

419. *Reactions of Macromolecules. Part II.*¹ *Halogeno- and Thio-substitution of Diazo-derivatives of Poly-(*m*-aminostyrene) and the Copolymer with Styrene.*

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Poly-(*m*-aminostyrene) and 2:1 styrene-*m*-aminostyrene copolymer have been converted, by standard diazo-reactions, into the chloro-, bromo-, iodo-, and thio-substituted polymer and copolymer, respectively. Cross-linking accompanies these reactions.

In order to ascertain how far substitution is effective when a diazo-compound is polymeric, replacements by chlorine, bromine, iodine, and, *via* the xanthate, thiol, have been carried out with diazotised poly-(*m*-aminostyrene) and 2:1 styrene-*m*-aminostyrene copolymer.

Replacements by thiol and chlorine have been accomplished by Gregor, Dolar, and Hoeschele,² and Manecke and Singer,³ respectively. The latter authors obtained poly-(aminostyrene) from the Norsk Hydro Company, who are presumed to use Skogseid's patent⁴ whereby polystyrene is dissolved, and kept, in 90% nitric acid below 10°, the nitrated polymer then being reduced with sodium disulphide at 150° to poly(aminostyrene). Gregor *et al.* prepared poly(nitrostyrene) as above, but catalytically hydrogenated it to the amino-polymer.

Treatment of the poly(aminostyrenes) with hydrochloric acid and sodium nitrite gave the diazonium chlorides; Gregor and his co-workers's amine hydrochloride and diazonium

¹ Part I, Arcus and Halliwell, *J.*, 1961, 3708.

² Gregor, Dolar, and Hoeschele, *J. Amer. Chem. Soc.*, 1955, **77**, 3675.

³ Manecke and Singer, *Makromol. Chem.*, 1960, **37**, 119.

⁴ Skogseid, U.S.P. 2,592,349.

chloride appear to have been soluble in water, but it is clear that those of Manecke and Singer were not. This insolubility points to cross-linking during reduction with sodium disulphide. The former authors's polythiol, prepared *via* the xanthate, contained 93% of the theoretical amount of sulphur, but was insoluble in all common solvents. The insolubility was ascribed to cross-linking during diazo-decomposition, since poly-(*p*-mercaptostyrene), when prepared by polymerisation of *p*-vinylphenyl thioacetate and hydrolysis of the polymer, was soluble in alkali and partly so in benzene and cyclohexanone.⁵ Manecke and Singer's chloro-polymer, prepared by the Sandmeyer reaction, contained chlorine equivalent to 91% of the original amino-groups.

Substitution in the above nitration is probably mainly *para*, but substantial *ortho*-nitration is likely, and, further, it cannot be certain that each phenyl group contains one, and only one, nitro-group. The preparation of polymers and the 2 : 1 styrene copolymer of *m*-aminostyrene has been described in Part I. These polymeric aromatic amines are uniform in position of substitution, and the polymers are substituted in each phenyl group. In the copolymer neighbouring *m*-aminophenyl groups are on average separated by two phenyl groups; if interaction between adjacent reactive groups had been a feature of the present reactions, it would have been detectable by comparison of reactions of the polymer with those of the copolymer.

In each of the present reactions, the amine hydrochloride was initially in homogeneous solution, and so far as possible the diazonium derivatives were also so obtained. For poly-(*m*-aminostyrene) diazotisation was carried out in water, and the polymeric diazonium chloride and bromide formed homogeneous solutions. The copolymer, which is insoluble in water and methanol, yields, on being heated with hydrochloric acid, a hydrochloride; this is insoluble in water but dissolves in methanol; the methanolic solution tolerates considerable dilution with water, and diazotisation yields a homogeneous solution of the copolymer diazonium chloride; the copolymeric amine hydrobromide is similarly soluble but on diazotisation yields a suspension of the diazonium bromide.

Substitution with chlorine and bromine was effected by the Sandmeyer reaction, and that with iodine by warming the diazonium chlorides with potassium iodide. The diazonium chlorides, treated with potassium xanthate, gave the aryl xanthates, which, on alkaline hydrolysis and acidification, yielded the arenethiols.

From the analyses of the substituted polymers and copolymers (Table) there has been calculated the atomic fraction of halogen or sulphur which is present for every repeating unit of 8 carbon atoms for the polymer, and (on average) of 24 carbon atoms for the copolymer. In the latter, some of the diazo-groups not replaced by halogen or thiol are probably replaced by methoxyl (Part I), whence the correct basis for calculation would be $(24 + x)$ carbon atoms, where x is less than $(1 - y)$, y being the fraction of an equivalent of halogen or thiol which combines; the error involved in neglecting x is small.

For the polymer, replacement by chlorine and bromine proceeded to ~85%, by iodine to 70%, and by thiol to 55%. Percentage replacements for the copolymer were lower, except for the thiol, for which they were higher. Of the substituted polymers and copolymers, only the thiol copolymers contained nitrogen.

Dissolution of a selection of the substituted polymers and copolymers of the Table was attempted in three or more of the following solvents: chloroform, carbon tetrachloride, *sym*-tetrachloroethane, 95% formic acid, dimethylformamide, benzene, toluene, benzyl alcohol, *m*-cresol, chlorobenzene, aniline, and pyridine; but none dissolved. The insolubility indicates cross-linking and, for the halogeno-polymers, this is borne out by known solubilities; for example, poly-(*o*-, *m*-, and *p*-chloro- and *o*-, *m*-, and *p*-bromostyrene)⁶ and chlorinated polystyrene⁷ are all soluble in chloroform. Cross-linking is

⁵ Overberger and Lebovits, *J. Amer. Chem. Soc.*, 1955, **77**, 3675.

⁶ Laitinen, Miller, and Parks, *J. Amer. Chem. Soc.*, 1947, **69**, 2707.

⁷ Bachman, Hellman, Robinson, Finholt, Kahlar, Filar, Heisey, Lewis, and Micuci, *J. Org. Chem.*, 1947, **12**, 108.

Replacement in diazotised poly-(*m*-aminostyrene) and 2 : 1 styrene-*m*-aminostyrene copolymer.

Polymer	Reagent	Prepn. no.	Substituted polymer or copolymer					
			Found (%)			Atomic ratios		
			C	H	Hal or S	C	H	Hal or S
Polymer	CuCl	i	70.75	5.4	Cl, 22.15	8	7.3	Cl, 0.85
		ii	70.5	5.25	Cl, 22.3	8	7.1	Cl, 0.86
	CuBr	i	53.8	4.2	Br, 39.55	8	7.4	Br, 0.88
		ii	53.95	4.1	Br, 37.35	8	7.2	Br, 0.83
	KI	i	45.6	3.5	I, 38.6	8	7.3	I, 0.64
		ii	46.4	3.75	I, 45.9	8	7.7	I, 0.75
Copolymer	KS ₂ C·OEt	i	74.2	6.0	S, 13.35	8	7.7	S, 0.54
		ii	71.75	6.1	S, 13.25	8	8.1	S, 0.55
	CuCl	i	84.6	7.0	Cl, 6.0	24	23.7	Cl, 0.58
		ii	84.35	6.7	Cl, 7.3	24	22.8	Cl, 0.71
	CuBr	i	77.05	6.15	Br, 16.5	24	22.8	Br, 0.77
		ii	77.85	6.3	Br, 16.6	24	23.2	Br, 0.77
KI	i	74.1	6.0	I,* 17.8	24	23.1	I, 0.55	
	ii	76.75	6.55	I, 13.0	24	24.4	I, 0.38	
KS ₂ C·OEt	i	82.5	6.85	S,† 5.95	24	23.8	S, 0.65	
	ii	82.25	6.85	S,† 6.35	24	23.8	S, 0.70	

* Contained Cl, 0.3%; the other iodo-copolymer and the iodo-polymers contained no chlorine.

† Contained N: (i) 1.1, (ii) 1.05%.

ascribed to Pschorr-type attack by some of the phenyldiazonium groups on phenyl or substituted phenyl side-groups.

The 1.1% of nitrogen contained by the thio-copolymers is presumed to be present as azo cross-linkages. With respect to the thio-polymers and -copolymers, it is possible that some mercapto-groups become oxidised to disulphide links during the preparation, but determination of the state of the thio-sulphur proved impracticable owing to the insolubility of these polymers.

A notable feature of the present group of reactions is that replacement is generally considerable, in half the examples to over 70%, despite the insolubility of the final products. Clearly, a fast substitution and a relatively slow rate of separation from solution favour a high degree of replacement, but precipitation cannot be regarded as a simple withdrawal from reaction. Reagent may associate with reactive groups of the macromolecule before precipitation, and may also be adsorbed on the precipitate. Further, such groups probably continue to be solvated, whereby reagent diffuses into the swollen material. Hence the onset of precipitation may not greatly lower the rate of reaction.

EXPERIMENTAL

Hydrochloric acid, unless otherwise stated, refers to 12N-acid.

Diazonium Chlorides.—A solution of poly-(*m*-aminostyrene) (0.596 g.) in 1.0N-hydrochloric acid (25 ml.) was cooled to 0–5°, and sodium nitrite (0.346 g.) in water (10 ml.) was added with stirring; the whole was kept for 1 hr. at 0–5°. A clear, pale-yellow solution resulted. 2 : 1 Styrene-*m*-aminostyrene copolymer (1.64 g.) was boiled with hydrochloric acid (15 ml.) for 15 min. The whole was diluted with water (100 ml.), and the copolymeric hydrochloride collected, washed with water, drained, and dissolved in methanol (100 ml.); water (100 ml.) was added and the solution filtered from a trace of insoluble material. Hydrochloric acid (2 ml.) was added to the filtrate, which was then diazotised as above. Solutions so prepared were used for the replacements by chlorine, iodine, and thiol.

Diazonium Bromides.—The procedure for the polymer was that for the chloride, hydrochloric acid being replaced by 1.0N-hydrobromic acid; addition of water (10 ml.) was necessary to dissolve the polymer hydrobromide completely at 0–5°; a clear diazonium bromide solution was obtained. The copolymer was treated as for the chloride, but the portions of hydrochloric acid were replaced by 20 and 4 ml. of 5N-hydrobromic acid. A suspension of the diazonium bromide was obtained.

Replacements.—The reactions were carried out with polymer (ii) and copolymer (ii) of Part I, except that polymer (i) was used for the replacements by chlorine and thiol.

Chlorine. The polymeric diazonium chloride solution was added dropwise, in 10 min., to a solution, at 60°, of cuprous chloride (0.99 g.) in hydrochloric acid (20 ml.); the mixture was kept at 60° for a further 20 min., and the chloro-polymer was filtered off. It was washed with hot water until the washings were free from halide ions, and was dried at 70° (all the substituted polymers and copolymers were finally so washed and dried). The copolymeric diazonium chloride was allowed to react similarly, but addition was made under reflux during 30 min., and the mixture was refluxed for a further 30 min. The chloro-polymer [(i), (ii) 0.65 g.] and -copolymer [(i) 1.60, (ii) 1.61 g.] formed grey powders.

Bromine. The polymeric diazonium bromide solution was added dropwise to a solution, at 70°, of cuprous bromide (1.44 g.) and potassium bromide (4.2 g.) in concentrated hydrobromic acid (20 ml.) and water (20 ml.); the mixture was kept at this temperature for 20 min. The bromo-polymer was then collected; it formed a buff powder [(i), (ii) 0.84 g.].

The copolymeric diazonium bromide was added to the reagents as above, and the mixture refluxed for 30 min.; the product was then filtered off and washed with 5*N*-hydrobromic acid (20 ml.). It yielded the bromo-copolymer, a white powder [(i) 1.79, (ii) 1.76 g.].

The chloro- and bromo-polymers and -copolymers gave on ignition a small residue, $\approx 0.03\%$, containing copper.

Iodine. Potassium iodide (1.04 g.) in water (10 ml.) was added at 0–5° with stirring to the polymeric or copolymeric diazonium chloride solution; precipitation occurred. After 20 min., the whole was heated to 80° and kept thereat for 30 min.; the product was then filtered off and washed with 5% aqueous sodium carbonate (100 ml.). The iodo-polymer [(i), (ii) 1.01 g.] and -copolymer [(i) 1.86, (ii) 1.83 g.] formed cream powders.

Thiol. The acidity of the diazonium chloride solution (polymeric and copolymeric) was reduced by the addition of sodium carbonate solution (10%), until it was just acid to Congo Red. Some precipitation occurred with the copolymer but not with the polymer. Potassium ethyl xanthate (1.13 g.) in water (15 ml.) was added with stirring during 5 min. at 0–5°, giving a yellow precipitate. The whole was heated to 80° and so kept for 30 min.; the product was filtered off and washed with water. It was next refluxed for 2 hr. with 20% aqueous potassium hydroxide (20 ml.), filtered off, washed with water, then heated for 10 min. with 6*N*-hydrochloric acid (10 ml.), collected, and washed with hot water and hot methanol (200 ml.). The thio-polymer [(i) 0.62, (ii) 0.68 g.] and -copolymer [(i) 1.76, (ii) 1.74 g.] formed yellow powders.

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