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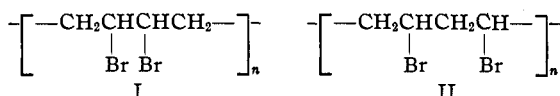
NUMBER 12

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

## The Structure of Vinyl Polymers. VI.<sup>1</sup> Polyvinyl Halides

BY C. S. MARVEL, J. H. SAMPLE AND MAX F. ROY

The earliest work on the structure of the polyvinyl halides was that of Ostromyslenski<sup>2</sup> who showed that zinc removes bromine from polyvinyl bromide in chlorobenzene solution. He stated that this reaction showed that polyvinyl bromide had the same structural unit which occurred in the perbromide of polybutadiene (I).



The properties of the two bromine-containing products were compared and it was stated that they were identical. Somewhat later a patent<sup>3</sup> was granted on the preparation of a caoutchouc-like product by the action of zinc on polyvinyl halides.

Harries<sup>4</sup> made a vigorous attack on the authenticity of Ostromyslenski's work. He pointed out that the perbromide of polybutadiene never can be obtained with the theoretical bromine content of 74.7% corresponding to that of polyvinyl bromide. Actually bromination of polybutadiene gave a product with a bromine content of 62.4 to 71.8%. The difficulties of proving the identity of two polymeric products were pointed out by Harries.

Later Staudinger, Brunner and Feisst<sup>5</sup> studied

(1) For the fifth communication in this series, see *THIS JOURNAL*, **61**, 3234 (1939).

(2) Ostromyslenski, *J. Russ. Phys.-Chem. Soc.*, **44**, 204, 240 (1912); *Chem. Zentr.*, **83**, (I), 1980, 1982 (1912).

(3) Ostromyslenski, German Patent 264,123 (1913); *Chem. Zentr.*, **84**, II, 1187 (1913).

(4) Harries, *Ann.*, **395**, 216 (1913).

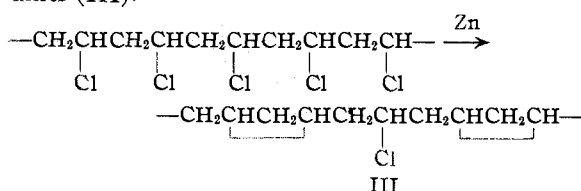
(5) Staudinger, Brunner and Feisst, *Helv. Chim. Acta*, **13**, 805 (1930).

the reactions of polyvinyl bromide and concluded that it was a 1,3-dihalide (II). They confirmed the observation of Ostromyslenski that zinc removes the halogen from a polyvinyl halide and accounted for this by ring formation. They also noted that zinc alkyls removed bromine from polyvinyl bromide and that reduction produced paraffin-like products.

In the present study of the structure of the polyvinyl halides most of the work has been done with polyvinyl chloride. When a saturated solution in dioxane of this polymer was heated with zinc, an insoluble product still containing most of the halogen was formed. When a very dilute solution of polyvinyl chloride in dioxane was heated with zinc the cross-linking reaction which produced the insoluble material was avoided and a smooth dehalogenation reaction occurred. It was never possible to remove all of the chlorine under the conditions used, but the amount removed under the most favorable conditions varied from 84 to 87%. Similarly, zinc removed 85.9% of the bromine from polyvinyl bromide. These facts are particularly significant, since Flory<sup>6</sup> has shown that random removal of pairs of halogens in a polymeric 1,3-dihalide should take out 86.47% of the halogen and leave 13.53% of the halogen isolated from reactive neighbors and non-removable except by cross-linking of the carbon chains. The polymeric material left after the reaction of polyvinyl chloride with zinc was still soluble in dioxane. It did not decolorize an alkaline solu-

(6) Flory, *THIS JOURNAL*, **61**, 1518 (1939).

tion of potassium permanganate if care was taken to avoid contamination with peroxides from the dioxane. Treatment of the dehalogenated polymer with ozone and subsequent hydrolysis in the presence of an oxidizing agent did not give definite products, whereas under the same conditions polybutadiene gave succinic acid.<sup>7</sup> Nitric acid did not attack the dehalogenated polymer readily. Chlorine would attack the dehalogenated polymer and both addition and substitution of chlorine occurred. All of these reactions indicate that the dehalogenated polymer consists of cyclopropane units with occasional isolated  $-\text{CH}_2\text{CHCl}-$  units (III).



Another fact which supports the 1,3-dihalide structure for the polyvinyl halides is that neither the chloride nor the bromide liberates iodine from a peroxide-free dioxane solution of potassium iodide, a reaction which is characteristic of 1,2-dihalides.<sup>8</sup>

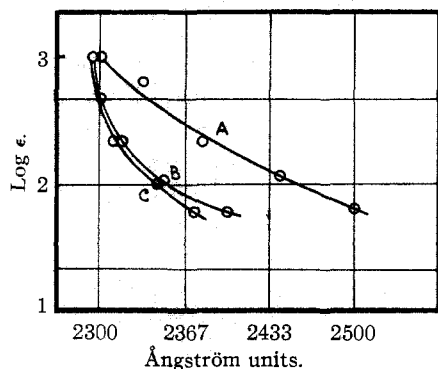
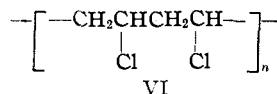
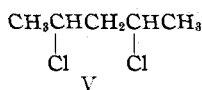
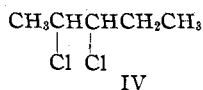
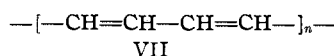


Fig. 1.—Ultraviolet absorption spectra,  $\epsilon$  = extinction coefficient: A, 2,3-dichloropentane; B, 2,4-dichloropentane; C, polyvinyl chloride.

Further evidence for the 1,3-dihalide structure is obtained by a comparison of the ultraviolet absorption spectra of 2,3-dichloropentane (IV), 2,4-dichloropentane (V) and polyvinyl chloride (VI). The absorption curves are given in Fig. 1.



It is interesting to note that treatment of a "Cellosolve" solution of polyvinyl chloride with potassium hydroxide removes halogen acid and leads to the formation of an insoluble shiny reddish-brown polymer which corresponds to the polymer  $(\text{CH})_x$  reported by Ostromysslenski.<sup>3</sup> This product is probably a very long chain polyene (VII). We have not investigated this polymer in any detail.



All of the reactions and properties of the polyvinyl halides are thus best accounted for on the basis of the 1,3-dihalide structure which was first proposed by Staudinger, Brunner and Feisst.<sup>5</sup>

### Experimental

The polyvinyl chloride used in this investigation was furnished by the Carbide and Carbon Chemicals Corporation.<sup>9</sup> It had been prepared by the polymerization of vinyl chloride in the presence of peroxides. Its chlorine content was 56.7%. The polymer was stable to boiling water. It was insoluble in most solvents but did dissolve slowly in dioxane.

**Reaction of Polyvinyl Chloride with Zinc.**—Ordinary zinc dust was purified by treating it with dilute hydrochloric acid to remove oxide and sulfide, then by washing with water to remove acid and with acetone to remove water. The zinc was dried in a desiccator and used without long exposure to air. In the air the zinc became unreactive in about two months.

When a saturated solution of polyvinyl chloride in dioxane was boiled with zinc, a rubbery gray mass separated out. This material contained halogen and a great deal of occluded zinc. It was not soluble in organic solvents and no satisfactory procedure could be devised to separate the organic and inorganic constituents.

When a very dilute solution of polyvinyl chloride in peroxide-free dioxane was boiled with zinc, halogen was

TABLE I

REMOVAL OF CHLORINE FROM POLYVINYL CHLORIDE BY TREATMENT WITH ZINC

Polyvinyl chloride, g.	Peroxide-free dioxane, cc.	Active zinc, g.	Time of reflux, hours	Chlorine removed, %
1.1060	500	6	39.5	57.6
7.6292	3400	37.2	83	67
4.2315	2000	35.6	76	80
1.895	650	7	150	85
0.2899	115	4	155.5	84.5
.4651	150	4	155.5	84
.4719	150	4	155.5	87.2

(9) The authors desire to express their thanks to Mr. H. B. McClure of Carbide and Carbon Chemicals Corporation for his aid in this connection.

(7) Ref. 4; also Harries, *Chem. Ztg.*, **36**, 654 (1912).

(8) Davis and Heggie, *J. Org. Chem.*, **2**, 470 (1937).

removed and the organic residue remained soluble. The dehalogenation reaction proceeded rather slowly and seemed to stop after about one hundred fifty to one hundred sixty hours. The excess zinc could be removed by filtration and the addition of water to the filtrate precipitated a rubbery polymer. Analysis of this polymer and of the remaining solution showed that the zinc treatment had removed about 85% of the chlorine from the polyvinyl chloride. Some typical experiments are listed in the table.

**Properties of the Dehalogenated Polymer.**—The dehalogenated polymer was precipitated from the dioxane solution as a rubbery mass by the addition of water. This polymer dissolved slowly in carbon tetrachloride. Its dioxane solution did not give a test for unsaturation when shaken with 2% alkaline potassium permanganate solution.

A carbon tetrachloride solution of the rubbery polymer was treated with ozone and then hydrolyzed but no evidence of ozonolysis was obtained. Treatment with nitric acid caused some oxidation but did not yield crystalline products. When the dioxane solution from the zinc treatment was mixed with a solution of chlorine in carbon tetrachloride, it was found that chlorine added again to the polymer but also chlorination occurred as more chlorine was taken up for the solution than had been removed from the polyvinyl chloride by the zinc.

**Polyvinyl Bromide and Zinc.**—Vinyl bromide was prepared by the method of Kharasch<sup>10</sup> and polymerized by warming it with benzoyl peroxide. The white amorphous powder thus obtained was washed with ether, dilute hydrochloric acid, distilled water, and finally with ethyl alcohol and ether. The bromine content of the polymer was 74.45%.

A solution of 0.0667 g. of polyvinyl bromide in 50 cc. of peroxide-free dioxane was refluxed with a slight excess of active zinc for one hundred and forty-six hours. The solution was filtered and the bromide ion was determined by titration. This treatment removed 85.9% of the bromine from the sample of polyvinyl bromide.

**Treatment of Polyvinyl Halides with Potassium Iodide.**—Heating a solution of 1.2109 g. of polyvinyl chloride and 9.0227 g. of potassium iodide in 500 cc. of peroxide-free dioxane to boiling under a reflux condenser for two hundred and twenty-three hours did not liberate enough iodine to give a test with starch paste. Similarly heating a solution of 0.2 g. of polyvinyl bromide and excess potassium iodide in 100 cc. of peroxide-free dioxane to boiling under reflux for eighty-two hours liberated only a trace of free iodine.

**Action of Potassium Hydroxide on Polyvinyl Chloride.**—A solution of potassium hydroxide in "Cellosolve" was added to a solution of polyvinyl chloride in the same solvent and the resulting clear colorless solution was boiled under reflux. Almost immediately it turned a light yellow which quickly changed to dark yellow, to orange, and finally to a reddish-brown with the formation of a brown gelatinous precipitate. On further heating, the color of the solution became darker and the gelatinous precipitate coagulated to a black stringy mass.

After several hours, heating was stopped, the solution was cooled and the black precipitate removed by filtration

and discarded. Acidification of the dark reddish-brown filtrate with concentrated nitric acid discharged most of the color, and addition of silver nitrate to the acidified solution gave a copious precipitate of silver chloride.

A mixture of 3.000 g. of polyvinyl chloride in 100 cc. of 5% solution of potassium hydroxide in "Cellosolve" was refluxed for thirty hours. (The solubility of polyvinyl chloride in "Cellosolve" is considerably less than 3 g. in 100 cc. so that most of the polyvinyl chloride was present at the start of the reaction as undissolved polyvinyl chloride.)

As refluxing was started, the color of the solution and of the undissolved solid quickly became a dark reddish-brown and remained so throughout the period of refluxing.

The solution was cooled and the dark red-brown solid was collected on a sintered-glass filter, washed with "Cellosolve" and with water, and dried in a vacuum desiccator over concentrated sulfuric acid for forty-eight hours. During this period the color of the material changed from deep red-brown to deep orange. The weight of the dried material was 1.746 g., indicating a loss in weight of 1.254 g. from the original weight of polyvinyl chloride.

This orange material burned with a smoky flame without any visible melting and, unlike the original polyvinyl chloride, was insoluble in hot dioxane. On further standing the color became lighter and lighter and after two weeks was a faint yellow. Some of the material was heated with concentrated nitric acid on a steam-bath. All of the solid slowly dissolved with the evolution of gas. Evaporation to dryness left no appreciable residue.

The filtrate and washings from the above were combined and the resulting solution was acidified with nitric acid. Silver nitrate solution was then added until no further precipitation of silver chloride occurred. The silver chloride was collected on a sintered-glass filter, dried in a vacuum desiccator over concentrated sulfuric acid, and weighed. The weight of silver chloride was 6.744 g., equivalent to 1.668 g. of chlorine. The original 3.000 g. of polyvinyl chloride (56.73% chlorine) contained 1.702 g. of chlorine which was removed to the extent of 98% by the action of the potassium hydroxide in "Cellosolve" solution.

**Ultraviolet Absorption Spectra Studies.**—The spectra were taken with a Bausch and Lomb ultraviolet spectrograph. A hydrogen discharge tube operating on 15,000 volts gave a continuous ultraviolet source and the  $H\alpha$ ,  $H\beta$ , and  $H\gamma$  lines served to calibrate the wave length scale of the instrument. Eastman Kodak Company D-O (double coated) Ortho plates were used and the pictures were taken with a slit opening of  $10\mu \times 4$  mm. and a 1-cm. quartz cell. Each exposure was for one and one-quarter minutes. The absorption coefficient was determined by comparison with the blackness of a trace in a  $10^{-4}$  molar solution of naphthalene. A concentration of 0.02 *M* for the dichloropentanes was used. The concentration of the polymer was 0.02 *M* on the basis of a dimer unit.

### Summary

Zinc removes 84–87% of the halogen from polyvinyl halides in dilute solution to yield a rubbery

(10) Kharasch, *THIS JOURNAL*, **55**, 2521 (1933).

polymer which does not decolorize aqueous potassium permanganate solution. Polyvinyl halides do not liberate iodine from potassium iodide. The ultraviolet absorption spectrum of polyvinyl chloride is very similar to that of 2,4-dichloro-

pentane and somewhat different from that of 2,3-dichloropentane. All of these facts support the view that polyvinyl chloride has the 1,3-dihalide structure.

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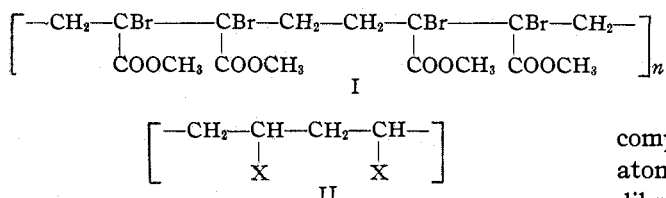
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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## The Structure of Vinyl Polymers. VII. Polyacrylyl Chloride<sup>1</sup>

BY C. S. MARVEL AND CHARLES L. LEVESQUE<sup>2</sup>

Recent work from this Laboratory<sup>3</sup> has shown that the polymers of alkyl  $\alpha$ -haloacrylates have a "head to head, tail to tail" structure (I), in contrast to many other vinyl polymers which have a "head to tail" structure (II, X = halogen, OH, COCH<sub>3</sub>).<sup>4</sup>



Since the vinyl halides are known to form "head to tail" polymers,<sup>4a</sup> this anomalous behavior of the haloacrylates must be due either to the presence of two activating groups attached to the vinyl group, or it must be peculiar to acrylic acid derivatives. The results reported in this paper support the latter explanation.

Acrylyl chloride prepared from sodium acrylate and phosphorus oxychloride<sup>5</sup> may be polymerized either by peroxides or ultraviolet light. When thionyl chloride is substituted for the phosphorus oxychloride in the preparation of the acrylyl chloride, the product obtained is polymerizable only by ultraviolet light. It is probable that this acrylyl chloride was contaminated with a little thionyl chloride, which inactivated the peroxide catalyst. The polymers obtained are all brittle, pale yellow solids, soluble in phosphorus oxychloride and dioxane, but insoluble in other common solvents.

By treating a phosphorus oxychloride solution

(1) For the sixth communication in this series, see *THIS JOURNAL*, **61**, 3241 (1939).

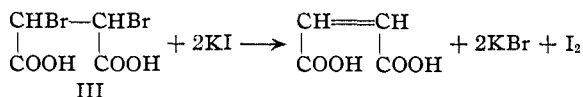
(2) Du Pont Fellow in Chemistry (1938-1939).

(3) Marvel and Cowan, *THIS JOURNAL*, **61**, 3156 (1939).

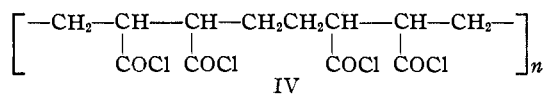
(4) (a) Marvel and Sample, *ibid.*, **61**, in press (1939); (b) Marvel and Denoon, *ibid.*, **60**, 1045 (1938); Marvel and Levesque, *ibid.*, **60**, 280 (1938).

(5) Moureu, *Ann. chim.*, [7] **2**, 145 (1894).

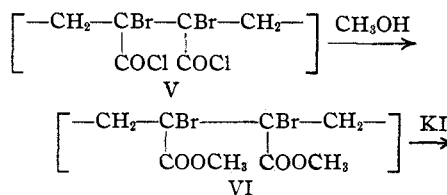
of photopolymerized acrylyl chloride with bromine, it was possible to introduce into the polymer bromine equivalent to one atom for every 3.4 acrylyl chloride units. When this brominated polymer was transformed into the corresponding methyl ester and heated with potassium iodide in acetone solution, free iodine was released. The amount of iodine was equivalent to 46% of the bromine in the polymer. This reaction is characteristic of 1,2-dibromo compounds, especially those in which the bromine atoms are adjacent to a negative group, as in dibromosuccinic acid (III).<sup>6</sup>



The production of 1,2-dibromo units by the bromination of polyacrylyl chloride is most logically explained by assuming a "head to head, tail to tail" structure for this polymer (IV).



Since bromine readily substitutes in the  $\alpha$ -position of an acid chloride, bromination of IV would give rise to 1,2-dibromo units (V). The corresponding methyl ester (VI) would release iodine from potassium iodide, forming an unsaturated ester (VII).



(6) Davis and Heggie, *J. Org. Chem.*, **2**, 470 (1937); see also ref. 3.