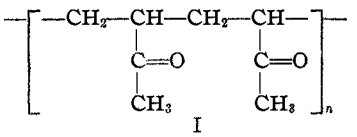
NOTES

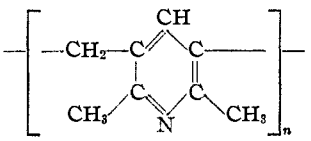
Structure of Vinyl Polymers. V.[1] Some Reactions of the Polymer of Methyl Vinyl Ketone

By C. S. Marvel and Charles L. Levesque[2]

Work from this Laboratory has shown[3] that the polymer of methyl vinyl ketone has a "head to tail" structure (I), and hence contains 1,5-diketone units. However, when this polyketone was treated with hydroxylamine, the corresponding polyketoxime rather than the expected polypyridine (II)[4] was obtained. It has now been found possible to prepare the polypyridine (II) by heating the polyketoxime with alcoholic hydrogen chloride.[5] Flory has shown[6] that no more than 86.47% of the ketoxime groups can participate in this reaction. Analytical results support the conclusion that under the conditions employed in our experiment, the remaining 13.53% of the ketoxime groups were hydrolyzed.

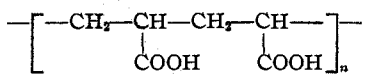


I



II

By treating a dioxane solution of the polymer of methyl vinyl ketone with aqueous sodium hypochlorite,[7] a polyacrylic acid (III) has been obtained. Attempts to compare this polyacid with that obtained by the polymerization of acrylic acid are now in progress.



III

Experimental

Preparation of the Polypyridine.[5]—A solution of 3.2 g. of the oxime of the polymer of methyl vinyl ketone[3] in 50 cc. of concentrated hydrochloric acid was placed in a 1-liter flask and a solution of 135 g. of hydrogen chloride in 500 cc. of alcohol was added. A reflux condenser was attached, and the milky solution was heated to boiling. Enough water to effect complete solution (40 cc.) was added and the mixture was refluxed for nineteen hours. The clear red reaction mixture was concentrated to 15 cc. and neutralized with ammonium hydroxide. The solid which precipitated was collected on a filter and dried under reduced pressure over solid potassium hydroxide. The product was 2.0 g. of light brown powder, readily soluble in acids, but insoluble in aqueous sodium hydroxide.

Anal. Calcd. for 0.4323 mole of C_8H_9N + 0.1353 mole of C_4H_6O: N, 9.94. Found: N, 9.53.

This product may be identical with the basic polymer which Balthis has obtained by the action of ammonia on the polymer of methyl vinyl ketone.[8]

Preparation of the Polyacid.[7]—A solution of sodium hypochlorite was prepared by bubbling chlorine into 160 g. of cold 10% sodium hydroxide until the gain in weight was 12 g. This solution was cooled by an ice-bath and stirred while a solution of 2.8 g. of the polymer of methyl vinyl ketone in 450 cc. of dioxane was added slowly. After the addition was complete, the mixture was stirred at room temperature for six hours. The lower aqueous layer was separated and concentrated under reduced pressure to 35 cc. The concentrate was filtered and the filtrate was acidified with concentrated hydrochloric acid. A white precipitate formed. The mixture of solution and precipitate was placed in a parchment paper sack and dialyzed until freed from chloride ion. The yellow solution remaining in the sack was filtered and the filtrate was evaporated to dryness. The residue was 1.15 g. of brittle, brown solid.

Anal. Calcd. for $(C_3H_4O_2)_n$: C, 50.0; H, 5.55. Found: C, 53.19; H, 5.92. The analysis indicates that about 90% of the methyl ketone groups have been oxidized.

(1) For the fourth communication in this series see This Journal, **61**, 3156 (1939).
(2) Du Pont Fellow in Chemistry.
(3) Marvel and Levesque, This Journal, **60**, 280 (1938).
(4) Knoevenagel, *Ann.*, **281**, 56 (1894).
(5) Blaise and Montagne, *Compt. rend.*, **180**, 1760 (1925).
(6) Flory, This Journal, **61**, 1518 (1939).
(7) Fuson and Tullock, *ibid.*, **56**, 1638 (1934).
(8) Balthis, U. S. Patent 2,122,707 (1938).

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The Rotatory Power of Zinc Lactate[1]

By W. Dayton Maclay, Raymond M. Hann and C. S. Hudson

In a recent article[2] we published measurements of the specific rotation of pure zinc D-lactate dihydrate in water for the concentrations 3.2 and 5.2%, which indicated that the change in rotation with concentration is a small one. Professor

(1) Publication authorized by the Surgeon General, U. S. Public Health Service.
(2) Maclay, Hann and Hudson, This Journal, **61**, 1666 (1939).