# Emulsion Polymerization of Linseed and Safflower Acrylates and Methacrylates

**S.K. JOSHI** and **P.C. CHATTERJEE,** Bank Note Press, Dewas, Madhya Pradesh, India

## ABSTRACT

Acrylic and methacrylic esters of mixed fatty alcohols derived from linseed and safflower oils were homopolymerized, by emulsion polymerization technique, yielding polymers that gave hard, gloosy films with excellent flexibility and good water and chemical resistance.

## INTRODUCTION

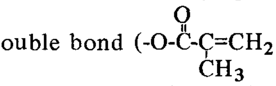
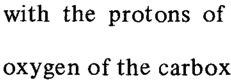
Polymerization studies on long chain vinyl monomers derived from oils and fats have not only extended our knowledge of polymer chemistry but have also given rise to products of potential commercial importance. For instance, polymers of acrylic and methacrylic esters of saturated fatty alcohols, and their copolymers with a wide range of commonly available low molecular weight vinyl monomers such as styrene, methyl methacrylate, vinyl acetate, etc., have shown considerable promise as plasticizers, adhesives, chewing-gum bases, textile assistants, water-proofing agents, and lubricating oil additives (1,2). However, no attempt seems to have been made toward polymerization of acrylates and methacrylates of polyunsaturated fatty alcohols. This is probably because unsaturation in the fatty chain is known to affect adversely the polymerization of these monomers. Harrison and Wheeler (3), during their studies on the polymerization of vinyl and allyl esters of fatty acids, observed that the polymerization decreases as the degree of unsaturation in the fatty vinyl monomer increases. The work of Port et al. (4) further confirms this view since they found that the presence of even 5% vinyl oleate in vinyl palmitate retards polymerization of the latter considerably.

Accordingly, our attempt (5) to homopolymerize acrylic and methacrylic esters of mixed alcohols derived from linseed and safflower oil, by solution polymerization technique, did not succeed, although they could be successfully copolymerized with vinyl acetate to yield copolymers having reasonably good coating characteristics. The present communication describes the work carried out to homopolymerize, by emulsion polymerization technique, the linseed and safflower acrylates and methacrylates which yielded homopolymers having interesting coating characteristics.

## EXPERIMENTAL SECTION

### Materials

Mixed fatty alcohols of linseed and safflower oils were obtained by sodium reduction (6) of the corresponding oils (acid value $\leqslant 1$) and purified by distillation under reduced pressure. Compositions of the fatty alcohols were determined by gas liquid chromatography (GLC) analysis of their acetates, on a polyester column, and compared with those of the corresponding methyl esters of the oils taken. The fatty chain distribution of the linseed and safflower alcohols agreed with that of the corresponding methyl esters within 0.5-1.0%.

Acrylic and methacrylic esters of the alcohols were prepared by Rheberg's procedure (7) involving alcoholysis of methyl acrylate or methyl methacrylate in the presence of an acid catalyst such as naphthalene-2-sulfonic acid, and a polymerization inhibitor such as hydroquinone. Each monomer was purified by one or two distillations under reduced pressures (0.1-0.5 mm Hg) over 0.1% copper rosinate. The distillate was pure enough (~99%) to respond satisfactorily to the polymerization technique adopted in the study. The products were characterized by IR (Perkin-Elmer Model 221) and nuclear magnetic resonance (NMR) (Varian 60 MC) spectroscopy, and the purity was checked by the chromatographic methods. IR spectra of the acrylic esters exhibited the following bands, characteristic of the acrylates, besides showing the usual bands due to the presence of the methylene linkages and unsaturation in the fatty chain: strong bands due to C=O and C-O stretching vibrations at 1725 and 1190 $cm^{-1}$, respectively; *two* weak bands due to C=C stretching vibrations at 1640 and 1620 $cm^{-1}$; one strong band due to C-H deformation vibrations ($C\text{-}CH_3$) at 1400 $cm^{-1}$; two medium-strong bands due to C-H in-plane deformation vibrations at 1295 and 1270 $cm^{-1}$; and two medium-strong bands due to C-H out-of-plane deformation vibrations at 980 and 960 $cm^{-1}$. The doubling of the C=C stretching vibrations to give rise to two bands (at 1640 and 1620 $cm^{-1}$), instead of one, is very characteristic of an acrylic ester. IR spectra of the methacrylic esters exhibited the following bands, characteristic of the methacrylates: strong bands due to C=O and C-O stretching vibrations at 1725 and 1165 $cm^{-1}$, respectively; one medium-strong band due to C=C stretching vibrations at 1640 $cm^{-1}$; *two* weak bands due to C-H deformation vibrations ($C\text{-}CH_3$) at 1400 and 1375 $cm^{-1}$; two strong bands due to C-H in-plane deformation vibrations at 1320 and 1300 $cm^{-1}$; and one C-H out-of-plane deformation vibration at 940 $cm^{-1}$. Occurrence of two C-H deformation bands for $C\text{-}CH_3$ (at 1400 and 1375 $cm^{-1}$) are very characteristic of the methacrylic esters since they possess two different types of methyl groups – one terminal and one in conjugation with the vinyl double bond. In the NMR spectra of the methacrylates too, the two sets of methyl protons existing under different environments gave rise to signals at two different fields, viz., the protons of the terminal methyl group ($CH_3\text{-}CH_2\text{-}$) appeared at 0.79 δ and the protons of the methyl group in conjugation with the vinyl double bond  $(\text{-O-}\overset{O}{\overset{\|}{C}}\text{-}\underset{CH_3}{\underset{|}{C}}\text{=}CH_2)$ appeared at 1.76 δ along with the protons of the methylene group adjacent to the oxygen of the carboxyl group  $(-CH_2\text{-O-}\overset{O}{\overset{\|}{C}}\text{-})$.

The emulsifier, Hyoxyd X-301 (an alkylarylether sulfonate marketed by the HICO Products Pvt., Ltd., Bombay), the penetrant, SLS-Liquid (also from HICO Products PVT., Ltd.,) and ammonium presulfate (E. Merck, GR Grade) were all used as supplied, without further purification.

### Polymerization and Films

All polymerization reactions were carried out in emulsion using the standard procedure of Fisher and Mast (8) suitably modified to meet our requirements. The exact procedure followed is described below.

A 250 ml capacity ground-glass joint Erlenmeyer flask, carrying a Teflon-enclosed magnetized stirring paddle and

TABLE I

Refractive Indices and Intrinsic Viscosities of the Monomers and Their Corresponding Polymers[a]

| Monomer | Properties of the monomer | | Properties of the polymer | |
|---|---|---|---|---|
| | $n_D^{30}$ | $[\eta] \times 10^4$ | $n_D^{30}$ | $[\eta] \times 10^4$ |
| Linseed acrylate | 1.4608 | 98 | 1.4760 | 216 |
| Linseed methacrylate | 1.4617 | 106 | 1.4802 | 227 |
| Safflower acrylate | 1.4572 | 96 | 1.4790 | 237 |
| Safflower methacrylate | 1.4584 | 102 | 1.4806 | 243 |

[a] Intrinsic viscosities were measured in benzene at 30 ± 0.01 C.

TABLE II

Characteristics of the Baked Films of the Polymers of Linseed and Safflower Acrylates and Methacrylates

| Polymer | Scratch hardness (g) | No effect in[a] | | |
|---|---|---|---|---|
| | | Chloroform | 1% NaOH | 5% $Na_2CO_3$ |
| Poly (linseed acrylate) | 2300-2500 | 30-40 min | 2-3 hr | 24-28 hr |
| Poly (linseed methacrylate) | 2500-2800 | 40-45 min | 2-3 hr | 24-28 hr |
| Poly (safflower acrylate) | 2000-2200 | 5-10 min | 20-25 min | 12-16 hr |
| Poly (safflower methacrylate) | 2200-2400 | 10-15 min | 40-45 min | 18-20 hr |

[a] The films were not affected in water, 5% sulfuric acid, white spirit, xylene, *n*-butanol, ethyl acetate, acetone, and trichloroethylene for more than 72 hr.

fitted with a reflux condenser, was charged with 40 ml of deionized water, 200 mg of Hyoxyd X-301, 200 mg of SLS-Liquid, and 1-2 mg of ammonium persulfate. The solution was stirred slowly on a hot plate with magnetic stirring, and 20 g of distilled monomer was added into it. Heat was initially applied to induce polymerization and thereafter continued at a rate just sufficient to cause gentle refluxing. The polymerization was considered to be completed when the emulsion became very viscous which took about 2-3 hr depending on the monomer chosen. Prolonged reaction period either resulted in a gelled product or reduced the yield of the desired fraction of the polymer considerably.

At the end of the reaction period, the flask was cooled to room temperature and its contents centrifuged. The contents separated out into three distinctly different layers, viz., a clear upper oily layer, a thick curdy precipitate in the middle, and a water layer at the bottom. The upper oily layer (65-70% on the weight of the monomer), which essentially consisted of low molecular weight polymers, was found to possess excellent coating characteristics. Nevertheless, the curdy precipitate (30-35% on the weight of the monomer) also was worked up, for academic interest, to study its properties. The precipitate was shaken with warm water and the suspension centrifuged. The process was repeated two to three times to remove the surfactants completely. Thereafter the precipitate was dried in a vacuum desiccator. The dried mass consisted of highly polymerized material and could not be dissolved completely in any of the common organic solvents such as toluene, xylene, methyl ethyl ketone, butanol, etc. To proceed further, the precipitate was shaken with a mixture of xylene and butanol (1:1) and the mixture centrifuged to remove the undissolved portion. The solution thus obtained (15-20% solids) also failed to produce uniform films because the highly polymerized molecules tended to separeate out as discrete particles during the evaporation of the solvent from the surface of the substrate. It may, therefore, be emphasized that all polymerization reactions were so controlled as to get low molecular weight polymers (the upper oily liquid) in maximum yield (65-70% on the weight of the monomer). The refractive indices and the intrinsic viscosities (at 30 C in benzene) of the polymers (upper oily layer) together with those of the corresponding monomers are given in Table I.

The upper oily layer, obtained during the centrifugation of the reaction product, was reduced to 60-80% nonvolatile with a mixture of xylene and butanol (1:1). The driers added (as octoates) were 0.03% Co and 0.3% Pb on the weight of the polymer. Films were cast on tin plates (1 mil, dry) for physical resistance tests and dip-coated on Pyrex test tubes for chemical resistance tests. Tin plates and test tubes thus coated were baked at 120 C for 60 min. The films were tested for their film properties after 24 hr.

## RESULTS AND DISCUSSION

The polymers studied gave bright, golden yellow films having excellent gloss, flexibility, and adhesion on metal substrates. The panels remained unaffected when subjected to (a) 1/8 in. conical mandrel bend test, and (b) cross-cut adhesion test using Scotch tape to pull out the films from the squares. The impact resistance (falling weight method) of the films was satisfactory at the maximum load of 2.81 kg falling from a distance of 20 cm. The films also exhibited excellent scratch hardness (Sheen's automatic scratch test machine). In general, the methacrylates gave harder films than the corresponding acrylates. The films remained unaffected in water, 5% sulfuric acid (w/v), white spirit, xylene, *n*-butanol, ethyl acetate, acetone, and trichloroethylene for over 72 hr. However, their resistance to 1% sodium hydroxide solution, 5% sodium carbonate solution and chloroform were different for different polymers. Some of the important film properties of the polymers of linseed and safflower acrylates and methacrylates are given in Table II. These are an average of at least three experiments. The products have good storage stability when stored in closed containers without the addition of drier compounds. No pickup of viscosity was noticed when stored at room temperature for 3 months or in an oven at 60 C for 12 hr.

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