

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

Copolymerization of Alkyl Acrylates and Alkyl Maleates. Some Kinetic Studies on Copolymerization<sup>1</sup>BY C. S. MARVEL AND ROBERT L. FRANK<sup>2</sup>

In order to learn more about copolymerization an attempt has been made to extend the method of kinetic study of the polymerization of optically active monomers<sup>3</sup> to mixtures of monomers. The work reported in this communication deals with copolymers of acrylates and maleates. These were selected for study because of ready availability and because it was thought that when these two monomer units entered a growing chain, they would do so in a 1:1 ratio as this seemed to be the tendency for such heteropolymers as styrene-maleic anhydride, stilbene-maleic anhydride<sup>4</sup> and the less closely related olefin-sulfur dioxide<sup>5</sup> copolymers. It was to be expected that excess acrylate units might appear in the polymer but the maleate being unable to polymerize alone should never exceed the 1:1 ratio.

The polymerization of various mixtures of *l*-monomethyl maleate and ethyl acrylate was carried out in water-jacketed polarimeter tubes at 55° and the change in rotation was followed to determine the rate of each reaction. The change in concentration of the maleate could then be calculated by means of the equation

$$C_T = \frac{C_0(\gamma_T - \gamma_p)}{\gamma_m - \gamma_p}$$

in which  $C_T$  is the concentration of the maleate at time  $T$  (in grams per 100 cc.),  $C_0$  is the initial concentration, and  $\gamma_m$ ,  $\gamma_p$ , and  $\gamma_T$  are the specific rotations of the monomer, the polymer, and the solution at time  $T$ , respectively. It should be noted that what is being measured here is not necessarily the rate of polymer formation, but the rate of entrance of the maleate units into the chain.

Benzoyl peroxide was used to catalyze the polymerizations, and rather large amounts (up to 5% of the solutions) were employed in order to eliminate as much as possible the induction period and to speed up the polymerizations. Anhydrous di-

oxane was the solvent and the solutions contained from 6 to 16% of the combined monomers.

The entrance of maleate units into the polymer chains appears to be a zero order reaction and gives a straight line when the change in concentration ( $C_0 - C_T$ ) is plotted against time (Fig. 1, Curve 1). This indicates that the rate should be independent of the concentration of the maleate, and this was found to be the case. When the concentration of the maleate was varied, the slope of the straight line did not change (Figs. 1 (Curve 2) and 2).

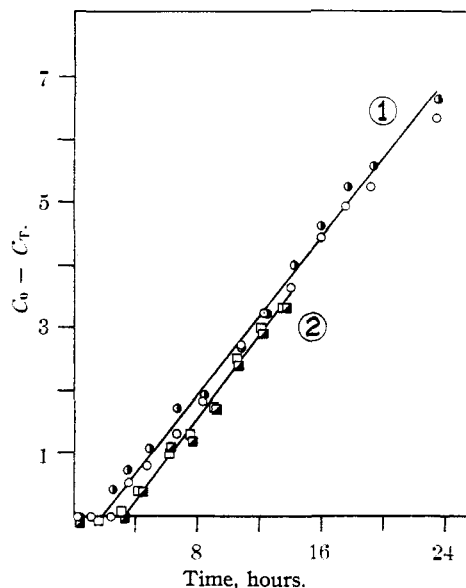


Fig. 1.—Curve 1: 0.26 molar ethyl acrylate, 0.26 molar *l*-monomethyl maleate, 5% benzoyl peroxide; Curve 2: 0.26 molar ethyl acrylate, 0.13 molar *l*-monomethyl maleate, 5% benzoyl peroxide.

When two equivalents of *l*-monomethyl maleate to one of ethyl acrylate were used, it was expected that the rotation would change until half the maleate had copolymerized with the acrylate, to give a 1:1 polymer, and that the rotation would then show no further change, as indicated by the dotted line in Fig. 2. As shown by the curve obtained in Fig. 2, this was not the case. The rotation changed according to zero order kinetics until one equivalent of maleate had been used up, and then continued to decrease slowly.

(1) This is the thirteenth communication on vinyl polymers. For the twelfth see *THIS JOURNAL*, **64**, 92 (1942).

(2) du Pont Post-Doctorate Research Assistant, University of Illinois, 1940-1941.

(3) (a) Marvel, Dec and Cooke, *THIS JOURNAL*, **62**, 3499 (1940); (b) Price and Kell, *ibid.*, **63**, 2798 (1941).

(4) Wagner-Jauregg, *Ber.*, **63**, 3213 (1930).

(5) Frederick, Cogan and Marvel, *THIS JOURNAL*, **56**, 1815 (1934).

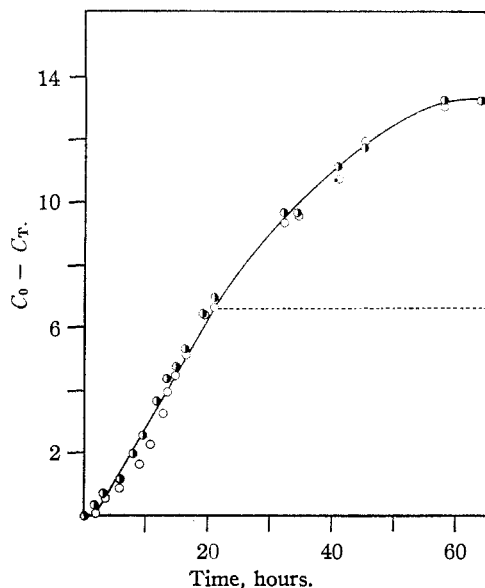


Fig. 2.—0.26 molar ethyl acrylate, 0.52 molar *l*-monomethyl maleate, 5% benzoyl peroxide.

In order to investigate this behavior, *l*-monomethyl maleate was heated in dioxane alone for a week to determine whether or not an ester interchange might be taking place. The rotation was unchanged at the end of this time.

The maleate was then treated with benzoyl peroxide without having any acrylate present. The rotation changed and, when the data were plotted, a first-order curve was obtained (Fig. 3). This result indicated that the maleate was polymerizing itself or that perhaps the monomer was

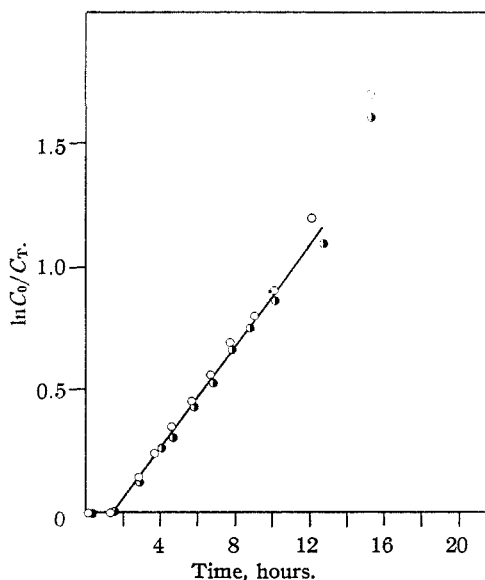


Fig. 3.—0.26 molar *l*-monomethyl maleate, 0.21 (5%) molar benzoyl peroxide.

reacting in some way with the benzoyl peroxide. In experiments using a limited amount of peroxide it was found that the latter alternative was the correct one. When less than one mole of peroxide was used for two of maleate, the rotation changed only in proportion to the amount of peroxide which would combine in this ratio. When the acrylate is present, this first order reaction is apparently superseded by the zero-order copolymerization, but takes place when the acrylate is absent. This reaction is being investigated further.

By doubling the concentration of acrylate and keeping the peroxide and maleate concentrations the same as in the experiments plotted in Fig. 1, it was found that the rate of reaction is independent of the acrylate concentration (Fig. 4, Curve 1).

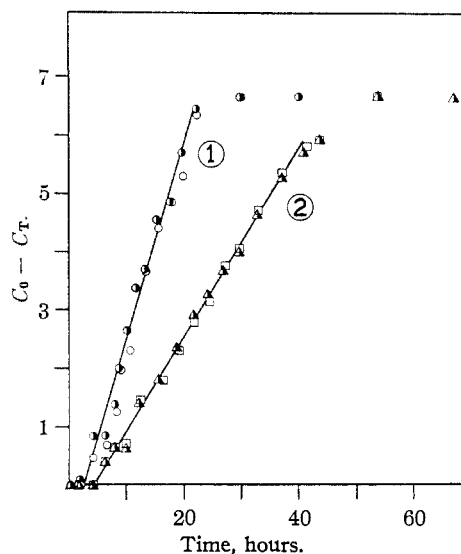


Fig. 4.—Curve 1: 0.52 molar ethyl acrylate, 0.26 molar *l*-monomethyl maleate, 5% benzoyl peroxide; Curve 2: 0.26 molar ethyl acrylate, 0.26 molar *l*-monomethyl maleate, 2.5% benzoyl peroxide.

When mole per mole of acrylate and maleate were used at the same concentration as in Fig. 1, and the peroxide concentration was halved, the rate of reaction was also cut in half, as illustrated in Fig. 4, Curve 2. Thus the rate of this polymerization appears to be directly proportional to peroxide concentration and not to the square root of the peroxide concentration as found by Price and Kell for *d-s*-butyl  $\alpha$ -chloroacrylate.<sup>8b</sup>

It is possible to explain these kinetics, zero order with respect to maleate, if one makes the assumption that the reaction of *l*-monomethyl maleate with the growing polymer chains occasionally forms a non-polymerizing product.

Polymers were isolated from the reaction mixtures containing equimolar amounts of acrylate and maleate and also from the mixtures containing two moles of maleate for one of acrylate. These polymers were found to have specific rotations of  $-29.2^\circ$  and  $-39.2^\circ$ , respectively. By calculating the specific rotation of a 1:1 copolymer from the actual rotation of the reaction mixtures at the end of the reaction, a figure of  $-43.2^\circ$  is obtained, which is higher than the values found. This would indicate that the polymer chains contain less than one maleate unit for each acrylate unit, even when the maleate monomer is used in excess. This conclusion is in agreement with the analytical data obtained for the copolymers.

A second series of experiments was carried out with *l*-menthyl acrylate and ethyl maleate, in order to study the kinetics of the entrance of acrylate units into the polymer chain. These reactions, however, did not give clean-cut curves and it was impossible to ascertain whether the reactions were zero order or first order. *l*-Menthyl acrylate alone was found to polymerize according to first-order kinetics, as shown in Fig. 5. This is the expected result and similar to the polymerization of *s*-butyl  $\alpha$ -chloroacrylate and vinyl  $\beta$ -phenylbutyrate.<sup>3a</sup>

### Experimental

**Kinetic Studies on Polymerization of Optically Active Esters.**—Special water-jacketed 1-dm. polarimeter tubes of Pyrex glass were used for the rotation studies. These were made by the Macalaster Bicknell Company of Cambridge, Massachusetts. Between polarimeter readings these tubes were kept in a constant temperature bath at  $55^\circ$ . When a reading was to be taken, a tube was removed from the bath and connected by means of rubber tubing to a small centrifugal pump. Water from the bath was then circulated through the jacket.

Some difficulty was experienced in the readings at  $55^\circ$  because of convection currents, but by averaging a number of readings it was possible to obtain reproducible results. All the experiments were carried out in duplicate except the polymerization of *l*-menthyl acrylate.

The first experiment was made with 0.750 g. of benzoyl peroxide, 0.999 g. of *l*-monomenthyl maleate, and 0.403 g. of ethyl acrylate in 15 ml. of dry dioxane solution. The data are plotted in Fig. 1, Curve 1.

The second experiment was carried out with 0.750 g. of benzoyl peroxide, 0.499 g. of *l*-monomenthyl maleate, and 0.399 g. of ethyl acrylate in 15 ml. of dry dioxane solution. These results are plotted in Fig. 1, Curve 2.

In the third kinetic study 0.750 g. of benzoyl peroxide, 2.000 g. of *l*-monomenthyl maleate, and 0.402 g. of ethyl acrylate in 15 ml. of dry dioxane were used. These data are plotted in Fig. 2.

The reaction between peroxide and maleate alone was

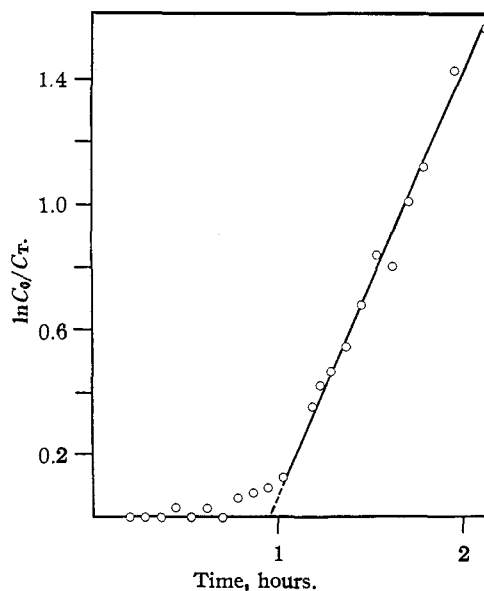


Fig. 5.—0.26 molar *l*-menthyl acrylate, 5% benzoyl peroxide.

carried out using 0.500 g. of benzoyl peroxide and 0.667 g. of *l*-monomenthyl maleate in 10 ml. of dry dioxane solution. The results are plotted in Fig. 3.

The data represented in Curve 1 of Fig. 4 were obtained with a 15-ml. solution of dry dioxane containing 0.750 g. of benzoyl peroxide, 1.000 g. of *l*-monomenthyl maleate, and 0.787 g. of ethyl acrylate. These are represented in Fig. 4, Curve 1.

In the experiment represented by Curve 2 of Fig. 4, the reaction was carried out with a 15-ml. dry dioxane solution containing 0.375 g. of benzoyl peroxide, 1.000 g. of *l*-monomenthyl maleate, and 0.394 g. of ethyl acrylate. The results are shown in Fig. 4, Curve 2.

The final experiment, the polymerization of *l*-menthyl acrylate, was made using a 5-ml. dry dioxane solution of 0.250 g. of benzoyl peroxide and 0.277 g. of *l*-menthyl acrylate. These data are represented in Fig. 5.

The final reading in each experiment was taken after the cell had been heated overnight in order to determine the rotation of the polymer itself.

***l*-Monomenthyl Maleate.**—This was prepared by the method of Wassermann<sup>6</sup> and on recrystallization from petroleum ether melted at  $86-87^\circ$  ( $[\alpha]^{25D} -74.3^\circ$ , 0.1053 g. in 5 cc. of ethanol solution). The yield was 38.6%.

**Ethyl Acrylate.**—Röhm and Haas ethyl acrylate was distilled once through a modified Widmer column at atmospheric pressure; b. p.  $98-99^\circ$ .

***l*-Menthyl  $\beta$ -Chloropropionate.**—To 125 g. of *l*-menthol dissolved in 200 cc. of dry benzene was added 98.2 g. of  $\beta$ -chloropropionyl chloride. The reaction mixture became warm and hydrogen chloride was evolved. The reaction flask, fitted with a calcium chloride tube, was allowed to stand for forty-eight hours.

The reaction mixture was fractionally distilled under reduced pressure through a modified Widmer column. The main fraction distilled at  $105-107^\circ$  (4 mm.) and weighed

(6) Wassermann, *Ann.*, **488**, 211 (1931).

146.4 g. (77%);  $n^{20}_D$  1.4642;  $d^{25}_4$  1.011;  $[\alpha]^{25}_D +25.8^\circ$  (no solvent).

*Anal.* Calcd. for  $C_{13}H_{23}ClO_2$ : C, 63.30; H, 9.39. Found: C, 63.55; H, 9.60.

***l*-Menthyl Acrylate.**—A mixture of 30 g. of *l*-menthyl  $\beta$ -chloropropionate and 66 g. of quinoline was heated for three hours at a bath temperature of 170–180°. Crystalline quinoline hydrochloride separated from the reaction mixture on cooling. One hundred cubic centimeters of benzene was added and the solution was extracted with three 100-cc. portions of water and five 60-cc. portions of 50% sulfuric acid. It was then washed with ten 50-cc. portions of water, in order to remove the last traces of quinoline salts.

The dark oily solution was fractionally distilled through a modified Widmer column and 10.2 g. (39.5%) of product boiling at 64–67° (3 mm.) was obtained. This was re-distilled at 78–80° (5 mm.);  $n^{20}_D$  1.4628;  $d^{20}_4$  0.927;  $[\alpha]^{25}_D -80.2^\circ$  (1.002 g. in 10 cc. of dioxane solution).

*Anal.* Calcd. for  $C_{13}H_{22}O_2$ : C, 74.29; H, 10.55. Found: C, 74.53; H, 10.57.

**Isolation of Polymers.**—The collected washings from all the polarimeter tubes containing 1:1 ethyl acrylate and *l*-monomenthyl maleate were evaporated nearly to dryness and the viscous mixture was dissolved in 50 cc. of methanol. This was poured into 100 cc. of water and the mixture became milky. Polymer droplets adhered to the sides of the beaker and the milky supernatant liquid was

poured off. This procedure was repeated and the polymer was then dried overnight at 70°. The result was a clear, light yellow, tacky plastic mass,  $[\alpha]^{55}_D -29.2^\circ$  (0.0992 g. in 5 cc. of dioxane solution).

*Anal.* Found: C, 63.15; H, 8.39.

The contents of the two polarimeter tubes used in the experiments described in Fig. 2 (two parts maleate and one part acrylate) were washed into a beaker with dioxane. Water was added and the polymer separated as an oil which stuck to the bottom and sides of the beaker. The milky supernatant liquid was poured off. This procedure was repeated once with dioxane and once with acetone, in which the polymer was soluble. The polymer was then dried overnight at 70°, yielding a clear, amber, brittle resin (0.4 g.);  $[\alpha]^{55}_D -39.5^\circ$  (0.1030 g. in 5 cc. of dioxane solution).

*Anal.* Found: C, 64.42, 64.48; H, 8.55, 8.57.

### Summary

Some preliminary kinetic studies on mixtures of ethyl acrylate and *l*-monomenthyl maleate and of ethyl maleate and *l*-menthyl acrylate have been recorded. Evidence that *l*-monomenthyl maleate reacts with benzoyl peroxide to give a non-polymeric product has been reported.

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## The Synthesis of the Three Isomeric *dl*- $\beta$ -Pyridylalanines

BY CARL NIEMANN, RICHARD N. LEWIS AND JOHN T. HAYS

The knowledge that the known  $\alpha$ -amino acids containing heterocyclic ring systems are intimately associated with a number of important biological processes<sup>1</sup> has led us to consider the chemical and physiological properties of  $\alpha$ -amino acids containing the pyridine nucleus, a heterocyclic ring system which, to date, has not been found in any naturally occurring  $\alpha$ -amino acid,<sup>2</sup> but which is present in other compounds isolated from natural sources.<sup>1,4</sup> In this communication we wish to describe the synthesis of *dl*- $\beta$ -(2-pyridyl)-alanine, *dl*- $\beta$ -(3-pyridyl)-alanine, and *dl*- $\beta$ -(4-pyridyl)-alanine, and to record some of the properties of these amino acids.

(1) M. Guggenheim, "Die biogenen Amine," S. Karger, Basel, 1940.

(2) It has been suggested<sup>3</sup> that the compound mimosine, obtained from the leaves of *Mimosa pudica*, is a dihydroxypyridylalanine, but this characterization has not been confirmed.

(3) (a) H. Nienburg and K. Tauböck, *Z. physiol. Chem.*, **250**, 80 (1937); (b) J. Renz, *ibid.*, **244**, 153 (1936).

(4) T. A. Henry, "The Plant Alkaloids," 3rd edition, Blakiston's Sons, Philadelphia, Pa., 1939.

Overhoff, Boeke and Gorter,<sup>5</sup> starting with (2-pyridyl)-methyl chloride, prepared *dl*- $\beta$ -(2-pyridyl)-alanine *via* the phthalimidomalonic ester synthesis of Sørensen.<sup>6</sup> The authors also reported that all attempts to prepare the amino acid from  $\beta$ -(2-pyridyl)- $\alpha$ -chloropropionic acid or from picolinaldehyde were unsuccessful. Our experiences have been similar to those described above, but we have found that *dl*- $\beta$ -(2-pyridyl)-alanine can be prepared in considerably better yield than that reported by Overhoff, Boeke and Gorter<sup>5</sup> by substituting the benzamidomalonic ester synthesis of Redemann and Dunn<sup>7</sup> for the procedure of Sørensen.<sup>6</sup> The failure of picolinaldehyde to condense with hippuric acid<sup>5</sup> or with diketopiperazine in the desired fashion is not due to a lack of reac-

(5) J. Overhoff, J. Boeke and A. Gorter, *Rec. trav. chim.*, **55**, 293 (1936).

(6) S. P. L. Sørensen, *Z. physiol. Chem.*, **44**, 448 (1905).

(7) C. E. Redemann and M. S. Dunn, *J. Biol. Chem.*, **130**, 341 (1939).