[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

COPOLYMERIZATION OF *TRANS*-METHYL β-BENZOYLACRYLATE

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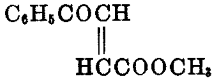
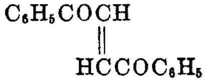
In a recent publication we reported the radical initiated copolymerization of *cis*- and *trans*-dibenzoylethylene in emulsion with various vinyl monomers (1). The results were interpreted in terms of the ease of formation and stabilities of the free dibenzoylethylene radical. Similarly one might expect the free radical from *trans*-methyl β-benzoylacrylate (I) to form with a facility similar to that of *trans*-dibenzoylethylene (II) because it too should be able to assume a planar structure and give a resonance stabilized complex (2). This keto ester free radical should be somewhat less stable than that from the diketone since the ester has only one phenyl group and therefore less possibilities for resonance.



$$\begin{array}{l} C_6H_5COCH \\ \quad\;\; \| \\ \quad HCCOOCH_3 \end{array}$$

I



$$\begin{array}{l} C_6H_5COCH \\ \quad\;\; \| \\ \quad HCCOC_6H_5 \end{array}$$

II

These assumptions are borne out by the experimental facts in copolymerizations with butadiene and styrene. Generally speaking, *trans*-methyl β-benzoylacrylate resembles *trans*-dibenzoylethylene, with the exception that the former shows higher incorporation, calculated on a molar basis, as would be expected for a compound of higher free radical activity. This monomer could not be homopolymerized in emulsion using the Mutual recipe (3). It formed rubber-like copolymers with butadiene. A decrease of molecular weight with increasing incorporation of the ketone in the copolymer was observed. This appears to be the result of a higher incorporation of a unit of low free radical reactivity which has no tendency for self addition.

This association of a higher percentage of incorporated ester with a lower molecular weight polymer indicates a higher probability of a termination reaction the moment the growing chain ends with a methyl β-benzoylacrylate unit. Actually, it would be expected that many collisions would be required before a butadiene molecule would attach itself to a chain terminated by a methyl β-benzoylacrylate unit since this would involve going from a more stable to a less stable radical end group. Copolymers of higher ester content showed a higher benzene solubility, indicating that the effect of the lower molecular weight overshadowed the polar effect of the carbonyl groups, which would be expected to decrease the benzene solubility.

Methyl β-benzoylacrylate copolymerized with styrene in emulsions without the retardation observed with *trans*-dibenzoylethylene. Again, because its free radical is less stable than that of dibenzoylethylene, a styrene molecule can add to a chain having a free methyl β-benzoylacrylate radical at its end with greater facility (the free energy difference between the radicals formed is not so great). The copolymers produced were tough and elastic, not resembling polystyrene. This elasticity increased with higher incorporations of the keto ester.

Acrylonitrile could not be polymerized in emulsion in the presence of *trans*-methyl β-benzoylacrylate using the Mutual recipe (3) at 50° for as much as three days. *trans*-Methyl β-benzoylacrylate is much more likely to attach itself to a growing chain than acrylonitrile. The free radical thus formed is sufficiently stable to prevent the addition of an acrylonitrile molecule and thereby form a much less stable free radical. Since the dicarbonyl compound shows little tendency for self addition, the chances are very favorable for immediate termination.

EXPERIMENTAL

Materials. Butadiene. Phillips Petroleum Company, special purity grade, was distilled from the tank and condensed in a Dry Ice-trap.

Acrylonitrile. Material obtained from Eastman Kodak Company was fractionated, and the part boiling between 77° and 77.5° was used.

Methyl β-benzoylacrylate. It was found most convenient to prepare this ester by modification of the silver salt method first proposed by R. E. Lutz and G. W. Scott (4). β-Benzoylacrylic acid (110 g.) was mixed with 53 g. of sodium bicarbonate and dissolved slowly in about 1000 ml. of water. A concentrated solution of 110 g. of silver nitrate in water was added and the precipitated silver salt was collected and washed with water until the washings contained no silver ions. The salt then was washed with acetone and dried in a vacuum desiccator lined with aluminum foil for ten days. The crumbs then were powdered, suspended in dry benzene, 178 g. of methyl iodide was added, and the mixture was stirred under reflux for 30 minutes and filtered. The benzene solution was shaken first with a bicarbonate solution, then with water, separated, and evaporated under a vacuum until only a heavy oil remained. The ester distilled at 150° at 5 mm. pressure, and crystallized in long yellow needles which melted at 35°. The yield was 97 g. or 82%.

Anal. Calc'd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30.
Found: C, 69.62; H, 5.50.

4-Carbomethoxy-5-benzoylcyclohexene. The compound was prepared by a method devised by Fieser and Fieser for similar derivatives (5). A solution of 2 g. of methyl β-benzoylacrylate, a trace of hydroquinone, and 1.8 g. of butadiene in 10 ml. of absolute ethanol was heated in a sealed bottle for five days in a steam-cone. After cooling to room temperature, the bottle was carefully opened and the excess butadiene allowed to escape. The solution was boiled for three minutes with a little Norit and filtered. After evaporation of the solvent, an oil remained which distilled at 128° under 1 mm. pressure. Only 0.642 g. of the product was collected; n_D^{20} 1.5453. This oil showed infrared bands at 1680 and 1735 cm.$^{-1}$.

Anal. Calc'd for $C_{15}H_{16}O_3$: C, 73.76; H, 6.60.
Found: C, 74.06; H, 6.51.

Polymerization technique. The monomers and reagents were placed in four-ounce bottles equipped with self sealing rubber gaskets, the air was swept out, and the bottles were rotated end over end at 50°. At the end of the polymerization time the latices were coagulated in the usual manner (3). The polymers were shredded into a large volume of water, soaked for one hour, filtered, and dried under 0.5 mm. Hg.

All polymerizations were run in the Mutual recipe (3) using 17 ml. of a 2.9% soap solution, one ml. of a 3% potassium persulfate solution, and 7 mg. of Hooker's lauryl mercaptan for a charge of 10 g. of monomers.

Copolymerizations with butadiene. The molecular weight of the copolymers decreased with increasing charge ratios (ester/butadiene). This was indicated by the viscosities as well as by the appearance of the product. After 15½ hours some of the copolymers were still slightly sticky. By increasing the polymerization time to 16½ hours very tough elastic solids were obtained. In no charge could any unreacted ester be detected after 16½ hours, apparently all of it was copolymerized as confirmed by infrared analysis which was carried out in benzene solution using 4-carbomethoxy-5-benzoylcyclohexene as model compound. For analysis the material was precipitated four times from a very concentrated benzene solution into a large volume of ethanol. *Analysis* by the infrared method was carried out as described before (1) using the 1680 cm.$^{-1}$ band of 4-carbomethoxy-5-benzoylcyclohexene as the standard and the 1682 cm.$^{-1}$ absorption of the polymer for comparison.

COPOLYMERIZATION OF *trans*-METHYL β-BENZOYLACRYLATE WITH BUTADIENE USING THE MUTUAL RECIPE AT 50° (16½ hours)

Charge[a] ratio	Weight of copolymer (g.)	Solubility	Inherent viscosity	Incorporation[b], %
6/4	9.7	98.4	1.00	61.5
4/6	9.0	84.8	1.31	—[c]
2/8	8.0	73.6	1.35	25.0
0/10	10.0	93.2	1.61	0.0

[a] The numerators and denominators are grams of ester and diene respectively

[b] In weight of methyl β-benzoylpropionate units per 100 g. of copolymer.

[c] After four reprecipitations the solubility of this sample was only 10%, so that no reliable analysis could be carried out.

Copolymerizations with styrene. The regular increase in molecular weight with decreasing ester content was even more pronounced with styrene, as indicated by the sharp increase in viscosity. The copolymer of charge ratio 8/2 came down as an oil and solidified only after washing with ethanol. Charge ratios 4/6 and 2/8 gave very tough rubber-like solids differing markedly from polystyrene which is a powder. At the end of 12½ hours the two copolymers of charge ratios 8/2 and 6/4 were still slightly yellow indicating the presence of unreacted ester, which was also confirmed by ultraviolet analysis of the crude copolymers. The absorption bands of the unreacted ester disappeared after one precipitation from a 10% benzene solution into a 100-fold volume of methanol. The final analysis was carried out on material which was purified by four reprecipitations. In the course of this operation much of the elasticity of the copolymers was lost, probably due to removal of some low molecular weight material which had a plasticizing action.

All copolymers were practically insoluble in carbon disulfide but exhibited a very high benzene solubility (20% solutions could easily be prepared). The solubility can be expected to decrease with longer polymerization times.

The incorporations were determined by ultraviolet analysis according to the procedure suggested by Meehan (6), using the formula

$$X = \frac{E - E_s}{E_m - E_s}$$

in which X is the incorporation of ester in the copolymer, E is the extinction coefficient of the copolymer solution and E_m and E_s are the extinction coefficients of methyl β-benzoylpropionate and polystyrene respectively. All measurements were taken at 2420 Å in tetrahydrofuran solution. E_m and E_s were found to be 65.8 and 0.69 (liter/g. cm.) respectively.

COPOLYMERIZATION OF *trans*-METHYL β-BENZOYLACRYLATE WITH STYRENE USING THE MUTUAL RECIPE AT 50° (12½ hours)

Charge[a] ratio	Weight of polymer (g.)	Inherent viscosity	*E*	Incorporation, %	
8/2	—	0.14	24.7 23.7	35.1 33.6	34.3
6/4	—	.20	—	—	
4/6	8.2	.30	23.0 22.4	32.5 31.6	32.0
2/8	8.8	.86	9.99 9.99	13.0 13.0	13.0
0/10	10.0	.92	0.00	0.0	

[a] The numerators and denominators are grams of ester and styrene respectively.

The microanalyses reported herein were done by Mr. J. Nemeth. Mr. J. Brader did the infrared measurements for us. We are indebted to the National Aniline Division of the Allied Chemical and Dye Corporation for a generous supply of β-benzoylacrylic acid.

SUMMARY

trans-Methyl β-benzoylacrylate was copolymerized in emulsion with butadiene and styrene, yielding in both cases tough rubber-like copolymers, the composition of which was determined by absorption spectroscopy. The ester was found to inhibit the polymerization of acrylonitrile.

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