216. *Reactions of Macromolecules. Part IV.*[1] *Poly-(4-mercaptomethylstyrene).*

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Poly-(4-chloromethylstyrene) has been converted, *via* the thiouronium chloride, into poly-(4-mercaptomethylstyrene). Reactions of the polythiol in alkaline solution have yielded poly[di(vinylbenzylthio)mercury], poly-(carbamoylmethyl vinylbenzyl sulphide), and poly-(2-cyanoethyl vinylbenzyl sulphide).

The formation of thiouronium salts, by the action of alkyl halides on thiourea, and their decomposition by alkali into thiols and dicyandiamide are well established. The replacement of halogen is probably by an S_N2 mechanism, the sulphur atom of the thiourea acting as nucleophilic reagent.[2] The following applications of these reactions to polymers have been recorded. Parrish[3] chloromethylated a cross-linked styrene–divinylbenzene copolymer and converted the product, by reaction as above, into a resin, containing 20·5% of sulphur, which bound mercury from a solution of mercuric nitrate. Okawara, Nakagawa,

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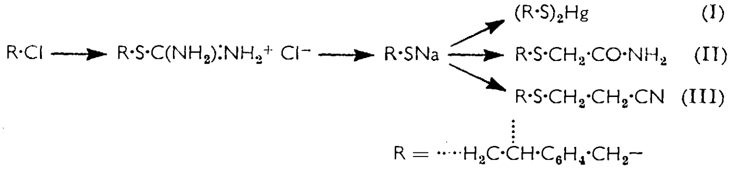
[1] Part III, Arcus and Randall, preceding paper.
[2] Arcus and Hallgarten, *J.*, 1956, 2987.
[3] Parrish, *Chem. and Ind.*, 1956, 137.

and Imoto[4] allowed a chloromethylated polystyrene to react with thiourea in dioxan–acetone solution; alkaline decomposition of the product yielded a polythiol containing 7·1% of thiol groups (the mercaptomethylstyrene unit contains 22·0%). Černý and Wichterle[5] have converted a cross-linked chloromethylated polystyrene containing 14·7% of chlorine into a polythiouronium anion-exchange resin.

We described[6] the preparation and polymerisation, initiated by αα′-azoisobutyronitrile, of 4-chloromethylstyrene. The known chloromethylation of polystyrene by chloromethyl methyl ether in the presence of zinc chloride[7] has been modified by Mr. M. S. M. Alger to yield a substituted polymer, soluble and free from cross-linking, having the ratio of chloromethyl groups to styrene units close to unity. Although *para*-substitution almost certainly preponderates during chloromethylation, it is not known how completely this is so; the infrared absorption spectra of polymerised 4-chloromethylstyrene and the chloromethylated polystyrene are closely similar, but do not exclude the presence of non-*para*-groups in the latter polymer.

The thiouronium- and thiol-forming reactions have now been applied to the substantially linear polymeric benzyl chlorides prepared by polymerisation of 4-chloromethylstyrene and by the above chloromethylation of polystyrene. Conversion of chloromethyl into mercaptomethyl groups was substantially complete. The polythiol was soluble in alkali, and remained in solution provided that the pH was not reduced to less than 12. By the action of oxygen on the alkaline solution, an insoluble material was formed; analysis showed the reaction to be more complex than oxidation of thiol to disulphide groups. There was little difference between the polythiol prepared from poly-(4-chloromethylstyrene) and that from the chloromethylated polystyrene.



The polythiol gave, with mercuric cyanide, poly[di(vinylbenzylthio)mercury] (I); with iodoacetamide, poly(carbamoylmethyl vinylbenzyl sulphide) (II); and with acrylonitrile, poly-(2-cyanoethyl vinylbenzyl sulphide) (III).

In these three reactions the thiol anion is the actual reagent, and conversion was substantially complete in each instance. In the mercury sulphide, the mercury–sulphur bonds are presumably sufficiently ionic to permit mercuric ions to migrate until virtually all vacant sites are filled. Were this not so, and on the contrary a pair of thiol groups combined rigidly with a mercury atom, then unchanged thiol groups, too far apart to form a covalent sulphide bridge, would be expected to remain. Iodoacetamide is an efficient reagent for alkylating thiol groups in proteins,[8] probably by an S_N2 mechanism. Cyanoethylation is an addition of the Michael type, initiated by attack by the thiol anion.[9]

The derived polymers were precipitated from each of the above reaction solutions, yet virtually all of the thiol groups reacted. A similar result with polymeric diazo-reactions has been discussed in Part II;[10] the factors contributing to high conversion are inferred to be: (*a*) a rate of reaction which is fast relative to that of precipitation; (*b*) association of reagent with reactive groups on the macromolecule before precipitation; (*c*) continued solvation of these groups in the precipitate, allowing reagent to diffuse into the locally

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[4] Okawara, Nakagawa, and Imoto, *Kôgyô Kagaku Zasshi*, 1957, **60**, 73; *Chem. Abs.*, 1959, **53**, 5730.
[5] Černý and Wichterle, *J. Polymer. Sci.*, 1958, **30**, 501.
[6] Arcus and Salomons, *J.*, 1962, 1515.
[7] Jones, *Ind. Eng. Chem.*, 1952, **44**, 2686; Charlton, Cundall, and Selby, B.P. 810,026.
[8] Dixon and Webb, "Enzymes," Longmans, Green and Co., London, 1958, pp. 377—378.
[9] Bruson, *Org. Reactions*, 1949, **5**, 79.
[10] Arcus and Halliwell, *J.*, 1962, 2187.

swollen macromolecule. It is noteworthy that, in the present and the earlier group of reactions, the polymer was initially in solution as a polyelectrolyte, the polythiol anion or a polymeric diazonium ion, the polar forces of which would promote factors (*b*) and (*c*).

The course of oxidation of the polythiol under different conditions, its oxidation–reduction potential, and its behaviour as a weak polyacid, are being investigated.

EXPERIMENTAL

During the preparation and reactions of the polythiol, exclusion of air was essential. Apparatus was either purged with nitrogen before use, or a current of nitrogen was passed continuously. Water for solutions and washing precipitates was boiled for 2 hr., with passage of nitrogen which was continued as it cooled. Sodium hydroxide was dissolved in oxygen-free water, and the solution boiled for 45 min. as above. Dilute hydrochloric acid was prepared by adding the concentrated acid to oxygen-free water. Water and solutions were kept under nitrogen.

The polythiols and derived polymers were dried at reduced pressure over phosphoric oxide, the former under nitrogen.

Poly(mercaptomethylstyrene).—A solution of poly-(4-chloromethylstyrene) (0·445 g.) in benzene (15 ml.) and one of thiourea (0·295 g.) in ethanol (6 ml.) were gradually mixed at 70—75° and stirring was continued for a further 3 hr. The polymeric thiouronium chloride separated. Passage of nitrogen through the flask was then commenced, the solvent was distilled off, 6N-sodium hydroxide (25 ml.) was added, and the whole was stirred for 1 hr. at 100°.

The following units were connected successively, vertically downwards: a sintered-glass filter, a tap-funnel, a second filter comprising paper supported on sintered glass, and a flask. The funnel and flask were fitted with side-tubes. (This apparatus was also used in the preparation of the derived polymers, below.) The alkaline thiol solution was aspirated from the reaction-flask, through a Polythene tube and the first filter, into the funnel. 6N-Hydrochloric acid was added dropwise through the side-tube of the funnel, with agitation, until pH 1 was attained. The side-tube was then closed, the tap opened, and the white precipitate of *poly-(4-mercaptomethylstyrene)* collected, by aspiration at the lower flask, on the second filter; it was washed with water until no sulphide or chloride was present in the washing.

The following specimens of poly(chloromethylstyrene) were converted into the polythiol:

	Poly(chloromethylstyrene)			Poly(mercaptomethylstyrene)		
			Found [b] (%)	Found [c] (%)		
Specimen	Origin	$[\eta]_c$ [a]	Cl	C	H	S
1	Polymerisation	0·255	23·05	72·25	6·4	21·35
2	Polymerisation	0·157	23·0	72·4	6·7	20·55
3	Chloromethylation	0·150	23·4	71·1	6·6	22·1

[a] The intrinsic viscosity, $[\eta]_c = (1/c) \ln (\eta_{soln.}/\eta_{solv.})$ (c = g. of solute in 100 ml. of solution), was determined for the polymer in solution in toluene at 25° and c 1·0. [b] Calc. for C_9H_9Cl: Cl, 23·25%. [c] $C_9H_{10}S$ requires C, 71·95; H, 6·7; S, 21·35%.

Derived Polymers.—Polythiol, freshly prepared from poly-(4-chloromethylstyrene) (0·455 g.), was dissolved in N-sodium hydroxide (25 ml.). N-Hydrochloric acid was added dropwise until a permanent white precipitate formed; this was immediately redissolved by adding a minimum of alkali. The solution was filtered into an agitated solution of mercuric cyanide (0·41 g.) in water (21 ml.). Precipitation commenced at once. Next day the *poly[di-(4-vinylbenzylthio)-mercury]* was collected and washed with aqueous methanol until the washings were free from mercury and chloride (Found: C, 43·7; H, 3·9. $C_{18}H_{18}HgS_2$ requires C, 43·3; H, 3·65%).

0·05N-Sodium thiosulphate was added dropwise to a solution of iodoacetamide (1·69 g.) in water (67 ml.) until the colour was discharged, and a few drops were added in excess. To this solution was added, with shaking, a slightly alkaline solution of the polythiol prepared as above from poly(chloromethylstyrene) (specimen 3, 1·11 g.). After a further 30 min., the precipitated *poly-(carbamoylmethyl vinylbenzyl sulphide)* was collected, and washed with water, 0·2N-hydrochloric acid, and water until free from halide (Found: C, 62·7; H, 6·0; N, 6·5; S, 15·45. $C_{11}H_{13}NOS$ requires C, 63·75; H, 6·3; N, 6·75; S, 15·45%).

Polythiol, freshly prepared from poly(chloromethylstyrene) (specimen 3, 0·51 g.), was passed in N-sodium hydroxide (60 ml.), through a filter into an agitated solution of acrylonitrile (0·265 g.) in water (26 ml.). Precipitation occurred at once. Next day the *poly-(2-cyanoethyl* *vinylbenzyl sulphide*) was collected and washed with water (Found: C, 71·35; H, 6·6; N, 6·4; S, 15·45. $C_{12}H_{13}NS$ requires C, 70·9; H, 6·45; N, 6·9; S, 15·75%).

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