

220. *The Polymerizability of Methyl α -tert.-Butylacrylate.*

By J. W. C. CRAWFORD and (Miss) S. D. SWIFT.

Slow polymerization to low polymers, which appears to be generally characteristic of esters of higher α -alkylacrylic acids, may be due to steric hindrance by the α -alkyl groups in formation of the polymer chain. Degradative chain transfer on the monomer may be a contributory cause of the behaviour. In methyl α -tert.-butylacrylate, the magnitude of steric hindrance would probably be exceptionally high; the degradative chain-transfer reaction would not occur.

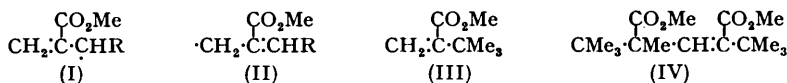
Methyl α -tert.-butylacrylate has been synthesized by dehydration of methyl tetramethyl-lactate. Attempts to produce polymers from the ester have been unsuccessful under a variety of conditions, and it is concluded that repulsion by the α -tert.-butyl group is sufficiently great to prevent polymerization.

It appears to be generally the case that esters of α -alkylacrylic acids, when exposed to usual polymerizing conditions, very slowly yield polymers of low molecular weight. This has been observed on heating the methyl esters at 100° with benzoyl peroxide, for the cases where the α -alkyl group was ethyl, *n*- and *iso*-propyl, *n*-butyl, *n*- and *iso*-amyl, and cetyl. Methyl methacrylate is exceptional, since under such conditions it polymerizes readily and virtually completely to a macromolecular product.

The polymerization behaviour of the higher α -alkylacrylic esters can be a consequence of steric hindrance in chain formation, by the 1 : 1-substituents in the ethylene. Existence of this hindrance can be demonstrated by constructing sections of polymer with Stuart atom models, but conclusions from the model about the size of the repulsive forces can only be qualitative. The presence of strain as a result of steric hindrance is also shown in the Stuart model of sections of poly(methyl methacrylate), and Evans and Tyrrell (*J. Polymer Sci.*, 1947, **2**, 387) have found that the heat of polymerization of methyl methacrylate is 7.3 kcal./mole less than that of methyl acrylate, which can form an unstrained polymer. They have brought evidence that the lower heat of polymerization of the methacrylate is associated with steric hindrance in polymer chain formation by the α -methyl group.

Allyl acetate, when heated with benzoyl peroxide, slowly passes into a low polymer. Poly(allyl acetate) would be expected to be strain-free. To account for the behaviour of the acetate, Bartlett and Altschul (*J. Amer. Chem. Soc.*, 1945, **67**, 816) suggested that the growing poly(allyl acetate) radical reacts readily with the monomer, and the reaction is

terminated by union with hydrogen from the α -carbon atom of the monomer. The latter is thereby converted into a resonance-stabilized allylic radical incapable or barely capable of initiating further polymerization of allyl acetate. A similar "degradative chain transfer" seems feasible for α -alkylacrylic esters and would supplement steric hindrance in producing a tendency for slow polymerization to low polymers. Reaction of the polymer radical with the 1-hydrogen atom of the α -alkyl group in the monomer would end polymerization and convert the monomer into a radical (I) stabilized by resonance with (II).



The ready polymerization of methyl methacrylate to a macromolecular product might be due to unimportance of the above transfer reaction in its case, because of the higher C-H bond energy in the α -methyl group than of the C-H bond energy of hydrogen combined with the 1-carbon atom in the higher α -alkyls. There are, however, no suitable bond-energy data from which to check this proposition. The values given by Roberts and Skinner (*Trans. Faraday Soc.*, 1949, **45**, 339) for R-H bond dissociation energies in ethane and propane suggest that the removal of hydrogen from the α -methyl group in methacrylate might require some 6 kcal./mole more than for removal of the 1-hydrogen atom from the α -ethyl group of α -ethylacrylate, but this conclusion would involve neglecting the effects of the adjacent vinyl and carboxymethyl group. No information is available for the activation energies of these processes.

The polymerizability of methyl α -tert.-butylacrylate (III) is of interest in this general connection. If steric hindrance is important in limiting the polymerizability of the α -alkylacrylic esters to macromolecular products, the α -tert.-butylacrylate should show the effects of this markedly, because of the bulkiness of the tert.-butyl group. Further, the degradative transfer reaction cannot occur in this case.

By using Stuart models, it was not found possible to construct model sections of poly(methyl α -tert.-butylacrylate), whether of head-to-tail, head-to-head, or tail-to-tail types, because of interference of the tert.-butyl groups with chain formation. It appeared indeed uncertain whether the ester would polymerize at all.

The polymerizability of methyl α -tert.-butyl acrylate was examined experimentally, material synthesized as described later being used.

The ester showed no visible signs of polymerization—passage to solid resin, deposition of polymer, or increase of viscosity—when heated at 100° with free-radical catalysts (benzoyl peroxide or azodiisobutyronitrile), or when exposed in borosilicate glass to ultraviolet radiation, with or without the presence in solution of benzoin photopolymerization catalyst. After prolonged exposure of the ester in glass to ultra-violet radiation at ordinary temperatures, its measured refractive index and viscosity were not significantly altered, no precipitate of polymer was obtained on addition of methanol or light petroleum, and the residue after evaporation of monomer was 0.04% of the weight of the latter.

In the absence of response to polymerizing conditions at ordinary or elevated temperatures, an attempt was made to polymerize methyl α -tert.-butylacrylate at a low temperature, at which, given effective activation, the free energy of the desired polymerization might be more favourable for its progress. Beaman (*J. Amer. Chem. Soc.*, 1948, **70**, 3115) has shown that methyl methacrylate is polymerized very rapidly and completely to a macromolecular product under conditions of anionic activation (sodium in liquid ammonia) at -80°. Application of Beaman's conditions to methyl α -tert.-butylacrylate produced only 0.8% of non-volatile residue, and this had a molecular weight little greater than that of the dimer (a head-to-head dimer could be formed, with some steric hindrance). It must be concluded from the experimental work that methyl α -tert.-butylacrylate is unable to furnish a polymer.

For polyisobutylene, Evans and Tyrrell (*loc. cit.*) were able to calculate a hypothetical value for the heat of polymerization in absence of strain, because of the existence of the strain-free head-to-tail dimer, 2:4:4-trimethylpent-1-ene. The value thus obtained, about 20 kcal./mole of monomer, was the same as that found experimentally in the

polymerization of monosubstituted ethylenes (*e.g.*, methyl acrylate) to unstrained polymers, and supported further the view that the lower value (12.8 kcal.) measured directly in the polymerization of *isobutylene* could be referred to steric hindrance of methyl groups. This treatment could not be followed in the present case, since it was apparent from the model that the possible head-to-tail dimer (IV) of methyl α -*tert.*-butylacrylate would be strained.

Methyl α -*tert.*-butylacrylate is readily hydrogenated to methyl α -*tert.*-butylpropionate ($\alpha\beta$ -trimethylbutyrate) at ordinary pressure and temperature, on use of palladium-barium sulphate catalyst. The boiling point of the propionate is only 2° lower than that of the acrylate, and separation of the two esters would not occur significantly under the conditions used for purification of the hydrogenation product. Mr. H. A. Willis has examined the infra-red absorption of this, and of pure methyl α -*tert.*-butylacrylate. The latter showed strong absorption at the C=C stretching frequency 1640 ν , corresponding closely to the same vibration for methyl methacrylate. This absorption was absent from the spectrum of the propionate. Examination of solutions of the acrylate of varying concentrations showed that the threshold of recognition of the C=C absorption would be at concentrations of acrylate of about 1%, from which it is concluded that the hydrogenation proceeds to the extent of 99% or better.

The heat of hydrogenation of methyl α -*tert.*-butylacrylate has been calculated, from the heats of combustion of acrylate and propionate, as 20.4 kcal./mole at 25°. This is lower than the calorimetrically measured heat of hydrogenation of methyl methacrylate—28.64 kcal./mole at 82° (Dollivier, Gresham, Kistiakowsky, Smith, and Vaughan *J. Amer. Chem. Soc.*, 1938, **60**, 440), but is liable to greater error. Although it may be that the heat of hydrogenation, and by inference the hypothetical strain-free heat of polymerization, is rather low, the inability to construct models of the polymer, because of interference by the α -*tert.*-butyl groups, suggests that steric hindrance is the primary cause of the non-polymerizability of methyl α -*tert.*-butylacrylate.

EXPERIMENTAL

Synthesis of Methyl α -tert.-Butylacrylate.—This followed the scheme



Trimethylpyruvic acid and methyl ester. The acid was prepared by oxidizing pinacone with potassium permanganate (Richard, *Ann. Chim.*, 1910, **21**, 360). Richard's claim of an 80% yield of distilled acid was substantiated with 80-g. batches of ketone, provided that the alkaline oxidation product, filtered from manganese dioxide, was neutralized to litmus with hydrochloric acid before concentration and liberation of the trimethylpyruvic acid: neglect of neutralization resulted in yields of 50–60%. The methyl ester, prepared as described by Richard, had b. p. 44–45°/12 mm. (yield, 82%).

Methyl tetramethyl-lactate. Methyl trimethylpyruvate (81 g., 0.56 mole), in an equal volume of ether, was added to a solution of methylmagnesium iodide [from magnesium, 27.3 g. (1.14 g.-atom), and methyl iodide, 160 g.] in ether (500 c.c.), the reaction mixture being stirred, and cooled to below –10° during the addition. Vigorous reaction and formation of a precipitate, which at once redissolved, accompanied addition of each drop of ester. 10 Minutes after addition was complete, the mixture was poured on 900 g. of cracked ice, magnesia dissolved by addition of hydrochloric acid, the ethereal layer washed four times with water and dried (Na_2SO_4), the solvent removed, and the residue fractionated through a 9-inch Vigreux column. After a few drops of forerun, almost all distilled at 64–64.5°/14 mm. (yield 73 g., 81%). Use of an equimolar amount of Grignard reagent gave yields around 50%.

The redistilled ester had b. p. 58.5°/10 mm., n_D^{20} 1.4275, d_4^{20} 0.9801, $[R_L]_D$ 42.00 (Calc. : 42.32); when cooled to –80°, it formed a glass [Found : C, 60.1; H, 9.9%; *M* (cryoscopic in benzene), 158. Calc. for $\text{C}_8\text{H}_{16}\text{O}_3$: C, 60.0; H, 10.0%; *M*, 160]. The ester is only slowly hydrolyzed by boiling 0.5*N*-alcoholic potash (Sap. val. : 2 hours' reflux, 286.3; 4 hours' reflux, 345.2; 8 hours' reflux, 352.3. Calc. : 350).

Methyl α -tert.-butylacrylate. Methyl tetramethyl-lactate (75 g., 0.47 mole), phosphoric oxide (77 g., 0.54 mole), and dimethylaniline (77 g., 0.64 mole) were heated for 22 hours on the water-bath. The product was distilled from a metal-bath, a simple distillation head being used,

at such a rate that the vapour temperature did not exceed 170°. This occupied 1—2 hours. The distillate (88 g.) was washed four times with dilute hydrochloric acid, twice with water, and dried (CaCl₂), and the product (60 g.) fractionally distilled at atmospheric pressure, a 6-inch precision column of 12 plates' rating (Dixon, *J. Soc. Chem. Ind.*, 1949, **68**, 299) being used. After a moist fore-run (4 g.) had passed over, methyl α -tert.-butylacrylate was collected at 146—149°/755 mm. (29 g., 40.6%). The residue was unchanged methyl tetramethyl-lactate, containing some butylacrylate. Mixed with fresh lactate, it was used in a subsequent preparation of butylacrylate, the yield being the same as with pure lactate.

On redistillation, *methyl α -tert.-butylacrylate* had b. p. 147—147.4°/757 mm., m. p. —36°, n_D^{20} 1.4273, d_4^{20} 0.9126, $[R_L]_D$ 40.00 (Calc.: 40.33) [Found: C, 67.2; H, 10.0%; M (cryoscopic in benzene), 139. Calc. for C₈H₁₄O₂: C, 67.6; H, 9.8%; M , 142]; like methyl tetramethyl-lactate, it is only slowly hydrolyzed by boiling alcoholic potash (Sap. val.: 2 hours' reflux, 330.1; 4 hours', 357; 8 hours', 383; 16 hours', 397. Calc., 396).

Polymerizability.—(a) 1-g. samples of the ester, containing in solution 1% of benzoyl peroxide or azodiisobutyronitrile [CMe₂C(CN)·N]₂, were sealed under nitrogen in glass tubes and heated at 100° for 72 and 118 hours, respectively. No visual evidence of polymerization was obtained. Similar results followed exposure of ester, with or without 0.1% of benzoin in solution, and sealed under nitrogen in Pyrex-glass tubes, to the radiation from a 250-watt Mazda compact-source mercury-in-silica lamp (type ME/D) at 12 in. distance.

(b) The ester used had been prepared 4 days previously, and stored meanwhile in the dark at ordinary temperature. Through 6 ml. of this, in a Pyrex tube (13 mm. outside diam.), a stream of oxygen-free nitrogen was passed for 5 minutes, the ester frozen, and the tube sealed off with exclusion of air. The tube was placed vertically in a cold water-jacket of transparent silica (internal diam. 25 mm.), and exposed to the radiation from the Mazda lamp at 10 inches for 88½ hours. Values of refractive index and absolute viscosity found for the ester before and after the above irradiation were, respectively: n_D^{20} 1.4273, 1.4274; η^{20} 1.24, 1.26 c.p. The irradiated ester gave clear solutions when mixed with 4 volumes of methanol or light petroleum (b. p. 100—120°). The irradiated ester was evaporated in a basin in an oven at 110°, heating being continued for 15 minutes after disappearance of liquid (the limited heating period being to minimize effects of possible depolymerization). The residue amounted to 0.04% of the weight of monomer, and was a tacky invisible film, removed by cold chloroform. A sample of the original ester, now about 15 days old, gave also 0.04% of residue when subjected to the same evaporation procedure; the residue in either case might have been an autoxidation product. In a control irradiation under the same conditions, methyl methacrylate was syrupy after 10 hours.

(c) Sodium (0.1 g.), dissolved in liquid ammonia (25 ml.), was cooled to —80° in solid carbon dioxide-methanol, and methyl α -tert.-butylacrylate (4 g.) added. The blue sodium solution was immediately decolorized. After 30 minutes at —80°, ammonium chloride (0.5 g.) was added, and ammonia removed by allowing the mixture to warm to room temperature. The residue, a mixture of liquid and white solid, was treated with water (20 ml.), which dissolved all the solids. The sharply demarcated ester layer was separated, washed three times with water, and dried (Na₂SO₄). The dried ester was evaporated in a basin in an oven at 110° for 15 minutes after disappearance of liquid, and left 0.8% of residue; continuation of heating until constant weight was reached left 0.5% of residue. This was a light brown gum [M (Rast), 327. Calc. for dimeric methyl α -tert.-butylacrylate: M , 284].

Hydrogenation of Methyl α -tert.-Butylacrylate.—Methyl α -tert.-butylacrylate (20 g., 0.14 mole), dissolved in methanol (80 g.), was hydrogenated in a shaker in presence of 5% palladium-barium sulphate (5 g.) at an initial temperature of 24°. After saturation, the liquid was filtered from catalyst, and methanol removed by fractional distillation through an 18-inch Vigreux column with 10:1 reflux ratio. The slightly moist residue was fractionated at atmospheric pressure through a 6-inch Dixon column (*loc. cit.*). After removal of further methanol, and moist ester (1 g.), methyl 1-tert.-butylpropionate (13 g., 64%) was collected at 145—146°/758.5 mm.; it had n_D^{20} 1.4122, d_4^{20} 0.8809, $[R_L]_D$ 40.40 (Calc.: 40.80).

Heats of Combustion (1 atm.).—Methyl α -tert.-butylacrylate: 21.0°, 1132.8; 21.2°, 1132.4; 27.5°, 1127.7; 27.7°, 1128.3 kcal./mole; linear interpolation gave 1129.9 kcal./mole at 25°. Methyl α -tert.-butylpropionate: 20.0°, 1177.5; 22.3°, 1177.7 kcal./mole; linear extrapolation gave 1177.9 kcal./mole at 25°.