

Some Polymers and Copolymers of Vinyl Ketostearates*

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The ready availability of some of the ketostearic acids, the known fact that ketones are good plasticizing agents for vinyl polymers¹ and the discovery that copolymers of vinyl stearate and vinyl chloride show some attractive properties has led to this study of some of the vinyl ketostearates.

4-Ketostearic acid was obtained from oiticica oil.† The hydrogenated oil was converted to the methyl esters of the fatty acids by the action of methanol and sodium methoxide. These esters were distilled and hydrolyzed according to the procedure of Calderon et al.² The free acid thus obtained was recrystallized from heptane to remove an unsaturated impurity which was probably unhydrogenated or partially hydrogenated licanic acid. Then by a slight modification of the process of Adelman³ as described by Calderon et al.,² the pure 4-ketostearic acid was converted to the vinyl ester.

9(10)-Ketostearic acid was prepared by hydrating oleic acid by the procedure of Knight et al.⁴ and oxidizing the mixed hydroxy acids by the method of Rockett.⁵ The mixed 9- and 10-acids were used in this study. The mixed vinyl esters were made as in the case of the 4-keto isomer.

12-Ketostearic acid and its vinyl ester were made by the method of Calderon et al.² from 12-hydroxystearic acid.

Homopolymerization studies were conducted first with vinyl 12-ketostearate. Bulk polymerization with benzoyl peroxide produced an insoluble polymer. When azobisisobutyronitrile was used as an initiator a partially soluble polymer was obtained. Polymerization in solution with

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benzoyl peroxide as an initiator gave a soluble polymer which had a low inherent viscosity (0.12 to 0.17). Emulsion polymerization with potassium persulfate-lauryl mercaptan as initiator gave polymers with inherent viscosities in the 0.3 to 0.5 range. Similar results were obtained with vinyl 4-ketostearate and vinyl 9(10)-ketostearate.

Polyvinyl 4-ketostearate is a white powder softening at 68–70°C., but it does not melt to a clear mass until the temperature reaches 140°C. Polyvinyl 9(10)-ketostearate is a soft fluffy solid which softens at 47–50°C. and becomes clear at about 72°C. Polyvinyl 12-ketostearate is also a fluffy solid which softens at 58–60°C. and becomes clear at 61°C.

The vinyl 4- and 12-ketostearates yield polymers which are slightly soluble in acetone. The vinyl 9(10)-ketostearate polymers are quite soluble in acetone and also in hexane which is not a good solvent for the other two materials. All of the polymers dissolve in carbon tetrachloride, chloroform, benzene, and tetrahydrofuran. None is soluble in methanol.

TABLE I
Reactivity Ratios of Vinyl Ketostearates and Typical Vinyl Monomers

| m_1 | m_2 | r_1 | r_2 |
|--------------------------|---------------------|-------------------|-------------------|
| Vinyl 4-ketostearate | Vinyl acetate | 1.18 \pm 0.22 | 1.04 \pm 0.2 |
| Vinyl 9(10)-ketostearate | Vinyl acetate | 1.49 \pm 0.25 | 1.03 \pm 0.05 |
| Vinyl 12-ketostearate | Vinyl acetate | 1.26 \pm 0.08 | 1.07 \pm 0.02 |
| Vinyl 4-ketostearate | Vinylidene chloride | 0.0 \pm 0.17 | 3.8 \pm 0.6 |
| Vinyl 9(10)-ketostearate | Vinylidene chloride | 0.01 \pm 0.09 | 3.7 \pm 0.3 |
| Vinyl 12-ketostearate | Vinylidene chloride | 0.0 \pm 0.16 | 4.0 \pm 0.5 |
| Vinyl 4-ketostearate | Vinyl chloride | 0.320 \pm 0.076 | 0.874 \pm 0.044 |
| Vinyl 12-ketostearate | Vinyl chloride | 0.248 \pm 0.01 | 0.963 \pm 0.01 |
| Vinyl 9(10)-ketostearate | Acrylonitrile | 0.0 \pm 0.091 | 2.96 \pm 0.12 |
| Vinyl 12-ketostearate | Acrylonitrile | 0.0 \pm 0.02 | 3.11 \pm 0.05 |

Vinyl 12-ketostearate copolymerized readily with vinyl stearate to form a soluble copolymer with essentially the composition of the reaction mixture. All of the vinyl ketostearates copolymerized readily with vinyl chloride and samples of these copolymers have been evaluated to determine the degree of effectiveness of the vinyl ketostearates as internal plasticizers.

Reactivity ratios for the vinyl ketostearates with vinyl acetate, vinylidene chloride, vinyl chloride, and acrylonitrile were determined by the general procedure of Mayo and Lewis.⁶ When conversion exceeded 6% the initial concentrations were corrected for drift during copolymerization by use of the equation of Overberger et al.⁷ The results are given in Table I. They are, in general, in line with values obtained for vinyl esters of other fatty acids.

Experimental

Vinyl 4-Ketostearate

Following the procedure of Calderon et al.,² 1 kg. of hydrogenated oiticica oil was treated with 650 ml. of methanol and 6.5 g. of sodium methoxide at reflux temperature for about 22 hr. The impure methyl ester was hydrolyzed to yield an impure acid which melted at 72–74°C. (literature m.p. 96.5–97.1°C.).² The crude acid was recrystallized from seven volumes of *n*-heptane to yield pure 4-ketostearic acid m.p. 98.5–100°C.

ANAL. Calc.: for $C_{18}H_{34}O_3$: C, 72.43%; H, 11.40%. Found: C, 72.59%; H, 11.33%.

The yield based on the crude methyl ester was about 45–46%.

The method of Adelman³ was modified by using a tenfold rather than fivefold excess of vinyl acetate; sulfuric acid was added in a nitrogen atmosphere and the reaction flask was wrapped in aluminum foil to exclude light. These modifications gave a less discolored reaction mixture and less polymerization during the reaction. The yields were usually in the 50–52% range; m.p. 51.9–52.9°C.

Vinyl 9(10)-Ketostearate

Following the method of Knight and co-workers⁴ 50 g. of oleic acid gave 25.6 g. (48.2%) of mixed hydroxystearic acids. Oxidation of 110 g. of this mixture by the procedure of Rockett⁵ gave 77 g. (70.6%) of mixed 9(10)-ketostearic acids, m.p. 65.2–66.0°C. By the same process used for the 4-keto isomer, 74.5 g. of the 9(10)-ketostearic acid gave 32.6 g. (40.2%) of vinyl esters; m.p. 38.7–40.3°C.

Vinyl 12-Ketostearate

Technical 12-hydroxystearic acid was recrystallized from 3 volumes of acetone to give a pure acid melting at 81.8–83.4°C. Oxidation of 150 g. of this acid by the method used for the mixed 9–10 acids gave 76.7 g. (51.5%) of 12-ketostearic acid m.p. 80.2–81.4°C. The vinyl ester was obtained in 46.7% yield, m.p. 48–49.7°C.

Homopolymerization

Bulk Polymerization of Vinyl 12-Ketostearate

Heating 5 g. of vinyl ester with 50 mg. of benzoyl peroxide for 21 hr. at 78.2°C. gave an insoluble gel which was not further characterized. Heating 5 g. of vinyl ester with 3 mg. of azobisisobutyronitrile at 78.2°C. for 21 hr. gave 60% conversion to partially soluble polymer which was isolated by pouring the benzene solution of the reaction product into a 3:1 mixture of methanol and acetone. The dried polymer softened at 51–59°C. and was clear at 60–61°C. The inherent viscosity (of soluble portion) (0.2 g. in 100 ml. carbon tetrachloride at 25°C.) was 0.177.

ANAL. Calc.: for $C_{20}H_{36}O_3$: C, 74.02%; H, 11.18%. Found: C, 73.73%; H, 10.99%.

Solution Polymerization of Vinyl 12-Ketostearate

A solution of 4 g. of vinyl ester and 50 mg. of benzoyl peroxide in 20 ml. of low boiling petroleum ether was refluxed under nitrogen at 38°C. for about 15 hr. Much of the solvent was lost leaving a viscous mass which was dissolved in benzene. The polymer was precipitated by pouring this solution into a 3:1 mixture of methanol and acetone. A white powdery solid was obtained in 30% yield. It softened at 58–63°C. and was clear at 63–64°C. The inherent viscosity in carbon tetrachloride was 0.17.

A solution of 2 g. of the vinyl ester and 6 mg. of benzoyl peroxide in 4 ml. of *p*-xylene was heated in boiling water for 157 hr. The solution was poured into 100 ml. of methanol to yield a white solid polymer. The dried product (24.6%) softened at 58–62°C. and became clear at 64°C. The inherent viscosity was 0.12.

Emulsion Polymerization of Vinyl Ketostearates

The emulsion polymerization of vinyl 12-ketostearate was studied first and the satisfactory recipe which was developed was then used for all three esters. The best results were obtained using a charge of 2 g. of monomer, 0.2 g. of sodium chloride, 2 ml. of oxygen-free water, 2 ml. of a 0.5% solution of potassium persulfate, 0.3 g. of Triton X-301, and 1 drop of lauryl mercaptan (Hooker technical grade) in a screw-cap polymerization bottle. The reaction mixtures were then tumbled in a constant temperature bath at the specified temperature and for the time indicated in Table II. The polymers were isolated by pouring the reaction mixture into 50 ml. of a 4.28% solution of sulfuric acid in water saturated with sodium chloride. Each polymer was collected on a filter, washed with water and methanol, redissolved in chloroform, and finally reprecipitated by pouring this solution into 300 ml. of methanol. After filtering the polymer was dried under reduced pressure. The properties of the products are given in Table II.

TABLE II
Emulsion Polymerization of Vinyl Ketostearates

| Monomer | Vinyl 12-keto- stearate | Vinyl 4-keto- stearate | Vinyl 9(10)-keto- stearate |
|--|----------------------------|---------------------------|-------------------------------|
| Temp. of polymerization, °C. | 60 | 50 | 50 |
| Time, hr. | 165 | 168 | 168 |
| Conversion, % | 76.2 | 34.6 | 57.6 |
| Inherent viscosity (0.125 g. in 100 ml. $CHCl_3$ at 25°C.) | 0.48 | 0.10 | 0.2 |
| Softening point, °C. | 58–62 | 68.2–70.5 | 47.3–50.5 |
| Clear point, °C. | 64 | 140 | 72 |

Copolymerization Experiments

Vinyl 12-Ketostearate with Vinyl Stearate

A polymerization bottle was charged with 3 g. of vinyl 12-ketostearate, 5 g. of vinyl stearate, 0.8 g. of sodium chloride, 14 ml. of oxygen-free water, 2 ml. of 2% aqueous potassium persulfate solution, 1.2 g. of Triton X-301 and a drop of Hooker technical lauryl mercaptan. The bottle was tumbled at 60°C. for 76.5 hr. and the polymer isolated as described for the homopolymers. The conversion was 64.6%. The polymer softened at 48–57°C. Its inherent viscosity (0.125 g. in 100 ml. CHCl_3 at 25°C.) was 0.234. The carbon content (76.05%) indicates a vinyl stearate content of approximately 60.8% in the copolymer which is very close to the charging ratio.

Vinyl Chloride Copolymers

A standard charge of 20 g. of mixed monomers, 0.6 g. of sodium chloride, 38 ml. of oxygen-free water, 3 g. of Triton X-301, and 2 ml. of 5% aqueous potassium persulfate was used in the experiments. All the ingredients except the vinyl chloride were introduced into the polymerization bottle. The bottle was flushed with nitrogen and cooled to -78°C . An excess of liquefied vinyl chloride was added, the cooled polymerization bottle placed on a balance and vinyl chloride was allowed to evaporate to sweep out the air until the desired charge was left in the bottle. The bottle was then sealed and tumbled for the specified time at 50°C. The copolymers were isolated as described for the homopolymers except tetrahydrofuran was used as the polymer solvent. The results are recorded in Table III.

TABLE III
Copolymerization of Vinyl Chloride and Vinyl Ketostearate

| | 4-Keto | 12-Keto | 12-Keto | 9(10)-Keto |
|---------------------------------|---------|---------|---------|------------|
| Vinyl ketostearate, g. | 6 | 6 | 8 | 6 |
| Vinyl chloride, g. | 14 | 14 | 12 | 14 |
| Time of polymerization, hr. | 168 | 168 | 168 | 168 |
| Conversion, % | 66 | 70 | 75 | 85.5 |
| Inherent viscosity | 0.67 | 1.16 | 1.38 | 1.19 |
| Chlorine content, % | 45.41 | 44.59 | 36.12 | 41.55 |
| Ester in corporation, wt.-% | 19.94 | 21.5 | 36.44 | 26.75 |
| Softening range of polymer, °C. | 140–160 | 155–175 | 125–155 | 130–175 |

The copolymers were fibrous materials. Several runs of each of the types given in Table III were carried out to provide adequate samples for the evaluation of the copolymers.

Reactivity Ratios

The reactivity ratios were determined at 60°C. in 4-oz. bottles sealed with nitrile rubber gaskets and screw-caps. Approximately 14–17 mg. of benzoyl peroxide was used as the initiator in each copolymerization. The

reactions were carried out under a nitrogen atmosphere with the exception of the vinyl chloride copolymerizations in which case excess vinyl chloride was allowed to boil off, thus sweeping air from the system. Purification

TABLE IV
Data from Reactivity Ratio Experiments

| m_1 | g. | m_2 | g. | Time, hr. | Con- ver- sion, % | Car- bon, % | Mole frac- tion of m_1 in polymer |
|--------------------------|------|------------------------|------|--------------|----------------------------|-------------------|--|
| Vinyl 4-ketostearate | 7.00 | Vinyl acetate | 3.00 | 6.75 | 2.2 | 69.83 | 0.406 |
| Vinyl 4-ketostearate | 3.00 | Vinyl acetate | 7.09 | 6.75 | 0.4 | 61.13 | 0.0987 |
| Vinyl 4-ketostearate | 1.00 | Vinyl acetate | 9.06 | 6.75 | 10.7 | 57.60 | 0.0280 |
| Vinyl 9(10)-ketostearate | 7.00 | Vinyl acetate | 3.02 | 5.00 | 5.4 | 69.02 | 0.411 |
| Vinyl 9(10)-ketostearate | 5.00 | Vinyl acetate | 5.00 | 5.00 | 2.0 | 64.49 | 0.195 |
| Vinyl 9(10)-ketostearate | 1.00 | Vinyl acetate | 9.07 | 5.00 | 3.4 | 57.53 | 0.0269 |
| Vinyl 12-ketostearate | 7.00 | Vinyl acetate | 3.00 | 6.75 | 16.4 | 68.67 | 0.389 |
| Vinyl 12-ketostearate | 5.00 | Vinyl acetate | 5.02 | 6.75 | 3.5 | 64.88 | 0.208 |
| Vinyl 12-ketostearate | 1.00 | Vinyl acetate | 9.13 | 6.75 | 9.6 | 57.52 | 0.268 |
| Chlorine, % | | | | | | | |
| Vinyl 4-ketostearate | 9.00 | Vinylidene chloride | 1.04 | 5.00 | 1.1 | 28.72 | 0.316 |
| Vinyl 4-ketostearate | 7.00 | Vinylidene chloride | 3.00 | 6.5 | 1.5 | 49.22 | 0.127 |
| Vinyl 4-ketostearate | 5.00 | Vinylidene chloride | 5.03 | 6.5 | 1.6 | 58.11 | 0.072 |
| Vinyl 9(10)-ketostearate | 9.00 | Vinylidene chloride | 1.00 | 6.5 | 1.0 | 27.53 | 0.331 |
| Vinyl 9(10)-ketostearate | 7.00 | Vinylidene chloride | 3.03 | 6.5 | 1.8 | 47.96 | 0.136 |
| Vinyl 9(10)-ketostearate | 5.00 | Vinylidene chloride | 5.11 | 6.5 | 0.9 | 57.80 | 0.080 |
| Vinyl 12-ketostearate | 9.00 | Vinylidene chloride | 1.00 | 6.5 | 1.2 | 28.21 | 0.322 |
| Vinyl 12-ketostearate | 7.00 | Vinylidene chloride | 3.19 | 6.5 | 3.8 | 50.22 | 0.120 |
| Vinyl 12-ketostearate | 5.00 | Vinylidene chloride | 5.02 | 5.00 | 1.3 | 63.41 | 0.069 |
| Vinyl 4-ketostearate | 8.99 | Vinyl chloride | 1.00 | 5.00 | 10.4 | 8.59 | 0.520 |
| Vinyl 4-ketostearate | 7.92 | Vinyl chloride | 1.80 | 5.00 | 12.1 | 13.22 | 0.388 |
| Vinyl 4-ketostearate | 1.15 | Vinyl chloride | 9.00 | 5.00 | 13.8 | 49.51 | 0.027 |
| Vinyl 12-ketostearate | 9.00 | Vinyl chloride | 1.00 | 5.00 | 19.3 | 9.36 | 0.493 |
| Vinyl 12-ketostearate | 7.99 | Vinyl chloride | 1.80 | 5.00 | 10.2 | 14.28 | 0.363 |
| Vinyl 12-ketostearate | 1.20 | Vinyl chloride | 9.00 | 5.00 | 12.0 | 49.92 | 0.252 |
| Nitrogen, % | | | | | | | |
| Vinyl 9(10)-ketostearate | 9.00 | Acrylonitrile | 1.02 | 5.5 | <0.1 | 10.30 | 0.187 |
| Vinyl 9(10)-ketostearate | 7.00 | Acrylonitrile | 3.04 | 5.5 | 1.4 | 19.86 | 0.092 |
| Vinyl 9(10)-ketostearate | 5.00 | Acrylonitrile | 4.97 | 3.5 | 3.4 | 20.55 | 0.048 |
| Vinyl 12-ketostearate | 9.00 | Acrylonitrile | 1.03 | 5.5 | <0.1 | 11.15 | 0.183 |
| Vinyl 12-ketostearate | 7.00 | Acrylonitrile | 3.00 | 3.5 | 2.5 | 16.26 | 0.093 |
| Vinyl 12-ketostearate | 5.00 | Acrylonitrile | 5.08 | 3.5 | 0.4 | 20.42 | 0.045 |

was attained through reprecipitation. When possible, the freeze-drying technique⁶ was used. Otherwise the polymers were placed under high vacuum for an extended length of time. The pertinent data are collected in Table IV.

Evaluation of Vinyl Chloride Copolymers

The vinyl ketostearate copolymer compositions were compounded on a rubber mill with 0.68% stearic acid and 1.66% barium-cadmium dilaurate (Mark XI) stabilizer at the temperatures reported in Table V. The milled sheets were then molded into 6 by 6 by 0.0625 in. panels under an ultimate pressure of 500 psi. Test specimens were die-cut at room temperature from these panels. All compositions were tested as rigid plastics in conformance with ASTM Test 638-52T except for the use of a 1-in. gage length instead of the standard 2 in. called for in the test. The 36.4% vinyl 12-ketostea-

TABLE V
Comparison of the Mechanical Properties of Vinyl Chloride-Vinyl Ketostearate Copolymers, Vinyl Chloride-Vinyl Stearate Copolymers, and an Externally Plasticized Vinyl Chloride-Vinyl Acetate Copolymer

| Test | Vinyl ketostearate in copolymer | | | | Vinyl stearate ^b in copolymer | | PVCA ^c plasti- cized with 35% DOP |
|---|------------------------------------|-------------------------|------------------|----------------------|---|-------|---|
| | 4- Keto ^a 19.9% | 9(10)- Keto 26.7% | 12-Keto 21.5% | 36.4% | 19.1% | 35.3% | |
| Tensile strength, psi (original cross section) (Instron) | | 4,400 | 4,400 | 3,200 | 3,400 | 1,500 | |
| Tensile strength, psi (rupture cross section) (Instron) | | 8,900 | 8,900 | 8,100 | | | |
| Tensile strength, psi (original cross section) (Scott IP-4) | | | | 3,300 | 4,200 | 2,200 | 3,100 |
| 100% modulus, psi (Scott IP-4) | | | | 3,100 | | 1,800 | 1,600 |
| Yield point, psi (Instron) | | 4,000 | 4,700 | (1,900) ^d | | | |
| Modulus of elasticity- tension (Instron) | | 102,000 | 106,000 | 46,400 | 212,000 | 4,300 | |
| Elongation, % (Instron) | | 200 | 150 | 340 | 65 | 310 | |
| Elongation, % (Scott IP-4) | | | | 280 | | | 310 |
| T _f (135,000), °C. | | 27 | 36 | 8 | 27 | 2 | -28 |
| T ₁ (10,000) °C. | | 39 | 50 | 27 | | | |
| Milling and molding temp., °F. | 260 | 300 | 320 | 295 | 220 | 200 | 310 |

^a Too brittle to test.

^b Data from ref. 8.

^c Vinylite VYDR-35% di-2-ethylnexylphthalate.

^d Observed at 10 times normal rate of elongation.

rate copolymer was also tested as a nonrigid composition in conformance to ASTM test 412-51T. All the vinyl ketostearate compositions milled readily and satisfactorily at the temperatures reported in Table V. The amount of ketostearate monomer incorporated as well as the particular isomer employed were significant factors affecting the fluxing temperature. Vinyl 4-ketostearate was the most effective of the three isomeric monomers in this respect and gave a copolymer having the lowest fluxing temperature. The influence of the keto group apparently tapers off as it becomes more removed from the ester group and becomes negligible at the 9(10) position since the effectiveness of the vinyl 9(10)- or 12-ketostearate are about equal.

Internal plasticization has been achieved to a limited degree in the vinyl 12-ketostearate copolymer by incorporation of 36.4% vinyl 12-ketostearate monomer. On the basis of an interpolative analysis (T_f versus composition) one would expect essentially the same degree of plasticization when the 9(10)-ketostearate monomer is incorporated to the same extent. The vinyl 4-ketostearate copolymer on the other hand is a brittle composition at room temperature. Proximity of the keto group to the carbonyl oxygen of the ester group, again appears as a factor influencing the physical characteristics of these copolymers, in this case adversely affecting internal plasticization.

The vinyl 9(10)- and 12-ketostearate copolymers compare favorably with vinyl stearate copolymers of similar composition⁸ in the degree of internal plasticization, as shown by the respective T_f values of Table V, but do not approach the plasticization achieved by employing 35% DOP, an external plasticizer, in a vinyl chloride-vinyl acetate copolymer.

At the 21-27% level of monomer incorporation the relative elastic modulus of the 12-ketostearate copolymer is lower by a 2:1 ratio than that reported for a vinyl stearate copolymer,⁸ but at higher levels the reverse is true by a 10:1 ratio. This amounts to a 50-fold decrease in elastic modulus for the vinyl stearate as compared to a mere halving in the ketostearate copolymers over the same composition range.

It can be concluded on the basis of values observed for the elastic and 100% moduli as well as for changes in T_f with composition that vinyl 12-ketostearate is a somewhat less effective plasticizing monomer than vinyl stearate. The same may be inferred of the 9(10)-ketostearate because of its close similarity to the 12-ketostearate. Whether an improvement in internal plasticization might be expected in a vinyl 17-ketostearate copolymer is open to speculation; however, the absence of any significant difference between the 9(10)- and 12-ketostearate raises a reasonable doubt of achieving any material improvement in the 17-ketostearate copolymer.

A comparison of the vinyl 9(10)- and 12-ketostearates as well as the vinyl stearate copolymers⁸ with the various vinyl pinate and pinonate copolymers previously reported^{9,10} substantiates the observation that long chain aliphatic vinyl monomers are the more effective promoters of internal plasticity in a vinyl chloride copolymer.⁸

References

1. Walter, A. T., *J. Polymer Sci.*, **13**, 207 (1954).
2. Calderon, R., H. DuPuy, E. McCall, R. O'Connor, and L. Goldblatt, *J. Am. Oil Chemists' Soc.*, **37**, 132 (1960).
3. Adelman, R. L., *J. Org. Chem.*, **14**, 1057 (1949).
4. Knight, H. B., R. E. Koos, and D. Swern, *J. Am. Chem. Soc.*, **75**, 6212 (1953).
5. Rockett, J., *J. Am. Chem. Soc.*, **78**, 3191 (1957).
6. Mayo, F. R., and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).
7. Overberger, C. G., D. Tanner, and E. M. Pearce, *J. Am. Chem. Soc.*, **80**, 4566 (1958).
8. Port, W. S., E. F. Jordan, Jr., W. E. Palm, L. P. Witnauer, J. E. Hansen, and D. Swern, *Ind. Eng. Chem.*, **47**, 472 (1955).
9. Marvel, C. S., E. D. Vessel, and F. C. Magne, *J. Polymer Sci.*, **36**, 35 (1959).
10. Marvel, C. S., Y. Shimura, and F. C. Magne, *J. Polymer Sci.*, **45**, 13 (1960).

Synopsis

Vinyl esters of 4-ketostearic acid, 9(10)-ketostearic acid, and 12-ketostearic acid have been homopolymerized and copolymerized with vinyl chloride. Reactivity ratios have been determined for the three vinyl ketostearates with vinyl acetate and vinylidene chloride. Also reactivity ratios for the 4- and 10-ketostearates with vinyl chloride and those of the 9(10)-ketostearates and 12-ketostearate with acrylonitrile were determined. The mechanical properties of typical vinyl chloride-vinyl ketostearate copolymers have been examined and compared with a similar vinyl chloride-vinyl stearate copolymer and with a plasticized vinyl chloride-vinyl acetate copolymer. The copolymers of vinyl chloride with vinyl 9(10)-ketostearate and with vinyl 12-ketostearate compare favorably with the copolymer of vinyl chloride and vinyl stearate in general properties.

Résumé

Les esters vinyliques des acides 4-cétostéarique, 9(10) cétostéarique et 12 cétostéarique ont été homopolymérisés et copolymérisés avec le chlorure de vinyle. On a déterminé les rapports de réactivité pour les trois cétostéarates de vinyle avec l'acétate de vinyle et le chlorure de vinylidène. On a aussi déterminé les rapports de réactivité pour les 4- et 10-cétostéarates avec le chlorure de vinyle et ceux pour les 9(10) cétostéarates avec le chlorure de vinyle et ceux pour les 9(10)-cétostéarates et 12-cétostéarates avec l'acrylonitrile. Les propriétés mécaniques des copolymères typiques chlorure de vinyle-cétostéarate de vinyle ont été examinés et comparés avec un copolymère similaire chlorure de vinyle-stéarate de vinyle et avec un copolymère plastifié chlorure de vinyle-acétate de vinyle. Les copolymères de chlorure de vinyle avec le 9(10)-cétostéarates de vinyle et le 12-cétostéarate de vinyle sont comparés favorablement du point de vue des propriétés générales avec le copolymère de chlorure de vinyle et de stéarate de vinyle.

Zusammenfassung

Die Polymerisation von Vinyestern der 4-Ketostearinsäure, 9(10)-Ketostearinsäure und 12-Ketostearinsäure und ihre Copolymerisation mit Vinylchlorid wurde durchgeführt. Die Reaktivitätsverhältnisse der drei Vinylketostearate mit Vinylacetat und Vinylidenchlorid wurden bestimmt. Ebenso wurden Reaktivitätsverhältnisse für 4- und 10-Ketostearat mit Vinylchlorid und für 9(10)-Ketostearat und 12-Ketostearat mit Acrylonitril bestimmt. Die mechanischen Eigenschaften typischer Vinylchlorid-Vinylketostearatcopolymerer wurden untersucht und mit einem ähnlichen Vinylchlorid-Vinylstearatcopolymeren und einem weichgemachten Vinylchlorid-Vinylacetatcopolymeren verglichen. Die Copolymeren von Vinylchlorid und Vinyl-9(10)-Ketostearat und mit Vinyl-12-Ketostearat besitzen im Vergleich zu Copolymeren von Vinylchlorid und Vinylstearat in allgemeinen günstige Eigenschaften.

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