501. *Chelating Polymers Derived from Poly-4-hydroxystyrene.*

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Cross-linked copolymers of 4-acetoxystyrene and divinylbenzene have been prepared. Hydrolysis of the polymers yielded insoluble poly-4-hydroxy-styrene with different degrees of cross-linking. It has been shown that many reactions of phenol can be carried out on the insoluble polymers. Normal electrophilic substitution reactions on poly-4-hydroxystyrene are restricted to the position *ortho* to the hydroxyl group, and thus lead to polymers with potential chelating functions. Physicochemical studies have shown that most of the polymers prepared in this way have ion-exchange and chelating properties in aqueous solution.

NUMEROUS polymers containing chelating or complexing groups have been described.[1] The majority are based on polymers of indefinite structure. For example, chelating polystyrenes are generally prepared by substitution of the polymer and, as a result, the chelating groups are in unknown ring positions. This Paper describes the preparation of cross-linked polymers derived from 4-hydroxystyrene. Normal electrophilic aromatic substitution reactions with poly-4-hydroxystyrene should result in substitution exclusively in the position *ortho* to the hydroxyl group. It has thus been found possible to prepare polymers of known chemical structure, some of which have potential interest as ion-exchange or chelating materials.

RESULTS AND DISCUSSION

Preparation of Polymers.—The preparation of hydroxystyrenes has been described by Flood and Nieuwland,[2] Dale and Hennis,[3] and Corson *et al.*[4] Stern, English, and Cassidy [5] reported a general method for poly(hydroxystyrenes). Dale and Hennis described 4-hydroxystyrene as a very unstable solid that rapidly softened at room temperature, presumably because of polymerisation. The controlled polymerisation of 4-hydroxy-styrene, and its copolymerisation leading to cross-linked polymers, has not been previously described. Indeed, its rate of polymerisation is too high to permit controlled polymeris-ation. However, the precursor in the preparation described by Corson *et al.*,[4] namely 4-acetoxystyrene, was relatively stable at room temperature, and could be polymerised under controlled conditions at 65° using a suitable free-radical initiator. Hydrolysis of cross-linked poly-4-acetoxystyrene, to the hydroxyl analogue was readily achieved. Subsequent reactions on the insoluble polymer led to seventeen new polymers. Some physicochemical properties of the polymers, including swelling data, and sodium–potassium and copper–nickel capacities, are described.

4-Acetoxystyrene polymerised smoothly in benzene at 65° in the presence of $\alpha\alpha'$-azo-bisisobutyronitrile. Its rate of polymerisation was of the same order as that of divinyl-benzene under similar conditions. Copolymerisation of the two monomers led to insoluble cross-linked polymers. The reproducibility of the polymerisation products indicated a statistical distribution of the divinylbenzene, and random cross-linking. A series of cross-linked 4-acetoxystyrene polymers containing nominally 2, 5, and 10 moles % of divinyl-benzene was prepared, and their swelling in benzene was measured (see Table 1). As expected, increased cross-linking resulted in decreased swelling. Elemental analyses and infrared spectra of the polymers confirmed the postulated structure (I).

Hydrolysis of cross-linked poly-4-acetoxystyrene proceeded smoothly in alkaline

[1] Millar, *Chem. and Ind.*, 1957, 606.
[2] Aquinas Flood and Nieuwland, *J. Amer. Chem. Soc.*, 1928, **50**, 2566.
[3] Dale and Hennis, *J. Amer. Chem. Soc.*, 1958, **80**, 3645.
[4] Corson, Heintzelman, Schwartzman, Tiefenthal, Lokken, Nickels, Atwood, and Pavlik, *J., Org. Chem.*, 1958, **23**, 544.
[5] Stern, English, and Cassidy, *J. Amer. Chem. Soc.*, 1957, **79**, 5792.

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aqueous dioxan, to give the required cross-linked poly-4-hydroxystyrene (II), characterised by analysis and infrared spectrum. Indeed, infrared analysis was a useful means of following the hydrolysis. Several samples of polymers containing a nominal 5 moles % of divinylbenzene had swelling characteristics [6] in reasonable agreement (see Table 1).

TABLE 1.

Solvent uptake of (a) poly-4-acetoxystyrene and (b) poly-4-hydroxystyrene.

	(a)			(b)					
Divinylbenzene (moles %)	1	2	10	1	2	10	5	5	5	5
Solvent		Benzene			Ethanol		Water		Ethanol	
Solvent uptake (g./g.)	7	3·6	1·16	5·1	3·9	1·6	1·25	1·30	3·15	2·94

Sulphonation. The cross-linked poly(hydroxystyrene) reacted smoothly with concentrated sulphuric acid. Sulphonation, for 5 hours at room temperature, gave a polymer containing sulphur slightly in excess of that required for cross-linked poly-4-hydroxystyrene-3-sulphonic acid (III). The ion-exchange capacity of the polymer in neutral solution was 95% of that calculated for the sulphonic acid group, and 65% of the calculated exchange for the hydroxyl group was obtained in alkaline solution. Poly-4-hydroxystyrene itself had an exchange capacity of approximately 3·5 mequiv./g. in 0·1N-sodium hydroxide solution. The low dissociation constant of phenol, and the slow rate of equilibration of the exchange OH $\longrightarrow$ ONa in the polymer, could account for the low capacity in alkaline solution.

Reaction between concentrated sulphuric acid and poly-4-acetoxystyrene at 100° resulted in sulphonation of the polymer and hydrolysis of the O-acetyl group. The sulphur content of this polymer approached that required for a disulphonic acid. The water uptake of the polymer (5·48 g./g.) was considerably higher than that for the monosulphonic acid polymer, whilst the ion-exchange capacities in neutral and alkaline solution were 92% of those calculated for poly-4-hydroxystyrene-3,5-disulphonic acid (IV).

Sulphonation of the poly(hydroxystyrene) at 100° with either concentrated sulphuric acid or oleum, gave polymers with high sulphur contents but markedly decreased swelling in water (see Table 2). Similarly, the reaction between oleum and poly(acetoxystyrene)

TABLE 2.

Properties of sulphonated polymers: (a) before hydrolysis; (b) after hydrolysis.

Polymer *	Conditions	Sulphur content (%) †		Water uptake (g./g.)		Ion-exchange capacities (mequiv./g.) †			
						(a)		(b)	
		(a)	(b)	(a)	(b)	NaCl	NaOH	NaCl	NaOH
PHS	Conc. H₂SO₄ at 25° for 5 hr.	18·3 (16)	—	3	—	5·35 (5)	8·65 (10)	—	—
PAS	Conc. H₂SO₄ at 100° for 7 hr.	20·2 (22·5)	19·75	5·48	5·4	6·5 (7·1)	9·8 (10·7)	5·7	8·4
PHS	Conc. H₂SO₄ at 100° for 7 hr.	20·4	21·0	1·75	4·0	5·4	9·3	5·4	8·7
PHS	Oleum at 100° for 1 day	22·0	21·05	1·77	4·0	4·3	6·3	5·7	8·5
PAS	Oleum at 100° for 1 day	23·2 (24·1)	22·0	1·59	5·45	3·9 (3·8)	6·7 (3·8)	6·1	9·0

* PHS = poly-4-hydroxystyrene; PAS = poly-4-acetoxystyrene. † Calc. values in parentheses.

at 100° gave a polymer with a high sulphur content, but with decreased swelling in water and a low ion-exchange capacity. Hydrolysis of these polymers, by heating in alkaline solution, resulted in products with slightly decreased sulphur contents, but with much increased water uptake and ion-exchange capacity. Most polymers contained some inactive sulphur, in amounts from 1·1% in the polymers where sulphonation had been carried out at room temperature, to 10·7% in cases where it was effected with oleum at

[6] Pepper, Reichenberg, and Hale, *J.*, 1952, 3129.

100°. Alkaline hydrolysis of the polymers in all cases reduced the amount of inactive sulphur. The results obtained in the sulphonations are given in Table 2. It is apparent that vigorous sulphonation may lead to additional cross-linking within the polymers, and that the mechanism necessarily involves the sulphonic acid group.

Sulphonation of *p*-cresol with an equal weight of sulphuric acid at 100° yields the *o*-hydroxy-sulphonic acid.[7] With an excess of oleum at 100°, *p*-cresol is converted in 87% yield into the sulphonylide.[7,8] Only at higher temperatures (*ca.* 160—180°) is sulphone formation significant.[9] Even when heated with oleum,[10] *p*-cresol is said to form less than 10% of the sulphone.

In a study of the chemical nature of sulphonated Novolac ion-exchange resins, Vasil'ev and Vansheidt [11] postulated the formation of sulphonylides to explain the presence of inactive sulphur. In their work, however, the reactions were obscured by the presence of sodium sulphite and formaldehyde, and the possible introduction of sulphomethyl groups $(CH_2 \cdot SO_3H)$. It is possible that sulphones and/or sulphonylides may be present in the sulphonated polyhydroxystyrenes. The facile hydrolysis of the polymers suggests that cross-linking occurs by the formation of sulphonylides rather than the more stable sulphones.[12] Although analytical data indicate a slight decrease in sulphur content with hydrolysis, this may be explained by the increase in molecular weight accompanying the hydrolysis of a sulphonylide. The calculated sulphur content of polymer (V) is 24·4%. Hydrolysis without any loss of sulphur would give the polymer(IV), with a calculated sulphur content of 22·5%. Thus, the decreased water-swelling of the polymers with increased sulphur content and increased inactive sulphur, and the changes that accompany hydrolysis, including the decrease in sulphur content, may all be explained by the formation of sulphonylides.

(I: R = Ac) (III) (IV) (V)
(II: R = H)
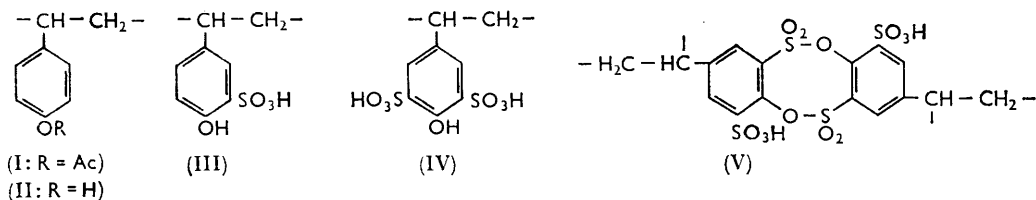
Polymers Containing Nitrogen.—Nitration of cross-linked poly-4-hydroxystyrene proceeded smoothly at room temperature to give a stable yellow polymer. The nitrogen content and the infrared spectrum of the polymer were as expected for poly-4-hydroxy-3-nitrostyrene (VI). As predicted, the introduction of the nitro-group *ortho* to the hydroxyl group enhanced the dissociation constant of the phenol, a fact reflected in the increased ion-exchange capacity of the polymer. The polymer was potassium-selective as expected.[13]

Reduction of the nitrophenol polymer to the *o*-amino-analogue required carefully controlled conditions. The ease of oxidation of *o*-aminophenol is well known, and it is not surprising that the polymer should likewise be susceptible to oxidation and side-reactions. Complete reduction was achieved, however, by reaction with a mixture of sulphur and sodium sulphide. The properties of the reduced polymer agreed with those postulated for poly-3-amino-4-hydroxystyrene (VII). Infrared spectra, elemental analysis, and the

[7] Steinkopf and Hübner, *J. prakt. Chem.*, 1934, **2**, 141, 193; Gibson, *ibid.*, 1935, **2**, 142, 218; Anchütz and Hodenius, *Annalen*, 1918, **415**, 74.
[8] Bischoff, *Ber.*, 1897, **30**, 487; Fromm, Forster, and Scherschewitzki, *Annalen*, 1912, **394**, 344.
[9] Zehenter, *Monatsh.*, 1912, **33**, 333.
[10] Zehenter, *Monatsh.*, 1916, **37**, 587.
[11] Vasil'ev and Vansheidt, *J. Appl. Chem.* (U.S.S.R.), 1959, **31**, 1510; **32**, 2650.
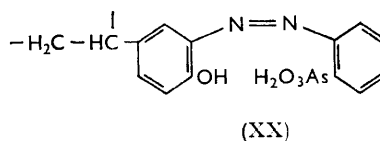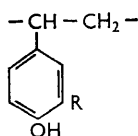[12] Suter, " The Organic Chemistry of Sulfur," Wiley, New York, 1944.
[13] Skogseid, " Noen Derivater Av Polystyrol," Aas and Wahls, Oslo, 1948, Ph.D. Thesis, Trondheim, 1946.

base-exchange capacity confirmed the structure. The amino-group could be diazotised in the normal manner.

Polymers Containing Halogen.—Chlorination and bromination of poly(hydroxystyrene) proceeded smoothly at room temperatures to give poly-3-chloro (IX) and -bromo-4-hydroxystyrene (X), respectively, as shown by infrared spectroscopy. In both cases, analyses indicated approximately the theoretical halogen content for the postulated structures. As expected, the nuclear substituted halogens were rather stable, and attempts to replace the chlorine by nitrile and phthalimide groups were only partly (15—20%) successful.

Reaction of poly-4-hydroxystyrene with chloromethyl ether gave the poly(chloromethyl-4-hydroxystyrene) (XI). In this compound, as expected, the chlorine was very reactive. Even dilute aqueous alkali at room temperature hydrolysed the polymer to the corresponding 3-hydroxymethyl derivative (XII). The chloromethylated polymer reacted exothermally with ammonia to give the aminomethyl analogue (XIII). Reaction with potassium cyanide afforded a product containing 65% of the nitrogen calculated for poly-3-cyanomethyl-4-hydroxystyrene (XIV). Likewise, reaction with potassium phthalimide led to a polymer containing 78% of the nitrogen calculated for the phthalimidomethyl-derivative (XV).

(VI) R = NO$_2$
(VII) R = NH$_2$
(VIII) R = AsO$_3$H$_2$
(IX) R = Cl
(X) R = Br
(XI) R = CH$_2$Cl
(XII) R = CH$_2\cdot$OH

(XIII) R = CH$_2\cdot$NH$_2$
(XIV) R = CH$_2\cdot$CN
(XV) R = phthalimidomethyl
(XVI) R = CHO
(XVII) R = CH:N·OH
(XVIII) R = CO·Me
(XIX) R = C(Me):N·OH

Polymers Containing a Carbonyl Group.—Reaction of poly-3-chloromethyl-4-hydroxystyrene with hexamethylenetetramine and glyceroboric acid gave the corresponding salicylaldehyde polymer (XVI). Oximation of the product yielded a polymer containing 60% of the nitrogen calculated for poly-4-hydroxy-3-hydroxyiminomethylstyrene (XVII). The presence of the aldehyde and oxime groups was confirmed by infrared spectroscopy. A more convenient synthesis of poly-3-formyl-4-hydroxystyrene (XVI), by an analogous reaction on poly-4-hydroxystyrene, was partly successful, as judged by infrared spectroscopy and by formation of the oxime.

Introduction of the acetyl group in the 3-position was also partly successful. Reaction of either the phenolic polymer or the poly(acetoxystyrene) with acetic acid containing zinc chloride gave polymers containing the 3-acetyl group, *e.g.*, (XVIII). Subsequent conversion into the oximes resulted in polymers containing 45% of the nitrogen required for poly-4-hydroxy-3-(1-hydroxyiminoethyl)styrene (XIX).

Polymers Containing Acid Groups.—The sulphonation of poly(hydroxystyrene) has already been described. Attempts to prepare the arsonic and phosphonic acid derivatives directly were not successful. However, some success was achieved in the preparation of poly-4-hydroxystyrene-3-arsonic acid (VIII), by a modified Bart reaction. The polymer (XX) was also prepared, thus indicating that conventional diazo-coupling reactions can be carried out on the phenolic polymer. Whilst the conditions used in these experiments were not necessarily optimal, the apparently low degree of substitution in some cases might be expected, and in part explained, on the basis of steric hindrance.

Effect of Polymer Structure on Solvent Absorption.—The solvent absorption of some of the polymers was measured by a modification of the centrifugal method described by Pepper,

Reichenberg, and Hale.[6] The results obtained on some of the polymers containing a nominal 5 moles % of divinylbenzene are given in Table 3.

The water weight-swelling of the phenolic polymer (1·2 g./g.) can be compared with that of sulphonated polystyrene with a similar degree of cross-linking (1·5 g./g.). The slight difference is somewhat deceptive unless one calculates the swelling on a molecular basis. In this case, the difference then represents a decrease in the number of molecules of water of hydration per hydrophilic group, from approximately 15 in the case of the sulphonic acid to 8·3 in the case of the phenol. Despite this lower degree of hydration, the phenolic polymer should form a suitable basis for hydrophilic chelating polymers.

The weight-swelling of the phenolic polymer in ethanol (3·15 g./g.) was substantially higher gravimetrically than in water, but in excellent agreement on a molecular basis, *i.e.*, 8·2 moles/mole for ethanol and 8·3 moles/mole for water. It thus appears that the polymer would also be useful in alcohol or aqueous alcohol.

The effect of *ortho*-substituents on the water absorption of substituted phenol polymers is indicated in Table 3. It is considered that the solvent absorption of the polymers is

TABLE 3.

Solvent absorption of polystyrenes.

Substituent	Water (g./g.)	Water (moles/mole)	Ethanol (g./g.)	Ethanol (moles/mole)
4-Hydroxy	1·25	8·3	3·15	8·2
4-Hydroxy-3-nitro	0·68	6·2	0	0
3-Amino-4-hydroxy	0·53	4·0	0·15	—
3-Chloro-4-hydroxy	0·80	6·9	1·71	5·8

influenced both by steric factors and by the change in the dissociation constant of the phenolic hydroxyl group due to the inductive effect of the *ortho*-substituent.

Apart from the striking similarity in the solvation of poly-4-hydroxystyrene with ethanol and with water, no general correlation was observed between the structure and the alcohol-absorption of the substituted polymers. It is interesting, however, that the 4-hydroxy-3-nitro- and 3-amino-4-hydroxy-polymers have virtually no affinity for alcohol.

Ion-exchange Studies.—The relative affinities of some of the polymers for sodium and potassium ions in aqueous solution were measured. The polymers, contained in columns, were equilibrated for 1 month by passing a solution containing equimolar quantities of sodium and potassium hydroxides through the column. The alkali metals were subsequently eluted with hydrochloric acid, and the amounts of sodium and potassium taken up by the resins determined by flame photometry. The results are given in Table 4. In no instance was the theoretical capacity achieved. Poly-4-hydroxy-3-nitrostyrene proved to be potassium-selective, whilst the parent polymer and the aminophenol showed a slight preference for sodium ions.

TABLE 4.

Ion affinities of some poly-4-hydroxystyrenes.

3 Subst.	SO_3H	Cl	NO_2	—	NH_2
$K_{R,K}/K_{R,Na}$ (g. atom/g. atom)	0·970	1·050	1·725	0·905	0·880
Total capacity (mequiv./g.)	5·56	3·84	4·57	2·41	3·84

Skogseid [13] described some potassium-selective picrylamine and nitrophenol polymers. However, his figures are considerably higher than ours. As the structure and the degree of cross-linking of Skogseid's polymers are not given, the discrepancy may be explained by differences in the polymer matrix.

Chelation Studies.—A cursory examination of the chelating properties of some of the polymers was made. The results (Table 5) were obtained from batch-wise experiments,

TABLE 5.

Chelation of copper and nickel ions by poly-4-hydroxystyrenes (after 7 days).

3-Subst.	Cu^{2+} uptake (mequiv./g.)	Ni^{2+} uptake (mequiv./g.)	Combined uptake	$K_{R,Cu}/K_{R,Ni}$ (g. atom/g. atom)
—	0·43	0·68	1·11	0·6
NO$_2$	0·46	0·81	1·27	0·6
NH$_2$	1·51	0·63	2·14	2·4
Cl	0·32	0·55	0·87	0·6
Br	0·00	1·25	1·25	~0
SO$_3$H	2·39	2·94	5·33	0·8
3,5-(SO$_3$H)$_2$	2·87	3·10	5·97	0·9
CO·Me	0·00	0·00	0·00	—
C(Me):N·OH	0·41	0·77	1·18	0·5
CHO	0·46	0·63	1·09	0·7
CH:N·OH	0·84	0·42	1·26	2·0
CH$_2$·CN	0·64	0·73	1·37	0·9

in which a sample of the polymer was shaken for 7 days with an aqueous solution containing equimolar quantities of cupric and nickel chloride, after which the pH of the solutions and the copper and nickel remaining in solution were measured by standard techniques. As expected, the capacities were generally less than the theoretical values. Most of the polymers were selective for nickel. The bromophenol polymer was, in fact, entirely specific for nickel within the accuracy of the experiments. Only poly-3-amino- and -4-hydroxy-3-hydroxyiminomethylstyrene were copper-selective. The results indicate that some of the materials described have interesting properties which warrant further examination.

EXPERIMENTAL

Cross-linked Poly-4-acetoxystyrene (I).—4-Acetoxystyrene [4] was distilled immediately before use, the fraction boiling at 74—79°/0·35 mm. being used. A solution of 4-acetoxystyrene (28·1 g.), αα'-azobisisobutyronitrile (0·17 g.), and divinylbenzene (1·125 g.), in benzene (38 ml.), was heated for 4 hr. at 65°, with stirring, and kept at 65° for 20 hr. The gel was granulated, washed with benzene, ethanol, and ether, and dried, to yield cross-linked poly-4-acetoxystyrene (29·0 g.) (Found: C, 75·1; H, 6·3. Calc. for poly-4-acetoxystyrene containing 5 moles % of divinylbenzene: C, 75·0; H, 6·3%).

Cross-linked Poly-4-hydroxystyrene (II).—Cross-linked poly-4-acetoxystyrene (29·0 g.) was refluxed for 2 days with sodium hydroxide (14 g.) in 50% aqueous dioxan (700 ml.). The white product was filtered off, washed with 2N-sulphuric acid and distilled water, and dried, to yield cross-linked poly-4-hydroxystyrene (20·0 g.) (Found: C, 79·1; H, 6·9. Calc. for poly-4-hydroxystyrene containing 5 moles % of divinylbenzene: C, 80·6; H, 6·8%).

Sulphonations.—(a) *Monosulphonation.* Cross-linked poly-4-hydroxystyrene (1 g.) was stirred with concentrated sulphuric acid (40 ml.) for 5 hr. at room temperature. The mixture was poured on to ice, and the insoluble polymer filtered off, washed free from acid with distilled water, and dried, to yield a dark insoluble polymer (1·4 g.) (Found: S, 18·3. Calc. for cross-linked poly-4-hydroxystyrene-3-sulphonic acid: S, 16%).

(b) *Polysulphonation.* Samples of poly-4-hydroxystyrene and poly-4-acetoxystyrene were sulphonated using the conditions described in the text and in Table 2. In all cases a polymer : acid ratio similar to that in (a) was used.

(c) *Hydrolyses.* The sulphonated polymers were hydrolysed by refluxing a sample (0·5 g.) with dioxan (50 ml.) and sodium hydroxide (50 ml.; 1N).

Cross-linked Poly-4-hydroxy-3-nitrostyrene (VI).—Cross-linked poly-4-hydroxystyrene (10·3 g.) was stirred for 5 hr. at 25° with concentrated nitric acid (500 ml.). The mixture was poured into distilled water, and the polymer filtered off, washed repeatedly with distilled water, ethanol, and ether, and dried, to yield a yellow product (15·4 g.) (Found: N, 8·6. Calc. for cross-linked poly-4-hydroxy-3-nitrostyrene: N, 8·2%).

Cross-linked Poly-3-amino-4-hydroxystyrene (VII).—Cross-linked poly-4-hydroxy-3-nitrostyrene (2 g.) was refluxed for 24 hr. with sodium sulphide (12 g.) in water (12 ml.) containing sulphur (1·7 g.). The supernatant liquid was decanted from the cooled mixture, and the product washed with sodium hydroxide, water, acetic acid, and water, and dried, to give a

black polymer (1·44 g.). The polymer had a base-exchange capacity of 7·1 mequiv./g. in 0·1N-hydrochloric acid (Found: N, 8·9. Calc. for cross-linked poly-3-amino-4-hydroxystyrene: N, 9·8%).

Cross-linked Poly-3-chloro-4-hydroxystyrene (IX).—Cross-linked poly-4-hydroxystyrene (1 g.) was added to a solution of chloramine T (2·4 g.) in glacial acetic acid (20 ml.) containing a trace of concentrated hydrochloric acid (0·05 ml.), and the mixture was shaken at 25° for 48 hr. The polymer was filtered off, washed with water, and dried, to give a light brown product (1·21 g.) (Found: Cl, 20·6. Calc. for cross-linked poly-3-chloro-4-hydroxystyrene: Cl, 21·9%).

Cross-linked Poly-3-bromo-4-hydroxystyrene (X).—Cross-linked poly-4-hydroxystyrene (1 g.) was stirred with a solution of bromine (1·5 g.) in hydrobromic acid (10·0 ml.) containing a trace of ferric chloride, in a darkened flask, at 25° for 4 hr. and set aside for 68 hr. at 25°. The polymer was filtered off, washed with water, and dried, to give a brown product (1·62 g.) (Found: Br, 38·8. Calc. for cross-linked poly-3-bromo-4-hydroxystyrene: Br, 38·7%).

Cross-linked Poly-3-chloromethyl-4-hydroxystyrene (XI).—Cross-linked poly-4-hydroxystyrene (2 g.) was stirred with freshly distilled chloromethyl ether (15 ml.) for 3 hr. at 25°, and set aside at 25° for 48 hr. The polymer was filtered off, washed with chloroform and ether, and dried, to give a light brown product (2·7 g.) (Found: Cl, 20·1. Calc. for cross-linked poly-3-chloromethyl-4-hydroxystyrene: Cl, 20·3%). The chloromethyl polymer (0·59 g.) was shaken with N-sodium hydroxide (20 ml.) at 25° overnight. The polymer was filtered off and washed with dilute sulphuric acid and water. The filtrate gave a chloride precipitate with silver nitrate, and analysis of the polymer showed the absence of chlorine. The chloromethyl polymer (0·91 g.) was stirred with ammonia (20 ml.; *d* 0·88) at 25° for 3 hr. and set aside overnight. The product was filtered off, washed with water, dilute acetic acid, and water, and dried, to yield a dark yellow polymer (0·76 g.) (Found: N, 5·8. Calc. for cross-linked poly-4-hydroxy-3-aminomethylstyrene: N, 9·0%).

Cross-linked Poly-3-cyanomethyl-4-hydroxystyrene (XIV).—Cross-linked poly-3-chloromethyl-4-hydroxystyrene (1·4 g.) was refluxed with potassium cyanide (3 g.) in acetonitrile (20 ml.) for 5 days. The product was filtered off, washed with alcohol, water, acetic acid, and water, and dried, to give an insoluble polymer (1·24 g.) (Found: N, 5·8. Calc. for cross-linked poly-3-cyanomethyl-4-hydroxystyrene: N, 8·5%).

Cross-linked Poly-4-hydroxy-3-phthalimidomethylstyrene (XV).—Cross-linked poly-3-chloromethyl-4-hydroxystyrene (1·21 g.) was heated at 100° for 2 days with a solution of potassium phthalimide (2·4 g.) in dimethylformamide (12 ml.). The product was filtered off from the hot solution, washed with ethanol, water, dilute hydrochloride acid, water, and ethanol, and dried, to yield an insoluble polymer (1·11 g.) (Found: N, 3·8. Calc. for cross-linked poly-4-hydroxy-3-phthalimidomethylstyrene: N, 4·9%).

Cross-linked Poly-3-formyl-4-hydroxystyrene (XVI).—Cross-linked poly-3-chloromethyl-4-hydroxystyrene (1 g.) was stirred with glyceroboric acid [from glycerol (6 g.) and boric acid (1·4 g.)] and hexamethylenetetramine (1 g.) at 150° for 30 min. N-Sulphuric acid (5 ml.) was added to the cooled mixture. The polymer was filtered off, washed with distilled water, and dried, to give a brown product (0·9 g.). The infrared spectrum of the polymer indicated the presence of carbonyl groups.

Cross-linked Poly-3-hydroxyiminomethyl-4-hydroxystyrene (XVII).—The foregoing formyl compound (0·4 g.) was refluxed for 18 hr. with hydroxylamine hydrochloride (2·5 g.) and sodium acetate (2·5 g.) in 50% aqueous ethanol (15 ml.). The polymer was filtered off, washed with ethanol and water, and dried, to give an insoluble product (0·43 g.) (Found: N, 4·9. Calc. for cross-linked poly-4-hydroxy-3-hydroxyiminomethylstyrene: N, 8·2%).

A similar reaction sequence using cross-linked poly-4-hydroxystyrene gave a product containing 3·8% of nitrogen.

Cross-linked Poly-3-acetyl-4-hydroxystyrene (XVIII).—Cross-linked poly-4-hydroxystyrene (4·0 g.) was refluxed with a solution of anhydrous zinc chloride (40 g.) in glacial acetic acid (40 ml.) for 5 days. The insoluble material was filtered off, washed with water, hydrochloric acid (2N), water, ethanol, and ether, and dried, to yield an insoluble polymer (3·87 g.). Infrared analysis indicated the presence of carbonyl groups.

Reaction of the product with hydroxylamine hydrochloride as for the formyl derivative yielded an insoluble product containing 3·2% of nitrogen [Calc. for cross-linked poly-4-hydroxy-3-(1-hydroxyiminoethyl)styrene (XIX): N, 7·6%].

Cross-linked Poly-4-hydroxystyrene-3-arsonic acid (VIII).—A suspension of cross-linked

poly-3-amino-4-hydroxystyrene (0·9 g.) in 2N-hydrochloric acid (11 ml.) at 0° was diazotised by the gradual addition (1 hr.) of an ice-cold solution of sodium nitrite (0·5 g.) in water (10 ml.). The polymer was filtered off, washed with water, and stirred at room temperature for 1 hr. with a solution of sodium arsenite (2 g.), sodium carbonate (2 g.), and copper sulphate (0·5 g.) in water (17 ml.). The mixture was slowly warmed to 60° and kept at that temperature for 5 hr. The insoluble product was filtered off, washed with dilute hydrochloric acid and water, and dried to yield a polymer (0·97 g.) (Found: As, 6·7%. Calc. for cross-linked poly-4-hydroxy-styrene-3-arsonic acid: As, 30·0%).

The Cross-linked Arsonic Acid (XX).—To a solution of *o*-arsanilic acid (2 g.) in N-hydrochloric acid (10 ml.) was added sodium nitrite solution at 0°. The cold solution of the diazonium salt was added to a suspension of cross-linked poly-4-hydroxystyrene (1 g.) in a solution of sodium carbonate (2 g.) in 2N-sodium hydroxide (10 ml.). The mixture was warmed to room temperature, with stirring, during 16 hr. The product was filtered off, washed with water, dilute acetic acid, water, and alcohol, and dried, to give a red polymer (1·24 g.) (Found: As, 5·2. Calc. for the cross-linked arsonic acid: As, 20·5%).