

liters of dilute (6 *N*) hydrochloric acid was added to a solution of 0.1 g. (0.00045 mole) of the tetrahydro-6-aminodibenzofuran hydrochloride in 15 ml. of water. Diazotization was effected by cautiously adding a 5% solution of sodium nitrite to the ice-cold, well-stirred solution until cadmium iodide-starch paper immediately turned blue when moistened with the stirring rod. After the clear yellow diazonium solution had stood for thirty minutes, it was slowly added to a cold solution of 0.1 g. of β -naphthol in 25 ml. of 10% sodium hydroxide. A brilliant carmine red dye, m. p. 199–201°, immediately precipitated in quantitative yield (0.15 g.).

Summary

Incidental to studies concerned with the bridging of the 1- and 9-positions in dibenzofuran types, series of 1,4- and 1,4,6-derivatives have been synthesized. In these compounds the 4- and the 4,6-substituents are strong ortho-para directors. Among other compounds described are 4,6-dimethoxy-1-dibenzofurylacetic acid and 1,2,3,4-tetrahydro-6-aminodibenzofuran.

AMES, IOWA

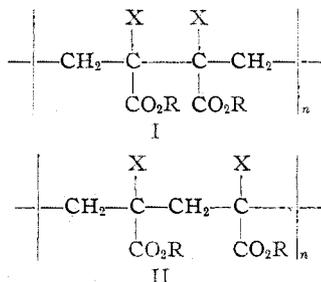
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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

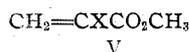
The Structure of Vinyl Polymers. IV.¹ The Polymers of the Methyl α -Haloacrylates

BY C. S. MARVEL AND JOHN CHARLES COWAN²

The polymers of the α -haloacrylates are especially suitable for a study of the arrangement of the structural units in the polymeric chain, since the reactions of the simple 1,2- and 1,3-dihalogen esters which correspond to the two most probable arrangements (I and II) of the structural units in these polymers are well known.



The polymer of methyl α -chloroacrylate has been described³ but the corresponding bromo compound apparently has not been prepared previously. In the present work the α,β -dihaloacrylates (IV) were treated with quinoline to give the α -haloacrylates (V).



The monomeric esters polymerized readily on standing or more rapidly on warming in the presence of peroxides. The polymers could be obtained either as clear, pale amber glassy solids or

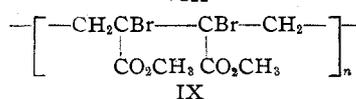
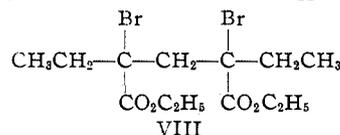
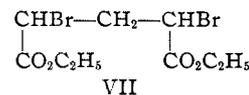
(1) For the third communication in this series, see *THIS JOURNAL*, **61**, 1682 (1939).

(2) Du Pont Special Research Assistant in Chemistry, 1937–1939.

(3) British Patent 411,860; *C. A.*, **28**, 6956 (1934).

as white powders. They were readily soluble in dioxane and acetone. Viscosity measurements on 0.606% (0.0368 molar, based on monomeric unit) solutions indicated a molecular weight of about 11,500. One sample of methyl α -chloroacrylate which polymerized slowly at room temperature over a period of nine months gave a polymer insoluble in acetone, benzene and dioxane; this insolubility indicates a very high molecular weight.

When either the chloro or bromo polymer was treated with potassium iodide in peroxide-free acetone or dioxane, iodine was liberated. This reaction is characteristic for 1,2-dihalogen compounds⁴ and indicates that the methyl α -haloacrylate polymers have structure I above and thus do not have the usual 1,3-distribution of the functional groups which has been accepted as the structural feature of most vinyl polymers. A comparison of the amount of iodine liberated from potassium iodide by ethyl α,α' -dibromosuccinate (VI), ethyl α,α' -dibromoglutarate (VII),



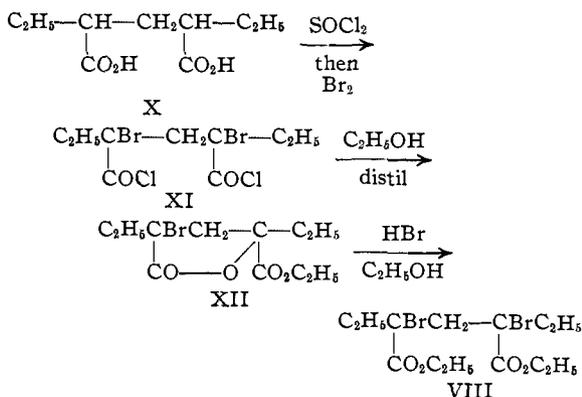
(4) Davis and Heggie, *J. Org. Chem.*, **2**, 470 (1937).

ethyl α, α' -dibromo- α, α' -diethylglutarate (VIII) and the polymer of methyl α -bromoacrylate (IX) is given in Table I.

TABLE I
LIBERATION OF IODINE FROM POTASSIUM IODIDE BY
VARIOUS DIBROMO ESTERS

Ester used	% iodine liberated			
	Acetone soln. 24 hr. 25°	Boiling acetone soln. 24 hr.	Dioxane 24 hr. 25°	Boiling dioxane 72 hr.
Polymer of methyl α -bromoacrylate	30	49	24	92
Ethyl α, α' -dibromo-succinate	33	53	26	96
Ethyl α, α' -dibromo-glutarate	4	6	4	21
Ethyl α, α' -dibromo- α, α' -diethylglutarate	2	5

The comparison with ethyl α, α' -dibromo- α, α' -diethylglutarate seemed to be desirable in order to be sure that a substituted bromoglutarate of this type did not react with potassium iodide. This ester was prepared by the reactions indicated. The starting acid (X) was prepared by methods described in earlier literature.⁵



Evidence to support the "head to head, tail to tail" formulation of these α -haloacrylate polymers (I) was obtained by the use of zinc. This reagent readily removed 97% of the bromine from the bromo polymer, an amount far above that which could be removed from a 1,3-dibromopolymer as shown by the calculation of Flory.⁶

Additional evidence supporting the 1,2-dihalogen structure was found in a comparison of the effect of heat on the polymer of methyl α -bromoacrylate, ethyl α, α' -dibromosuccinate (VI), and ethyl α, α' -dibromo- α, α' -diethylglutarate (VIII). The polymer and the succinate

(VI)⁷ lost hydrogen bromide at a much lower temperature than did the glutarate (VIII). During the preparation of the glutarate (VIII), it was noticed that the ester on distillation under reduced pressure lost ethyl bromide. During the pyrolysis of the polymer of methyl α -bromoacrylate, methyl bromide was formed but only after the appearance of hydrogen bromide. Heating the polymer of methyl α -bromoacrylate with quinoline removed half of the bromine as hydrogen bromide.

Further evidence supporting the 1,2-dihalogen structure (I) for the polymers was obtained by a comparison of the ultraviolet absorption spectra of the polymers of methyl α -bromoacrylate, ethyl α, α' -dibromosuccinate and ethyl α, α' -dibromo-glutarate. Figure 1 shows the absorption curves for these compounds.

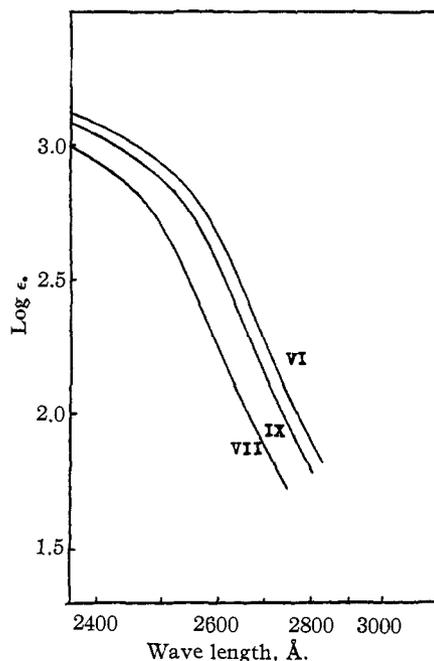
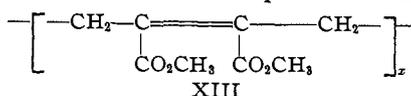


Fig. 1.—Absorption spectra.

The unsaturated polymeric ester (XIII) which undoubtedly results from the action with potassium iodide apparently undergoes some further polymerization to give a cross-linked product, as the debrominated compound is insoluble.



However, it does decolorize aqueous potassium permanganate solution slowly, thus indicating

(5) Dressel, *Ann.*, **256**, 185 (1889); Redeman and Lucas, *Ind. Eng. Chem., Anal. Ed.*, **9**, 521 (1937).

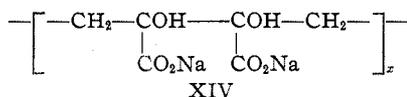
(6) Flory, *THIS JOURNAL*, **61**, 1518 (1939).

(7) Anschütz, *Ber.*, **12**, 2282 (1879).

unsaturation. All attempts to isolate definite products from the oxidation have been unsuccessful.

When zinc reacts with the bromo polymer there is apparently some cross-linking. This would account for the fact that not quite all of the halogen is eliminated from the polymer. For each halogen which is used up in the cross-linking reaction, an isolated halogen will remain in the polymer after the reaction is complete. The debrominated product is again an insoluble product as would be expected if cross-linking had occurred.

The polymers on alkaline hydrolysis yielded the salt of a 1,2-dihydroxy dibasic acid (XIV). The



product (XIV) reduces periodic acid to iodic acid in approximately forty-eight hours. This oxidation is characteristic of 1,2-glycols.⁸ Reduction of the iodic acid also occurs; this observation has also been noted by Jackson and Hudson⁹ in a study of the oxidation of cellulose. The amount and rate of oxidation varied with different samples of the polymers, but in every test some oxidation occurred.

Experimental

Methyl α -Bromoacrylate.—In a 250-cc. modified Claisen flask was placed 73 g. (0.3 mole) of methyl α,β -dibromopropionate (prepared by addition of bromine to methyl acrylate)¹⁰ and 39 g. (0.3 mole) of freshly distilled quinoline.¹¹ The methyl α -bromoacrylate was distilled out of this mixture at once. The yield was 40 g. (82% of the theoretical amount) of a colorless liquid which boiled at 72.5–74° (78 mm.); d_{20}^{20} 1.61; n_D^{20} 1.4840.

Anal. Calcd. for $C_4H_5O_2Br$: Br, 48.48. Found: Br, 47.90.

Methyl α -Chloroacrylate.—The same method was used for the preparation of methyl α -bromoacrylate.^{10,11} The yield from 47 g. (0.3 mole) of methyl α,β -dichloropropionate was 33 g. (73% of the theoretical amount). The ester boiled at 57–59° (55 mm.); d_{20}^{20} 1.189; n_D^{20} 1.4400.

Anal. Calcd. for $C_4H_5O_2Cl$: Cl, 29.43. Found: Cl, 29.02.

Synthesis of Ethyl α,α' -Dibromo- α,α' -diethylglutarate.—Ethyl propane-1,1,3,3-tetracarboxylate¹² was treated with sodium ethoxide and ethyl iodide⁵ to form ethyl heptane-3,3,5,5-tetracarboxylate. The latter was hydrolyzed with potassium hydroxide in diethylene glycol⁵ and decarboxylated by refluxing in dilute hydrochloric acid.⁵

The crude diethylglutaric acid (33 g.) was warmed (60–80°) with thionyl chloride for twenty-four hours, and the excess thionyl chloride was removed by distillation. Dried bromine (21 cc.) was added to the residual acid chloride and the mixture was heated at 70° for five hours. The bromine treatment was repeated with 15 cc. of dried bromine. The bromination mixture was allowed to stand for two days, and the bromo acid chloride was poured into absolute ethyl alcohol. This solution was distilled and after the removal of all the low-boiling material a fraction boiling at 134–138° (3 mm.) was obtained as the main product: d_{20}^{20} 1.358; n_D^{20} 1.4775. The yield was 25 g. (48% of the theoretical amount). The analysis showed that this product was the bromo-lactone (XII).

Anal. Calcd. for $C_{11}H_{17}O_4Br$: C, 45.05; H, 5.71. Found: C, 45.14; H, 5.98.

The bromo-lactone (25 g.) was dissolved in absolute ethyl alcohol and saturated with dry hydrogen bromide.¹³ The reaction mixture was allowed to stand for twenty-four hours. All low-boiling material was removed from the reaction mixture under diminished pressure. Analysis showed the residue was mainly the ethyl α,α' -dibromo- α,α' -diethylglutarate.

Anal. Calcd. for $C_{13}H_{22}O_4Br_2$: Br, 39.81. Found: Br, 38.70.

Polymerization of the Methyl α -Haloacrylates.—The monomers were polymerized either without solvent or in dioxane or toluene solution. Forty grams of methyl α -bromoacrylate was allowed to stand in a glass container at room temperature for three weeks; the liquid gradually became viscous and finally turned to a clear, pale amber, brittle solid.

Anal. Calcd. for $(C_4H_5O_2Br)_n$: C, 29.09; H, 3.03; Br, 48.48. Found: C, 29.20; H, 3.20; Br, 47.88.

Twenty grams of methyl α -bromoacrylate was dissolved in 100 cc. of dry dioxane and 0.48 g. of benzoyl peroxide was added. The solution was warmed at 35° for forty-eight hours and the addition of benzoyl peroxide repeated. After an additional forty-eight hours at 35°, the reaction mixture was diluted with approximately 500 cc. of ether and the polymer was precipitated as a white powder. It was collected on a filter, washed with ether, and dried; the yield was 15 g. When toluene was used as a solvent for polymerization, the yields were lower than when dioxane was used.

The methyl α -chloroacrylate gave a clear, pale amber, brittle solid when the monomer was allowed to stand in a glass container for one month. The methyl α -chloroacrylate also polymerized in dioxane or toluene solution. Ten grams of the methyl α -chloroacrylate was dissolved in 100 cc. of toluene, and 0.5 g. of benzoyl peroxide was added. The solution was warmed at 35° for twenty-four hours and the polymer precipitated as a white powder by the addition of approximately 500 cc. of ether. The yield was 3 g.

Anal. Calcd. for $(C_4H_5O_2Cl)_n$: C, 39.85; H, 4.19; Cl, 29.43. Found: C, 39.51; H, 4.48; Cl, 27.26.

Anal. Calcd. for $(C_4H_5O_2Cl)_n$: C, 39.85; H, 4.19; Cl, 29.43. Found: C, 39.51; H, 4.48; Cl, 27.26.

(13) Noyes, *Am. Chem. J.*, **22**, 258 (1899).

(8) Malaprade, *Compt. rend.*, **186**, 382 (1928); Fleury and Boisson, *ibid.*, **204**, 1264 (1937).

(9) Jackson and Hudson, *This Journal*, **59**, 2049 (1937).

(10) Moureu, Murat and Tampier, *Ann. chim.*, **15**, 221 (1921).

(11) Crossley, *J. Chem. Soc.*, **85**, 1416 (1904).

(12) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 284.

Both the bromo and chloro polymers were soluble in acetone and dioxane when freshly prepared. Both polymers were insoluble in ether, ethyl alcohol, and carbon tetrachloride. One sample of methyl α -chloroacrylate which stood for ten months gave a polymer that did not dissolve when shaken with dioxane for forty-eight hours. This insolubility indicates that the polymer had a very high molecular weight.

The molecular weight of one sample of methyl α -bromoacrylate was determined by viscosity measurement. The sample which was used was prepared in dioxane with benzoyl peroxide at 35°. The relative viscosity of a 0.0368 molar dioxane solution (molarity based on the monomeric unit) was found to be 1.11. Using 2.6×10^{-4} for the value of K_m^{14} in the equation $N_{sp}/C = K_m M$, the molecular weight was found to be approximately 11,500.

Study of the Reaction of Potassium Iodide with the Polymers of α -Haloacrylates and with the Esters of Dibromosuccinic and Dibromoglutaric Acids.—Standard solutions of the polymers and the esters were prepared in peroxide-free dioxane or acetone and to each of these solutions was added a measured amount of an aqueous solution of potassium iodide. Each of the reaction mixtures was placed in an all-glass apparatus and subjected to conditions as shown in Table II.

The iodine liberated was determined with standard thiosulfate. In some of the determinations, the procedure was modified further by using an acetone solution of potassium iodide instead of an aqueous solution. The results are summarized in Table II.

TABLE II

LIBERATION OF IODINE FROM POTASSIUM IODIDE BY HALOGENATED ESTERS

Compound	Molality in dioxane	Treatment Time, hr.	Temp., °C.	Molality of iodine liberated	Conversion, %
Polymer of methyl α -bromoacrylate	0.0171 ^a	1	100	0.0061	36
Ethyl α, α' -dibromosuccinate (VI)	.0290	1	100	.0115	40
Ethyl α, α' -dibromoglutarate (VII)	.0185	72	100	.0130	96
	.0304	1	100	.0009	3
	.0142	72	100	.0029	20
In acetone					
Polymer of methyl α -bromoacrylate	0.0098	16	25	0.0029	30
Ethyl α, α' -dibromosuccinate (VI)	.0049	21	55	.0024	49
Ethyl α, α' -dibromoglutarate (VII)	.0101	16	25	.0033	33
Ethyl α, α' -diethylglutarate (VIII)	.0051	21	55	.0027	53
	.0127	16	25	.0005	4
	.0085	21	55	.0005	6
	.0114	24	25	.0002	2
	.0114	24	55	.0005	5

^a Based on the polymeric unit I.

A 0.0084 molal acetone solution of the polymer of methyl α -chloroacrylate was heated to 90° for five days in a sealed tube with aqueous potassium iodide and approximately 58% of the calculated amount of iodine was liberated. The amount of iodine liberated in this experiment was determined colorimetrically.

Debrominated Polymers from the Polymer of Methyl α -Bromoacrylate.—The debrominated polymers were obtained by the action of potassium iodide and by the action of zinc dust on the polymer of methyl α -bromoacrylate.

To a solution of 3 g. of the polymer in 100 cc. of peroxide-free dioxane was added 10 cc. of 30% aqueous potassium iodide. The mixture was warmed at 80–85° for three days. The solution became deeply colored by the liberation of iodine, and a polymeric precipitate formed in the reaction flask. It was isolated, washed with water and alcohol and dried. Analysis showed that 93% of the bromine had been removed.

Anal. Calcd. for $(C_8H_{10}O_4)_n$: C, 56.47; H, 5.88. Found: C, 52.10; H, 4.36; Br, 3.77.

This debrominated polymer decolorized an aqueous solution of potassium permanganate in a period of about forty-eight hours. A 5-g. sample of the polymer of methyl α -bromoacrylate was dissolved in 100 cc. of dioxane and 4 g. of purified zinc dust was added. The mixture was refluxed gently for forty-eight hours. After the solution cooled, the unreacted zinc and the precipitated organic material were separated from the dioxane by filtration.

The filtrate gave a positive test for halogen ion, indicating that the zinc had reacted. The residue was suspended in dilute hydrochloric acid for forty-eight hours in order to dissolve the zinc. The residue was collected on a filter and washed thoroughly with water. It burned with a smoky flame, decolorized aqueous permanganate at room temperature within forty-eight hours, and gave a slight test for halogen. The yield was 2 g.

Anal. Calcd. for $(C_8H_{10}O_4)_n$ (XIII): C, 56.47; H, 5.88. Found: C, 50.61; H, 5.24; Br, 3.20. A portion of the polymer which had precipitated on the sides of the flask and which was not contaminated with zinc was analyzed. Found: C, 53.52; H, 5.62; Br, 1.42.

Effect of Heat on the Polymers of Methyl α -Bromoacrylate, Methyl α -Chloroacrylate, and on the Esters of Halogenated Succinic and Glutaric Acids.—The materials were heated in 50-cc. Erlenmeyer flasks and the vapors passed into water and then through a trap immersed in a dry-ice-acetone bath. The liberation of hydrogen bromide was noted by an indicator (congo red) which was placed in the water, and the dry-ice-acetone trap was used to catch any low-boiling substances which were liberated. The polymer of methyl α -bromoacrylate began to lose hydrogen bromide when heated to 110°, and the reaction was rapid between 120 and 150°. The hydrogen bromide appeared before any loss of methyl bromide was noticed. Finally, the polymer was heated to 220° to give a shiny, dark brown residue.

Anal. Calcd. for $(C_7H_8O_4)_n$: C, 54.50; H, 3.90. Found: C, 55.18; H, 4.00.

The ethyl α, α' -dibromosuccinate (VI) lost hydrogen bromide at 130–170°, which is in agreement with observations recorded in the literature.⁷ The ethyl α, α' -dibromo- α, α' -diethylglutarate (VIII) began to lose hydrogen bromide at approximately 175°, the major portion of the decomposition occurring at 190–200°.

The polymer of methyl α -chloroacrylate was heated to 330° under pressure of 3 mm. for one hour. The residue was a shiny dark brown material which was very brittle. It burned with a smoky flame, contained no chlorine, and was insoluble in organic solvents.

Anal. Calcd. for $(C_4H_4O_2)_n$: C, 57.10; H, 4.76. Found: C, 59.37; H, 4.65.

(14) Staudinger and Schwalbach, *Ann.*, **488**, 8 (1931).

Reaction of the Polymer of Methyl α -Bromoacrylate with Quinoline.—One and one-half grams of methyl α -bromoacrylate was dissolved in 100 cc. of dried dioxane and 3 g. of quinoline was added. The reaction mixture was warmed at 60° for eight hours. It was diluted with 300 cc. of ether and a polymeric material was precipitated. The precipitate was washed alternately with water and alcohol to remove impurities. Analysis of the polymer showed that a molecule of hydrogen bromide had been removed for each unit (see formula IX).

Anal. Calcd. for $(C_8H_8O_4Br)_n$: C, 38.50; H, 3.61; Br, 32.10. Found: C, 39.10; H, 3.94; Br, 30.40.

Absorption Spectra.—The spectra were taken on a Bausch and Lomb ultraviolet spectrograph. A hydrogen discharge tube operating on 15,000 volts was used as the source of ultraviolet light and the hydrogen lines were used to calibrate the wave length scale. The absorption coefficients were determined by comparing the absorption of the compounds with the absorption of a 10^{-4} molal naphthalene solution. Dioxane, which had been carefully purified, was used as the solvent.¹⁵ The results are shown in Fig. 1.

Hydrolysis and Subsequent Oxidation of the Polymer of Methyl α -Bromoacrylate.—A 14-g. sample of the polymer of methyl α -bromoacrylate was warmed with 150 cc. of aqueous sodium hydroxide (8 g. of sodium hydroxide) for twenty hours. The polymer dissolved slowly to give a dark brown solution. This was cooled and the alkali neutralized with hydrochloric acid. The solution was inclosed in parchment paper and dialyzed for seventy hours, when the solution gave a negative test for halogen ion. The solution was evaporated to dryness on a steam-bath to give a brown residue. This residue burned with a luminous flame and gave a white residue on ignition. The white residue when dissolved in water gave an alkaline reaction. Analysis of the material indicated that it was the sodium salt of a polymeric hydroxy acid (XIV).

Anal. Calcd. for $(C_3H_3O_2Na)_n$: C, 32.80; H, 2.73; Na₂O, 28.20; Na₂O₂, 35.45. Found: C, 35.20; H, 3.31; ash, 34.50.

A 0.5375-g. sample of the brown residue was dissolved in 50 cc. of water and the solution was cooled to 17°. To this solution was added 50 cc. of periodic acid solution containing 5 cc. of dilute hydrochloric acid, and the mixture

was immersed in a water-bath at 17°. A 25-cc. sample was removed immediately and titrated with standard sodium thiosulfate. This value was used to determine the normality of the periodic acid (0.75 *N*) in the reaction mixture. After thirty minutes, another 25-cc. sample was titrated. The difference in titrations was 3.00 (35.50–32.50) cc. of 0.528 *N* sodium thiosulfate. This difference amounts to 33.8% reduction of the periodic acid to iodic acid.

A 7.095-g. sample of the polymer of methyl α -bromoacrylate was treated with hot dilute alkali for twenty-four hours. The solution was acidified with an excess of dilute hydrochloric acid and the volume diluted to 250 cc. After cooling the solution to 16°, 100 cc. of periodic solution (cooled to 16°) was added. Throughout the oxidation the mixture was kept at 16°. A 25-cc. sample was immediately titrated. Table III gives the change in titration in cubic centimeters of 0.269 *N* sodium thiosulfate with time.

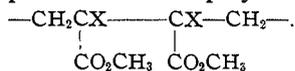
TABLE III

Time	Cc. of 0.269 <i>N</i> Na ₂ S ₂ O ₃ per 25 cc. sample	% reduction of HIO ₄
0	41.20	0
15 min.	40.98	3.1
47 min.	40.05	11.9
107 min.	39.85	14.0
6.5 hours	37.95	33.8
46.5 hours	31.30	103
52.5 hours	30.45	..
53.5 hours	30.30	..
71.5 hours	28.25	..

At the end of approximately forty-six hours all of the periodic acid had been reduced to iodic acid but the titration value in terms of thiosulfate slowly decreased, indicating that the iodic acid was being reduced further.

Summary

The structures of the polymers of methyl α -chloroacrylate and methyl α -bromoacrylate have been determined. The structural unit present in these polymers has been shown to be



(15) Oxford, *Biochem. J.*, **28**, 1325 (1934).