

The chlorine was stopped, and air blown through the reaction mixture for 0.5 hour to remove dissolved chlorine and hydrogen chloride. The chlorine was distilled from the Dry Ice cooled trap and any high boiling residue was returned to the reaction mixture. The reaction mixture was then rectified on a Todd precision fractionating assembly. When all the solvent was removed, rectification was continued at reduced pressure. This procedure was followed in each of the cases described.

2,2,3,3,4,4,4-Heptafluoro-1-butanol Chlorination.—Forty-three grams of 2,2,3,3,4,4,4-heptafluoro-1-butanol in carbon tetrachloride was treated with chlorine for 2 hours. Ice-water was passed through the reflux condenser. The reaction mixture was distilled to yield 10 g. of heptafluorobutanol boiling at 29° at 745 mm. pressure, and 24 g. of unreacted alcohol or a yield of 80% and a conversion of 24%.

Chlorination of 3,3,4,4,5,5,5-Heptafluoro-2-pentanol.—Sixty-seven grams (0.31 mole) of 3,3,4,4,5,5,5-heptafluoro-2-pentanol in carbon tetrachloride was chlorinated for 2 hours and fractionation of the resulting mixture resulted in 63 g. of a product boiling at 60° at 745 mm. pressure, which was an azeotrope of 3,3,4,4,5,5,5-heptafluoro-2-pentanone and carbon tetrachloride. The 2,4-dinitrophenylhydrazone of the ketone was prepared, m.p. 76–76.5°.

Anal. Calcd. for $C_{11}H_7F_7O_4N_4$: N, 14.30. Found: N, 14.47.

The 2,4-dinitrophenylhydrazone was hydrolyzed with concentrated sulfuric acid and the pure ketone isolated, boiling at 63.5° at 740 mm. The yield was 70%.

4,4,5,5,6,6,6-Heptafluoro-3-hexanol.—Sixty-four grams of 4,4,5,5,6,6,6-heptafluoro-3-hexanol in 88.5 g. of carbon tetrachloride was chlorinated as previously described. The reaction time was 2.5 hours. The fraction boiling at 70–74° during rectification was identified as a mixture of 4,4,5,5,6,6,6-heptafluoro-3-hexanone and carbon tetrachloride, by means of the 2,4-dinitrophenylhydrazone, m.p. 70–71°.

Anal. Calcd. for $C_{13}H_9F_7O_4N_4$: N, 13.80. Found: N, 13.70.

Fractions boiling over the range 135–156° were monochloro alcohols, isomers of the general formula $C_3F_7CHOH-C_2H_4Cl$. The monochloroalcohols were combined and rectified to yield two main fractions, alcohol (I) b.p. 136–140° at 745 mm. pressure (with decomposition), alcohol (II) b.p. 156° at 745 mm. pressure (68% yield).

Alcohols (I) and (II) were each refluxed for 24 hours with 10 g. of potassium carbonate in 50 ml. of water. The lower organic layers were separated, the water layers, containing much chloride ion, were extracted with ether, the ether extract combined with the organic layer and the mixture dried over Drierite. The dried extracts were distilled at atmospheric pressure. Alcohol (II) yielded, besides unreacted starting material, a chlorine-free solid, m.p. 90–91° after recrystallization from benzene. This solid gave a negative test with periodic acid even after heating, and was therefore identified as 4,4,5,5,6,6,6-heptafluoro-1,3-hexanediol.

The distillation of the hydrolysis product of alcohol (I) did not yield a product completely free of chlorine, but a high boiling liquid, b.p. 170–175°, was obtained. It did not give a positive test with silver nitrate solution but did give a positive periodic acid test. On the basis of these results, the chlorohydrins (I) and (II) were assigned the following structures: $C_3F_7CHOHCH_2Cl$ (I), $C_3F_7CHOHCH_2-CH_2Cl$ (II).

Chlorination of 3,3,4,4,5,5,5-Heptafluoro-2-methyl-2-pentanol.—A solution of 100 g. (0.44 mole) of 3,3,4,4,5,5,5-heptafluoro-2-methyl-2-pentanol in carbon tetrachloride was treated with chlorine for 5 hours. Fractionation of the products gave 43.1 g. (0.16 mole) of 1-chloro-3,3,4,4,5,5,5-heptafluoro-2-methyl-2-pentanol (37% yield) and 37.5 g. of the dichloro compound.

1,2-Epoxy-3,3,4,4,5,5,5-heptafluoro-2-methylpentane.—Thirty-nine grams of 1-chloro-3,3,4,4,5,5,5-heptafluoro-2-methyl-2-pentanol was added slowly through a dropping funnel to 50 g. of a 20% sodium hydroxide solution in a distilling flask maintained at 100°. When half of the chlorohydrin had been added, a liquid began steam distilling from the mixture. The distillation began at 78° and was continued until no more organic material was evident in the distillate. The water layer in the distillate was separated and the crude product was dried over Drierite. The product was rectified and 32.1 g. (93% yield) of 1,2-epoxy-3,3,4,4,5,5,5-heptafluoro-2-methylpentane was obtained.

Acknowledgment.—The authors wish to acknowledge the financial support of this work received from the Petroleum Branch, Materials Laboratory, Wright Air Development Center, Dayton, Ohio.

LAFAYETTE, INDIANA

[CONTRIBUTION NO. 1123 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Electron Exchange-Polymers. III. Polymers and Copolymers of Vinylhydroquinone

BY MYER EZRIN, IVOR H. UPDEGRAFF AND HAROLD G. CASSIDY

RECEIVED SEPTEMBER 18, 1952

The preparation and properties of vinylhydroquinone dibenzoate and diacetate, of polyvinylhydroquinone, and copolymers of the dibenzoate and of the free hydroquinone with styrene, with α -methylstyrene, with vinyl pyridine; and with styrene, cross-linked with divinylbenzene are described. The oxidation behaviors of some of these substances are shown and discussed. It is established that high polymers capable of showing oxidation-reduction properties have been prepared, and some physical and chemical properties of these substances are discussed.

In this paper are reported the preparation and properties of polyvinylhydroquinone and copolymers with styrene, α -methylstyrene, vinylpyridine and styrene and divinylbenzene.

In previous reports the concept of the electron exchange-polymer ("redox resin") was presented¹ and the preparation of vinylhydroquinone and its polymerization by heat were described.² Titration curves for the oxidation of the product of this polymerization alone, in suspension, and dispersed in the presence of bovine serum albumin were reported. While it turned out that the polymerized vinylhydroquinone prepared in this way

was of low molecular weight (corresponding largely to the dimer and trimer) the oxidation findings as well as the general discussions of the experimental work^{1,2} are supported by the results obtained with high polymer and reported here. This is because the low molecular weight material "polymerized vinylhydroquinone" is quite insoluble in aqueous solvents, so that over at least part of the titration curves in such solvents a heterogeneous system was present (precipitation occurred) and because, also, the substance contained a range of molecular sizes, and at least two chemical groupings with different oxidizabilities.³ Nevertheless, these re-

(1) H. G. Cassidy, *THIS JOURNAL*, **71**, 402 (1949).

(2) I. H. Updegraff and H. G. Cassidy, *ibid.*, **71**, 407 (1949).

(3) I. H. Updegraff and H. G. Cassidy, presented before the Organic Division at the Philadelphia Meeting of the American Chemical Society, April, 1950.

sults, which it is hoped later to present in detail, require a revision of some interpretations given in the earlier papers. Thus, the shape and increased slope of the titration curves of the "polymerized vinylhydroquinone" can be interpreted satisfactorily as due to the presence of the substances with different values of the mid-point potential. None of these need be free radical (as had been postulated). The red color produced during the titration must then most likely be laid to quinhydrone formation. The suggestion that in suitable cases free radical may accumulate in a system when groups are held sufficiently far apart by being attached to a polymeric structure so that dismutation is hampered, remains a reasonable supposition, but loses some of its force in this connection. The entire effect of the heterogeneity of the system is not known.

Upon protecting the hydroxyl groups of vinylhydroquinone, as described in this paper, subsequent polymerization readily produced high polymer.

Experimental

Vinylhydroquinone.—This was prepared from coumarin by the method already described.² Despite numerous studies utilizing the findings of Baker and Brown⁴ in their study of the Elbs persulfate oxidation, the yield in the step involving the preparation of dihydroxycinnamic acid could not be improved.

Vinylhydroquinone Dibenzoate.—Vinylhydroquinone, 2.65 g. (0.0195 mole), was benzoylated in 15 ml. of pyridine with 4.8 ml. of benzoyl chloride. The product was washed with water, dried and recrystallized from 36 ml. of 95% alcohol; yield 5.24 g. (0.0152 mole), 78% based on vinylhydroquinone.

Vinylhydroquinone dibenzoate has not been previously described. It is colorless and crystalline, melting at 94°. Hydrogenation at atmospheric pressure with Adams catalyst indicated one olefinic double bond; 183.5 mg. absorbed 11.8 ml. of hydrogen (S.T.P.); calcd., 12.0 ml.

Anal. Calcd. for $C_{22}H_{16}O_4$: C, 76.7; H, 4.7; sapon. equiv., 172. Found: C, 76.3; H, 5.1; sapon. equiv., 176.

Vinylhydroquinone Diacetate.—Vinylhydroquinone, 3.0 g. (0.022 mole) was treated with 4.8 ml. of acetic anhydride. A very small drop of concd. sulfuric acid was added and the mixture stirred. After 3–4 min., water containing a trace of sodium chloride was added and the mixture stirred thoroughly. The oily product was washed six times with water, then the last product layer was removed from the tube with three 10-ml. portions of ether. Through the ether solution, cooled to 0°, nitrogen was bubbled for 15–20 min. Nitrogen was at the same time bubbled through a cooled 1% sodium hydroxide solution to which a trace of sodium hydrosulfite had been added. The ether solution was quickly extracted with the alkaline hydrosulfite then washed with water four times, dried, the solvent removed on the steam-bath and the product crystallized twice from 95% ethyl alcohol; colorless crystals, m.p. 48–49°.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.4; H, 5.5. Found: C, 65.7; H, 5.8.

Styrene (E. K. Co.), α -Methylstyrene (E. K. Co.), 4-Vinylpyridine (Reilly).—These were distilled *in vacuo* under nitrogen just before use, or in a few instances were distilled and stored in the refrigerator overnight before use.

Divinylbenzene.—We are indebted to Koppers Co., Inc., for this material. The commercial product contained 40–50% divinylbenzene isomers. The inhibitor was removed by washing three times with an equal volume of 5% sodium hydroxide and three times with water. The reagent was dried over anhydrous potassium carbonate and stored under nitrogen at –10°.

Method of Polymerization of Polymer and Copolymers (Not Cross-linked).—The conventional polymerization procedure was used, with very careful exclusion of oxygen. Examples of the procedure are given below.

Preparation of Cross-linked Polymers.—The polymerization was carried out in a 50-ml. flask equipped with stirrer, reflux condenser, nitrogen inlet and exit, and an inlet tube for adding reagents. The flask was heated in a glycerol bath contained in a depression in a 1-l. flask equipped with a reflux condenser. The flask contained a liquid of suitable boiling point, which, refluxing, maintained the glycerol-bath at a fixed temperature.⁵

The aqueous polymerization medium consisted of 1% polyvinyl alcohol.⁶ This was stirred vigorously at the polymerization temperature, the mixture of monomers and benzoyl peroxide, warmed to ensure fluidity, was added, and the mixture stirred for the desired period under nitrogen. The granules ("beads") of cross-linked copolymer were removed by filtration and thoroughly washed with water.

Determination of Molecular Weights.—Molecular weights were determined by the static elevation method with a Zimm-Myerson osmometer.⁷ The membrane used was #300 cellophane undried.⁸ The instrument was thermostated at $27.35 \pm 0.005^\circ$. Four points were taken over a concentration range of 0.001–0.005 g. per ml., using toluene as the solvent. The recommendations of Wagner⁹ were followed. The osmometer was standardized using a sample of standard polystyrene of mol. wt. 78,000, kindly supplied by Prof. R. M. Fuoss. The number average molecular weight obtained with this osmometer was 69,000.

The esterified polymers were used for determination of molecular weight to avoid complications which would arise with the free hydroquinone polymers because of their easy oxidation.

Saponification Methods.—After trying various methods, including the use of concd. sulfuric acid, the following was found satisfactory. The reaction must be carried out in the absence of oxygen, and is conveniently done in a sealed tube when the saponification equivalent is required or, for larger quantities, in a special apparatus. This latter is essentially an H-shaped vessel with bulbs at the bases, and stopcock equipped stoppers (glass) at the tops of each leg; with a stopcock and condenser on the cross-tube, and with a condenser on one leg. The polymer is introduced in the leg with the condenser; sodium ethylate, approximately 0.2 N in the other.¹⁰ The bulbs are cooled in freezing mixture and the apparatus evacuated and filled with nitrogen several times, being finally evacuated and closed. By tipping the vessel, the alkali is transferred through the cross-tube on to the polymer. There is usually developed a transient blue color. If air is present in any amount, or if the apparatus leaks, the blue color remains or intensifies. By means of the stopcocks at the top of this leg and on the cross-tube, the mixture is isolated. It is now refluxed on the steam-bath. Twenty-four hours of reflux has been used. After reflux, excess acid, e.g., 1 N sulfuric acid, is introduced into the empty leg of the apparatus, evacuated and flushed with nitrogen several times, then the stopcock on the cross-tube is opened under vacuum and the acid is transferred to the saponification mixture. Following this step it is permissible to work in the air, though even under acid conditions the free polymer tends to become pink on exposure to the atmosphere.

The saponified polymer is precipitated by adding the acidified saponification mixture (in which the polymer remains soluble due to the alcohol present) to a large excess of water, centrifuging and washing the precipitate twice by centrifugation. The polymer is purified further by dissolving it in

(5) H. G. Cassidy, *Ind. Eng. Chem., Anal. Ed.*, **10**, 456 (1938).

(6) du Pont "Elvanol," Grade 71-24 for which we are indebted to the Electrochemicals Department of E. I. du Pont de Nemours and Company.

(7) B. H. Zimm and I. Myerson, *THIS JOURNAL*, **68**, 911 (1946).

(8) We are indebted to the Sylvania Division, American Viscose Corp., Fredericksburg, Virginia, for this material.

(9) R. H. Wagner, (a) *Ind. Eng. Chem., Anal. Ed.*, **16**, 520 (1944); (b) "Physical Methods of Organic Chemistry," A. Weissberger, ed., Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945, p. 253.

(10) All the free polymers develop a deep blue color in the presence of air and alkali. The pH at which this color begins to appear seems to vary with the different polymers, being ca. pH 10.5–10.6 for polyvinylhydroquinone; 11.8–12 for the copolymer with styrene, and 11.55–11.75 for that with vinylpyridine. S. J. French and D. J. Saunders (*THIS JOURNAL*, **58**, 689 (1936)) studied the relation between production of colors with hydroquinone and pH. They found no color produced below pH 10.5.

(4) W. Baker and N. C. Brown, *J. Chem. Soc.*, 2303 (1948).

a suitable solvent, usually 90% acetic acid, and precipitating it by addition to an excess of water. This is repeated at least once. During these manipulations the polymers tend to become slightly pink (slightly oxidized). To prepare the essentially completely reduced form the polymer is suspended in a little air-free water, a freshly prepared 5% solution of sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$) containing a trace of alkali¹¹ is added and stirred with it under purified nitrogen for a short time.¹² The reduced polymer is quickly removed by centrifugation (or filtration) and washed several times with water. It may be dissolved and reprecipitated for further purification. Finally it is dissolved in 90% acetic acid or *t*-butyl alcohol containing a little water, and freeze-dried.

Purified Nitrogen.—For ordinary work Fieser's solution¹³ was used in gas bubblers. For the electrometric titrations, a Kautsky¹⁴ apparatus was used with Fieser's solution, but omitting the phosphorus pentoxide drying tube.

Polyvinylhydroquinone Dibenzoate.—A 20% solution in toluene (0.4 g. monomer) containing 4 mg. of benzoyl peroxide was heated 48 hours at 85°. This was diluted with toluene and precipitated by addition to ligroin. The purified, freeze-dried, polymer was a white, fluffy material, soluble in aromatic solvents, insoluble in alcohol, acetic acid and water; molecular weight 52,000 (*ca.* 160 monomer units).¹⁵

Anal. Calcd. for $(\text{C}_{22}\text{H}_{16}\text{O}_4)_n$: C, 76.7; H, 4.7; sapn. equiv., 172. Found: C, 75.4; H, 4.7; sapn. equiv., 180.

Saponified with subsequent reduction and purification, freeze-dried from 90% acetic acid the free polymer was obtained as a fluffy white material which slowly turns light pink on exposure to air. It is insoluble in benzene, slightly soluble in water, soluble in 90% acetic acid, 95% ethanol and *t*-butyl alcohol containing a little water.

Anal. Calcd. for $(\text{C}_8\text{H}_8\text{O}_2)_n$: C, 70.6; H, 5.9. Found: C, 64.9; H, 6.5; ash, 1.9.

The ash is presumably from the glass saponification vessel.

Polyvinylhydroquinone Diacetate.—The monomer (0.2 g.) as a 10% solution in benzene, with 0.3 mg. of benzoyl peroxide was heated 63 hours at 67°. Polymer separated on cooling. Dissolved in acetone, it was added to excess ligroin for precipitation; white, fluffy material was freeze-dried from glacial acetic acid; insoluble in aromatic solvents (cold), soluble in acetic acid and acetone.

Anal. Calcd. for $(\text{C}_{12}\text{H}_{12}\text{O}_4)_n$: C, 65.4; H, 5.5; sapn. equiv., 110.1. Found: C, 64.5; H, 5.7; sapn. equiv., 107.

After saponification, reduction, purification and freeze-drying from 90% acetic acid, it appeared as a white fluffy material soluble in 90% acetic, and in *t*-butyl alcohol containing a little water; slightly soluble in water; insoluble in benzene. After saponification, about half of the material in a hard coarse, lumpy red form resisted reduction. With the improved apparatus described above none of this need be present.

Copolymer of Vinylhydroquinone Dibenzoate with Styrene.¹⁶—A *ca.* 1:1 molar ratio of vinylhydroquinone diben-

zoate (0.40 g.) and styrene (0.126 g.) as a 20% solution in toluene, with 5.2 mg. of benzoyl peroxide was heated 72 hours at 85°. On dilution with toluene, precipitation by addition to ligroin, purification, and freeze-drying from benzene the polymer was obtained as white fluffy material, soluble in aromatic solvents, insoluble in alcohol, acetic acid and water; molecular weight 41,300 (about 200 units on 1:1 basis).

Anal. Calcd. for $(\text{C}_{30}\text{H}_{24}\text{O}_4)_n$: C, 80.3; H, 5.4; sapn. equiv. (1:1 basis), 224. Found: C, 79.0; H, 5.4; sapn. equiv., 242.

That the substance is a copolymer is indicated by the observation that the substance is completely soluble in concentrated sulfuric acid. A mixture of polystyrene and polyvinylhydroquinone dibenzoate treated under the same conditions with concentrated sulfuric acid leaves the polystyrene undissolved.

After saponification, reduction, purification and freeze-drying from 90% acetic acid a fluffy light tan material is obtained, soluble in 90% acetic acid, insoluble in benzene.

Anal. Calcd. for $(\text{C}_{16}\text{H}_{16}\text{O}_2)_n$, (1:1 ratio): C, 78.0; H, 6.7. Found: C, 72.3; H, 7.1; ash, 1.72 (probably introduced from the glass during saponification).

Copolymer of Vinylhydroquinone Dibenzoate with 4-Vinylpyridine.—A 1:1 molar ratio of vinylhydroquinone dibenzoate (0.40 g.) and 4-vinylpyridine (0.122 g.) in 20% solution in toluene, with 5.2 mg. of benzoyl peroxide was heated 36 hours at 85°. The viscous and slightly turbid product was diluted with toluene and added to excess ligroin for precipitation. The product was fractionated as follows: fraction 1 (14 mg.) soluble in toluene at room temperature; fraction 2 (87 mg.) soluble in toluene at 100°; fraction 3 (196 mg.) insoluble in toluene at 100° (soluble in methyl ethyl ketone at room temperature.) Fraction 3 was much more highly charged statically than the other two, retaining its charge even after several months of storage in glass. All three fractions were soluble in benzene, from which they were separately freeze-dried as white, fluffy materials. None of them showed any solubility whatsoever in ethanol, indicating the absence of polyvinylpyridine, and thus the copolymer nature of the substances.

Anal. Calcd. for $(\text{C}_{29}\text{H}_{23}\text{O}_4\text{N})_n$, (1:1 ratio): C, 77.5; H, 5.2; N, 3.1; sapn. equiv. for 1:1 copolymer, 224.5. Found: C, fract. 1, 64.6; fract. 2, 76.3; fract. 3, 75.9; H, fract. 1, 5.3; fract. 2, 5.2; fract. 3, 5.2; N, fract. 3, 3.1; sapn. equiv., fract. 2, 218; fract. 3, 218.

After saponification the solutions of fractions 2 and 3 were made strongly acid with standard hydrochloric acid and back-titrated with standard sodium hydroxide. The copolymers precipitated when a pH of *ca.* 4.4 was reached, and they did not redissolve when again strongly acidified. Reduction with hydrosulfite converted the brick-red polymer to a light yellow material, insoluble in 90% acetic or *t*-butyl alcohol containing a little water. They were freeze-dried as suspensions in acetic acid.

When saponification of a sample of fraction 3 was carried out in the strict absence of air and the products neutralized with standard acetate buffer¹¹ the product was white, insoluble in water, or *t*-butyl alcohol alone or with a little water. It was readily soluble in wet acetic acid, from which it did not precipitate on addition to much water. This seemed to indicate the solubilizing effect of the pyridine acetate part of the polymer. It was partially dissolved by 6 *N* hydrochloric acid, and dissolved completely when the acid was removed and water added to the solid. The saponified polymer became light pink in a matter of a few hours after preparation, and continued to darken. It was freeze-dried as a suspension in water, and was then a pinkish red, and no longer soluble in wet acetic acid.

Copolymer of Vinylhydroquinone Dibenzoate and α -Methylstyrene.—A 1:1 molar solution of vinylhydroquinone dibenzoate (1.0 g.) and α -methylstyrene (0.34 g.) as a 50% solution in toluene, containing 1.4 mg. of benzoyl peroxide (*ca.* 0.1 mole %) was heated 6 hours at 70°. On dilution with toluene, addition to methanol for precipitation, purification and freeze-drying from benzene, the copolymer was obtained as a white fluffy material. It was soluble in aromatic solvents, insoluble in alcohol, acetic acid and water.

Anal. Calcd. for $(\text{C}_{31}\text{H}_{26}\text{O}_4)_n$, (1:1 ratio): C, 80.5; H, 5.6; sapn. equiv., 231. Found: C, 78.5; H, 5.2; sapn. equiv., 202.

(11) L. Michaelis, ref. 9b, Vol. I, Part II, 1949, p. 1713.

(12) This method of reduction has proved satisfactory in the preparation of pure polymers in the reduced form. Attempts to reduce with stannous chloride in hydrochloric acid yielded polymers which despite careful repeated precipitation contained up to 18% ash. Experiments with chromatographic columns suggest that satisfactory reduction would be clearly obtained with strongly acid potassium iodide (see following paper). Purification by dialysis was abandoned because of difficulties in excluding oxygen, and because the polymer was thrown down in a form which required further purification.

(13) L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, Mass., 1941, p. 395.

(14) H. Kautsky and H. Thiele, *Z. anorg. allgem. Chem.*, **152**, 342 (1926).

(15) The polyvinylhydroquinone dibenzoate of "molecular weight" 52,000, the preparation of which is reported above, was made under conditions not expected to produce very high molecular weight polymer. For this, lower mole per cent. catalyst, lower temperature and higher concentration would be needed.

(16) Due to the lack of sufficient material the rigorous proof that copolymers were obtained could not be demonstrated by the usual method of fractionation combined with elementary analysis of the fractions. However, solubility behaviors do indicate quite clearly the absence of polystyrene and of polyvinylpyridine from their respective copolymers and it seems reasonable to conclude provisionally that these substances are true copolymers.

After saponification, and reduction, purification and freeze-drying from 90% acetic acid the copolymer was obtained as a fluffy white material which slowly became light tan. It was soluble in 90% acetic acid and insoluble in aromatic solvents and in water.

Anal. Calcd. for $(C_{17}H_{18}O_2)_n$, (1:1 ratio): C, 80.3; H, 7.1. Found: C, 71.3; H, 7.2.

Cross-linked Terpolymer.¹⁷—A 1:1 molar ratio of vinylhydroquinone dibenzoate (0.40 g.) and styrene (0.122 g.) was mixed with a small ratio of "divinylbenzene" (0.024 g. of the commercial mixture) and 5.5 mg. of benzoyl peroxide (1% by wt.). The mixture was warmed and added to 5 ml. of 1% polyvinyl alcohol solution rapidly stirred under nitrogen at 82°. The droplets first formed soon coalesced to some extent so that the polymerization mixture contained beads of quite different sizes. After 5 hours the product was separated, crushed to small white granules, washed and dried over P_2O_5 .

Anal. Calcd. for $(C_{20}H_{24}O_4)_n$, (1:1 ratio neglecting the divinylbenzene): C, 80.3; H, 5.4. Found: C, 77.8; H, 5.0.

The polymer was saponified, subjected to reduction with hydrosulfite and isolated as a light tan material insoluble in all solvents tried, even when hot.

Effect of Exposure to Air.—All the polymers after saponification except one tended to turn tan or pink in the air, especially so if wet or in the presence of alkali. The product seems under some conditions to be reducible to the colorless form. It is not yet profitable to propose a detailed explanation, but it appears that the red color may be associated with conditions which would conduce to quinhydrone formation.

Electrometric Titrations.—These were carried out according to the general procedure described by Michaelis.¹¹ The experiments were often of long duration when heterogeneous systems were present, and the use of a Leeds and Northrup Company "Speedomax" recording potentiometer was extremely convenient since the course of the reactions could be followed without errors due to fatigue. The instrument has a range of 200 mv. and was connected to a student potentiometer which permitted setting the range from 0 to 1.5 v. The instrument could be read to 0.5 mv.; however, the potential changes were such that readings to 1 mv. sufficed.

Representative data, obtained in the electrometric titration of these polymers, are shown in the Figs. 1 and 2. In general, the behaviors observed are of two types: what might be classed as "common" oxidation behavior, and oxidation with precipitation. An extreme type, which seems to be related to the second of these is sometimes observed. Here the potential reaches a certain value fairly early in the titration, *ca.* at 25–30% oxidation. It then falls steadily with further addition of oxidant to the endpoint, when there is an extremely rapid rise. This type is not discussed below. The protein behavior of these substances combined with the present lack of complete understanding of them is the reason for this arbitrary classification.

The more or less normal or common behavior seems to be associated with polymer which remains in solution during the course of the titration or which is present in extremely finely dispersed form—for example, as an opalescent "solution." This kind of behavior is sometimes observed with polyvinylhydroquinone, Fig. 1. For example, 5.23 mg. of white, freshly prepared polyvinylhydroquinone dissolved in 90% (v.:v.) acetic acid¹¹ (pH 0) and having a total volume of 200 ml., gave a faintly opalescent solution. Two platinum electrodes gave the same potential at the start and at the end of the titration. The solution was titrated with bromine in 90% acetic acid, taking 40 readings (additions of oxidant) over 1 hour and 10 minutes. The potentials were quite stable except near the end (above 0.467 v.), when there was a tendency to drift downward slowly. After about 0.60 ml. of oxidant (end-point 2.30 ml.) the solution was observed to take on a pink tinge which intensified to about the mid-point, with increasing turbidity, then decreased. At the end-point the substance was largely in a yellow form and precipitated out. It was then found to resist reduction with colloidal palladium and hydrogen. The sample (calcd., 0.0768 meq.) used 2.30 ml. of 0.0279 *N*

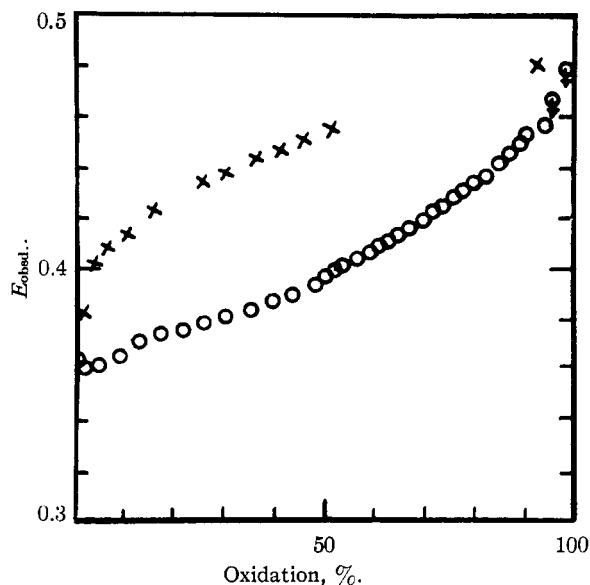


Fig. 1.—Lower curve, titration of 5.23 mg. of polyvinylhydroquinone in 200 ml. of 90% acetic acid using bromine in 90% acetic acid as oxidizing agent; upper curve, titration of hydroquinone in 200 ml. of 90% acetic acid using the same titrating agent; the small arrows indicate direction of drift of potential.

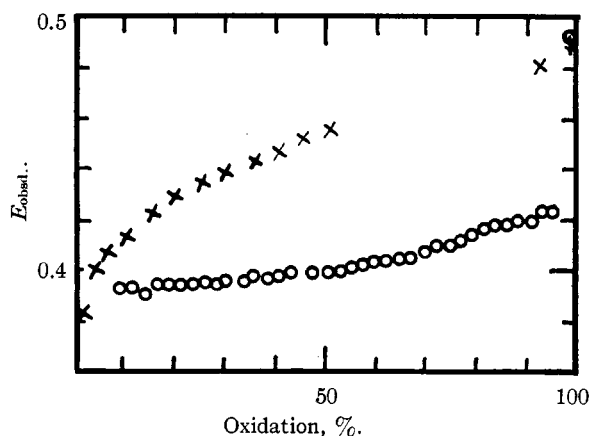


Fig. 2.—Lower curve, titration of 14.765 mg. of vinylhydroquinone- α -methylstyrene copolymer in 200 ml. of 90% acetic acid, with bromine in 90% acetic acid. The polymer precipitated during the titration; upper curve, titration of hydroquinone in 200 ml. of 90% acetic acid with bromine in 90% acetic acid; the small arrow indicates direction of drift of potential.

bromine solution, thus accounting for 0.0641 meq., or 83.5% of theoretical. Whether the color change was due solely to changes in particle size, or to quinhydrone formation, or related phenomena is not established.

Titrations with polymer which had been stored for some time in a closed dark bottle, and had taken on a pale tan color indicated, for example, 41% of the theoretical oxidizable groups available.

Many of the titrations did not give as stable potentials as the one described, and there was considerable difficulty in obtaining electrodes which agreed with each other, though in other cases stable, duplicatable systems were found. The common observation was that on addition of oxidant the potential shot up. It returned more or less rapidly (depending on whether the substance was finely dispersed or not) to a value which might be stable. In other cases a stable value was not reached, but a slow drift continued, and the titration was continued in these cases when the drift

(17) We are indebted to Dr. D. L. Schoene, Naugatuck Chemical Div., U. S. Rubber Co., for much valuable advice on methods.

had slowed to *ca.* 1–2 mv./2.5 min. For this reason, and others associated with uncertainties about the physical state of the system, the potentials are not to be considered as other than relative, semi-quantitative, values for comparison of the systems. They are plotted as observed, with the hydroquinone curves obtained under the same conditions for reference.

If the polymer precipitates during the titration, while still leaving some in solution, or if it starts as an opalescent solution and becomes flocculated during the titration, curves such as that shown in Fig. 2 are obtained.¹⁸ These are quite regularly obtained in aqueous media such as Fieser's alcoholic buffer¹⁹ or in phosphate buffers, etc.

As an example, 14.765 mg. of vinylhydroquinone- α -methylstyrene copolymer was dissolved in 90% acetic acid and titrated in 200-ml. solution. The solution was slightly tinged with pink, and there were a few minute fibrous particles present. On titration with bromine in 90% acetic, quite stable potentials were obtained except at the beginning and end of the titration, where some drifting, downward in both cases, occurred. At one point during the titration (44 additions of oxidant, 2 hours and 5 minutes duration) two platinum electrodes were compared and found to give the same value. The solution became gradually opalescent and took on an orange-pink cast. At the end of the titration the solution was faintly yellow with white flocs floating in it, and orange-colored filamentous material wound around the electrodes. The sample (0.116 meq. calcd. for a 1:1 ratio of monomers) utilized 4.15 ml. of 0.0277 *N* oxidant, indicating 0.115 meq. reactive groups. The substance was treated with colloidal palladium and hydrogen overnight but retitration was difficult, and the unsharp end-point (drifting upward of the potential) indicated at most 0.035 meq. reactive groups.

The titration of the copolymer of vinylhydroquinone with styrene would be expected to yield results like those with the α -methylstyrene copolymer. The polymer with vinylpyridine was oxidized, but more experience with this substance is needed before we are ready to report on it. Oxidation behavior of the cross-linked polymer is described in the following paper.

Discussion

Accumulated experience in working with electron exchange-polymers based on data of which only a small representative part has been given above, makes it possible to describe some of the general characteristics of these substances. The phenomena observed have not all been clearly understood so that many of the conclusions which can be drawn at present must be of a tentative kind.

In general, the *physical properties* of the linear polymers so far prepared are such as would be expected from high molecular weight substances with polar groups. They are all insoluble in water. The benzoylated polymers are more soluble in toluene and less in acetic acid; the acetylated polymers, the reverse. The free hydroquinone polymers are not very soluble in glacial acetic acid, but if a little water is added they dissolve readily, suggesting that intermolecular interactions of the polar groups may cross-link the chains but be readily replaced by interactions with water molecules, thus breaking down the network structure. The oxidized forms of the polymers are quite insoluble in the usual solvents.

(18) A. Geake, *Trans. Faraday Soc.*, **34**, 1395 (1938); A. Geake and J. T. Lemon, *ibid.*, **34**, 1409 (1938).

(19) L. F. Fieser, *This Journal*, **52**, 5204 (1930).

The *chemical properties* of the esterified polymers are as expected. Considering that they are high molecular weight substances they give reasonable saponification equivalents.

The free hydroquinone polymers exhibit some instability to oxidizing conditions. Reversible behavior has been demonstrated (see also the following paper) but there appears to be a tendency in the present polymers for some change to prevent all the initially present groups, once oxidized, from becoming readily reduced and available for re-oxidation. Reductive titration of the oxidized polymers with titanous sulfate (the very acid solutions) or chromous acetate has not usually been successful. Sodium hydrosulfite in neutral or slightly alkaline solution seems promising, but the side reactions may be undesirable in long experiments.

The titrations were carried out in quite dilute solutions (*ca.* 0.001 *N*), and this may in part account for the instability of the electrodes where observed. The necessary long duration of the experiments resulted, apparently, from the heterogeneity of the systems, and seemed related to the state of subdivision as observed with the eye. The following paper shows how, with the proper conditions, rapid quantitative reactions can be achieved.

The growing interest in oxidation-reduction polymers prompts calling attention to several other substances which should show these properties. Cairns and co-workers²⁰ converted *N*-methoxymethylpolyamides into the *N*-mercaptomethyl form and obtained substances which were readily oxidizable to the disulfide form, with cross-linking and consequent insolubility. The disulfides could be reduced to the mercapto state by suitable reagents such as an excess of mercaptan.

Certain photographic colloids have been prepared which should show oxidation-reduction polymer properties.²¹ These substances are prepared, in general, by forming cyclic acetals from aldehydes and polyvinyl alcohol. The aldehydes are coupled with color-developer molecules to form what should behave as an oxidation-reduction system. Many variations on this theme have been described by the authors²¹ as well as the scheme of using aldehydes with solubilizing groups.

Lautsch and co-workers²² have described high polymers in which active groups of the hemin series are incorporated. These show interesting catalytic and optical properties.

NEW HAVEN, CONN.

(20) T. L. Cairns, H. W. Gray, A. K. Schneider and R. S. Schreiber, *ibid.*, **71**, 655 (1949).

(21) G. L. Dorough and D. M. McQueen, U. S. Patent 2,310,943 (Feb. 16, 1943), and D. M. McQueen and D. W. Woodward, *This Journal*, **73**, 4930 (1931), give examples and references. We are indebted to Dr. D. W. Sargent for calling this work to our attention.

(22) W. Lautsch, W. Broser, W. Rothkegel, W. Biedermann, U. Doering and H. Zoschke, *J. Polymer Sci.*, **8**, 191 (1952).