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Electron Exchange Polymers. VI. Preparation of Water-soluble and Water-swellable Polymers

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The preparations of sulfonated linear copolymers of vinylhydroquinone and α-methylstyrene are described. Vinylhydroquinone dibenzoate is polymerized in toluene solution with α-methylstyrene to form a linear polymer; the cross-linked polymers are produced in bead form by suspension polymerization using divinylbenzene as cross-linking agent, and starch as protective colloid. These polymers are purified, then sulfonated with concentrated sulfuric acid, the bead polymers being first swollen with benzene or toluene. The resulting linear polymers may be made soluble in water; the cross-linked polymers swell in water or aqueous solutions. Both types show reasonable oxidation–reduction capacities.

In the first paper of this series, a variety of types of electron exchange-polymers was proposed.[2] Several representatives of these types have been specifically prepared as electron exchangers. Hydroquinone–formaldehyde polymers, and copolymers with other phenols have been prepared by Manecke and others.[3] Thiol derivatives have been reported by Gregor, Overberger and their co-workers.[4] Further, Lautsch and co-workers[5] have described the preparation and properties of high molecular weight substances incorporating porphyrin groups. Although we have carried out some preliminary investigations on hydroquinone–formaldehyde polymers, on butyl polyvinylpyridinium bromide and a N-mercaptomethylpolyamide,[6] representing the types of exchangers initially suggested, we have centered our attention chiefly on derivatives of vinylhydroquinone for the reasons already laid down.[2] One limitation to many polymers and copolymers of vinylhydroquinone, however, is their poor solubility and even wettability in water. This paper describes methods for overcoming this limitation.

One obvious method is to copolymerize the oxidation–reduction monomer with an appropriate monomer which contains solubilizing, or potentially solubilizing groups, such as vinyl pyridine[7] or ethyl fumarate. Another method is to convert already-formed copolymers into more soluble forms by introducing suitable groups. This has turned out to be a simple and elegant method.

The suitable copolymer[7] is treated with concentrated sulfuric acid for an appropriate period of time and is then transferred by stages to pure water. If the initial copolymer is a linear one, the sulfonation treatment can result in a water-soluble electron and ion-exchange polymer, or if the molecular weight of the original copolymer was very high, the sulfonation product yields a swollen gel in water. If the original copolymer is cross-linked, the sulfonated product is readily wetted by water and swells in water. The extent of swelling is sensitive to acid and salt concentration as with any ion-exchange resin.

These water-wettable polymers have been prepared in bead form, and as such have shown both oxidation–reduction and ion-exchange behavior when utilized in a chromatographic tube in break-through experiments,[8] as will be reported further.

Experimental and Results

Starting materials and methods were the same as described previously.[7]

Linear Copolymer (I).—This was prepared by polymerizing 2,5-dibenzoxystyrene with α-methylstyrene in the molecular ratio 1:1. Forty g. of vinylhydroquinone dibenzoate (2,5-dibenzoxystyrene) and 14.7 g. of α-methylstyrene, as a 40% solution in toluene, was treated with 57.1 mg. of benzoyl peroxide (*ca.* 0.1 mole %) and heated 106 hr. at 58° followed by 48 hr. at 70°; 24 hr. at 85° and 23 hr. at 90°. The resulting viscous solution was diluted with toluene and precipitated by addition to more than 5 volumes of methanol. In order to get thorough contact between solution and precipitant the precipitated mass was vigorously agitated with methanol in a Waring Blendor. The mass was thoroughly broken up and became easily manageable. It was redissolved in toluene and reprecipitated a total of 5 times to remove soluble and low molecular weight material. Very high molecular weight, insoluble material was centrifuged from the toluene supernatant before precipitation. The purified polymer was dissolved in benzene, centrifuged from a little insoluble material and freeze-dried, yielding 35.5 g. (65% yield) of fluffy, white material.

Saponification equivalent[7] for a 1:1 ratio of vinylhydroquinone dibenzoate: α-methylstyrene 231; found, 207, which implies a ratio of 1.71:1.00.

Anal. Calcd. for $(1.71 \times C_{22}H_{16}O_4 + C_9H_{10})_n$: C, 79.2; H, 5.3. Found: C, 78.9; H, 5.3.

Saponified Linear Copolymer (II).—The above copolymer (1.25 g.) was saponified with 10 ml. of 1.09 *N* sodium ethylate, purified, reduced and freeze-dried from 90% *t*-butyl alcohol, as previously described,[7] giving 0.535 g. of light pink material. This was readily soluble in 90% acetic acid, dioxane and 90% *t*-butyl alcohol.

Anal. Calcd. for $(1.71 \times C_8H_8O_2 + C_9H_{10})_n$: C, 77.6; H, 6.79. Found: C, 73.7; H, 6.9.

Potentiometric oxidation of 26.0 mg. of this copolymer (0.253 meq., basis 1.71:1 ratio) in 90% acetic acid with bromine in 90% acetic acid indicated 67% (0.172 meq.) of theoretically present oxidizable groups available. Precipitation occurred from the beginning of the experiment. Potentiometric oxidation of 26.3 mg. (0.256 meq., same basis) in 80% dioxane 0.2 *M* in HCl and 0.2 *M* in LiCl by bromine in the same solvent indicated 92% (0.234 meq.) of groups available. Precipitation did not occur until the end of the titration. Apparently, when precipitation occurs early, some oxidizable groups become unavailable to the oxidant.

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[1] This work is largely taken from the Dissertation presented to the Graduate School, Yale University, in partial fulfillment of the requirements for the Ph.D. degree, as also was the work referred to in references 7 and 8.

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

(3) V. Verplanck, M.S. Thesis, 1948; G. Manecke, *Z. Elektrochem.*, **57**, 189 (1953); **58**, 363, 369 (1954); S. Soloway and L. Schwartz, *Science*, **121**, 730 (1955); V. Verplanck and H. G. Cassidy, *J. Polymer Sci.* **19**, 307 (1956).

(4) H. P. Gregor, D. Dolar and G. K. Hoeschele, THIS JOURNAL, **77**, 3675 (1955); C. G. Overberger and A. Lebovits, *ibid.*, **77**, 3675 (1955).

(5) For bibliography see W. Lautsch, W. Broser, W. Biedermann and H. Gnichtel, *J. Polymer Sci.*, **17**, 479 (1955); *Angew. Chem.*, **66**, 123 (1954).

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

(7) M. Ezrin, I. H. Updegraff and H. G. Cassidy, *ibid.*, **75**, 1610 (1953).

(8) H. G. Cassidy, M. Ezrin and I. H. Updegraff, *ibid.*, **75**, 1615 (1953).

Sulfonated Linear Copolymer (III).—Linear copolymer (I), *ca.* 40 mg. was treated with 1.0 ml. of concentrated sulfuric acid at 0–5° for 35–40 minutes. The polymer was dispersed with stirring, after addition of the acid, and formed a clear solution. Progress of the sulfonation could be followed by taking a small drop of the liquid and putting it in water. At the end of the process it dissolved completely. The mixture was then diluted and titrated potentiometrically, or the *p*H was adjusted before titration. No attempt was made to isolate the sulfonated polymer.

Copolymer (I), 42.7 mg. sulfonated with 1.8 ml. concd. sulfuric acid 35 min. at 0–5°, added to 100 ml. of water, *p*H brought to 0.53 with 0.8 ml. of concd. sulfuric acid, titrated with ceric sulfate in 0.048 *N* sulfuric acid, *p*H 0.54, consumed 0.205 meq. oxidant. This accounts for 99.5% of the theoretically oxidizable groups in a 1.71:1 ratio copolymer (the ratio found by saponification). This indicated that in the sulfonation procedure the protecting benzoyl groups were cleaved off. In another experiment 79.5% of the theoretical was accounted for, but here a few flecks of polymer failed to dissolve.

Cross-linked Copolymer (IV).—This preparation was modified from that given for a cross-linked terpolymer.[7] Vinylhydroquinone dibenzoate (5.00 g.) and α-methylstyrene (1.737 g., mole ratio 1:1) were mixed with 0.712 g. of divinylbenzene mixture (*ca.* 5% divinylbenzene isomers on a weight basis to the total monomers) and 0.111 g. of benzoyl peroxide. The mixture was gently warmed to give a clear solution, and this was introduced into a stirred mixture of 62 ml. of water and 1.85 g. of soluble starch heated to *ca.* 80° under nitrogen. After 2.75 hr. the droplets, formed under the stirring action, had hardened, and after 6 hr. stirring was stopped. The heating was continued for 4 hr. more.

The mixture was left overnight to cool. The hard, white, opaque beads were washed many times with cold water to remove starch; dried weight, 6.84 g. They were then thoroughly extracted with toluene, in which they swelled considerably. This lot was set aside for special quantitative studies.

This preparation was repeated several times with substantially the same results. It was, however, difficult to obtain good sequences of analytical results on the polymers (see below). Two different preparations, prepared as described above, were repeatedly extracted with warm benzene, before drying.

Anal. Calcd. for $(C_{31}H_{26}O_4)_n$ (1:1 ratio, neglecting divinylbenzene): C, 80.5; H, 5.7. Found: C, 79.5, 79.8; H, 5.6, 5.9.

Saponified Cross-linked Copolymer (V).—The bead polymers of the type IV were saponified by heating at atmospheric pressure, under nitrogen for 2.5 hr. with sodium ethylate. After titration and further acidification the resin was washed thoroughly with water and then with warm 90% *t*-butyl alcohol. The addition of these last washes to water produced no precipitation, indicating that no soluble polymer had been present in the saponified polymer. The "bead" form was well retained. Swelled in *t*-butyl alcohol, the beads appeared translucent. They were not swelled by water, and were opaque and light tan in color. Saponification equivalent for one batch of V was 224, 227. Calcd. for 1:1 ratio, neglecting divinyl benzene, 231.

Anal. Calcd. for $(C_{17}H_{18}O_2)_n$ (1:1 ratio, neglecting divinylbenzene): C, 80.3; H, 7.1. Found: C, 75.6; H, 7.7, and for another batch, C, 75.2; H, 7.8. (These results are consistent with the presence of residual moisture inside the beads.) The generally poor analytical results obtained with beads is consistent with the extreme difficulty found in purifying them.

When the beads from one batch were placed in a chromatographic column and reduced with acid KI solution, a small amount of iodine was set free (*ca.* 0.034 meq. for 90.2 mg. of dry beads) indicating that some oxidation had occurred during working up. Subsequent oxidation with bromine in 90% acetic acid indicated a quite reproducible equivalent weight of 92, while the calculated weight on a 1:1 basis is 122. The oxidized beads were bright yellow.

Sulfonated Cross-linked Copolymer (VI).—The copolymer of type IV was sulfonated as follows. The beads (0.2058 g.) were swollen[9] by treatment with hot benzene several times in a sintered glass funnel attached to a suction flask for convenient removal of the liquid. The excess benzene was then removed, taking care to leave the resin in a swollen condition. The resin was then treated on the funnel with 2–3 ml. of concd. sulfuric acid for 2²/₃ hr., whereupon the color became reddish-brown. After removal of the excess acid the resin was treated successively for short periods with 90, 80, 60, 40, 20, 10 and 5% sulfuric acid, and washed with water several times. The color was now light pink. The particles (there had been some fragmentation of the beads) were washed with 95% alcohol, then water, and after filtering were placed in a desiccator. The resulting brown particles were hygroscopic. They became highly swollen and nearly colorless in water. They probably contained residual sulfuric acid, and possibly some benzoic acid or uncleaved benzoyl groups that may have become sulfonated, because on analysis, they yielded C, 44.9; H, 6.0; S, 12.2. On the basis of the sulfur analysis, this calculates for 1.4 SO_3H groups per assumed unit of vinylhydroquinone:α-methylstyrene (1:1), but this would calculate for C, 55.8; H, 4.95; S, 12.2. Further, this material was saponified by the usual procedure, with sodium ethylate in a sealed tube,[7] and after repeated treatment with hydrochloric acid, thorough washing with water, and drying *in vacuo*, the analysis found was C, 38.6; H, 6.8; S, 11.2. On the basis of sulfur this calculates for 1.23 SO_3H groups per assumed vinylhydroquinone:α-methylstyrene residue (1:1), when the calculated values would be: C, 57.8; H, 5.1; S, 11.2. That the problem was either one of purification, or that the poor analytical results may be laid to the analytical intractability of the substances, follows because on "saponification" the % S should have increased if any residual benzoyl groups had been present, but the C values would have been affected very little. When 99.5 mg. of dried particles was put on a pad of glass wool in a 10-ml. buret the resin formed a bed *ca.* 10.5 mm. deep. In this buret 1 ml. = 33.0 mm., thus the resin bed had a volume of 0.32 ml. When swollen with water the bed measured 34.5 mm. deep, *i.e.*, *ca.* 7.3 ml. of water was taken up per gram of the dried resin.

When this bed was treated with 2.5% KI in 0.1 *N* HCl no iodine was released, but the bed shrank to *ca.* 25 mm. Washing with water returned the bed depth to *ca.* 33 mm. When washed with *p*H 7.9 phosphate buffer the bed depth changed to *ca.* 25 mm. In this state a slow stream of 0.05 *N* iodine in KI, buffered at *p*H 7.9 was passed through the bed. The bed was washed with aqueous alcohol to remove sorbed iodine (bed height *ca.* 15 mm.). Total iodine reduced 0.551 meq. The resin was dark-reddish-orange. Reduction with acid KI showed a capacity of 0.392 meq., with the resin returning to its original light tan color.

These data show that oxidation–reduction polymers that are capable of dissolving in aqueous media, as well as cross-linked oxidation–reduction polymers that swell in water and respond to aqueous oxidizing and reducing agents have been prepared. The method of preparation seems straightforward. A subsequent report will demonstrate in a quantitative way that a new dimension, that of oxidation–reduction, has been in this way added to the acid–base properties of ion-exchange resins.

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[9] R. M. Wheaton and D. F. Harrington, *Ind. Eng. Chem.*, **44**, 1796 (1952).