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

The Structure of Butadiene–Styrene Type Copolymers. The Butadiene–*o*-Chlorostyrene Copolymer[1]

BY C. S. MARVEL AND RUPERT E. LIGHT, JR.

In the earlier investigation of the arrangement of structural units in a butadiene (75)–styrene (25) (GR-S) copolymer which was carried out in this Laboratory[2] about 67% of the butadiene was accounted for but only about 24% of the styrene was recovered in products of identifiable structure. It seemed possible that this might have been due to some destruction of benzene rings in the ozonolysis and subsequent oxidative cleavage or that, alternatively, the styrene units might have been bunched up in the polymer chain and then lost in high boiling residues during the ester distillation required to separate the products of oxidation. Recently the development of a satisfactory method for separating organic acid mixtures by means of partition chromatography[3] has given a new tool for the study of diene structure, and we have reopened the investigation of the structure of the GR-S type polymer.

In the work described here, a copolymer of *o*-chlorostyrene and butadiene was selected for study so that the benzene ring would be marked with chlorine and chlorine analyses could be used to tell whether the ring was remaining intact during the various operations involved in diene polymer cleavage. The polymer which was studied was essentially 69% butadiene and 31% *o*-chlorostyrene since this gave a product with the same molar ratio of butadiene units and styrene units that is found in a 75–25 butadiene styrene copolymer.

This copolymer was ozonized by the general procedure used in the earlier work.[2] The ozonide was decomposed in the presence of hydrogen peroxide and the excess hydrogen peroxide destroyed by treatment of the acid mixture with platinum oxide. The water-soluble and water-insoluble acids were separated. The solution of water-soluble acids was evaporated under reduced pressure in order to avoid charring. The formic acid was not collected. The water-soluble acids (112.7 g.) contained 1.86% chlorine which indicated that the percentage of aryl-substituted acid present in the water-soluble portion was not high. These acids were later separated by the partition chromatographic procedure.[3] The water-insoluble acids (38 g.) contained 14.11% of chlorine and the significant constituent identified proved to be β-(*o*-chlorophenyl)-adipic acid. The amount of chlorine in the two fractions of acids comprised over 94% of that in the original polymer. Analysis of first water-insoluble fraction of acids showed it contained oxygen in addition to that of the carboxyl groups. Either the cleavage of the ozonide was not complete or some oxygen containing acids were produced as side products of the oxidation. This fraction was accordingly reoxidized with hydrogen peroxide before final separation of the acids by chromatographic procedures.

The water-soluble acids were separated by adsorption on a silicic acid column to which had been added water and glycerol, and then by development with chloroform to which five per cent. additional ethanol was added for every 100 ml. of eluant. The amount of each acid was determined by titration of the different fractions of eluate coming through at the proper volumes. Succinic acid, 1,2,4-butanetricarboxylic acid and β-(*o*-chlorophenyl)-adipic acid were separated.

The water-insoluble acids were adsorbed on dry silicic acid and developed with chloroform, chloroform–ether, and chloroform–alcohol mixtures. The acids definitely characterized were traces of succinic acid and 1,2,4-butanetricarboxylic acid and considerable quantities of β-(*o*-chlorophenyl)-adipic acid. Some more complex acids have not been completely separated and are still under investigation.

Assuming a random distribution of the 1,4-butadiene units (80%), and 1,2-butadiene units (20%) and the *o*-chlorostyrene units along the chain, the amounts of succinic, 1,2,4-butanetricarboxylic and β-(*o*-chlorophenyl)-adipic acid that should be obtained can be calculated. The calculated quantities, and those actually isolated, are recorded in Table I. The amounts of the various products isolated were calculated from averages of a number of separations such as are described in the experimenta part. Since the over-all yield of acidic oxidation products only

TABLE I

OXIDATION PRODUCTS OF BUTADIENE (69) + *o*-CHLOROSTYRENE (31) COPOLYMER

	Succinic acid, g.	1,2,4-Butanetricarboxylic acid, g.	β-(*o*-Chlorophenyl)-adipic acid, g.
Calcd. for 100 g. of polymer	82.5	22.6	26.5
Found in water-soluble acids	69.2	10.6	16.2
Found in water-insoluble acids	0.16	.11	2.27
Total found	69.36	10.71	18.47
% of theory	84.1	47.3	69.6

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[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

[2] Rabjohn, Bryan, Inskeep, Johnson and Lawson, THIS JOURNAL, **69**, 314 (1947).

[3] Marvel and Rands, THIS JOURNAL, **72**, 2642 (1950).

amounted to 73% of the theoretical amount it will be seen that somewhat more succinic acid and somewhat less 1,2,4-butanetricarboxylic acid were obtained than was expected on the basis of 20% 1,2-addition of the butadiene units. This may be due to over oxidation of 1,2,4-butanetricarboxylic acid to give lower acids. The recovery of β-(*o*-chlorophenyl)-adipic acid is excellent and this is evidence that styrene units are distributed along the GR-S type polymer chain according to chance and no bunching together of such units is indicated.

Experimental

Preparation and Properties of Butadiene (69.2)-*o*-Chlorostyrene (30.8) Copolymer.—The copolymer was prepared from 160 g. of butadiene, 66.6 g. of *o*-chlorostyrene, 1 g. of dodecyl mercaptan, 10 g. of Procter and Gamble SF soap flakes, 340 ml. of water and 20 ml. of 3% potassium persulfate solution. Polymerization was carried on for ten and a half hours and then to the latex was added 5 g. of phenyl-β-naphthylamine in soap solution and finally the polymer was coagulated by adding sodium sulfate and sulfuric acid in water solution. The polymer was cut into small pieces and dried at 2 to 3 mm. pressure in a desiccator. The conversion was 80.3%; the copolymer was 98.8% soluble in benzene (static method) and it had an intrinsic viscosity (in benzene solution) of 1.83. For analysis a sample was purified by dissolving in chloroform and precipitating with methanol for three successive times.

Anal.[4] Calcd. for copolymer (69.2 butadiene/30.8 *o*-chlorostyrene), C, 82.8; H, 9.3; Cl, 7.87. Found: C, 82.91; H, 9.24; Cl, 7.91.

The ultraviolet adsorption curve for a solution of 80 mg. of the purified polymer in 100 ml. of chloroform is given in Fig. 1.

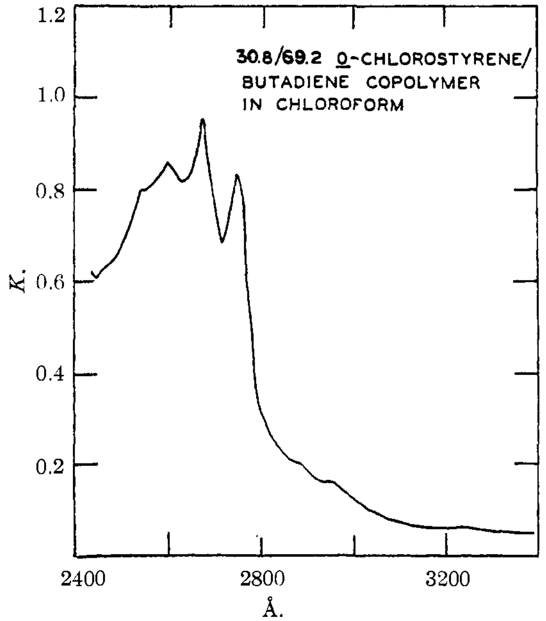

Fig. 1.

Preparation and Properties of Butadiene (75)-*o*-Chlorostyrene (25) Copolymer.—For some of the early experiments a 75–25 copolymer was prepared and used in ozonolysis. The procedure was that described above except only 50 g. of *o*-chlorostyrene was used in the recipe. The conversion was 80.7%, solubility—98.5%, [η] 1.7. The polymer was purified as described above.

Anal. Calcd. for copolymer (75 butadiene/25 *o*-chlorostyrene): C, 84.0; H, 9.58; Cl, 6.40. Found: C, 84.3, 83.7; H, 9.35, 9.72; Cl, 6.39, 6.53.

Ozonolysis.—To obtain homogeneous samples of polymer for ozonolysis 300 g. of the above type polymer was dissolved in 10 l. of chloroform, filtered and the solution stirred under nitrogen. Just before ozonolysis 750 ml. of this solution (containing 19.74 g. of polymer) was poured with stirring into a 4-l. beaker containing 3 l. of methanol. The precipitated polymer was redissolved without drying in 500 ml. of chloroform and poured very slowly into 3 l. of methanol. The treatment was repeated for another time and then the polymer (without drying) was taken up in chloroform and the solution made up to exactly 1 l. Three 5-ml. portions were pipetted into tared aluminum foil dishes, evaporated to dryness at 63° for two hours and weighed to determine the exact amount of polymer which was ozonized.

The remaining chloroform solution of the polymer was placed in a 1-l. flask, fitted with standard ground glass connections, which had an inlet tube for ozone leading to within 7 mm. of the bottom. The flask was placed in an ice-bath and this placed inside a wooden box made of 2 × 8 inch lumber. The top was open to the air so in case of explosion the operator at the side was protected.

Approximately 2% ozone was passed through the solution and the flow continued for about thirty to sixty minutes after a potassium iodide–starch solution indicated ozone was passing through the solution unabsorbed. The total ozonolysis time was about nine hours.

The flask was then fitted with a capillary for admitting air and a lead-off for chloroform vapors and the solvent removed by careful evaporation under reduced pressure at about 40°. This required about twelve hours. Toward the latter part of this operation the pressure was reduced to 18 mm. The viscous ozonide was treated with about 300 ml. of 3% hydrogen peroxide and finally boiled for about three hours to insure complete oxidation. The mixture was cooled to about 2°, and filtered through a 200 mesh screen. The soluble material was collected as the stock solution of water-soluble acids. The material remaining on the screen and in the ozonization flask was washed thoroughly with water which went into the above stock solution of water-soluble acids. The water-insoluble acids were collected in ether as a stock solution.

Altogether six portions (82.41 g. of the 69.2–30.8 copolymer) of the type described were combined to give a pair of stock solutions of water-soluble and insoluble acids. Another six portions (82.242 g. of the same polymer) gave a second pair of stock solutions.

As a safety precaution the ozonization, evaporation and decomposition of the ozonides were carried out in the heavy box of 2 × 8 inch lumber. No explosions occurred but extreme care was observed at all time to avoid accidental injury to the operator.

Properties of the Ozonide.—A sample of the ozonide from the butadiene (75)-*o*-chlorostyrene (25) copolymer was obtained by ozonization of 11.804 g. of copolymer in 1.2% solution in chloroform with 2% ozone as above. A test portion of the ozonide solution was evaporated to determine gain in weight of the polymer during ozonolysis. This gain in weight was 51.3% where the theoretical gain should be 39.9%.

The ozonide obtained by evaporating the remainder of the solution to dryness was a viscous liquid which would not pour without warming. It did not explode on striking with a hammer or on heating to its flash point.

Anal. Calcd. for copolymer ozonide: C, 50.5; H, 5.87; Cl, 3.85; O, 39.9. Found: C, 50.28; H, 6.58; Cl, 8.28; O (by difference), 34.86.

The high chlorine content and the abnormal gain in weight during ozonolysis show that some chloroform must

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[4] Analyses by Clark Microanalytical Laboratory, Urbana, Illinois.

have been retained in the ozonide. The ultraviolet absorption of a solution of 80 mg. of this ozonide in 100 ml. of chloroform is given in Fig. 2.

Destruction of Excess Hydrogen Peroxide in Aqueous Stock Solution.—The water-soluble oxidative degradation products were freed from excess hydrogen peroxide by treatment of 1 liter of stock solution with 1 g. of platinum oxide[5] for twenty-four hours at room temperature. Then another 1-g. portion of platinum oxide was added and the mixture again allowed to stand for twenty-four hours. Finally the solution was heated to 70–80° on a steam-bath for thirty minutes, cooled and filtered. Preliminary experiments showed that this treatment would destroy hydrogen peroxide without excessive destruction of the succinic acid expected from oxidative cleavage of the polymer.

Isolation of Water-Soluble Acids.—Several methods of isolating the water-soluble acids were tried and the following adopted as the standard procedure. About one-tenth of the hydrogen peroxide-free water stock solution (205.7 ml.) was placed in four tared 125-ml. filter flasks in an oil-bath carefully held at 15–25°. Air was carefully drawn over the surface so that evaporation occurred without spattering of the solution. The evaporation required about eight to twelve hours. The flasks were placed in a vacuum desiccator held at 0.1 to 0.4 mm. for thirty hours and at 0.05 mm. for six hours, and then weighed. The acid recovery was 9.1312 g. which on the basis of 100 g. of polymer is 112.3 g. of water-soluble acids. A slightly different method of isolation gave 112.7 g. of water-soluble acids for 100 g. of polymer.

The water-soluble acids obtained were white, had a neutral equivalent of 71.1 and a chlorine content of 1.86%. They were soluble in acetone, water, methyl alcohol, ethyl alcohol, ethyl acetate, and dioxane. They were partially soluble in ether, benzene, chloroform and toluene. They were apparently entirely insoluble in carbon tetrachloride, cyclohexane, ethylene chloride and petroleum ether. The water solution of these acids did not decolorize potassium permanganate solution.

Separation of Known Acids.—A column of moist silicic acid for partition chromatographic separation of acids[3] was prepared by grinding a 30-g. portion of Mallinckrodt 100-mesh silicic acid with a solution of 2 ml. of glycerol in 12 ml. of distilled water. After these ingredients were thoroughly mixed, 100 ml. of chloroform was added in portions and stirring maintained so that a uniform slurry of the silicic acid was obtained. The slurry was then poured into a Pyrex glass tube 52 cm. long with 2.2 cm. inside diameter. The tube was closed at the bottom with a two-way stopcock. The sides of the column were washed with chloroform and an air pressure of 4 to 9 p. s. i. was applied at the top or the column to force through the chloroform and settle the column of silicic acid. These operations gave a column about 17 cm. high.

To use this column for the separation of acids, the acid mixture was introduced at the top in a solution in a mixture of 1 ml. of alcohol and 0.5 ml. of chloroform. This solution was carefully introduced at the top of the column from a pipet without a tip. Care was necessary to avoid breaking the surface of the silicic acid. The flask containing the acid solution was rinsed with a mixture of 1.5 ml. of chloroform and 0.2 ml. of alcohol and this wash solution was introduced into the column. A third washing with a mixture of 0.1 ml. of alcohol in 3 ml. of chloroform and a fourth with 4 cc. of chloroform was used to ensure complete transfer of the acids to the column. The column was developed with chloroform to which was added successive increments of ethanol, under a pressure of about 4 to 9 pounds. The eluant consisted of successive 100-ml. portions of 100% chloroform, of 95% (by volume) chloroform-5% alcohol; 90% chloroform-10% alcohol; 85% chloroform-15% alcohol; 80% chloroform-20% alcohol; 75% chloroform-25% alcohol: and 70% chloroform-30% alcohol. Each 10-cc. portion coming through the column was titrated with standard sodium hydroxide solution.

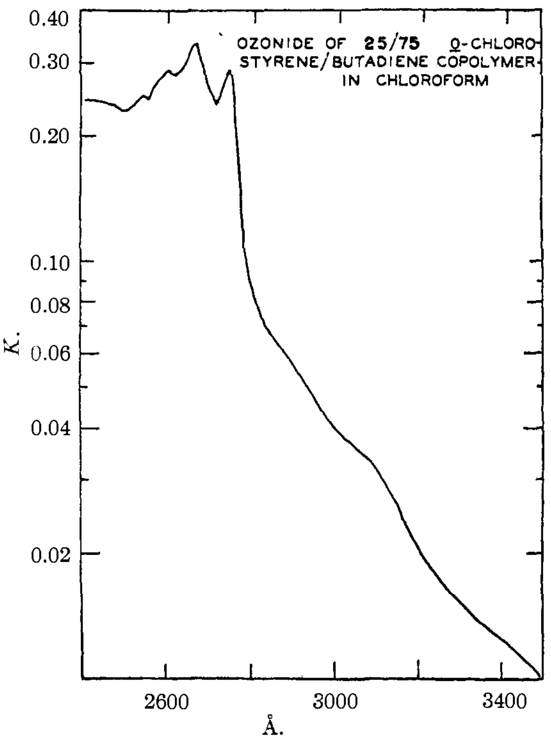

Fig. 2.

When this general procedure was used to separate a mixture of 0.1030 milliequivalent of β-phenyladipic acid, 1.5000 milliequivalents of succinic acid and 0.4000 milliequivalent of 1,2,4-butanetricarboxylic acid, the β-phenyladipic acid was found to have a peak effluent volume[3] of 60 ml.; the succinic acid of 330 ml. and the 1,2,4-butanetricarboxylic acid of 440 ml. There was recovered 0.1032 milliequivalent (100.2%) of β-phenyladipic acid, 1.5000 milliequivalents (100%) of succinic acid; and 0.3922 milliequivalent (98.1%) of 1,2,4-butanetricarboxylic acid. Other experiments indicated the same general recovery of these products from known mixtures.

Separation and Identification of Water-soluble Acids from the Oxidation of *o*-Chlorostyrene–Butadiene Copolymer.—A 70.0-mg. portion of the water-soluble acids from ozonolysis and oxidation was placed on the silicic acid column and developed in the standard fashion. The bands obtained and the fraction of the total acids are indicated in Table II and Fig. 3.

TABLE II

SEPARATION OF WATER-SOLUBLE ACIDS

Band	Ml. of eluant	Acid	Per cent. of starting mixture
1	80	Unknown	7.67
2	190	Unknown	3.85
3	260	Unknown	1.6
4	345	Succinic acid	74.5
5	450	1,2,4-Butanetricarboxylic acid	10.04
6	520	Unknown	2.18
7	540	Unknown	
8	560	Unknown	

The total recovery of the acid used amounted to 99%. The first two bands were thought to be due to a single component β-(*o*-chlorophenyl)-adipic acid which was separated at different levels because some washed through with the alcohol used to introduce the acids on the column.

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[5] "Organic Syntheses," Col. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 463.

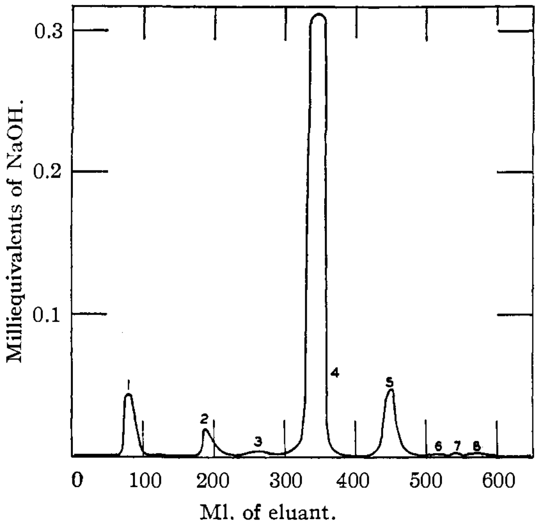

Fig. 3.

Later experience verified this view. The third band could be due to formic acid which had not been entirely removed by the drying process. Bands 4 and 5 correspond respectively with the expected bands for succinic acid and 1,2,4-butanetricarboxylic acid. These two acids were actually isolated from a portion of the eluant on a larger scale experiment. The succinic acid isolated from band 4 melted at 184.5–185° and the mixed melting point with an authentic sample of succinic acid was 184.5–185°. The isolated succinic acid had a neutral equivalent of 59 (calcd. 59). The 1,2,4-butanetricarboxylic acid isolated from band 5 melted at 119–120° and the mixed melting point with an authentic specimen was 119–121°. The isolated acid had a neutral equivalent of 64.7 (calcd. 63.4).

In order to identify the material which washed through the column in the first two bands the water-soluble acids were divided into a chloroform-soluble fraction and a chloroform-insoluble fraction and the chloroform-soluble fraction separated on a larger column. The large column was prepared by making a slurry of 426 g. of silicic acid in 170 ml. of water and 1400 ml. of chloroform. This was placed in a 6.5 cm. (inside diameter) glass tube and the chloroform was forced out of the column under slight pressure which left a column about 25 cm. high.

A 4.3612-g. sample of the water-soluble acids was extracted twice with 10-ml. portions of chloroform and once with a 20-ml. portion of chloroform and the combined extracts were added to the above column. The sides of the column were washed with another 20 ml. of chloroform. This column was then developed with 1600 ml. of chloroform, 1600 ml. of 95% chloroform–5% absolute ethanol, and 1200 ml. of 90% chloroform–10% absolute ethanol. The eluate was collected in 100-ml. fractions and titrated. The results are given in Table III.

Table III

Separation of Chloroform-soluble Fraction of Water-soluble Acids

Liters of eluate	Milli-equivalents of acid	% Based on acids added	% Based on acids recovered	% of acid in the original sample of acids
1.9	0.5383	0.88	9.36	1.08
2.4	0.2831	0.46	5.02	0.36
2.7	3.8883	6.34	67.60	7.77
3.3	1.0395	1.69	18.10	2.22

The 27th and 28th 100-ml. fractions were combined and the solvent removed in a current of air. The residue was dissolved in water, filtered to remove a little water-insoluble oil, evaporated and the residue finally recrystallized three times from hot water, m. p. 128–129°. The neutral equivalent and analysis indicated that this acid was the expected β-(*o*-chlorophenyl)-adipic acid.

Anal. Calcd. for $C_{12}H_{12}O_4Cl$: C, 56.15; H, 5.11: Cl, 13.81: neut. equiv., 128.3. Found: C, 56.39; H, 5.07; Cl, 13.81; neut. equiv., 128.5.

Reoxidation of the Water-Insoluble Acids.—Preliminary studies showed that the water-insoluble acid portion contained some undecomposed ozonide or other oxygen-rich non acidic portions. Accordingly aliquot portions were reoxidized to insure complete breakdown. This can be illustrated by the following experiment.

In a 300-ml. flask fitted with a stirrer was placed 10.3599 g. of water-insoluble acid mixture (neut. equiv. 345) and 100 ml. of 6% hydrogen peroxide solution. The mixture was stirred and heated to boiling under a reflux condenser for two hours. Then 70 ml. of 6% hydrogen peroxide was added and heating and stirring continued for another two hours. The mixture was then cooled to 0–2° and decanted through a sintered glass funnel. The residue on the funnel was boiled with 20 ml. of distilled water to collect as much water-soluble material as possible. The water solution was treated with platinum oxide as before to remove excess hydrogen peroxide and then evaporated to dryness. The water-insoluble material was dissolved in acetone and ether. The water-soluble fraction weighed 1.7877 g. and had a neutral equivalent of 135.3. The water-insoluble portion weighed 8.4966 g. and had a neutral equivalent of 354.

Separation of Water Insoluble Acids.—Preliminary experiments indicated that the water-insoluble acids could be separated better by straight adsorption chromatography using silicic acid and chloroform than by the use of the partition chromatography system with moist silicic acid. A large column (25 × 6.5) of silicic acid was prepared as before except no water was added. A 2.1345-g. sample of reoxidized acids was introduced onto this column in chloroform solution. The column was then developed by use of chloroform to which was added first increasing amounts of ether and then increasing amounts of ethanol. The composition of the eluant used is given in Table IV.

Table IV

Eluant for Water-insoluble Acid Separation

Quantity of eluant l.	Composition by volume, % Chloroform	
3.9	97	3 ether
2.0	94	6 ether
0.5	93	7 ether
2.1	92	8 ether
1.2	88	12 ether
3.0	97	3 ethanol
1.5	95	5 ethanol
0.6	92	8 ethanol
1.0	85	15 ethanol

Titration of the eluate gave the results plotted in Fig. 4. The acidic substance from each of the bands indicated in the figure were isolated by evaporation and the acids were analyzed. However the analytical results were only indicative as there was insufficient material for careful purification. Band 8 containing 17.46% of the total acids was identified as due to β-(*o*-chlorophenyl)-adipic acid. Further work on the other bands is in progress.

Water-Soluble Acids from the Reoxidation of Water-Insoluble Acids.—Separation of the water-soluble acids obtained from the reoxidized fraction of the water-insoluble acids yielded no additional succinic acid, but a small amount of additional 1,2,4-butanetricarboxylic acid was isolated.

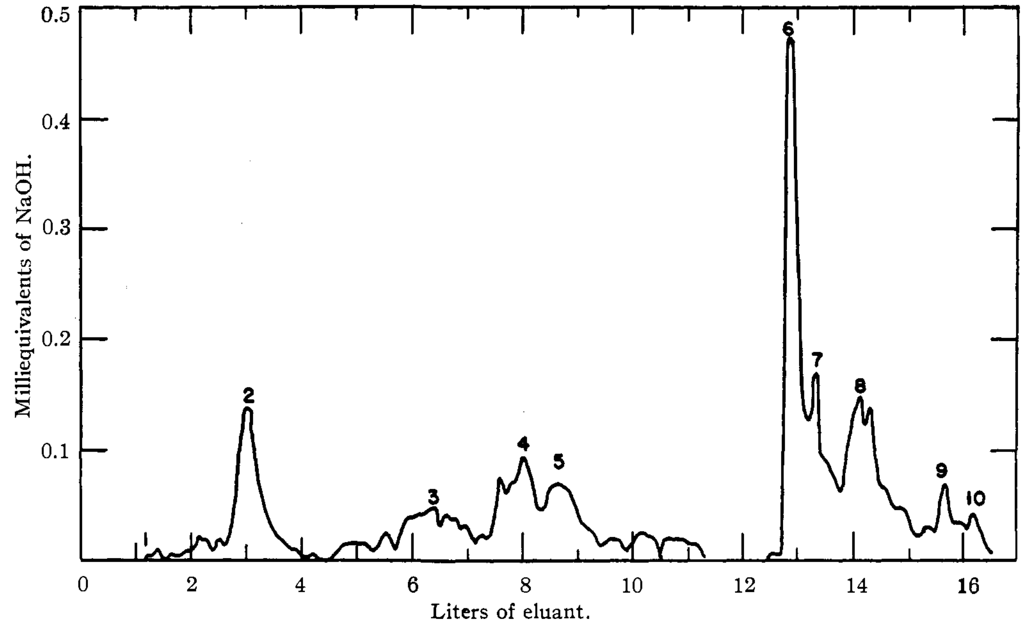

Fig. 4.

Summary

Ozonolysis followed by oxidative cleavage of a copolymer of butadiene and *o*-chlorostyrene has given a 73% yield of acidic products. Succinic acid was isolated in more than the expected amount and 1,2,4-butanetricarboxylic acid in less than the expected amount. This may indicate some overoxidation of the latter acid to yield succinic acid. β-(*o*-Chlorophenyl)-adipic acid was obtained in 69.6% yield which indicates a random distribution of the styrene units along the polymer chain. Some unidentified acids were also isolated and are under further study.

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[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Inhibition of Friedel–Crafts Polymerization[1]. I. The Mechanism of Inhibition

BY J. GEORGE, H. WECHSLER AND H. MARK

The polymerization of olefins by such catalysts as aluminum chloride, tin tetrachloride and boron trifluoride,[2–4] is a chain reaction, in the course of which the molecular weight of the polymer remains essentially constant, a high molecular weight material being obtained right at the start.[5] An indication of the chain character is its sensitivity to inhibitors. Hydrogen halides, hydrogen sulfide and paraffin hydrocarbons lower the molecular weight of polyisobutylene formed in the presence of boron trifluoride[6]; hydrogen chloride inhibits the polymerization of styrene by tin tetrachloride,[5] ethers and alcohols inhibit that of isobutylene[4] and butyl vinyl ether[7] and the passage of a stream of trimethylamine completely stops the absorption of acetylene by aluminum chloride.[8] Since electron deficient molecules are involved in Friedel–Crafts polymerizations, it is not surprising to find that electron pair donors such as amines and oxygen compounds act as inhibitors. In the present work the proportion of inhibitor never exceeded 10% on the catalyst; the marked effect observed notwithstanding indicates that the inhibitor does not merely neutralize the catalyst but somehow interferes with the reaction itself.

Polymerization of styrene and α-methylstyrene was carried out with tin tetrachloride as catalyst and mono-, di-, tri-*n*-butylamine and dimethylaniline as inhibitors. Mixtures of nitrobenzene

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(1) This paper is part of the dissertation presented by Harry Wechsler to the Faculty of the Graduate School, Polytechnic Institute of Brooklyn, in partial fulfillment of the degree of Ph.D.

(2) (a) H. M. Hulburt, R. A. Harman, A. V. Tobolsky and H. Eyring, *Ann. N. Y. Acad. Sci.*, **44**, 371 (1943); (b) C. C. Price, *ibid.*, **44**, 351 (1943).

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

(4) P. H. Plesch, M. Polanyi and H. A. Skinner, *J. Chem. Soc.*, 257 (1947).

(5) G. Williams, *ibid.*, 246 (1938); 1046 (1938); 775 (1940).

(6) R. M. Thomas, W. T. Sparks, P. K. Frolich, H. Otto and M. J. Mueller-Cunardi, THIS JOURNAL, **62**, 276 (1940).

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(8) Hunter and Yohe, THIS JOURNAL, **55**, 1248 (1933).