Homo- and Copolymers of Vinyl Esters, Acrylates, and Methacrylates of Some Derivatives of Fatty Acids

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Synopsis

Vinyl esters of some undecylenic acid derivatives and acrylates and methacrylates of undecyl and undecylenyl alcohols, which may be considered as derivatives of castor oil, have been polymerized and copolymerized with vinyl chloride to provide a variety of new polymers.   The acrylate and the methacrylate of undecylenyl alcohol have been epoxidized to yield two new polymerizable monomers of potential usefulness as crosslinking agents in finished copolymers.

INTRODUCTION

The main objective of this work is to explore the possibility of utilizing the various derivatives of castor oil, some as internal plasticizers and others as crosslinkers.   Thus it was undertaken to prepare and characterize homopolymers and vinyl chloride copolymers of monomers I to XIII listed in Table I.   The undecylenyl acrylate and methacrylate (XIV and XV), which are bifunctional monomers and potential crosslinkers, were epoxidized and copolymerized with a number of vinyl monomers.

The monomers (I to XV) were supplied by Dr. J. S. Aggarwal of Hyderabad-Deccan of India through the Western Utilization Research and Development Division, the U. S. Department of Agriculture.   Prior to polymerization, they were purified by vacuum distillation, or column chromatography on silica gel if the boiling point was too high to distill safely.   Their purity was checked by the thin layer chromatography. Some of the physical data are given in Table I.

Homopolymers of the vinyl esters initiated with α,α'-azobisisobutyronitrile (AIBN) or persulfate at 60°C were generally soft and sticky and of low molecular weight, whereas those of acrylates and methacrylates were often insoluble in conventional organic solvents.   As a result, these homopolymers did not show any promising properties for practical use.

Radical copolymerization with vinyl chloride and various other comonomers was conducted in emulsion systems, using such initiators as AIBN, potassium persulfate and benzoyl peroxide.   The latter, when used in conjunction with the redox system containing ferrous sulfate and sodium pyrophosphate, initiated the polymerization at room temperature.   In general,

TABLE I
Monomers and Their Physical Data

No.	Compound	$n_D(°C)$	b.p. °C/mm
I	Vinyl Undecanoate (VUA)	1.4344 (30)	85–89/0.2
II	Vinyl 10-/11-phenylundec- anoate (VPU)	1.4887 (30)	166–168/0.3
III	Vinyl 11-Methoxyundec- anoate (VMU)	1.4415 (28.5)	98/0.18
IV	Vinyl 11-Bromoundecanoate (VBU)	1.4685 (29)	180/0.2
V	Vinyl 10,11-Dichloroundec- anoate (VDCU)	1.4712 (26)	144–46/0.5
VI	Undecyl Acrylate (UAC)	1.4575 (30.5)	138/1
VII	10-/11-Phenylundecyl Acrylate (PUA)	1.4372 (30)	190/1
VIII	10,11-Dibromoundecyl Acrylate (DBUA)	1.4960 (26)	178/0.7
IX	Methyl 14-Acryloxyeico- sanoate (MAE)	1.4515 (31)	—
X	Undecyl methacrylate (UMA)	1.4475 (30.5)	145/1
XI	10-/11-Phenylundecyl Methacrylate (PUM)	1.4857 (28)	202/1
XII	10,11-Dibromoundecyl Methacrylate (DBUM)	1.4976 (26)	195/0.8
XIII	12-Methacryloxy-n-amyl- stearate (MAAS)	1.4480 (30.5)	ca. 245/2
XIV	Undecylenyl Acrylate	1.4475 (28.5)	85/0.2
XV	Undecylenyl Methacrylate	1.4489 (25.5)	90–109/0.5
XVI	10,11-Epoxyundecyl Acrylate	1.4534 (35)	115-127/0.35
XVII	10,11-Epoxyundecyl Meth- acrylate	1.4526 (29)	—

copolymers prepared by the redox initiation at room temperature had a higher molecular weight than those initiated with AIBN or potassium persulfate at 60°C.

A number of vinyl chloride copolymers thus prepared, shown in Tables II, III and IV, were made into films and examined in a preliminary manner. These films were obtained by casting tetrahydrofuran (THF) solutions on glass plates and subsequently drying in vacuum ovens. Insofar as plasticization and tensile strength are concerned, 25 to 30% modification by a comonomer seems to give the best balance. As the comonomer content goes up beyond this limit, the tensile strength drops rapidly, and the polymer eventually becomes too soft to form films.

Of the copolymers described in this communication, none seemed to exhibit any unusual properties. Hence they have not been recommended for further tests. The result suggested that the nature of the substituents on the alkyl group of a comonomer had little influence on the plasticity of the resulting copolymers. It may be concluded that vinyl esters, acrylates and methacrylates having structures similar to those discussed above

TABLE II
Emulsion Copolymerization of Vinyl Esters with Vinyl Chloride[a]

Run no.	Vinyl ester charged, %		Vinyl ester[d] found, %	Initiator[b] %	Time, hr	Temp., °C	Conversion, %	η_{inh}[c]
COVUA-1	VUA	37.5	35.3	1 P	3	60	62	0.67
COVUA-7	VUA	25	24.4	R	22	27	87	0.54
COVPU-3	VPU	37.5	37.1	1 A	70	60	70	0.46
COVPU-4	VPU	37.5	26.9	R	22	27	35	0.67
COVPU-5	VPU	37.5	40.5	1 P	40	60	96	0.50
COVMU-1	VMU	50	—	R	46	25	100	0.93
COVBU-2	VBU	37.5	38.4	1 P	5	60	91	0.75
COVBU-4	VBU	37.5	38.2	1 A	5	60	70	0.71
COVBU-1	VBU	37.5	30.0	R	22	27	67	0.97
COVDCU-2	VDCU	25	20.3	R	44	25	37	1.44
COVDCU-3	VDCU	25	35.3	1 P	4	60	93	0.67

[a] The polymerization was carried out in pressure bottles, using 5 parts of deaerated water, and 1% Siponate DS-10 as the emulsifier.
[b] Initiators: P = Potassium persulfate, A = α,α'-Azobisisobutyronitrile, R = Redox initiation system which consists of 1% ferrous sulfate heptahydrate, 10% sodium pyrophosphate decahydrate and 2% benzoyl peroxide.
[c] Inherent viscosities were measured on 0.2% THF solutions at 30°C.
[d] Based on carbon, hydrogen and chlorine analyses.

TABLE III
Emulsion Copolymerization of Acrylates and Vinyl Chloride[a]

Run no.	Acrylate charged, %		Acrylate[e] found, %	Initiator[b] %	Time, hr	Temp. °C	Conversion, %	η_{inh}[c]
COUAC-3	UAC	25	28.0	1 A	31	60	80	1.84
COUAC-6	UAC	25	32.7	R'	42	27	89	1.13
COPUA-1	PUA	25	—	R	20	25	50	Insoluble
CODBUA-5[d]	DBUA	25	32.2	1 A	16	60	75	0.41
CODBUA-2	DBUA	25	28	R	44	25	66	1.12
CODBUA-4	DBUA	25	—	1 P	4	60	68	0.92
COMAE-3	MAE	25	52.1	R''	45.5	27	21	1.60
COMAE-4	MAE	25	47.5	R	45.5	27	57	2.69

[a] The polymerization was carried out in pressure bottles, with 5 parts of deaerated water, and using 1% Siponate DS-10 as the emulsifier.

[b] Initiators: P = Potassium persulfate, A = α,α'-Azobisisobutyronitrile, R = Redox initiation system consisting of 1% ferrous sulfate heptahydrate, 10% sodium pyrophosphate decahydrate and 2% benzoyl peroxide; R' = redox initiation with 4% benzoyl peroxide; R'' = redox initiation with 1% benzoyl peroxide.

[c] Inherent viscosities were measured on 0.2% THF solutions at 30°C.

[d] Solution polymerization in 5 ml of benzene per 4 g of monomer.

[e] Based on carbon, hydrogen and chlorine analyses.

TABLE IV

Emulsion Copolymerization of Methacrylates and Vinyl Chloride[a]

Run no.	Methacrylate charged, %		Methacrylate[d] found, %	Initiator[b] %	Time, hr	Temp. °C	Conversion, %	$\eta_{inh.}$[c]
COUMA-2	UMA	25	30.3	1 P	17.5	60	71	2.00
COUMA-4	UMA	25	35.1	1 A	17.5	60	68	0.85
COUMA-5	UMA	25	26.4	R	42	27	75	1.17
COUMA-6	UMA	25	26.5	R'	42	27	76	1.54
COPUM-1	PUM	50	71.6	R	46	25	59	Insoluble
COPUM-2	PUM	25	61.8	R	46	25	37	Insoluble
CODBUM-1	DBUM	25	45.7	1 P	18	60	59	0.68
COMAAS-1	MAAS	23	23.5	R	22.5	27	90	0.82

[a] The polymerization was carried out in pressure bottles, with 5 parts of deaerated water, and 1% Siponate DS-10 or Office of Rubber Research Soap as the emulsifier.

[b] Initiators: P = potassium persulfate, A = α,α'-azobisisobutyronitrile, R = Redox initiation system containing 1% ferrous sulfate heptahydrate, 10% sodium pyrophosphate decahydrate and 2% benzoyl peroxide (4% in R').

[c] Inherent viscosities were measured on 0.2% THF solutions at 30°C.

[d] Based on carbon, hydrogen and chlorine analyses.

plasticize polyvinyl chloride to a certain degree, but are not effective enough to be considered as potential internal plasticizers.

Undecylenyl acrylate (UEAC, XIV) and methacrylate (UEMA, XV) were originally made available by the U. S. Department of Agriculture and later also prepared in our laboratory. The reaction of acrylyl chloride and undecylenyl alcohol with one mole of triethylamine in anhydrous ether at 0–25°C afforded undecylenyl acrylate, which after purification by column chromatography on silica gel was obtained in 65% yield. The corresponding methacrylate was prepared in a similar fashion and obtained in a comparable yield. Homopolymerization of these bifunctional monomers with potassium persulfate as an initiator at 60°C gave insoluble materials as expected.

To use UEAC and UEMA as crosslinkers, they were first epoxidized to 10,11-epoxyundecyl acrylate and methacrylate with m-chloroperbenzoic acid in weak basic media. The procedure described previously[1] for the epoxidation of vinyl 10,11-undecylenate was followed.

10,11-Epoxyundecyl acrylate was rather unstable chemically as well as thermally. Attempted purification of the crude material by column chromatography on silica gel or alumina led to the formation of an insoluble polymer. Vacuum distillation of the reaction product in the presence of copper resinate gave approximately 20% of the epoxy monomer. The epoxy ring was shown by its infrared absorptions at 3040 and 834 cm^{-1} and a positive thiosulfate test. That the acrylate double bond was intact was revealed by absorptions at 965 and 985 cm^{-1}, which did not change in going from the starting material to the expoxidized product.

Similarly, the epoxyundecyl methacrylate was prepared, and obtained in a better yield, presumably because it had a greater stability and could be purified by chromatography on alumina, using petroleum ether as an eluent. The epoxy ring structure was demonstrated by its infrared, nmr spectra and a positive thiosulfate test. Its elemental analysis also agreed with the empirical formula.

The epoxy acrylate and methacrylate were copolymerized with vinyl chloride, vinyl acetate and methyl methacrylate with radical initiation to give soluble polymers in most instances. But the vinyl chloride and vinyl acetate copolymers of 10,11-epoxyundecyl acrylate did not dissolve in THF completely. The insoluble material was removed by filtration under the aspirator pressure. Some of the results are shown collectively in Table V. Purification of the copolymers were generally done by several reprecipitations from THF and methanol, except copolymers of vinyl acetate which were soluble in methanol; water was used instead for the methanol soluble materials.

The infrared analysis of the epoxy copolymers suggested that the epoxy ring had remained intact throughout the polymerization by the presence of a very weak absorption at $ca.$ 830 cm^{-1}, attributable to the ring vibration.[2] The epoxy copolymers have been cured with concentrated sulfuric acid at room temperature, with p-phenylenediamine at about 120°C, and by heat-

TABLE V

Emulsion Copolymerization[a] of 10,11-Epoxyundecyl Acrylate and Methacrylate with Vinyl Monomers

Run no.	Comonomers[b] charged, %		EUAC or EUMA[f] found, %	Initiator[c]	Temp., °C	Time, hr	Conversion, %	$\eta_{inh.}$[d]
Acrylate								
COUEAC-5	VCl	90	9.6	R	20	44	100	1.79
COUEAC-3	VAc	95	—	R	25	44	31	1.09
COUEAC-1	MMA	95	—	R	25	24	70	3.69
COUEAC-2	MMA	87.5	—	R	25	24	74	2.33
Methacrylate								
COEUMA-14[e]	VCl	90	14.9	R	27	17	78	1.42
COEUMA-3	VAc	90	—	1 A	60	2.3	19	1.20
COEUMA-5[e]	VAc	90	13.8	R	60	15.5	51	0.44
COEUMA-15	MMA	90	13.7	1 P	60	2	31	3.18
COEUMA-16	MMA	90	18.4	1 A	60	2	54	3.84

[a] The polymerization was run in 5 parts of deaerated buffer solution of pH 7 or deaerated water with the redox system, and 1% Siponate DS-10 as the emulsifier.

[b] Comonomers: VCl = Vinyl Chloride; VAc = Vinyl Acetate; MMA = Methyl Methacrylate.

[c] Initiators: P = Potassium Persulfate; A = α,α-Azobisisobutyronitrile; R = Redox initiation system which consists of 1% ferrous ammonium sulfate hexahydrate and 10% sodium pyrophosphate decahydrate with 2% benzoyl peroxide.

[d] Viscosities were determined on 0.2% THF solutions at 30°C.

[e] In these runs, 1% Office Rubber Research Soap was used as the emulsifier.

[f] Based on carbon, hydrogen and chlorine analyses.

ing at 150°C for 30 min or longer. It was thought that epoxy copolymers of this kind may have some use in the field of coatings.

EXPERIMENTAL

Polymerization. The procedure of emulsion polymerization with free radical initiation was reported elsewhere.[1]

Preparation of Undecylenyl Acrylate. In a 1-liter round bottomed flask equipped with a magnetic stirrer and an addition funnel protected with a calcium chloride drying tube were placed 68 g (0.4 mole) of 11-undecylenyl alcohol (Aldrich Chemical), 36 g (0.4 mole) of acrylyl chloride (K and K), 0.035 g of copper resinate and 200 ml of anhydrous ether. To this solution, stirred and chilled at 0°C, was added dropwise over a period of about 1 hr a solution of 40.1 g (0.4 mole) of triethylamine (freshly distilled over sodium) in 200 ml of anhydrous ether. The reaction then continued for 22 hr at room temperature (*ca.* 25°C). On termination of the reaction, triethylamine hydrochloride was removed by filtration. And the filtrate, after washing with 2 l of 5% hydrochloric acid, 1 l of 2% sodium bicarbonate solution and water, drying over anhydrous magnesium sulfate, was evaporated on a "Rotovap" to leave behind a yellowish liquid. Chromatographing the crude product on 200 g of silica gel (Merck reagent, 28–80 mesh), and eluting with petroleum ether, yielded 58 g (0.259 mole, 65%) of undecylenyl acrylate whose infrared spectrum was superimposable with that of the authentic sample. The ester had a refractive index of $n_D^{28.5} =$ 1.4475, and TLC on silica gel, eluted with carbon tetrachloride, showed one spot at $r_f = 0.60$. This material boils at 85°C/0.2 mm and the distillate had $n_D^{29} = 1.4473$.

Epoxidation of Undecylenyl Acrylate. A mixture of 10 g (0.0045 mole) of undecylenyl acrylate, 10 g of sodium bicarbonate, approximately 0.1 g of copper resinate and 200 ml of benzene was stirred and to this was added dropwise a solution of 12 g of *m*-chloroperbenzoic acid (FMC product, min. assay 80%) in 200 ml of benzene over a period of 75 min at temperatures between 5 and 10°C. The reaction was allowed to continue at room temperature for 40 hr. At the end of this period, the reaction mixture was chilled at approximately 10°C and 10 g of sodium carbonate was added portionwise with vigorous stirring to neutralize the excess peracid. Stirring was continued for 1 hr. This mixture was filtered and the filtrate, after adding another portion of copper resinate, was washed with 2 l of 2% of sodium carbonate and water, and dried over magnesium sulfate. Benzene was removed by freeze-drying technique. The residue was a viscous oil which distilled at 115–127°C/0.35 mm, and had $n_D^{35} = 1.4534$. TLC on silica gel, eluted with carbon tetrachloride, showed a main spot at $r_f = 0.35$, and a very faint line at $r_f = 0.44$. The yield of the distilled product was approximately 20%, and the remaining portion was polymerized in the flask. The oxirane oxygen content, determined by the dioxane-hydrochloric acid method,[3] using pH meter for the end point determination, was 88.1 ± 1.4% of theory.

Preparation of Undecylenyl Methacrylate. The undecylenyl methacrylate was prepared in a similar fashion as the corresponding acrylate in approximately 50% yield, and had $n_D^{25.5} = 1.4489$.

Epoxidation of Undecylenyl Methacrylate. The procedure was similar to that for the synthesis of the corresponding acrylate. The product was chromatogrammed on alumina eluted with petroleum ether. There was obtained 68% of the purified material, which had $n_D^{29} = 1.4526$. Its infrared spectrum was characterized by absorptions at 1650, 940 and 920 cm^{-1}, due to the acryl function, and 1258 and 840 cm^{-1}, due to the epoxy ring. The nmr spectrum of this material had the following signals (τ): 3.85 and 4.42 (2 H) for the olefinic protons, 5.82 (2 H) triplet, for the methylene hydrogens adjacent to the acyloxy group, a multiplet centered at 7.52 (3 H) for the epoxy ring protons, a doublet at 8.07 (3 H) for the methyl group, and a singlet at 8.63 (16 H) for the remaining methylenes. This monomer gave a positive thiosulfate test.

ANAL. Calcd. for $C_{15}H_{26}O_3$: C, 70.88%; H, 10.23%. Found: C, 70.73%; H, 10.50%.

References

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