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Aldehyde Functionalization of Styrene Polymers

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Summary

Two methods of the introduction of aldehyde group into polystyrene skeleton are described.

Although aldehydes rank among the most widespread starting materials in organic synthesis, the use of poly(vinylbenzaldehydes) in the preparation of functionalized polystyrenes is not in accord with potentialities of the aldehyde group. The not entirely satisfactory methods for the polyaldehyde preparation (FRÉCHET and FARRALL 1977; MATHUR et al. 1980) may be to blame in this case.

Basically, only three methods of the preparation of linear or crosslinked poly(vinylbenzaldehydes) have been described in the literature, viz.,polymerization of the monomer (KINOSHITA and SCHULZ 1968),reaction of polystyryllithium with dimethylformamide (BRAUN 1961; FARRALL and FRÉCHET 1976) and oxidation of poly(vinylbenzyl chloride) with dimethyl sulfoxide (DMSO)(AYRES and MANN 1965; FRÉCHET and SCHUERCH 1971; FRÉCHET and HAQUE 1975; HARRISON et al. 1975; GIBSON and BAILEY 1975). Each of these methods has its drawbacks. The preparation via the monomer is lengthy, the synthesis of lithiated polystyrene requires the use of a special technique. The more frequently used DMSO oxidation is not smooth (HARRISON et al. 1975), in addition, even minute amounts of water in the reaction mixture cause hydrolysis of benzylic chlorine which is unusually facilitated by the DMSO medium. In both cases nonhomogeneous products result.

In this communication two novel syntheses of poly(vinylbenzaldehydes) are described. In the former, the aldehyde group is introduced by direct electrophilic substitution of polystyrene (reaction 1). In the latter, the polyaldehyde is obtained by the Sommelet reaction of chloromethylated polystyrene.

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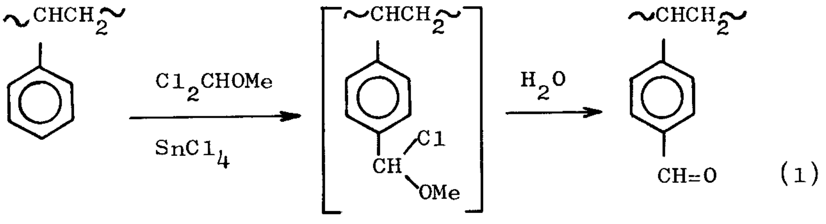

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In the direct formylation, polymer dissolved or swollen in dichloromethane or nitrobenzene was treated with methyl dichloromethyl ether in the presence of anhydrous tin(IV) chloride (mole ratio 1:1:2, 20-25°C, 3-4 hours) (RIECHE et al. 1960). After hydrolysis and washing with water, dioxane - conc. HCl mixture, dioxane and methanol, products exhibiting strong infrared absorption at 1690 and 2720cm^{-1} were obtained (cf. Table I). Some crosslinking, manifesting itself in the case of linear polystyrene by insolubility of the product, occurs, obviously due to the reaction of intermediate I with a further substrate molecule. The crosslinking could be suppressed by shortening the reaction time.

TABLE I

Direct formylation of styrene polymers

Starting polymer	Aldehyde content[a] (mmol/g)
Polystyrene[b]	5.11
Styrene - 2 % divinylbenzene copolymer	3.64
Divinylbenzene copolymer[c]	1.46

[a] Ex N content after oximation (NH$_2$OH.HCl in pyridine, 100°, 10 hrs, washed with H$_2$O, ethanol, dioxane); ir spectra demonstrate practically complete conversion of CHO except with the second polymer. [b] Molecular weight (viscometric) of the order 10^5. [c] Macroreticular (Amberlite XAD-2, Rohm and Haas), dried to constant weight before use.

Alternatively, the polyaldehyde was prepared as follows. Chloromethylated styrene - 1% divinylbenzene copolymer (0.79 meq Cl/g), previously swollen in chloroform, was refluxed with an excess of hexamethylenetetramine in chloroform for 24 hours. The hexamethylenetetraminium salt thus formed was decomposed by 10 h reflux with glacial acetic acid and 2 h reflux with conc. hydrochloric acid. The product obtained contained 0.67 mmol CHO/g (as determined by oximation) and no chlorine and nitrogen. Infrared spectra again reveal the presence of aldehyde groups (see above) and their absence in the oximated polymer.

Both reactions described here enrich the assortment of available reactions for the synthesis of aldehyde derivatives of styrene polymers. The direct formylation is particularly simple and the products obtained do not contain other reactive groups.

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