Poly(p-tert-butoxycarbonyloxystyrene): a convenient precursor to p-hydroxystyrene resins

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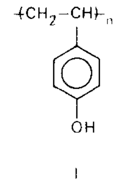
An efficient synthetic route to pure, high molecular weight poly(p-hydroxystyrene) is reported. The route involves synthesis of a new monomer, p-tert-butoxycarbonyloxystyrene, polymerization by radical initiation or by cationic initiation in liquid SO_2, followed by thermolysis or acidolysis of the tert-butoxycarbonyl protecting group. Porous, crosslinked resin beads containing the nucleophilic, phenol pendant group have been prepared in a similar fashion from the precursor terpolymer of p-tert-butoxycarbonyloxystyrene, styrene and divinylbenzene. The utility of this resin for solid-phase synthesis has been demonstrated.

Keywords Poly(p-tert-butoxycarbonyloxystyrene); poly(p-hydroxystyrene); p-tert-butoxycarbonyloxystyrene; p-tert-butoxycarbonyloxybenzaldehyde; polymerization; poly(vinyl phenol)

INTRODUCTION

Poly(p-hydroxystyrene) or poly(p-vinylphenol) (I) is an important and extremely versatile specialty polymer which has found numerous applications. For example, polymer I was used as a base soluble matrix resin in a recently described, two-component resist system[1]. We have also recently described the preparation of a cross-linked analogue to polymer I by chemical modification of polystyrene–divinylbenzene resins[2]. The p-hydroxystyrene resins have nucleophilic properties which make them useful in the field of polymer-supported reactions[3,4] or solid-phase syntheses[5,6]. A similar cross-linked resin has also been used as a separation medium in h.p.l.c. applications[7]. In other areas, the excellent dimensional stability of polymer I coupled with its chemical and thermal resistance have led to application as a curing agent for epoxy resins[8] and as a polymeric adsorbent for the removal of organic matters from aqueous wastes[9]. Modified forms of the polymer are useful in the formulation of fire-retardant polymer blends, electrical insulators, or in the preparation of membranes with selective permeability[10]. Polymer I has also been tested in several biomedical applications[11]. Numerous studies have focused on the preparation of derivatives of polymer I with hindered phenolic functionalities[12] for use as radical scavengers and antioxidants.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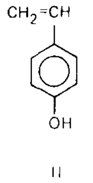
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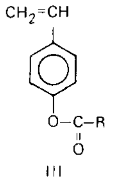
III

(a) $R = C_6H_5$
(b) $R = CH_3$
(c) $R = O{-}C(CH_3)_3$

Several procedures exist for the preparation of p-hydroxystyrene (II) or its p-acylated derivatives (III). Dale and Hennis[13] report the preparation of p-benzoyloxystyrene (IIIa) by decarboxylation of p-benzoyloxycinnamic acid or through a Grignard reaction on p-benzoyloxybenzaldehyde followed by dehydration of the resulting alcohol. Corson *et al.*[14] describe a two-step catalytic hydrogenation–dehydration method to produce p-acetoxystyrene (IIIb) from p-acetoxyacetophenone, and Sovish[15] prepared p-hydroxystyrene directly by distillation of a mixture of p-hydroxycinnamic acid, quinoline and copper powder. The latter procedure affords a distillate from which a 41% yield of II can be isolated; the author notes, however, that this isolation step is difficult as the product polymerizes extremely easily, especially in the presence of traces of the acidic reagents which may remain after isolation. This problem was partly overcome by Overberger *et al.*[16], who obtained an improved yield of II by sublimation of p-hydroxycinnamic acid. The Overberger procedure yields a mixture of starting material and II, which is free from acid impurities and thus is less prone to uncontrolled polymerization. Other routes to II include the dehydrogenation of p-ethylphenol at high temperature over a tin oxide catalyst, which proceeds in 35% conversion[17] and the thermal decomposition of 4,4′-ethylidenebisphenol over iron oxide–chromium oxide catalyst[18] or in the presence of sulphuric acid[18]. Although the preparation of I has been studied extensively, it remains a

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challenge, as it has proven difficult to obtain a pure polymer I. In most cases the polymer is coloured, suggesting the presence of oxidized impurities, and has a low molecular weight with a fairly broad distribution. A typical material obtained commercially[19] has $M_n = 1500$–3000 and $M_w = 3000$–7000; the polymer is brown and an analysis indicates that it contains approximately 2% more oxygen than would be calculated for pure I. Sovish[15] reported the spontaneous polymerization of II at temperatures as low as 0°C without any added initiator, to form a low molecular weight polymer. The self-polymerization of II at room temperature was also reported by Overberger *et al.*[16]; the polymerization proceeded in the solid state and afforded a polymer with $M_n = 4800$. In this instance, again, the polymer contained only 77.9% C *versus* a calculated 80% C content.

Although the phenolic functionality of II is expected to inhibit, or at least to disrupt, its free-radical polymerization, I has been prepared from II using AIBN as initiator[15,20,21]. The polymerization afforded a low molecular weight polymer which contained a significant excess of oxygen over the calculated amount.

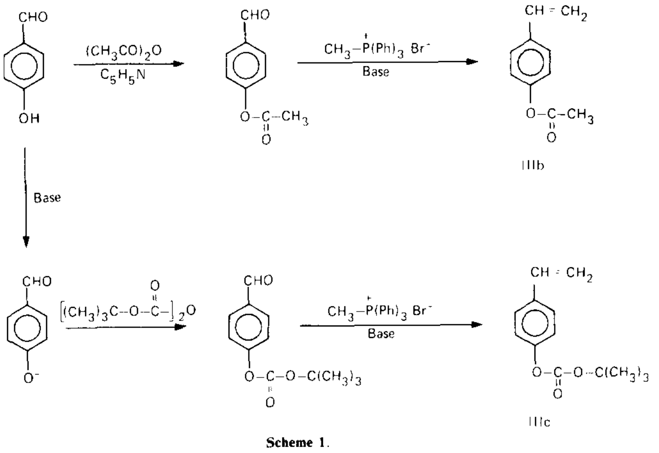
Some conflicting reports exist regarding the mechanism of polymerization of II in the presence of AIBN. Kato[21] reports that the polymerization proceeds by an 'almost normal free-radical mechanism', although little experimental evidence is given to support this claim. In fact, careful examination of the reported data shows that, in two otherwise similar polymerizations, a decrease in initiator concentration was accompanied by a decrease in the viscosity of the polymer rather than the increase which would normally be expected. The data reported by Still and Whitehead[22] point to an anomalous behaviour of II in its polymerization with AIBN as initiator. Thus, the viscosity of the polymer and the rate of polymerization seem to remain constant, regardless of initiator concentration; in fact, a polymer of similar viscosity can be obtained in the absence of AIBN or even in the presence of 5% tert-butylcatechol. Still and Whitehead conclude that II polymerizes through a non-radical mechanism and suggest an ionic mechanism involving self-initiation to produce a low molecular weight polymer.

Somewhat better results were obtained by Kato[23] using cationic initiators. However, owing to the strong phenolic activation of the aromatic rings of II, cationic polymerization was also accompanied by alkylation of the phenolic rings to yield a polymer with a structure which was not completely polyvinylic. Similar occurrences were also observed in the reactions of vinylhydroquinone and related monomers[24].

RESULTS AND DISCUSSION

Although the polymerization of II can yield materials useful in some applications, it is often desirable to prepare polymers containing *p*-hydroxystyrene units free from any side products and, in particular, oxidized byproducts. At first glance, the polymerization of *p*-acetoxystyrene followed by removal of the acetyl side groups seems like a satisfactory route. Indeed, IIIb can be polymerized by free-radical initiators[25], but we have observed that it cannot be polymerized cleanly by a cationic initiator such as boron trifluoride etherate as the polymerization reaction is accompanied by some loss of acetyl protecting groups. In addition, the preparation of the monomer itself is not ideal, as much polymerization occurs during the harsh dehydration step in the procedure of Corson *et al.*[14] Additional problems may be encountered during removal of the acetyl protecting groups especially in the case of copolymers of IIIb with other reactive monomers. For example, Ledwith *et al.*[5] had to use a hydrazinolysis reaction to remove the acetyl groups of a copolymer of IIIb with acrylonitrile to avoid reactions on the sensitive nitrile groups. We have encountered a similar problem in our work with bifunctional copolymers[4]. Thus, it is desirable to test a different protecting group for the phenolic functionalities of II. A first possibility involving the use of trimethylsilyl protecting groups was not fully explored as parallel work with *p*-hydroxy-α-methylstyrene had shown that the trialkylsilylated polymer cannot be conveniently deprotected under mild conditions[26]. A second interesting possibility involves the use of the tert-butoxycarbonyl group (t-BOC), which is one of the most versatile protecting groups used in peptide chemistry.

Several of the reagents developed specifically for introduction of the t-BOC group onto amines can potentially react just as well with good nucleophiles such as phenolates. We recently reported successful use of t-BOC as a phenol protecting group[27], but, to the best of our knowledge, this is the only prior use. The reagent we chose to test the protection of *p*-hydroxybenzaldehyde was di-tert-butyl dicarbonate, a readily available reagent which is both safe and easy to use. Indeed, the introduction of the t-BOC protecting group on *p*-hydroxybenzaldehyde proceeds readily to afford the desired protected phenol in essentially quantitative yield (Scheme 1). The corresponding vinyl compound IIIc is then prepared from *p*-tert-butoxycarbonyloxybenzaldehyde in one step by a Wittig reaction with methyltriphenylphosphonium bromide in good yield. In contrast, the Wittig reaction of *p*-acetoxybenzaldehyde with methyltriphenylphosphonium bromide gives a very low yield of the desired vinyl monomer IIIb as extensive attack on the acetyl protecting group is observed and results in the formation of *p*-hydroxybenzaldehyde as a major byproduct (Scheme 1). Monomer IIIc is stable at room temperature and can be polymerized readily by radical or certain cationic initiators to afford high molecular weight polymers (IVc) with M_n and M_w as high as 50 000 and 100 000, respectively (*Table 1*). The i.r. spectrum of IVc has a sharp carbonyl band at 1758 cm^{-1} and no hydroxyl absorption (*Figure 1*).



Scheme 1.

Table 1 Polymerization of *p*-tert-butoxycarbonyloxystyrene (IIIc)

Polymn. no.	Monomer (g)	Initiator (mol %)	Solvent (ml)	Temp. (°C)	Time (h)	Yield (%)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$
E067B[a]	5.0	AIBN (0.8)	Toluene (5.0)	65–75	24	82.0	43.0[c]	
84[b]	0.350	BF_3OEt_2 (1.0)	CH_2Cl_2 (1.0)	−78	72	4.9	27.5[d]	84.6[d]
86[b]	1.000	BF_3OEt_2 (0.8)	SO_2 (3.0)	−65	27	90.1	63.1[c]	89.8[d]

[a] Polymerization was carried out under inert atmosphere

[b] Polymerization was carried out under high vacuum

[c] Value determined by membrane osmometry

[d] Value determined by g.p.c. with THF as a solvent (relative to polystyrene)

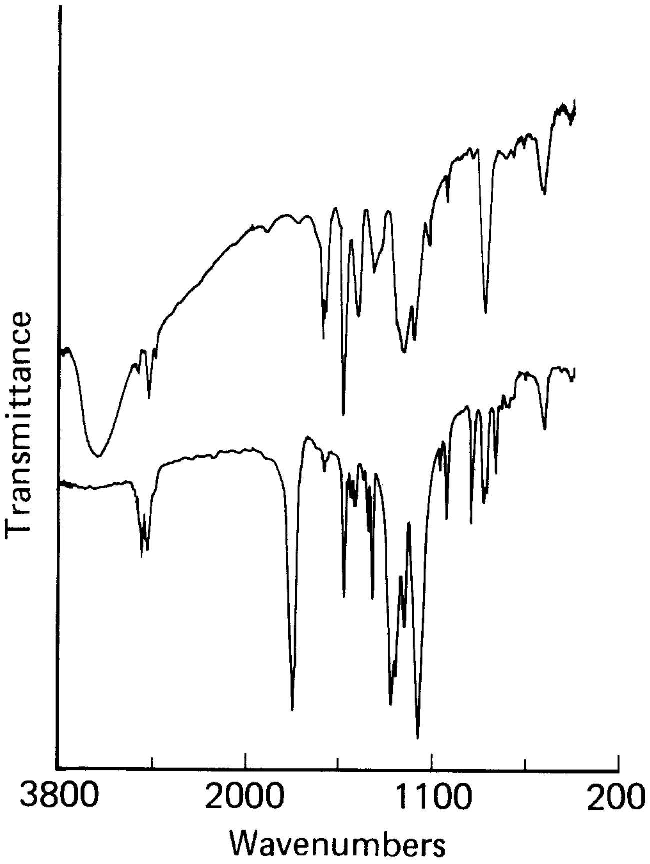


Figure 1 I.r. spectra of I (top) and IVc (bottom)

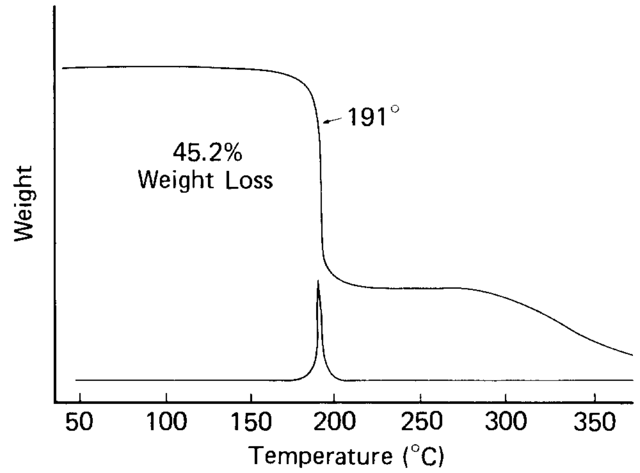


Figure 2 Thermogravimetric analysis (t.g.a.) of IVc

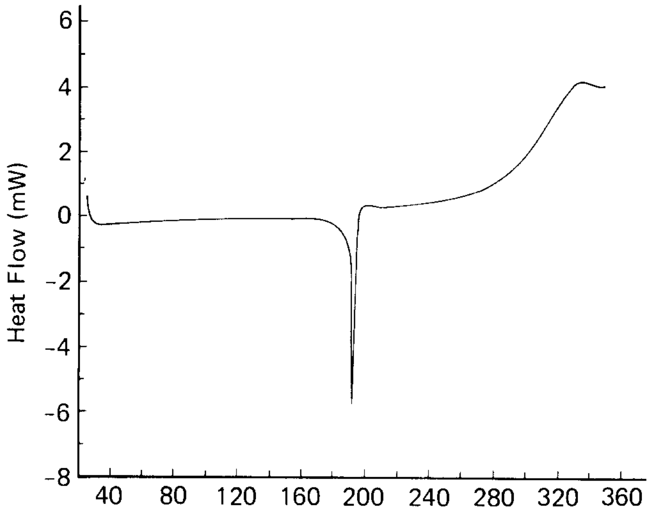
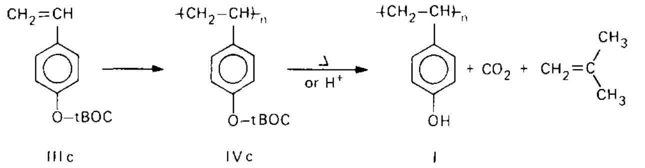


Figure 3 Differential scanning calorimetry (d.s.c.) of IVc

In an earlier paper[27] we described a cationic polymerization of *p*-tert-butoxycarbonyloxy-α-methylstyrene. We reported that attempts to carry out cationic polymerization of the monomer in dichloromethane resulted in low molecular weight polymer and that the polymerization was accompanied by a significant amount of acidolysis of the t-BOC protecting group. High molecular weight poly(*p*-tert-butoxycarbonyloxy-α-methylstryene) was, however, obtained in excellent yield and without loss of the protecting group when the polymerization was carried out in *liquid sulphur dioxide*[27]. Unlike the α-methylstyrene analogue, the styrene monomer IIIc can be readily polymerized by radical initiation. However, cationic polymerization of IIIc was also studied. The results parallel those detailed for the α-methylstyrene analogue. As shown in *Table 1*, cationic polymerization of IIIc in dichloromethane (no. 84) produces a low yield (4.9% in three days) of polymer IVc, whereas polymerization in *liquid sulphur dioxide* (no. 86) gave a high yield (90.1% in one day) of polymer IVc with a high molecular weight. The molecular weight of IVc prepared by BF_3OEt_2 polymerization in liquid sulphur dioxide is comparable to that obtained by radical polymerization and the protecting group is not lost during the polymerization.

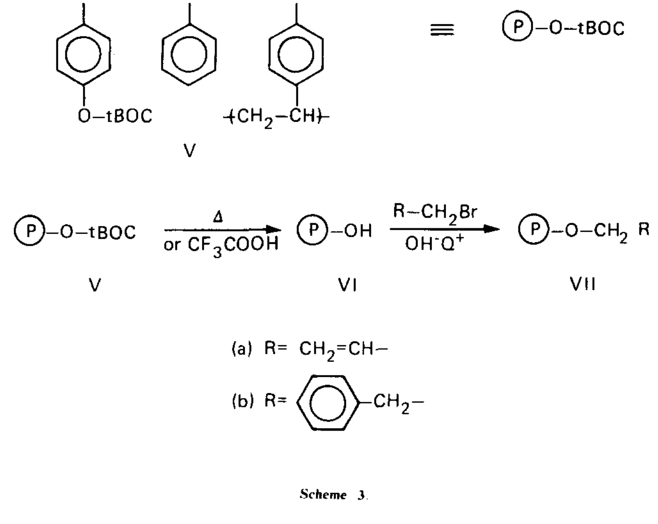
The thermal analysis of polymer IVc yields some interesting data (*Figure 2*). A sharp loss of 45% of the mass of the starting polymer is observed near 200°C, followed by a plateau, which indicates that the thermally modified polymer is stable to much higher temperatures. This thermal modification of IVc is confirmed by the d.s.c. data (*Figure 3*) which shows a sharp endotherm near 200°C followed by a return to the original baseline once the thermal event is completed. Analysis of the polymer after heating to 200°C shows that it consists of pure I produced by the thermolysis of the t-BOC protecting group with evolution of one molecule of carbon dioxide and one molecule of 2-methylpropene per t-BOC group (which amounts to 45% of the total mass of polymer IVc). The thermolysis reaction shown in Scheme 2 affords a polymer which has an elemental analysis in agreement with that expected for pure I, and is soluble in aqueous base as expected for a phenolic resin. The i.r. spectrum of I shows no remaining carbonate band and has a very large hydroxyl band centred near 3380 cm^{-1} (*Figure 1*). Difference spectroscopy shows the loss of large C–H, C=O, and C–O absorptions at 2982, 1758 and 1148–1276 cm^{-1}, corresponding to the loss of the t-BOC groups. As expected, the t-BOC protecting groups can also be removed under more classical conditions in acidic medium. Best results are obtained with trifluoroacetic acid, which removes the t-BOC groups very cleanly and is probably the chemical reagent of choice for the deprotection of IVc. In contrast to the poly(α-methylstyrene) derivative[27], the acidolysis of IVc is not accompanied by main chain degradation.



Scheme 2.

The finding that IVc can be deprotected cleanly and in quantitative yield by thermolysis is important as it opens a new avenue for the use of such t-BOC protected phenolic resins. We have recently applied this procedure to the protection and preparation of other polymers containing phenolic pendant groups[27]. We have also found that IVc is an extremely versatile resist material. The lithographic work will be reported elsewhere.

The applicability of IIIc to the preparation of porous crosslinked resin beads containing the nucleophilic pendant group was also tested. Suspension copolymerization of IIIc with styrene and divinylbenzene affords a porous bead polymer (structure V, Scheme 3) which contains the desired t-BOC functionalities. The extent of incorporation of IIIc in the terpolymer can be established either directly from the elemental analysis of the polymer or from a thermogravimetric analysis. In a typical preparation, the resin beads show a 20.5% loss of weight when heated briefly to 200°C due to the thermally induced decomposition of the t-BOC groups with evolution of carbon dioxide and 2-methylpropene as above. This corresponds to an incorporation of 45 wt% of IIIc in the terpolymer, or approximately 20 mol% for a functional loading of 2.05 mmol of t-BOC groups per gram of resin V. This figure is in exact agreement with that obtained through calculation from the elemental analysis data. After thermolysis, the i.r. spectrum of the resin has lost the large carbonyl band of its t-BOC precursor and shows a large hydroxyl band; the final functional group loading of resin VI is of approximately 2.5 mmol OH per gram. Accessibility of the reactive sites of insoluble resins V and VI to reagents in solution is confirmed by the successful removal of all the t-BOC groups of the resin by reaction with trifluoroacetic acid in dichloromethane and also through reactions involving the phenolic groups of the deprotected resin (Scheme 3). For example, VI could be O-alkylated by reaction with allyl bromide or *p*-nitrophenethyl bromide in toluene in the presence of powdered potassium hydroxide and tetrabutylammonium bromide or 18-crown-6. The alkylation is a solid–liquid–solid phase transfer reaction between two solid phases dispersed in an organic solvent[4].



Scheme 3.

EXPERIMENTAL

Di-tert-butyl dicarbonate, *p*-hydroxybenzaldehyde and methyltriphenylphosphonium chloride were obtained from Sigma Chemicals. Styrene and divinylbenzene (45–55% pure) were purchased from Polysciences Inc.; styrene was distilled immediately before use while divinylbenzene was used as received. All reactions were carried out under a dry nitrogen atmosphere unless otherwise stated. N.m.r. spectra were recorded in deuteriochloroform using Varian CFT-80, EM360 or HA-100 spectrometers. I.r. spectra were recorded on Nicolet MX-1 or Perkin–Elmer 283 i.r. spectrometers. Thermal analyses (t.g.a. and d.s.c.) were performed on a Dupont 951 or 1090 at a heating rate of 10°C min^{-1} with a flow of 30 ml air per minute from ambient temperature to 375°C. Chromatographic separations were performed on a Waters Model Prep-500 preparative high-pressure liquid chromatograph with silica gel columns and ethyl acetate–hexane mixtures for elution. Molecular weight measurements were made using a Wescan 230 or 231 recording membrane osmometer with toluene or THF as solvent while g.p.c. measurements were made on a Waters Model 150 chromatograph equipped with six or eight microstyragel columns at 30° or 40°C in THF.

Preparation of p-*acetoxystyrene* (*IIIb*)

p-Acetoxystyrene was prepared according to the literature[14]. In general, the dehydration step was accompanied by polymerization of a significant amount of IIIb, which affected the overall yield (42–45%) of the preparation.

Alternatively, IIIb was prepared by a Wittig reaction as follows. *p*-Hydroxybenzaldehyde (70 g) was dissolved in 624 ml of 7.5% NaOH in an ice bath. The mixture was then treated slowly with 80 ml of acetic anhydride, while keeping the internal temperature below 10°C. Once the addition was complete (thin-layer chromatography indicated that the reaction was over), the mixture was extracted with dichloromethane. After washing and drying the organic layer, evaporation of the solvent afforded a crude product, from which the pure material (73 g, 78%) was obtained by distillation at 90°C/1 mmHg. The n.m.r. spectrum of *p*-acetoxybenzaldehyde includes resonances at δ 2.86 (3H, s, acetyl); 7.72, 7.86, 8.36 and 8.50 (4H, *p*-subst. aromatic); 10.46 (1H, s, CHO).

A suspension of 28 g of methyltriphenylphosphonium bromide, 8.73 g of potassium tert-butoxide and 0.2 g of 18-crown-6 in 150 ml of THF freshly distilled over $LiAlH_4$ was stirred with external cooling while 11.5 g of *p*-acetoxybenzaldehyde in 100 ml of THF were added. After stirring overnight, THF was evaporated and the residue extracted with ethyl acetate and water. After washing and drying the organic phase, h.p.l.c. purification afforded 4.1 g (36%) of pure IIIb; a significant amount of *p*-hydroxybenzaldehyde was also isolated from the reaction mixture. Alternative preparations of IIIb using modifications of this procedure (including reverse addition of the reagents) gave similar results with yields of pure product varying from 12 to 42%. The n.m.r. spectrum of IIIb includes resonances at δ 2.36 (3H, s, acetyl); 5.28, 5.42, 5.66 and 5.95 (2H, βCH_2); 6.66, 6.86 and 6.95 (1H, αCH); 7.16, 7.33, 7.54 and 7.71 (4H, *p*-subst. aromatic).

Preparation of p-*tert-butoxycarbonyloxybenzaldehyde*

A solution of 21.7 g of *p*-hydroxybenzaldehyde in dry THF was treated with 19.94 g of potassium tert-butoxide under a nitrogen atmosphere. After stirring for a few minutes at room temperature, 42.8 g of di-tert-butyl dicarbonate were added and the mixture was stirred for another hour at room temperature. Thin-layer chromatography showed that the reaction was complete and the mixture was poured into ice water. The product was extracted with ethyl acetate, washed with water and dried over magnesium sulphate. Evaporation of the solvent afforded 39 g (99%) of a crude material which can be used directly for the preparation of IIIc. Alternatively, the product was purified by preparative h.p.l.c. to afford analytically pure material. The n.m.r. spectrum of *p*-tert-butoxycarbonyloxybenzaldehyde includes peaks at δ 1.57 (9H, s, tert-butyl); 7.26, 7.39, 7.78 and 7.96 (4H, *p*-subst. aromatic); 10.03 (1H, s, CHO). Mass spectrum: M+ not visible, m/e 207, 163, 122, 57. I.r. spectrum: sharp aldehydic C–H at 2733 cm^{-1}, C=O (carbonate) at 1758 cm^{-1}, and C=O (aldehydic) at 1702 cm^{-1}.

Preparation of p-*tert-butoxycarbonyloxystyrene* (*IIIc*)

A suspension of 34.1 g of methyltriphenylphosphonium bromide in 400 ml of dry THF was treated with 10.7 g of potassium tert-butoxide under a nitrogen atmosphere. After stirring for 10 min at room temperature, the yellow solution was treated with a solution of 21.2 g of *p*-tert-butoxycarbonyloxybenzaldehyde in 100 ml of dry THF. After stirring for 1 h, the mixture was poured into cold water and extracted with ethyl acetate. The organic phase was washed, dried over magnesium sulphate and concentrated. The crude product was purified by preparative h.p.l.c. to yield 16.6 g (79%) of pure IIIc. Alternatively, IIIc was purified by distillation under reduced pressure. The n.m.r. spectrum of IIIc has peaks at δ 1.60 (9H, s, tert-butyl); 5.25, 5.35, 5.69 and 5.96 (2H, βCH_2); 6.54, 6.65, 6.71 and 6.82 (1H, αCH). Mass spectrum: M+ not visible, m/e 205, 120, 103, 77, 57. The i.r. spectrum of IIIc has a sharp C=O band at 1758 cm^{-1} and a C=C band at 1630 cm^{-1}.

Free radical polymerization of IIIc

A solution of 5 g of IIIc in 5 ml of toluene containing 0.03 g of AIBN was heated to 65°–75°C under nitrogen. The mixture became very viscous overnight and, after being diluted with dichloromethane, the polymer was precipitated in petroleum ether. The white solid was washed with petroleum ether, then with methanol and dried. The polymer weighed 4.1 g (82% yield) and has $M_n = 43\,000$ (osmometry). The i.r. spectrum of IVc has a large C=O band at 1758 cm^{-1} as well as C–H and C–O bands at 2982 and 1148–1276 cm^{-1}, respectively. The n.m.r. and analytical data are in agreement with those expected for IVc; no deprotected moieties were detected in the polymer.

Cationic polymerization of IIIc

Purification of reagents and high-vacuum polymerization technique were described in our previous paper[27]. The monomer IIIc (1.000 g) was dried under high vacuum overnight and dissolved in 3.0 ml of liquid sulphur dioxide that was distilled *in vacuo* into the polymerization ampoule to give a yellow solution. With the monomer solution frozen at liquid-nitrogen temperature, BF_3OEt_2 (0.8 mol% to the monomer) was introduced by distillation *in vacuo*. The ampoule was placed in a bath maintained at −65°C and the reagents were thoroughly mixed. The solution became turbid and viscous. After 27 h, the ampoule was cut open and cold methanol was added at −65°C to precipitate the polymer. The precipitated polymer was dissolved in chloroform, precipitated in methanol, purified by reprecipitation in methanol, and dried *in vacuo* at 40°C to provide 0.901 g (90.1%) of product with $M_n = 63\,100$ (osmometry). The i.r. spectrum of the product did not show any evidence of cleavage of the t-BOC group.

Cationic polymerization in dichloromethane was carried out in a similar fashion at −78°C for 3 days. The polymer was purified by precipitations in hexanes and the yield amounted to only 4.9%.

Preparation of crosslinked resin (*V*)

To a solution of 2 g of poly(vinyl alcohol) in 300 ml of freshly boiled, distilled water was added a mixture of 10 g of styrene, 10 g of IIIc, 2 g of divinylbenzene, and 14 ml of toluene containing 0.2 g of AIBN. The mixture was stirred mechanically while the polymerization reactor was kept at 80°C. After stirring for 8 h at 80°C, the mixture was cooled and the polymer beads were filtered through a cloth filter which did not retain the finer particles. After washing the polymer with water and methanol, the beads were placed in a Soxhlet extractor and extracted with methanol. The final product weighed 12 g. An i.r. spectrum of polymer V confirms the presence of a significant amount of IIIc units in the beads, while elemental analysis indicates 82.7% C and 7.7% H, in good agreement with the calculated analysis, 82.6% C and 7.6% H, for a polymer containing 28 mol% of the *p*-t-BOC groups. The latter value was calculated from the data obtained by t.g.a. as thermolysis of the t-BOC protecting groups resulted in the loss of 20.5% of the weight of the starting polymer (V).

Preparation of I: removal of the t-BOC protecting groups

Since the t.g.a. of IVc shows that the t-BOC protecting groups of IVc can be removed in quantitative yield by thermolysis near 200°C, I was prepared by heating the polymer in bulk in an oven at 200°C for 15 min or less. The weight loss observed in a typical experiment amounted to 45.2% of the weight of the starting polymer, as expected from the t.g.a. study. Alternately, the t-BOC protecting groups were removed by treatment with trifluoroacetic acid as follows: The polymer was dissolved in dichloromethane and trifluoroacetic acid was added. A reaction occurred immediately with evolution of gas. The polymer was recovered by solvent evaporation or precipitation in petroleum ether. The n.m.r. and analytical data were in agreement with those expected for I.

Preparation of crosslinked poly(p-hydroxystyrene) (VI)

Removal of the t-BOC protecting groups of V was carried out as above by thermolysis at 200°C or by treating a suspension of polymer V in 1,2-dichloroethane with trifluoroacetic acid. Once the evolution of gas was complete, the polymer was filtered and washed repeatedly with 1,2-dichloroethane, dioxane–water 4:1, and methanol. The final product had lost 20% of its starting weight, confirming that removal of the protecting groups was essentially complete (theory: 20.5%).

Preparation of derivatives of VI under phase transfer conditions

To a suspension of 0.5 g of VI in 4 ml of dichloromethane were added 0.5 g of powdered KOH and 0.08 g of tetrabutylammonium chloride. After stirring for 30 min, 1 ml of allyl bromide was added and the mixture was stirred overnight. After extracting all soluble materials from the polymer and drying, i.r. spectroscopy shows a large decrease in the hydroxyl band and appearance of new, large bands at 1238 and 1028 cm^{-1} (C–O), a small C=O band at 1647 cm^{-1}, and bands at 999 and 924 cm^{-1} characteristic of the allyl group[28], with additional weak bands at 1303 and 1420 cm^{-1}. A similar reaction was carried out under solid–liquid–solid phase transfer conditions with 18-crown-6 as phase transfer catalyst in the presence of powdered KOH and using *p*-nitrophenethyl bromide as the electrophile. After filtration and thorough washing of the polymer, an i.r. spectrum confirmed the incorporation of *p*-nitrophenethyl groups evidenced by strong bands due to the nitro groups at 1514 and 1346 cm^{-1}, and a weaker C–N band at 860 cm^{-1}. In both cases, owing to the relatively short reaction time, the reaction was incomplete; nitrogen analysis on the *p*-nitrophenethyl derivative indicated that 67% of the phenolic groups had reacted.

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REFERENCES

1 Iwayanagi, T., Kohashi, T., Nonogaki, S., Matsuzawa, T., Douta, K. and Yanazawa, H. *IEEE Trans. Electron Devices* 1981, **ED-28**, 1306

2 Fréchet, J. M. J., de Smet, M. D. and Farrall, M. J. *Polymer* 1979, **20**, 675

3 Fréchet, J. M. J. *Tetrahedron* 1981, **37**, 663

4 Fréchet, J. M. J. 'Crown Ethers and Phase Transfer Catalysis in Polymer Science', (Eds. C. E. Carraher and L. Mathias), Plenum Press, New York, in press

5 Ledwith, A., Rahnema, M. and Sen Gupta, P. K. *J. Polym. Sci., Polym. Chem. Edn.* 1980, **18**, 2239; Arshady, R., Kenner, G. W. and Ledwith, A. *J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 2017

6 Fridkin, M., Patchornik, A. and Katchalski, E. *J. Am. Chem. Soc.* 1968, **90**, 2953; Williams, R. E. *J. Polym. Sci. A-1* 1972, **10**, 2123

7 Ono, Y., Nishishita, T. and Sekiya, M. *Jpn. Kokai Tokkyo Koho* 1978, **78**, 80291 (*Chem. Abstr.* **89**, 2257214y)

8 Fujiwara, H., Takahashi, A. and Suzuki, K. *Maruzen Sekiyu Giho* 1976, **21**, 1 (*Chem. Abstr.* **88**, 121944m)

9 Kawabata, N. and Taketani, Y. *Bull. Chem. Soc. Jpn.* 1980, **53**, 2986

10 Fujiwara, H. and Takahashi, A. *Yuki Gosei Kagaku Kyokaishi* 1977, **35**, 877

11 Ferruti, P. *Chim. Ind.* (*Milan*) 1973, **55**, 147

12 Kato, M., Takemoto, Y., Nakano, Y. and Masahiro, Y. *J. Polym. Sci. A-1* 1975, **13**, 1901; Braun, D., Tormalla, P. and Wittig, W. *Makromol. Chem.* 1981, **182**, 2217; Braun, D. and Meier, B. *Makromol. Chem.* 1974, **175**, 791

13 Dale, W. J. and Hennis, H. E. *J. Am. Chem. Soc.* 1958, **80**, 3645

14 Corson, B. B., Heintzelman, W. J., Swartzman, L. H., Teifenthal, H. E., Lokken, R. J., Nickels, J. E., Atwood, G. R. and Pavlik, F. J. *J. Org. Chem.* 1958, **23**, 544

15 Sovish, R. C. *J. Org. Chem.* 1959, **24**, 1345

16 Overberger, C. G., Salamone, J. C. and Yaroslavsky, S. *J. Am. Chem. Soc.* 1967, **89**, 6231

17 Tachibana, Y., Matsumoto, O. and Oshima, S. *Jpn. Kokai Tokkyo Koho* 1980, **80**, 28958 (*Chem. Abstr.* **93**, 185938y)

18 *Jpn. Kokai Tokkyo Koho* 1979, **79**, 84536 (*Chem. Abstr.* **91**, 15743); *Jpn. Kokai Tokkyo Koho* 1981, **81**, 53131 (*Chem. Abstr.* **95**, 187872n)

19 Resin M, manufactured by Maruzen Oil Co. (Tokyo)

20 Danusso, F., Ferruti, P. and Gazzaniga-Marabelli, C. *Chem. Ind.* (*Milan*) 1965, **47**, 55

21 Kato, M. *J. Polym. Sci. A-1* 1969, **7**, 2175

22 Still, R. H. and Whitehead, A. *J. Appl. Polym. Sci.* 1977, **21**, 1119

23 Kato, M. *J. Polym. Sci. A-1* 1969, **7**, 2405

24 Cassidy, H. G. and Kun, M. A. 'Oxydation–Reduction Polymers', Interscience, New York, 1965; Cassidy, H. G., Ezrin, M. and Updegraff, I. H. *J. Am. Chem. Soc.* 1953, **75**, 1615

25 Danusso, F., Ferruti, P. and Gazzaniga-Marabelli, C. *Chim. Ind.* (*Milan*) 1965, **47**, 493

26 Gipstein, E., unpublished data

27 Ito, H., Willson, C. G., Fréchet, J. M. J., Farrall, M. J. and Eichler, E., *Macromolecules*, in press

28 Kato, M. and Kamogawa, H. *J. Polym. Sci. A-1* 1968, **6**, 2993