposed a simple, graphic linear method for determining reactivity ratios. According to the method proposed, the following linear equation can be used:

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha} = r_1\xi - \frac{r_2}{\alpha}(1-\xi) \qquad (3)$$

where

$$\eta = \frac{G}{\alpha + F} \quad \text{and} \quad \xi = \frac{F}{\alpha + F}$$

and the transformed variables, F and G, are defined by

$$F = \frac{[P_1]}{[P_2]}\left(\log \frac{[M_2]_0 - [P_2]}{[M_2]_0} \middle/ \log \frac{[M_1]_0 - [P_1]^2}{[M_1]_0}\right)^2$$

$$G = \frac{[P_1] - [P_2]}{[P_1]} \log \frac{[M_2]_0 - [P_2]}{[M_2]_0} \middle/ \log \frac{[M_1]_0 - [P_1]}{[M_1]_0} \qquad (4)$$

Thus, α is a parameter of symmetrization, its optimal value for a given series of measurements being

$$\alpha = \sqrt{F_{\min} F_{\max}}$$

Copolymer Composition[18]

The copolymerization equation can be expressed in terms of mole fractions. If f_1 and f_2 are the mole fraction of monomers M_1 and M_2 in the feed and F_1 and F_2 the mole fractions of M_1 and M_2 in the copolymer, then

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \qquad (5)$$

Determination of Reactivity Ratios

The unreacted monomers remaining after partial copolymerization were determined by GLC and are reported in Table IV. From these data, the reactivity ratios were calculated using eq. (2) and (3) by a computer and are listed in Table V. The deviations of the reactivity ratios are described

TABLE III

Physical and Spectrometric Characteristics of Fatty Acrylates

| Monomer | Appearance | Purity (wt %) (by GLC) | Major infrared spectra (cm^{-1}) | | | | | Structure | Major nuclear Magnetic | | Resonance spectra intensity | |
| | | | C-H | | | | | | | | | |
			Olefinic	Other	C=O	C	C—O		index	δ (ppm)	Exptl data	Theor data
Linolenyl acrylate	Colorless liquid	96.2	3010 1453	2920 2850	1729	1620 1632	1185	H$_2$C=CH—COO— (a); CH$_2$—(CH$_2$)$_6$— (c); (CH$_2$—CH=CH)$_3$— (b); CH$_2$—CH$_3$	a b	5.5-6.4 5.2-5.5	12 25	12 24
(LA3)				1405 982 962					c	3.8-4.4	8	8
Linoleyl	Colorless	98.5	3001	2920	1721	1625	1186	H$_2$C=CH—COO— (a); CH$_2$—(CH$_2$)$_6$— (c); (CH$_2$—CH=CH)$_2$— (b); (CH$_2$)$_4$—CH$_3$	a	5.4-6.3	13	13

acrylate (LA2)	liquid		1460	2850 1405 983 963		1631			b	5.1–5.4	17	17.3
									c	3.8–4.2	9	8.6
Oleyl	Colorless	99.4	3000	2920	1730	1620	1184	H₂C=CH—COO— (a); CH₂—(CH₂)₆— (c); CH₂—; CH=CH— (b); (CH₂)₇—CH₃	a	5.4–6.3	11	11
acrylate (OA)	liquid		1462	2850 1405 980 960		1635			b	5.1–5.4	7	7.3
									c	3.7–4.2	7.5	7.3
Lauryl	Colorless	99.0	1462	2920	1728	1619	1182	H₂C=CH—COO— (a); CH₂—(CH₂)₁₀— (b); CH₃	a	5.3–6.3	13	13
acrylate (LA)	liquid			2830 1402 978 955		1630			b	3.7–4.2	9	8.6

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TABLE IV
Unreacted Monomers of Bulk Copolymerization of Ethyl Acrylate or Methyl Methacrylate
with Fatty Acrylate[a]

Monomer pair	$1-[M_1]/[M_1]_0$	$1-[M_2]/[M_2]_0$	$[M_1]_0/[M_2]_0$
MMA–OA	0.0612	0.0347	13.28
	0.45	0.28	4.8
	0.4875	0.375	0.66
	0.446	0.285	5.48
EA–OA	0.061	0.044	9.6
	0.06	0.04	1.29
	0.445	0.34	0.514
	0.231	0.2	0.14
MMA–LA2	0.493	0.41	0.8
	0.21	0.15	1.26
	0.38	0.26	9.82
	0.4	0.32	0.36
EA–LA2	0.38	0.296	0.69
	0.13	0.1	0.69
	0.325	0.2	6.58
	0.13	0.08	17.34
MMA–LA3	0.22	0.12	0.68
	0.15	0.11	5.56
	0.07	0.05	12.5
	0.102	0.07	2.2
EA–LA3	0.0754	0.05	10.3
	0.1	0.07	3.4
	0.15	0.1	1.3
	0.069	0.04	0.83

[a] M_1 = the first monomer of monomer pair, M_2 = the second monomer of monomer pair, 0 = the initial condition, EA = ethyl acrylate, MMA = methyl methacrylate, OA = Oleyl acrylate, LA2 = Linoleyl acrylate, LA3 = Linolenyl acrylate, and reaction temperature = 60°C.

by the standard deviation method. After the reactivity ratios were obtained, eq. (5) and r_1 and r_2 values from the Kelen–Tüdös (KT) method were used to calculate the mole fraction in the copolymer, and the results are plotted in Figures 2 and 3.

The results as recorded in Table V show that MMA and EA display high reactivities in copolymerization with fatty acrylates. This is also shown in

TABLE V
Reactivity Ratios of Bulk Copolymerization of Ethyl Acrylate or Methyl Methacrylate with
Fatty Acrylates at 60°C

Monomer pair	KT[a]		Integrated[b]	
	r_1	r_2	r_1	r_2
MMA–OA	1.9±0.2	0.9±0.3	1.8±0.1	0.7±0.3
EA–OA	1.5±0.4	0.8±0.3	1.7±0.3	0.8±0.1
MMA–LA2	1.6±0.2	0.9±0.2	1.7±0.3	0.9±0.2
EA–LA2	1.5±0.5	0.7±0.4	1.5±0.5	0.7±0.3
MMA–LA3	1.3±0.1	0.4±0.2	1.3±0.1	0.5±0.2
EA–LA3	1.5±0.2	0.5±0.3	1.4±0.2	0.5±0.2

[a] Kelen–Tüdös method.
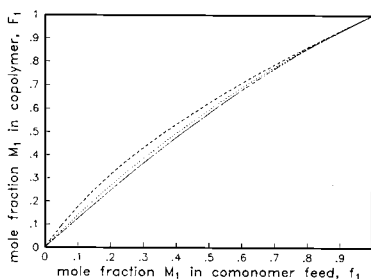[b] Integrated transformation method.

Fig. 2.   Dependence of the copolymer composition F_1 on the comonomer feed composition f_1: (—) EA(M$_1$)–OA(M$_2$); (· · ·) EA(M$_1$)–LA2(M$_2$); (- - -) EA(M$_1$)–LA3(M$_2$).

Figures 2 and 3. It is obvious that radicals terminated by a MMA or EA unit prefer to add to their own monomer over the comonomers. The bulky pendant 18 carbon chain of fatty acrylates is the cause to decrease the reactivity of fatty acrylates due to steric hindrance between monomers themselves and the radical to which they are adding.[22]

The introduction of unsaturation increases the polarity of fatty acrylates and therefore the differences in polarity between fatty acrylates and MMA or EA.[23] This lowers the energy of activation in the transition state and increases the tendency toward alternating copolymerization.[24] The $r_1 r_2$ values shown in Table VI decreases as the unsaturation in the side chain of fatty acrylates increases. LA3 has the highest unsaturated moiety in the side chain among these monomers, and so comonomers of EA or MMA and LA3 are expected to have the most alternating copolymers among the systems studied.

CONCLUSION

The purity of fatty alcohols from which the monomers are derived was determined by gas chromatography. Esterification of the above alcohols with acryloyl chloride was subsequently accomplished.

The study of reactivity ratios of comonomers of EA–LA3, MMA–LA3, EA–LA2, MMA–LA2, EA–OA, and MMA–OA was conducted by Kelen–Tüdös and integrated transformation methods. The unreacted monomer concentrations were determined by GLC.

A nonsolvent was difficult to find for precipitation of a low-molecular-weight and low-conversion copolymer. This problem was overcome by di-
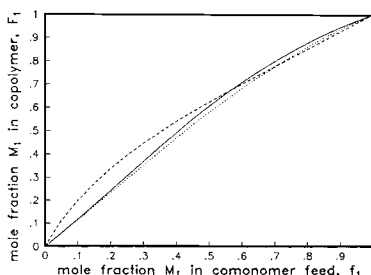

Fig. 3.   Dependence of the copolymer compositioin F_1 on the comonomer feed composition f_1: (—) MMA(M$_1$)–OA(M$_2$); (· · ·) MMA(M$_1$)–LA2(M$_2$); (- - -) MMA(M$_1$)–LA3(M$_2$).

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TABLE VI
Reactivity Ratio Product

Monomer pairs	$r_1 r_2^a$
A. MMA comonomers	
MMA–OA	1.71
MMA–LA2	1.44
MMA–LA3	0.52
B. EA comonomers	
EA–OA	1.2
EA–LA2	1.05
EA–LA3	0.75

^{a} r_1 and r_2 were obtained from KT method.

rectly analyzing the unreacted monomer by GLC. No attempt was made to remove the polymer before injecting the copolymer solutions into the chromatograph. In general, the long side-chain fatty acrylates have a stronger tendency toward copolymerization than do the short side-chain acrylates. The difference between the values of the reactivity ratios derived from both methods is small.

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