

835. Reactions of Macromolecules. Part VI.* Azo-Coupling by Poly-(*m*-styrenediazonium Chloride).

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Polymeric azo-compounds are formed by the coupling of poly-(*m*-styrenediazonium chloride) with 2-naphthol, 2,5-dimethylaniline, and 2,5-dimethoxyaniline. The aminoazo polymers, on diazotisation and coupling with 2-naphthol, yield bisazo polymers.

In the present series of studies, it has been shown that the rate of decomposition of poly-(*m*-styrenediazonium chloride) is of the first order and intermediate between those of benzene- and *m*-isopropylbenzenediazonium chlorides,¹ and that various substitutions in the polymeric diazonium cation by standard diazo-replacement reactions are effective to 54—88%.² These results indicate that attachment to a polymeric chain does not markedly alter the reactivity of the phenyldiazonium units. The course of some azo-coupling reactions of poly-(*m*-styrenediazonium chloride) are now reported.

Martynoff³ prepared poly-(*p*-aminostyrene) by thermal decarboxylation of *p*-aminocinnamic acid, diazotised the polymer, and found it to couple almost completely with phenol and dimethylaniline. Oda and Urata⁴ polymerised *m*-aminostyrene by heating it to 160°; they dissolved the polymer in concentrated sulphuric acid, diazotised the resultant solution, and, after dilution, effected coupling with 2-hydroxynaphthalene-3-carboxyanilide. The high temperature of polymerisation, together with the drastic means apparently necessary for dissolution, indicates that this polymer was not a linear poly-(*m*-aminostyrene).

Our polymers, on the other hand, were prepared by initiation with $\alpha\alpha'$ -azoisobutyronitrile at 73°, and were soluble in 1*N*-hydrochloric acid. 2-Naphthol, 2,5-dimethylaniline, and 2,5-dimethoxyaniline were selected as substrates; the amines because they are substituted directly to yield the *p*-aminoazo compounds,⁵ and because they and 2-naphthol couple only once;⁵ in this way we avoided the complication of two azo groups becoming bonded to a single phenol or amine molecule, forming a cyclic or cross-linked structure.

Reaction of a solution of poly-(*m*-styrenediazonium chloride) with alkaline 2-naphthol yielded poly-(*m*-styrene-1-azo-2-naphthol) (I), and reaction with ethanolic 2,5-dimethyl- and 2,5-dimethoxyaniline at 50°, the procedure for low-molecular-weight diazonium salts introduced by Troeger and Westerkamp,⁶ gave poly-(*m*-styrene-4-azo-2,5-dimethylaniline) (II) and poly-(*m*-styrene-4-azo-2,5-dimethoxyaniline) (III). The analyses show that coupling with 2-naphthol was complete. That with the amines was less so; as the course of side-reactions is uncertain, the extent of coupling cannot be computed exactly, but an approximate value is given by the nitrogen content expressed as a percentage of that for complete coupling; for the 2,5-dimethyl- and 2,5-dimethoxy-anilino polymers, these values are 57 and 91%, respectively. Greater susceptibility to electrophilic attack would be expected with methoxyl than with methyl as a substituent.

In our media, the poly(azonaphthol) was insoluble and the poly(azodimethoxyaniline hydrochloride) only slightly soluble, yet the extent of conversion was high. Examples of similar high conversion with ultimately-insoluble products have been discussed earlier,^{2,7} and it was inferred that the contributing factors are a fast rate of reaction relative to that of precipitation, and, as here, that the polymer should initially be in solution as a poly-electrolyte, the polar character of which promotes both association of reagent with reactive

* Part V, *J.*, 1963, 4199.

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

² Arcus and Halliwell, *J.*, 1962, 2187.

³ Martynoff, *Compt. rend.*, 1954, 239, 1512.

⁴ Oda and Urata, *Reports Inst. Chem. Res., Kyoto Univ.*, 1949, 19, 94; *Chem. Abs.*, 1951, 45, 5409.

⁵ Saunders, "The Aromatic Diazo-compounds." Arnold and Co., London, 2nd edn., 1949, pp. 199—

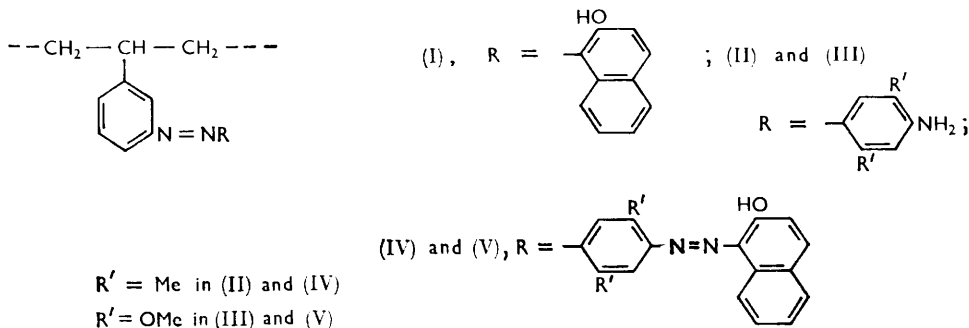
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⁶ Troeger and Westerkamp, *Arch. Pharm.*, 1909, 247, 684.

⁷ Arcus and Salomons, *J.*, 1963, 1175.

groups on the macromolecule before precipitation, and continued solvation of these groups in the precipitate, allowing reagent to diffuse into the locally swollen macromolecule.

Poly-(*m*-styrene-4-azo-2,5-dimethylaniline) and poly-(*m*-styrene-4-azo-2,5-dimethoxyaniline) were diazotised in suspension in dilute hydrochloric acid and allowed to couple



with alkaline 2-naphthol; the bisazo polymers (IV) and (V) were formed. Computation of the extent of the second coupling from the analyses is not practicable, but the conversion of the above monoazo into bisazo compounds is shown by deepening in colour from orange to purple-brown and violet-black, respectively.

EXPERIMENTAL

m-Aminostyrene (13.3 g.), on being heated under nitrogen at 73° for 90 min. with $\alpha\alpha'$ -azoisobutyronitrile (0.054 g.), polymerised to a pale yellow glass. Solution and precipitation¹ yielded white, fibrous poly-(*m*-aminostyrene) (7.0 g.) (Found: N, (i) 11.55, (ii) 11.75. Calc. for $\text{C}_8\text{H}_9\text{N}$: N, 11.75%). The logarithmic viscosity numbers, $(1/c) \ln(\eta_{\text{soln.}}/\eta_{\text{solv.}})$, where $c = \text{g. of solute in 100 ml. of solution}$, were determined for solutions of the polymer in aniline at 25.0° and $c = 1.2, 0.8, 0.6, 0.4$; extrapolation yielded the limiting intrinsic viscosity, $[\eta] 0.47$.

To a solution of poly-(*m*-aminostyrene) (0.583 g.) in 1.0*N*-hydrochloric acid (25 ml.) kept at <5°, sodium nitrite (0.332 g.) in water (10 ml.) was added dropwise with stirring; after 30 min., the slight excess of nitrous acid was removed by addition of aqueous urea (5%; 1.5 ml.); the solution was stirred for a further 15 min. It was then added dropwise with stirring during 10 min. to a solution of 2-naphthol (0.787 g.) in 0.125*N*-sodium hydroxide (200 ml.) at 15°. Coupling commenced immediately. The whole was stirred for 1 hr., then filtered. The product was washed with 0.02*N*-sodium hydroxide (500 ml.) until the washing gave no precipitate with benzenediazonium chloride, showing that excess of 2-naphthol had been removed, then with water (1 l.) until free of alkali. This gave bright red poly-(*m*-styrene-1-azo-2-naphthol) (0.769 g.) (Found: C, (i) 78.9, (ii) 78.95; H, (i) 5.15, (ii) 5.25; N, (i) 10.25, (ii) 10.15; O, (i) 5.85, (ii) 5.9. The unit corresponding to complete coupling, $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}$, requires C, 78.8; H, 5.15; N, 10.2; O, 5.85%).

To a solution of *p*-xylydine (0.348 g.) in ethanol (96%; 25 ml.) at 50°, diazonium solution from 0.296 g. of poly-(*m*-aminostyrene) was added dropwise with stirring, continued for 30 min.; coupling commenced immediately. After being cooled in ice, the whole was filtered. The product, the purple-red hydrochloride, was washed with 0.1*N*-hydrochloric acid (250 ml.), converted into the base by suspension in 2*N*-ammonia (150 ml.), and centrifuged; this was thrice repeated. Finally, the poly-(*m*-styrene-4-azo-2,5-dimethylaniline) was suspended in ammonia, collected on a filter, and washed first with ammonia and then water. It formed a dull orange powder (0.365 g.) (Found: C, (i) 77.5, (ii) 77.65; H, (i) 6.8, (ii) 6.9; N, (i) 9.4, (ii) 9.55%. The unit corresponding to complete coupling, $\text{C}_{16}\text{H}_{17}\text{N}_3$, requires C, 76.45; H, 6.8; N, 16.7%).

2,5-Dimethoxyaniline (0.425 g.) gave, by the same coupling-procedure, a red, gelatinous, and slightly soluble hydrochloride, which was collected by centrifugation and converted as above into the bright orange-red poly-(*m*-styrene-4-azo-2,5-dimethoxyaniline) (0.453 g.) (Found: C, (i) 67.5, (ii) 67.45; H, (i) 6.3, (ii) 6.4; N, (i) 13.5, (ii) 13.6%. The unit corresponding to complete coupling, $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_2$, requires C, 67.85; H, 6.05; N, 14.85%).

To a suspension of poly-(*m*-styrene-4-azo-2,4-dimethylaniline) (0.211 g.) in *N*-hydrochloric acid (20 ml.) at 0–5°, sodium nitrite (0.061 g.) in water (1.5 ml.) was added with stirring, continued for 1 hr. The diazotised suspension was then added to a stirred solution of 2-naphthol (0.158 g.) in 0.125*N*-sodium hydroxide (200 ml.) at 15°. After 1 hr. the poly-(*m*-styrene-4-azo-2,5-dimethylbenzene-1-azo-2-naphthol) was filtered off, washed with 0.02*N*-sodium hydroxide (500 ml.), and with water (1 l.); it formed a purple-brown powder (0.229 g.) (Found: C, (i) 76.45, (ii) 76.2; H, (i) 5.85, (ii) 5.7; N, (i) 9.6, (ii) 9.6%).

A similar procedure with poly-(*m*-styrene-4-azo-2,5-dimethoxyaniline) (0.182 g.), sodium nitrite (0.051 g.), and 2-naphthol (0.125 g.) yielded violet-black poly-(*m*-styrene-4-azo-2,5-dimethoxybenzene-1-azo-2-naphthol) (0.224 g.) (Found: C, (i) 69.9, (ii) 70.05; H, (i) 5.4, (ii) 5.25; N, (i) 12.6, (ii) 12.45%).

All the azo and bisazo polymers were swollen by boiling dimethylformamide, *m*-cresol, or formic acid, but only poly-(*m*-styrene-4-azo-2,5-dimethoxyaniline) was completely soluble.

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