Mercuriation and Thalliation of Polystyrene: Conversion of the Products into Polystyrenes containing Iodobenzene, Phenylboronic Acid, and Phenol Residues

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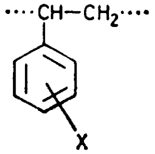
Linear and 1% crosslinked polystyrenes were mercuriated and thalliated. Treatment of the mercuriated products with iodine and the thalliated products with potassium iodide gave iodinated polystyrenes. The metallated polymers reacted with borane to give polymer-supported arylboranes, and these on treatment with water gave polystyrenes containing phenylboronic acid residues. The latter can be used as polymer-supported protecting groups for diols. Oxidation of the polymers containing phenylboronic acid residues with trimethylamine oxide or with alkaline hydrogen peroxide gave polymers containing phenol residues.

ARYLMERCURY and arylthallium compounds, prepared by the mercuriation [1] or thalliation [2] of aromatic compounds, react with borane to give arylboranes,[3,4,5] which can be oxidised to phenols [3,4,5] or hydrolysed to arylboronic acids.[3,4] The latter can also be oxidised to phenols.[6] We have studied analogous reactions starting with polystyrene because polymers containing phenylboronic acid residues (1) are useful as protecting groups for diols [7] and as stationary phases in chromatography [8] and because polymers containing phenol residues (2; R = H) are not otherwise easily prepared from unsubstituted polystyrenes.



(1) $X = B(OH)_2$
(2) $X = OR$
(3) $X = HgOAc$
(4) $X = HgOCOCF_3$
(5) $X = Tl(OCOCF_3)_2$
(6) $X = I$
(7) $X = BH_2$

Mercuriation of Polystyrene.—Both mercury(II) acetate and trifluoroacetate were used as mercuriating agents. The degrees of substitution † (DS) obtained were generally estimated by mercury analysis. In a few cases the results were confirmed by replacing (see a later section) the mercury-containing substituents by iodo-substituents [9,10] and analysing the products for iodine. The first method occasionally gave values a little lower than the second, probably because the analytical reagents used had difficulty penetrating the insoluble polymers.

Mercuriation of polystyrene with mercury(II) acetate gave products with variable DS values, generally much lower than those obtained by earlier workers.[9-12] A selection of the results are summarised in Table 1. The addition of perchloric acid, as expected,[10,12,13] catalysed the mercuriation (*cf.* entries 4 and 5 and 8 and 9 in Table 1), but it also lead to the formation of mercury(I) salts which could only be removed from the polymers by extensive washing with water. The observed catalytic effect was much less than that claimed by Stamberg *et. al.*,[12] but their products were only washed with methanol, a solvent which we found only partially removed the mercury(I) salts. The formation of mercury(I) salts suggests that the mechanism of perchloric acid-catalysed mercuriations may be more complex than previously thought.[13]

Mercury(II) trifluoroacetate proved to be a much more satisfactory mercuriating agent. It has only been used to mercuriate polystyrene once before and then, by choice, the DS obtained was extremely low.[14] We find it reacts smoothly with both linear and crosslinked polystyrene in tetrahydrofuran or dioxan to give polymers containing residues (4), and that with prolonged reaction times high DS values can be obtained. Our results are summarised in Table 1.

The reasons why mercury(II) trifluoroacetate is a more satisfactory reagent than the corresponding acetate in the above reactions are not clear. With the linear polymer a major factor is almost certainly the solubility of the product in the reaction medium. Thus, when the trifluoroacetate is used in tetrahydrofuran or dioxan the polymer remains in solution throughout the reaction, whereas when the acetate is used in tetrahydrofuran, acetic acid, or a mixture of the two, the polymer precipitates out when about 10% of the phenyl residues have been mercuriated.

Thalliation of Polystyrene.—The thalliation of polystyrene has not previously been reported. Both the linear and crosslinked polymers reacted smoothly with thallium(III) trifluoroacetate in methylene dichloride or carbon tetrachloride, and satisfactory DS values were obtained with reaction times of a few hours (see Table 2). The extent of thalliation was estimated by elemental analysis and the presence of residues (5) was confirmed by the infrared spectrum of the products which had bands at 1 640 (carbonyl) and 1 200 and 1 150 cm^{-1} (C–F bonds).

Preparation of Polystyrenes containing Iodobenzene Residues (6).—As noted above, several of the mercuriated polymers were converted into iodinated polystyrenes in

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† The degree of substitution is the fraction of the phenyl residues which have been substituted.

order to estimate the extent of mercuriation (see Table 1). This conversion was readily achieved using iodine in tetrahydrofuran and judging from the infrared spectra (no carbonyl band) of the products the yields were essentially quantitative. Indeed, mercuriation of polystyrene with mercury(II) trifluoroacetate followed by reaction of the product with iodine appears to be a useful method for preparing polystyrenes with iodobenzene residues (6).[15] The latter have been used for the preparation of polymer-supported reagents.[16]

Reaction of the thalliated polymers with potassium iodide also gave iodinated polystyrenes [17] (see Table 2) but these reactions were sluggish, probably because solvents which dissolved or swelled the thalliated polymer did not dissolve potassium iodide.

TABLE 1

Mercuriation of polystyrene

Entry	Polymer type [a]	Reaction conditions solvent, T °C, t/h	Catalyst [b]	DS of product [c]	DS of derived iodopolymer [d]
(a) Using mercury(II) acetate [e]					
1	L	PhNO$_2$, 150, 16	none	0.18	
2	L	AcOH, 110, 16	none	0.18	
3	L	THF, 66, 72	none	0.18	
4	L	THF–AA,[f] *ca.* 75, 6	HClO$_4$	0.16 [g]	0.24
5	L	THF–AA,[f] *ca.* 75, 6	none	*ca.* 0.02	
6	L	THF–AA,[f] *ca.* 75, 72	none	0.73	
7	XL	THF, 66, 72	none	*ca.* 0.01	
8	XL	THF–AA,[f] *ca.* 75, 6	HClO$_4$	0.21	0.21
9	XL	THF–AA,[f] *ca.* 75, 6	none	*ca.* 0.01	
(b) Using mercury(II) trifluoroacetate [e]					
10	L	THF, 66, 16	none	0.18	
11	L	THF, 66, 72 [h]	none	0.60	
12	L	THF, 66, 336	none	0.75	
13	XL	THF, 66, 24	HClO$_4$	0.12	0.13
14	XL	THF, 66, 24	none	0.17	0.20
15	XL	THF, 66, 72	none	0.34	0.39
16	XL	THF, 66, 120	none	0.65	
17	XL	dioxan, 101, 24	none	0.50	0.60

[a] L = linear polystyrene, $\bar{M}_n$ = 130 000; XL = 1% crosslinked polystyrene. [b] The catalyst added was approximately 1 mol per cent relative to the mercury salt, added as a 60% aqueous solution. [c] By elemental analysis for mercury. The DS calculated from the gain in weight of the polymer was generally in close agreement. [d] The mercuriated polymers were converted into the iodinated polystyrenes by reaction with iodine in THF. The DS was determined by elemental analysis for iodine. [e] Unless indicated otherwise 1.0 mol equiv. of mercury salt was used. [f] THF–AA = Tetrahydrofuran–acetic acid (5 : 1 v/v). [g] Estimated from the gain in weight of the polymer. [h] 1.25 Mol equiv. of mercury salt used.

TABLE 2

Thalliation of polystyrene using thallium(III) trifluoracetate

Entry	Polymer type [a]	Mol equiv. of reagent	Reaction conditions solvent, T °C, t/h	DS of thalliated polymer [b]	DS of derived iodopolymer [c]
1	L	0.5	CH$_2$Cl$_2$, 42, 4	0.33	
2	L	0.7	CCl$_4$, 78, 4	0.54	0.41
3	L	1.0	CCl$_4$, 78, 4	0.57	
4	L	1.0	CCl$_4$, 78, 10	0.65	
5	XL	0.7	CH$_2$Cl$_2$, 42, 20	0.38	0.23

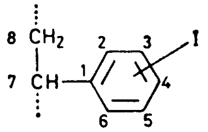
[a] See footnote *a* in Table 1. [b] By elemental analysis for thallium. The DS calculated from the gain in weight of the polymer was generally in close agreement. [c] The thalliated polymers were converted into iodinated polystyrenes by treatment with potassium iodide. The DS was determined by elemental analysis for iodine.

The iodinated linear polymers were sufficiently soluble in deuteriochloroform to allow ^{13}C n.m.r. spectra to be measured, and hence the sites of metallation to be determined. The results (Table 3) show that mercuriation and thalliation took place at the *meta*- and *para*-positions of the phenyl residues but not at the *ortho*-positions. Assuming the relaxation times of the iodo-bearing carbon atoms were very similar, the ratio of *para*- to *meta*-substitution was in all cases *ca.* 4 : 1. The infrared spectra of both the iodinated linear and cross-linked polystyrenes were consistent with this substitution pattern.

Preparation of Polymers containing Phenylboronic Acid Residues (1).—The mercuriated and thalliated polystyrenes reacted readily with borane in tetrahydrofuran to give polymers containing phenylborane residues (7) and these on hydrolysis gave polymers containing phenylboronic acid residues (1). The presence of these groups was evident from the chemical reactions discussed below and from the infrared spectra of the products which showed strong bands at 1 350 cm^{-1} due to B–O bonds. The amounts of boronic acid residues (1) present, as estimated by elemental analyses for boron, were substantially less than the theoretical maximum (see Table 4). As the infrared spectra of the final products did not contain any obvious bands due to functionalities other than the boronic acid residues, it is almost certain that some reduction (by diborane) to hydrocarbon accompanied the transmetallation. Reductions of this type are known to occur in related non-polymeric systems.[5] In agreement with this explanation it was found that treatment of one of the linear polymers containing boronic acid residues (1) (see Table 4) with iodine and alkali[6] gave an iodinated polystyrene with a DS very similar to that of the boronic acid polymer and an infrared spectrum essentially the same as that of the iodinated polystyrenes prepared directly from the metallated polymers.

TABLE 3

Chemical shifts in ^{13}C n.m.r. spectra of linear polystyrene and partially iodinated linear polystyrenes[a,b]



Carbon atom	Polystyrene	Partially iodinated polystyrene Phenyl residues[c]	 4-Iodophenyl residues[c]	 3-Iodophenyl residues
1	145.2	144.4	144.4	144.4
2	127.8	127.4, 128.1	129.5	(138.6)[e]
3	127.8	127.4, 128.1	137.1	94.3[d]
4	125.9	125.9	90.9[d]	(134.9)[e]
5	127.8	127.4, 128.1	137.1	
6	127.8	127.4, 128.1	129.5	

[a] δ Values measured for *ca.* 12% solutions in deuteriochloroform using a Varian CFT20 spectrometer with proton noise decoupling and gated undecoupling. [b] Chemical shifts of C-7 and C-8 are at δ 40.3 and 41.5–45.4 br in polystyrene and the iodinated polystyrene. [c] These data are in excellent agreement with those quoted previously (M. J. Farrall and J. M. J. Fréchet, *Macromolecules*, 1979, **12**, 426). [d] Chemical shifts of the iodinated carbon atoms in 4-, 3-, and 2-iodotoluenes are δ 90.1, 94.3, and 101.0 respectively. [e] Assignments of these small signals uncertain.

TABLE 4

Conversion of metallated polystyrenes into polystyrenes with phenylboronic acid residues[a]

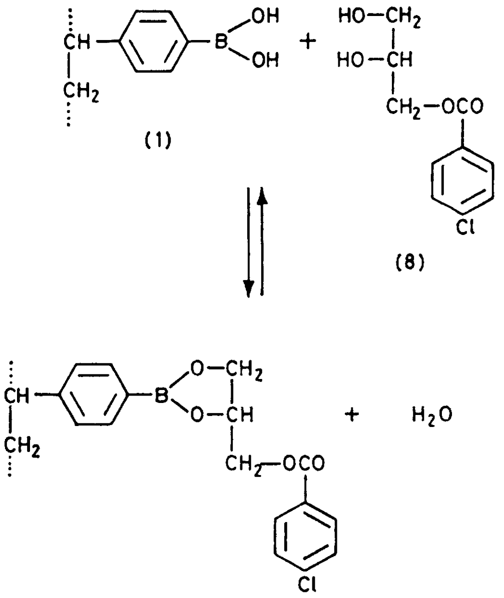
Entry	Polymer type[b]	Starting polymer Substituent group	 DS[c]	DS of final polymer[d]	% Conversion
1	L	HgOAc	0.73	0.42	57
2	L	$HgOCOCF_3$	0.71	0.38	54
3	L	HgOCOCF	0.60	0.38[e]	63
4	XL	$HgOCOCF_3$	0.47	0.23	49
5	XL	$HgOCOCF_3$	0.65	0.22	34
6	XL	$Tl(OCOCF_3)_2$	0.38	0.15	39

[a] Conversion achieved by treating the metallated polymer with 2 mol equiv. of borane followed by hydrolysis. [b] See footnote *a* of Table 1. [c] By elemental analysis for mercury or thallium. [d] By elemental analysis for boron. [e] This product reacted with sodium hydroxide and iodine[6] in aqueous THF to give a soluble iodinated polystyrene which, by elemental analysis for iodine, had DS 0.42.

It is interesting that the mercuriated linear polymers (4) were initially soluble in tetrahydrofuran but that on reaction with borane they became insoluble. This is probably the result of crosslinking due to the formation of a small amount of the diarylborane. The boronic acids derived from these polymers were also insoluble in all solvents tried, but they reacted with sodium hydroxide and iodine,[6] which cleaved the carbon–boron bonds, to give soluble iodinated polystyrenes.

Our three-step process [mercuriation with mercury(II) trifluoroacetate; reaction with borane; hydrolysis] for introducing boronic acid groups into polystyrene appears to be a useful alternative to the four-step process (bromination; lithiation with n-butyl-lithium; reaction with trimethylborate; hydrolysis) described by Fréchet *et al.*[18]

Fréchet *et al.* have used polymer-supported boronic acids as protecting groups for diols.[7] The polymer supported boronic acids prepared in the present work reacted similarly. Thus, treatment of a crosslinked polymer containing 1.9 mmol g^{-1} of residues (1) with the diol (8) in pyridine and azeotropic removal of water gave a polymer showing the expected infrared band at 1 720 cm^{-1} in 80% yield (by chlorine analysis). The reaction was reversed by treating the product with water.



Preparation of Polymers containing Phenol Residues (2; R = H).—The polymer-supported boronic acids described above were oxidised with trimethylamine oxide[19] or with alkaline hydrogen peroxide[6] to give polymers containing phenol residues (2; R = H). The infrared spectra of the products had bands at 3 450 cm^{-1} due to OH groups, but none at 1 340 cm^{-1} due to B–O bonds. The products were further identified by acetylation (product shows $\nu_{max.}$ 1 770 cm^{-1}) or by *p*-chlorobenzoylation ($\nu_{max.}$ 1 740 cm^{-1}). In the latter case elemental analysis for chlorine indicated that the conversion of boronic acid residues (1) into chlorobenzoate residues (2; R = *p*-chlorobenzoyl) was essentially quantitative.

The introduction of phenolic groups into preformed polystyrenes by the above method provides an alternative to the usual method of preparing such polymers, which is to carry out polymerisations or copolymerisations with *O*-protected vinylphenols followed by removal of the protecting groups.[20]

EXPERIMENTAL

I.r. spectra were measured for potassium bromide discs. Tetrahydrofuran (THF) was dried using calcium hydride and stored over molecular sieves. The linear polystyrene was a commercial sample, $\bar{M}_n$ 130 000. The 1% crosslinked polystyrene was Biobeads SX1 from Biorad Laboratories, Richmond, California. Thallium(III) trifluoroacetate[2] and diborane[21] were prepared as reported. Unless indicated otherwise the polymeric reaction products were dried to constant weight in a vacuum-oven at 60 °C and 2 mmHg. Metal analyses were carried out in duplicate by treating accurately weighed samples (*ca.* 0.2 g) of the metallated polymers with concentrated hydrochloric acid (10 ml) for 48 h at 60 °C, filtering the mixtures, and analysing the filtrates for mercury or thallium using standard procedures.[22]

Mercuriation of Polystyrene.—The following mercuriations are typical of those summarised in Table 1. In each experiment the mercuriated polymer was washed with water until it was free of mercury-(I) and -(II) salts, *i.e.*, until treatment of the washings with aqueous sodium hydroxide or with dilute hydrochloric acid gave no precipitate.[23]

(a) *Using linear polymer and mercury*(II) *acetate* (*entry* 6, *Table* 1). A solution of linear polystyrene (5.00 g) and mercury(II) acetate (15.9 g) in THF (50 ml) and acetic acid (10 ml) was vigorously stirred and heated under reflux for 72 h. The mixture was then added dropwise with stirring into methanol (500 ml). The polymer was filtered off, washed thoroughly with methanol then water, and dried. The product (12.6 g) had $\nu_{max.}$ 1 600 cm^{-1} (Found: Hg, 50.4%, indicating DS 0.73).

(b) *Using crosslinked polymer and mercury*(II) *acetate both with and without acid catalysis* (*entries* 8 *and* 9, *Table* 1). A mixture of crosslinked polystyrene (3.00 g), mercury(II) acetate (9.0 g), THF (30 ml), acetic acid (6 ml), and perchloric acid (2 drops, 60% aqueous solution) was vigorously stirred and heated under reflux for 6 h. The cold reaction mixture was filtered and the polymer washed repeatedly with ethanol and with water. The mercury(II) salts were easily washed out of the product but even after extensive washing with water mercury(I) salts were still present. Washing with methanol did not remove the inorganic impurities. The mercury(I) salts were eventually removed by stirring the product with water for several days. Finally the polymer was washed with ethanol, then THF, and dried. The product (4.8 g) had $\nu_{max.}$ 1 600 cm^{-1} (broad) (Found: Hg, 24.5%, indicating DS 0.19).

In a similar experiment from which the perchloric acid was omitted, the polymer obtained contained no mercury(I) salts and was easily washed free of mercury(II) salts. However, the product (3.1 g) weighed only slightly more than the starting material and its infrared spectrum did not have any discernbile carbonyl band at 1 600 cm^{-1}.

(c) *Using linear polymer and mercury*(II) *trifluoroacetate* (*entry* 11, *Table* 1). A solution of linear polystyrene (3.00 g) and mercury(II) trifluoroacetate (15.00 g) in THF (30 ml) was vigorously stirred and heated under reflux for 72 h. The mixture was then added dropwise with stirring into light petroleum (300 ml; b.p. 40—60 °C). The precipitated polymer was filtered off and washed with water, then ethanol, and dried. The product (9.90 g) had $\nu_{max.}$ 1 680 (C=O) and 1 150 and 1 190 cm^{-1} (C–F) (Found: Hg, 41.9%, corresponding to DS 0.60).

(d) *Using crosslinked polymer and mercury*(II) *trifluoroacetate* (*entry* 15, *Table* 1). A vigorously stirred mixture of crosslinked polystyrene (2.00 g) and mercury(II) trifluoroacetate (8.00 g) in THF (30 ml) was heated under reflux for 72 h. The mixture was cooled and the polymer filtered off. It was washed with water, ethanol, then THF, and dried. The product (4.50 g) had $\nu_{max.}$ 1 680, 1 150, and 1 190 cm^{-1} (Found: Hg, 32.2%, corresponding to DS 0.34).

Thalliation of Polystyrene.—The following experiments are typical of those summarised in Table 2.

(a) *Using linear polystyrene* (*entry* 3). A solution of linear polystyrene (2.00 g) and thallium(III) trifluoroacetate (11.00 g) in carbon tetrachloride (100 ml) was heated under reflux for 4 h. The precipitate which formed on cooling the reaction mixture was filtered off and then washed by stirring for several hours with each of the following solvents: THF, THF–water (3 : 1 v/v), methanol–water (3 : 1 v/v), methanol, and acetone. The dried product (6.30 g) had $\nu_{max.}$ 1 650 (carbonyl) and 1 150 and 1 200 cm^{-1} (C–F) (Found: Tl, 33.9%, corresponding to DS 0.57).

(b) *Using crosslinked polymer* (*entry* 5). A vigorously stirred mixture of crosslinked polystyrene (1.60 g) and thallium(III) trifluoroacetate (5.40 g) in dichloromethane (40 ml) was heated under reflux for 20 h. The polymer was then filtered off and washed successively with chloroform, THF, methanol, and ether, and dried. The product (4.70 g) had $\nu_{max.}$ 1 650, 1 150, and 1 200 cm^{-1} (Found: Tl, 29.0%, corresponding to DS 0.38).

Preparation of Polystyrenes containing Iodobenzene Residues (6).—The following procedures are typical. The results of other reactions with mercuriated polymers are given in Table 1 and with thalliated polymers in Table 2. The ^{13}C n.m.r. spectra of the products from the linear polymers were as summarised in Table 3.

(a) *Using mercuriated crosslinked polystyrene* (*entry* 15, *Table* 1). The mercuriated polymer (1.00 g) was stirred in THF (30 ml) with iodine (0.80 g) for 24 h at 20 °C. The polymer was collected and stirred with aqueous potassium iodide (50 ml, 10%) for 4 h. The polymer was then washed successively on a filter with water, ethanol, and THF. The dried polymer (0.42 g) had $\nu_{max.}$ 820 (s), 760 (s), and 700 cm^{-1} (s). It contained no mercury (Found: I, 32.6%, corresponding to DS 0.39).

(b) *Using thalliated linear polystyrene* (*entry* 2, *Table* 2). A mixture of the thalliated polymer (0.20 g), potassium iodide (0.30 g), dichloromethane (10 ml), and water (0.5 ml) was vigorously stirred for 24 h. The mixture was then cooled, filtered, and added dropwise to vigorously stirred methanol (100 ml). The precipitated polymer was filtered off, washed successively with water and methanol, and dried. The product (*ca.* 0.1 g) had $\nu_{max.}$ 820 (s), 780 (w), 760 (s), and 700 cm^{-1} (s) (Found: I, 33.3%, corresponding to DS 0.41).

Preparation of Polymers containing Phenylboronic Acid Residues (1).—The following are typical of the reactions summarised in Table 4.

(a) *Using a mercuriated linear polymer* (*entry* 1). Mercuriated linear polystyrene [1.00 g; DS 0.73; prepared using mercury(II) acetate] was stirred with THF (20 ml) for 2 h in a three-necked flask fitted with a nitrogen inlet, a septum cap, a drying tube, and a magnetic-stirrer bar. Diborane in THF (5.9 ml; 0.8M) was added using a syringe. The polymer immediately became dark grey and a gas was evolved. The mixture was stirred for 2 h at 20 °C then carefully treated with water (10 ml). The polymer was filtered off, washed thoroughly with water, THF, dioxan, methanol, acetone, and ether. To remove metallic mercury the polymer was dried in a vacuum oven (2 mmHg) at 150 °C for 20 h. The product (0.37 g) had $\nu_{max.}$ 1 350 cm^{-1} (broad; B–O) [there was no band at 1 600 cm^{-1}] (Found: B, 3.76% corresponding to DS 0.42).

(b) *Using mercuriated crosslinked polymer* (*entry* 4). Using a similar apparatus to that used in (a), mercuriated crosslinked polystyrene [4.0 g; DS 0.47; prepared using mercury(II) trifluoroacetate] was stirred with dry THF (30 ml) for 0.5 h to allow the polymer to swell. Diborane in THF (13 ml; 0.6M) was then added *via* the septum cap. The mixture immediately went black. It was stirred for 2 h at 20 °C then the reaction was worked up as above. The product (2.10 g) had $\nu_{max.}$ 1 340 cm^{-1} (broad) (there were no bands at 1 680, 1 150, or 1 190 cm^{-1}) (Found: B, 2.22% corresponding to DS 0.23).

Conversion of a Linear Polystyrene containing Phenylboronic Acid Residues (1) *into an Iodinated Polystyrene.*—Linear polystyrene containing phenylboronic acid residues (0.50 g, DS 0.38) was treated with sodium hydroxide (10 ml; 3M) and iodine (1.0 g) in THF (20 ml). The mixture was stirred at 20 °C for 16 h then added dropwise to vigorously stirred methanol (300 ml). The precipitate was collected and washed successively with THF–water (1 : 1 v/v), THF, methanol, and acetone. The dried polymer (0.58 g) had an infrared spectrum essentially the same as those of the iodinated polystyrenes described above. (Found: I, 34.3%, equivalent to DS 0.42).

2,3-*Dihydroxypropyl* p-*Chlorobenzoate* (8).—Reaction of solketal (the 1,2-acetanide of glycerol) with *p*-chlorobenzoyl chloride in pyridine gave the acetonide of 2,3-dihydroxypropyl *p*-chlorobenzoate (b.p. 195 °C at 20 mmHg). This on treatment with dilute hydrochloric acid at 20 °C for 12 h gave 2,3-*dihydroxypropyl* p-*chlorobenzoate* (8) (56% overall), m.p. 70—72 °C (from carbon tetrachloride), $\nu_{max.}$ (CCl_4) 3 250 and 1 720 cm^{-1} (Found: C, 52.2; H, 4.6. $C_{10}H_{11}ClO_4$ requires C, 52.1; H, 4.8%).

Attachment of 2,3-*Dihydroxypropyl* p-*Chlorobenzoate* (8) *to a Polymer containing Phenylboronic Acid Residues* (1) *and its Subsequent Detachment.*—These experiments are based on procedures described by Fréchet *et al.*[7]

(a) *Attachment.* A mixture of the crosslinked polymer (1.00 g; DS 0.23; 1.9 mmol of boronic acid groups), 2,3-dihydroxypropyl *p*-chlorobenzoate (0.45 g, 2.0 mmol), and dry pyridine (100 ml) was heated under reflux for 2 h whilst water was removed by azeotropic distillation. At the end of the reaction period the resin was filtered off and washed successively with THF and acetone. The dried product (1.36 g) had $\nu_{max.}$ 1 720 cm^{-1} (Found: B, 1.36; Cl, 4.57%, corresponding to DSs of 0.18 and 0.19 respectively).

(b) *Detachment.* The above polymer (1.00 g) was stirred with acetone–water (4 : 1 v/v; 30 ml) for 4 h at 20 °C. It was then filtered off, washed successively with THF and acetone, and dried. The polymer (0.72 g) had an i.r. spectrum identical to that of the original polymer containing boronic acid groups, and by elemental analysis B 1.83%, corresponding to DS 0.18. 2,3-Dihydroxypropyl *p*-chlorobenzoate (270 mg, 86%) was recovered from the washings. The spectroscopic properties (^{1}H n.m.r. and i.r.) of this material were identical to those of an authentic sample.

Preparation of Polymers containing Phenol Residues (2; R = H).—(a) *Using linear polymer.* A linear polymer containing phenylboronic acid residues (0.20 g; DS 0.42) was swollen in THF (15 ml) then treated with trimethylamine oxide (56 mg) for 19 h at reflux temperature. The cold reaction mixture was added to methanol and the product filtered off. The product was washed successively with methanol, acetone, THF, and ether. The dried polymer (0.18 g) had $\nu_{max.}$ 3 500 cm^{-1} (broad). A portion (0.10 g) was acetylated by treatment for 16 h with acetyl chloride in pyridine at 20 °C. The product (0.11 g), isolated as above, had $\nu_{max.}$ 1 770 cm^{-1} (strong).

(b) *Using crosslinked polymer.* A crosslinked polymer containing phenylboronic acid residues (0.40 g, DS 0.23) was swollen in THF (15 ml) then stirred with sodium hydroxide solution (2 ml; 3M) and hydrogen peroxide (1 ml; 30%) for 4 h at 20 °C. The polymer was filtered off and washed successively with water, THF, methanol, and ether. The dried product (0.34 g) had $\nu_{max.}$ 3 450 cm^{-1} (broad) and no absorption at 1 340 cm^{-1}.

The oxidised polymer was allowed to react with *p*-chlorobenzoyl chloride in dry pyridine at 80 °C for 10 h. The resin was filtered off and washed successively with THF, methanol, and ether. The dried product had $\nu_{max.}$ 1 740 cm^{-1} (Found: Cl, 7.0%, corresponding to DS 0.29).

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