

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.

URBANA, ILLINOIS

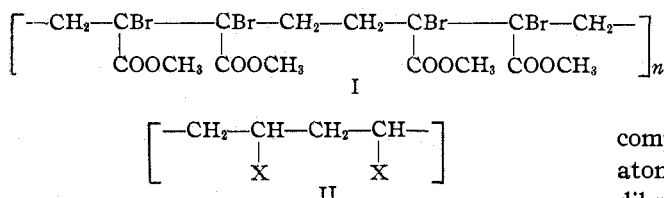
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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## 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).

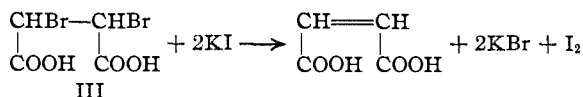
(2) Du Pont Fellow in Chemistry (1938-1939).

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

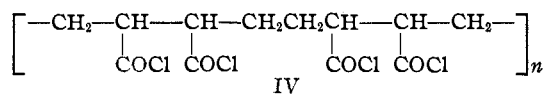
(4) (a) Marvel and Sample, *ibid.*, 61, in press (1939); (b) Marvel and Denoon, *ibid.*, 60, 1045 (1938); Marvel and Levesque, *ibid.*, 60, 280 (1938).

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

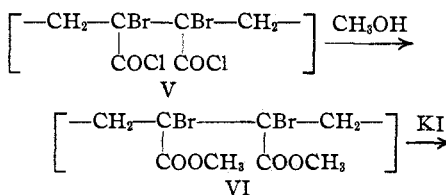
of photopolymerized acrylyl chloride with bromine, it was possible to introduce into the polymer bromine equivalent to one atom for every 3.4 acrylyl chloride units. When this brominated polymer was transformed into the corresponding methyl ester and heated with potassium iodide in acetone solution, 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>



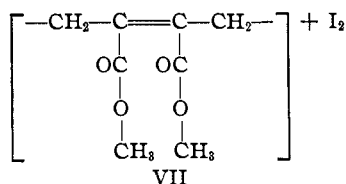
The production of 1,2-dibromo units by the bromination of polyacrylyl chloride is most logically explained by assuming a "head to head, tail to tail" structure for this polymer (IV).



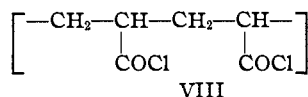
Since bromine readily substitutes in the  $\alpha$ -position of an acid chloride, bromination of IV would give rise to 1,2-dibromo units (V). The corresponding methyl ester (VI) would release iodine from potassium iodide, forming an unsaturated ester (VII).



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

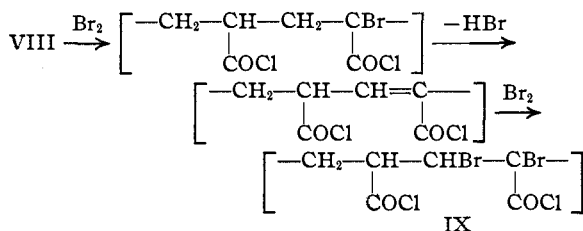


Since only a third of the hydrogen atoms in the  $\alpha$ -positions of the polymer were replaced by bromine, the possibility of the presence of some "head to tail" units (VIII) is not excluded. The



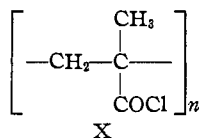
presence of any appreciable fraction of these units, however, would make it quite improbable that the substitution of bromine in only one-third of the  $\alpha$ -positions of the polymer would place nearly half of the bromine atoms on adjacent carbon atoms.

A polyacrylyl chloride having only the "head to tail" structure (VIII) might give rise to 1,2-dibromo units (IX) by the following series of reactions. However, the fact that even in the



presence of bases, ethyl  $\alpha$ -bromoglutarate is transformed into glutaconic acid in only very small yields argues against this mechanism.

Although the direct substitution of bromine in other than the  $\alpha$ -position of polyacrylyl chloride seemed unlikely, this possibility was investigated. Polymethacrylyl chloride (X) was treated with bromine under conditions identical with those



prevailing during the bromination of polyacrylyl chloride. The  $\alpha$ -positions of this polymer are not available for substitution and, as expected, no bromination occurred.

From these facts it is evident that at least a part of the units of polyacrylyl chloride are arranged in a "head to head, tail to tail" structure (IV).

## Experimental

**Preparation of Acrylyl Chloride.**—Acrylyl chloride was prepared from phosphorus oxychloride and sodium acrylate.<sup>5</sup> The first crude product was purified by careful fractionation. The yield of acrylyl chloride boiling from 72–73° was 22%. When thionyl chloride was substituted for the phosphorus oxychloride, the yield dropped to 19%.

**Polymerization of Acrylyl Chloride by Benzoyl Peroxide.**—In a round-bottomed flask connected by a ground joint to a reflux condenser carrying a calcium chloride tube was placed 3 cc. of acrylyl chloride prepared from phosphorus oxychloride, 50 cc. of dry carbon tetrachloride and a few crystals of benzoyl peroxide. The mixture was boiled for four hours. The polyacrylyl chloride separated as a pale yellow solid which adhered to the sides of the flask. The solvent was decanted and the polymer was scraped into a tared evaporating dish. After drying under reduced pressure, it weighed 1.1 g. (45%). The polymer was soluble in phosphorus oxychloride.

Acrylyl chloride prepared from thionyl chloride did not polymerize under similar conditions.

**Polymerization of Acrylyl Chloride by Ultraviolet Light.**—A solution of 15 g. of acrylyl chloride in an equal volume of dry carbon tetrachloride was placed in a tightly stoppered quartz test-tube and irradiated with light from a mercury vapor arc for thirty hours. The polyacrylyl chloride separated as a brittle, light yellow solid. It was isolated by removing the solvent under reduced pressure in a stream of dried air. It weighed 7.2 g. (48%).

**Bromination of Polyacrylyl Chloride.**—A solution of 7.2 g. of photopolymerized acrylyl chloride in 90 cc. of phosphorus oxychloride was placed in a 200-cc. round-bottomed flask and 6.3 cc. of bromine was added. A reflux condenser carrying a calcium chloride tube was attached to the flask by a ground joint, and the mixture was irradiated for seven days with light from a 100-watt lamp. Most of the phosphorus oxychloride was removed by distillation under reduced pressure and a mixture of 50 cc. of toluene and 50 cc. of methanol was added to the viscous residue. The mixture was refluxed for one hour. The excess methanol was removed by distillation and the residual toluene solution was filtered through a sintered glass funnel. The brown gel remaining on the funnel was treated with 150 cc. of acetone and most of it dissolved. The acetone solution was filtered and the filtrate was added to the toluene filtrate. The combined filtrates were diluted with four volumes of alcohol and the tacky, brown solid which separated was isolated by decantation. The solid was redissolved in 50 cc. of acetone and reprecipitated with alcohol. The precipitate was collected on a filter. After drying under reduced pressure over sulfuric acid, the product was 5.8 g. of a fibrous, light brown solid.

*Anal.* Calcd. for  $\text{C}_4\text{H}_5\text{O}_2\text{Br}$ : Br, 48.5. Found: Br, 21.26.

The analysis shows the presence of one bromine atom for every 3.4 methyl acrylate units.

**Reaction of the Brominated Polymer with Potassium Iodide.**<sup>6</sup>—A solution of 4.000 g. of the brominated polymer in acetone was made up to exactly 100 cc. This solution was placed in a flask containing 2.0 g. of powdered

potassium iodide and a reflux condenser was attached by a ground joint. The mixture was boiled gently on a steam cone. At intervals 25 cc. of the reaction mixture was removed with a pipet, diluted with 250 cc. of water and titrated with 0.03620 *N* sodium thiosulfate, using starch solution as an indicator. At seventeen, twenty-three and twenty-nine hours, 41.7, 46.3 and 46.0% of bromine, respectively, were removed from the polymer.

A solution of 1.677 g. of the brominated polymer in acetone was made up to exactly 50 cc. The solution was placed in a glass-stoppered Erlenmeyer flask containing 1.0 g. of powdered potassium iodide. The flask, which was allowed to stand at room temperature, was shaken occasionally. At intervals 10-cc. samples were removed, diluted with 125 cc. of water and titrated with 0.03620 *N* sodium thiosulfate.

Under these conditions the percentages of bromine removed from the polymer were 25.9, 26.8, 32.2 and 32.1 after twenty-one, twenty-four, forty-five and seventy-nine hours, respectively.

#### Attempted Bromination of Polymethacrylyl Chloride.—

A sample of polymethacrylyl chloride was obtained

through the courtesy of Dr. B. C. Pratt of the du Pont Experimental Station. Four grams of this polymer was dissolved in 50 cc. of phosphorus oxychloride contained in a 100-cc. flask and 3.2 cc. of bromine was added. A reflux condenser protected by a calcium chloride tube was attached to the flask by a ground joint, and the mixture was irradiated for eight days with light from a 100-watt lamp. The product, isolated by the methods employed for the brominated polyacrylyl chloride, was 2.2 g. of brittle, brown solid.

*Anal.* Found: Br, 0.23.

### Summary

Polyacrylyl chloride has been brominated and then esterified to give a polymeric bromoacrylic ester which liberated iodine from potassium iodide solution. This indicates that polyacrylyl chloride has some of its units arranged in a "head to head, tail to tail" fashion.

URBANA, ILLINOIS

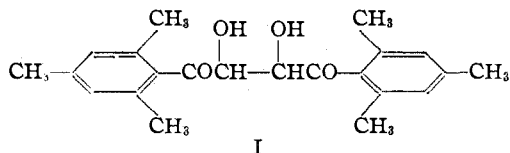
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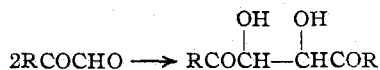
## 1,2-Diacylethylene Glycols

BY REYNOLD C. FUSON, C. H. MCBURNEY AND W. E. HOLLAND

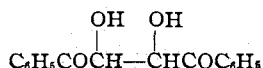
Mesitylgyoxal reacts with the binary mixture,  $Mg + MgI_2$ ,<sup>1</sup> in a very remarkable fashion; the reduction is entirely bimolecular, yielding 1,2-dimesityloethylene glycol (I).<sup>2</sup> In the pres-



ent work *t*-butylglyoxal, phenylglyoxal, 3,5-dibromomesitylgyoxal, 2,4,6-triethylphenylglyoxal and isodurylgyoxal have been found to behave in this same manner. In each case the product is the corresponding 1,2-diacylethylene glycol



The hindered glyoxals gave only one glycol while phenylglyoxal yielded two—presumably diastereoisomers



Thus it would seem that while steric hindrance is

(1) Gomberg and Bachmann, *THIS JOURNAL*, **49**, 236 (1927).

(2) Gray and Fuson, *ibid.*, **56**, 739 (1934).

not responsible for the success of the reaction it may influence its course.

Two of the glyoxals, isodurylgyoxal and 3,5-dibromomesitylgyoxal, have not been reported before. They were made from acetoisodurene and 3,5-dibromoacetomesitylene, respectively, by treatment with selenium dioxide. The semicarbazones and the phenylhydrazones of the two glyoxals were prepared. The glyoxals were found to undergo rearrangement to the corresponding glycolic acids when treated with 10% potassium hydroxide solution.

The yield of glycol was found to depend on the time of reaction and on the ether-benzene ratio of the solvent. For example, in one experiment with phenylglyoxal, using an ether-benzene ratio of 1:2, the yield of glycol was only 2% of the theoretical; in another experiment in which an ether-benzene ratio of 2:3 was used the yield was 55%. If too long a reaction time is employed, side reactions occur. When mesitylgyoxal was treated with the binary mixture,  $Mg + MgI_2$ , for one hour the resulting glycol was contaminated with 1,2-dimesitylformoin (II). In view of this fact a standard reaction time of fifteen minutes was used in all of the experiments.