Functionalization of crosslinked polystyrene resins: 2. Preparation of nucleophilic resins containing hydroxyl or thiol functionalities

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Crosslinked polystyrene resins containing thiol or hydroxyl functionalities on a fraction of their aromatic rings were prepared by reaction of crosslinked polystyryllithium with elemental sulphur or oxygen followed by reduction of the resulting polymer. Similarly, resins containing hydroxymethyl or thiomethyl functional groups were prepared from chloromethylated polystyrene by displacement of chloride in procedures involving three phase systems and the use of a phase transfer catalyst. The degree of functionalization could be controlled easily and the sulphur containing polymers were free of disulphide bonds.

The preparation of crosslinked polystyrene resins[1–4] containing various functionalities is of interest in several contexts including the use of polymers as supports in organic synthesis[5,6], in ion exchangers[7], reagents[6,8], protecting groups[9], supports for affinity chromatography[10] or catalysis[11], immobilizing media for drugs[12] or for the detection of unstable reaction intermediates[13], chelating agents[14], etc.

In general, resins containing functional groups are prepared by either of two procedures: preparation of reactive functional monomers and their copolymerization with a suitable crosslinking agent, or chemical modification of a preformed crosslinked polymer[1–14]. We favour the second approach which can be used with resins of controlled pore size and desirable physical properties. In addition, the chemical modification approach allows for a good control of the degree of functionalization of the resin.

Polystyrene resins which possess reactive handles such as the chloromethyl group are extremely useful in a number of applications in which a substrate is attached to the resin by nucleophilic displacement of chloride[4–6,11,12,14,18]. No other resin presently available is as versatile as chloromethylated polystyrene although lithiated polystyrene resins have recently found numerous applications[3,9,11,15–17]. The preparation of resins containing reactive hydroxyl or thiol functionalities has received little attention; yet, such resins might prove to be extremely useful in view of their ability to generate powerful nucleophilies which, in turn, can be used for the attachment of various substrates under very mild conditions.

PREPARATION OF PSt–SH

In a recent publication[3] we have reported very briefly on the reaction of polystyryllithium PSt–Li with elemental sulphur, a reaction which yields a polymer containing sulphur attached to the aromatic rings of polystyrene. We have now completed the study of this reaction and have also extended it to the synthesis of polymers containing oxygen.

$$\text{PSt–Li} \xrightarrow{S_8} \text{PSt–S}_x\text{H} \xrightarrow{\text{LiAlH}_4} \text{PSt–SH}$$

In all cases, the preparations are carried out in one-pot reactions using the special flask shown in *Figure 1* which allows for filtrations of intermediates without removal of the polymer from the reaction vessel. The polystyryllithium can be generated directly from polystyrene using the direct lithiation procedure[3,17] with n-butyllithium-tetramethylethylenediamine, or *via* the bromination–lithiation route[3]. In general, we prefer the second route which allows for a better control of the degree of functionalization but requires an additional step. In particular, it is easier to obtain polymers with high degrees of functionalization using the bromination–lithiation route (*Table 1*) rather than the direct lithiation procedure (*Table 2*).

By reaction of PSt–Li with an excess of sulphur, the product which is obtained often contains more sulphur than is theoretically possible as calculated from the bromine content of the PSt–Br precursor. This indicates that in addition to the desired thiol, di- and polysulphides are formed. To obtain the desired polymeric thiol, the polymer must be reduced to eliminate all sulphur–sulphur bonds. We have carried out this reduction with lithium aluminium hydride under reflux to ensure that no S–S bonds remain in the polymer. Although the polymer which is obtained can be used efficiently in a number of nucleophilic substitutions[18], we suspect that it still contains some unreactive sulphur-containing sites, perhaps in the form of sulphides which create additional crosslinks in the polymer. We have however determined that PSt–SH does not have a great tendency to form disulphides.

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Our first experiments using the bromination–lithiation route involved the use of a large excess of sulphur which had had to be removed from the resin prior to the reduction. This excess is not necessary as the yields which were obtained using only an equivalent amount of sulphur were practically identical to those obtained in reaction involving large excesses of sulphur (*Table 1*). In a typical experiment involving equivalent amounts of polystyryllithium and of sulphur, approximately 83% of the sulphur became attached to the polymer. After reduction of the sulphur–sulphur bonds, approximately 73% of the sulphur remained on the polymer, indicating that approximately 10% of the original sulphur had not been attached directly to the aromatic ring of the polymer. As can be seen in *Table 1*, the transformation of PSt–Br into PSt–SH was generally achieved in yields of 70–75% and thus the reaction can produce predictable results.

In the preparation of PSt–SH by direct lithiation of polystyrene followed by reaction with sulphur, best results are obtained using a 1:1 ratio of base to polymer (*Table 2, exp. 1*). Lowering the amount of base or of sulphur relative to polymer results in a decrease in the degree of functionalization (*Table 2, exp. 2* and *3*). In an attempt to increase functionalization, we substituted t-BuLi for n-BuLi, but found that a decrease in functionalization resulted (*Table 2, exp 2* and *6*), a result in marked contrast with that obtained for soluble polystyrene[28]

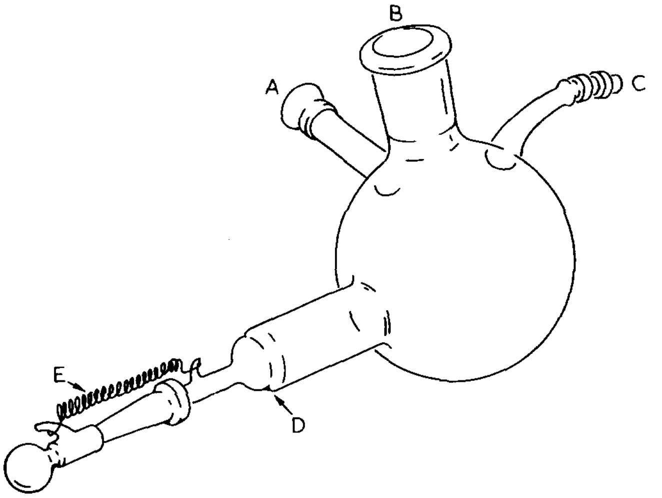


Figure 1 Flask for generation and reaction of PSt–Li. A, septum inlet; B, to condenser, drying tube, etc., C, inert gas inlet; D, fritted glass filter; E, outlet

PREPARATION OF PSt–OH

The first preparation of a crosslinked polystyrene resin containing p-hydroxystyrene units was reported by Letsinger and Hamilton in 1959[19]. Their product was obtained by copolymerization of the ethyl tartrate ester of p-vinylbenzeneboronic acid with styrene and diallyl maleate followed by oxidation of the copolymer with hydrogen peroxide. The final product had an infrared spectrum which indicated the presence of some hydroxyl as well as of some undesired functionalities. Another preparation[20] of PSt–OH which was reported more recently involved the copolymerization of p-acetoxystyrene with styrene and divinylbenzene followed by removal of the acetyl groups with hydrazine hydrate. There is no previous report of the preparation of crosslinked hydroxypolystyrene by chemical modification of crosslinked polystyrene. Our procedure for this reaction involves the addition of oxygen to a suspension of polystyryllithium in dry THF or benzene at room temperature. This reaction is easier to carry out than the corresponding preparation of PSt–SH since an excess of oxygen can be used without adversely affecting the ease of purification of the product. Although the reaction seemed to form little hydroperoxide, the polymers were routinely washed with sodium bisulphite to ensure their reduction to the desired hydroxyl polymers. The infrared spectrum of PSt–OH included a large hydroxyl absorption at 3590 and 3500 cm^{-1} and the polymer reacted easily with benzoyl chloride to yield the corresponding benzoate in which the hydroxyl absorption had disappeared and been replaced by a large absorption at 1740 cm^{-1}.

As was the case for the corresponding polystyryl mercaptan, the transformation of PSt–Br into PSt–OH via PSt–Li proceeded in approximately 75% yield. We have also studied the preparation of PSt–OH using the direct lithiation of

Table 2 Preparation of PSt–SH by direction lithiation

Exp. #	Base complex	Ratio polystyrene: base: sulphur	Reaction conditions	S analysis mequiv./g	D.F.
1	nBuLi:TMEDA	1 1:0:49	4 hr, 60° C	1.98	0.22
2	nBuLi:TMEDA	1.62:1:0.49	4 hr, 65° C	1.40	0.15
3	nBuLi:TMEDA	1.62:1:0.24	4 hr, 65° C	1.01	0.11
4	tBuLi:TMEDA	1.62:1:0.49	4 hr, RT	1.07	0.115
5	tBuLi:TMEDA	1.62:1:0.98	4 hr, RT	0.94	0.10
6	tBuLi:TMEDA	1.62:1:0.49	4 hr, 65° C	0.98	0.105

Table 1 Preparation of PSt–SH from PSt–Br

PSt–Br			Sulphur mequiv	ratio[b] PSt–Br/S	PSt–SH			Functional Yield[c] %
D. F.[a]	weight (g)	mequiv/g			% S	mequiv/g	D. F.[a]	
0.115	21	1.02	150	1:7	2.59	0.81	0.087	76
0.15	18	1.3	94	1:4	3.2	1.00	0.11	72
0.19	16	1.60	250	1:10	4.16	1.30	0.14	74
0.37	35	2.82	100	1:1	7.6	2.37	0.27	73
0.42	22	3.1	800	1:12	9.13	2.85	0.33	78
0.42	20	3.1	62	1:1	8.13	2.54	0.29	69

[a] Degree of functionalization: fraction of aromatic rings carrying the substituent
[b] Calculated from the number of mequiv. of PSt–Br and S
[c] (Final D.F./Initial D.F.) x 100

Table 3 Preparation of PSt–OH by direct lithiation

	Base complex	Ratio polystyrene:base:O_2	Reaction conditions	O analysis mequiv./g	D.F.
1	n-BuLi:TMEDA	0.95:1:large excess	4 h, 65°C	2.18	0.23
2	n-BuLi:TMEDA	1.62:1:large excess	4 h, 65°C	1.57	0.17
3	t-BuLi:TMEDA	1.62:1:large excess	4 h, 65°C	1.80	0.19
4	t-BuLi:TMEDA	1.62:1:large excess	4 h, RT	1.30	0.14

polystyrene followed by quenching with oxygen. Using this reaction, polymers containing approximately 1.3–2.2 mequiv of functional group per gram were obtained for degrees of functionalization of up to 0.24. In every case, for the same ratio of polystyrene to base, the reaction of the lithiated resin with oxygen was found to result in a higher functionalization than had been the case with the reactions involving sulphur quenching (*see Tables 2* and *3*). This may be due to an increased ease of access of the quenching agent to the reactive sites. Especially striking is the contrast between reactions carried out under similar conditions with t-BuLi-TMEDA where a D.F. of 0.10 was obtained with sulphur quenching (*Table 2, exp. 6*) while oxygen quenching gave almost twice as much functionalization with D.F. 0.19 (*Table 3, exp. 3*).

Applications of PSt–OH as a polymeric nucleophile will be described elsewhere[18].

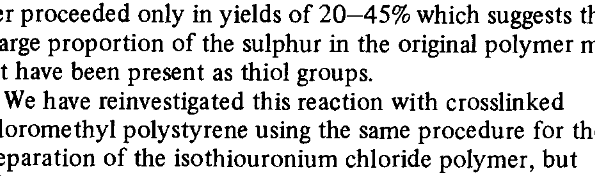
PREPARATION OF PSt–CH_2OH

The preparation of crosslinked hydroxymethyl polystyrene from the corresponding chloromethylated resin has been described by Shambhu and Digenis[21] who used a procedure similar to that developed by Bamford and Lindsey[22] for the corresponding soluble polymer. Their method involves a two-step reaction sequence in which the resin is first acetylated by nucleophilic substitution, then saponified to the desired hydroxymethyl polymer. We have attempted to carry out this reaction in one step using the direct displacement of chloride by hydroxyl ions but, as was the case in previous attempts[22,23], the reaction tried under a variety of conditions was unsuccessful. We have however succeeded in carrying out the one-pot conversion of chloromethylpolystyrene into the corresponding hydroxymethyl polymer using a three phase system consisting of the chloromethylated resin suspended in *o*-dichlorobenzene or 1,2-dichloroethane, and an aqueous solution of hydroxide and acetate ions in the presence of a phase transfer catalyst such as tetrabutylammonium hydroxide. After processing of the reaction mixture, the infrared spectrum of the polymer exhibited a large hydroxyl and no carbonyl absorption which would have been present had any acetylated species remained on the polymer. We describe this reaction as one-pot rather than a one-step reaction since we believe that it is the acetate ion which effects displacement of chloride, and that the acetylated polymer undergoes saponification as soon as it is formed, both acetate and hydroxide ions being transported by the phase transfer catalyst.

Chlorine analysis of the final polymer revealed that only approximately 90–95% of the chlorine had been removed from the polymer, suggesting that some of the chloromethyl groups were located in inaccessible positions within the resin. This finding was somewhat puzzling in view of the fact that quantitative replacement of chloride by a variety of nucleophiles including acetate ion can be obtained easily under phase transfer conditions[18]. The reason for this incomplete removal of chlorine became apparent when the reaction was carried out using soluble chloromethylated polystyrene as a polymer substrate. After a short time of reaction, a third phase appeared in the reaction mixture as the soluble polystyrene formed a gel, indicating that a crosslinking reaction was occurring. The final product of the reaction was completely insoluble in common organic solvents and still contained some chlorine. This crosslinking reaction is due to displacement of chloride ion by PSt–CH_2O^- which is the species formed in the saponification reaction. Attack of this species on a unit of acetylated polymer produces no net change in polymer composition while attack on a chloromethylated unit results in crosslinking. This crosslinking reaction probably occurs also in the case of the 1% crosslinked polystyrene which is used in this study since it is known[24] that site–site interactions are extensive in this type of polymer. To avoid this undesirable crosslinking and obtain quantitative removal of chlorine in the formation of PSt–CH_2OH, the reaction can be carried out in one-pot under phase transfer conditions by adding first the acetate ion. Then, after several hours when formation of the acetylated polymer is complete, addition of hydroxide to the aqueous phase leads smoothly to the desired hydroxymethyl polymer with complete removal of chlorine and without additional crosslinking.

PREPARATION OF PSt–CH_2SH

Soluble mercaptomethyl polystyrene was first prepared in 1957 by Okawara and coworkers[25] using the following reaction sequence:



$$\text{PSt–CH}_2\text{Cl} \xrightarrow{\text{S=C(NH}_2)_2}$$

$$\text{PSt–CH}_2\text{–S–C}\begin{matrix}\nearrow\text{NH}\\ \searrow\text{NH}_2\end{matrix}\cdot\text{HCl} \xrightarrow{\text{OH}^-} \text{PSt–CH}_2\text{SH}$$

More recently, Kieboom and coworkers[26] have adapted this reaction to the preparation of the corresponding crosslinked polymer and have carried out this reaction with a functional yield of 89%. However, subsequent reactions with this polymer proceeded only in yields of 20–45% which suggests that a large proportion of the sulphur in the original polymer may not have been present as thiol groups.

We have reinvestigated this reaction with crosslinked chloromethyl polystyrene using the same procedure for the preparation of the isothiouronium chloride polymer, but different conditions for the second, more critical step, in which the thiol is to be formed. Reaction with hydroxide ion was carried out under phase transfer conditions using a three phase system under an inert atmosphere to prevent the formation of disulphides through interaction between the functional groups of the polymer. Using this procedure, PSt–CH_2SH was obtained in better than 95% functional yield. The infrared spectrum of the polymer included an SH band centred at 2580 cm^{-1}. The reactivity of this polymer as a nucleophile was ascertained by reaction with *p*-nitrophenethyl bromide under phase transfer conditions. Nitrogen analysis on the product of this reaction indicated that the yield was quantitative. In contrast, when the isothiouronium chloride resin was treated with base under the conditions described above, but without exclusion of atmospheric oxygen, the product which was obtained also contained a large amount of sulphur which indicated a very high functional yield, but its infrared spectrum did not exhibit any SH band. This observation shows once again that extensive site–site interactions do exist in 1% crosslinked polystyrene due to the high mobility of the polymer chains. To avoid formation of undesired disulphides in applications involving the use of PSt–CH_2SH in basic medium, it is essential that all reactions be carried out under inert atmosphere.

EXPERIMENTAL

The resin used in this investigation was a solvent swellable 1% divinylbenzene–styrene copolymer, Bio-Beads SX-1, purchased from Bio-Rad Laboratories. The solvents used in the lithiation reactions were purified as follows: cyclohexane was dried over molecular sieves (Davison Type 4A), tetrahydrofuran was distilled from lithium aluminium hydride and benzene was distilled from calcium hydride. All other solvents were practical or reagent grade used without further purification unless specified. The phase transfer catalysts which were used, tetrabutylammonium hydroxide and Adogen-464 were obtained from Aldrich Chemical Company. Reactions involving lithiated intermediates were carried out in a one piece vessel/filtration apparatus shown in *Figure 1* under inert atmosphere.

Infrared spectra were recorded on a Pye-Unicam SP 1100 infrared spectrophotometer using potassium bromide pellets. Elemental analyses were carried out in this laboratory and by MHW Laboratories and Galbraith Laboratories.

Washing of the resins

All the resins used in experiments involving a lithiation step were washed thoroughly to remove surface impurities using a procedure described earlier[3]. All the organic solvents used in these and other washings of the resins were recycled after use.

Preparation of PSt–SH via bromination-lithiation

Bromination of 1% crosslinked polystyrene was carried out as described earlier[3] using the thallium (III) catalyzed bromination. The brominated resin was lithiated then allowed to react with elemental sulphur using an equimolar amount of functional polymer and sulphur as follows: to 35 g of PSt–Br (2.82 mequiv/g; D. F. = 0.377) swollen in 300 ml of dry benzene were added 125 ml (200 mequiv.) of n-butyllithium. After heating at 70°C for two h, the solvent was removed and the lithiated polymer was washed twice with dry benzene. After addition of 300 ml of dry THF and 3.2 g (100 mequiv.) of sulphur, the mixture was stirred at 60°C overnight. After filtration, the resin was washed with THF, THF/6N HCl 3:1, then water. The resin was then placed in a Soxhlet extractor and extracted with THF for 3 days. After a last wash with methanol, the polymer was dried *in vacuo*. The dry resin (29.9 g) had an infrared spectrum which included an S–H bond at 2560 cm^{-1} and contained 8.77% sulphur (2.74 mequiv/g suggesting a D. F. of 0.313) for an apparent functional yield of 83%.

The resin was then suspended in 250 ml dry THF and treated with 2 g $LiAlH_4$ under reflux for 5 h. After cooling, excess 3N hydrochloric acid was added to destroy all remaining hydride and dissolve the inorganic salts. The resin was then washed thoroughly with THF/6N HCl 3:1, THF/water 4:1, water, methanol, dichloromethane and finally, ether. The dry polymer contained 7.6% sulphur (2.37 mequiv/g; D. F. = 0.27) for a functional yield of 73%. A second treatment with lithium aluminium hydride did not cause any further loss of sulphur or change in the infrared spectrum of the polymer.

One-pot preparation of PSt–SH via direct lithiation

With n-BuLi-TMEDA. 15 g of 1% crosslinked polystyrene were lithiated using 37 ml of 2.6N n-BuLi and 15 ml TMEDA in 125 ml of dry cyclohexane. The reaction was allowed to proceed for 4 h at 65°C with stirring in the flask shown in *Figure 1*. After filtration, the lithiated resin was washed twice with dry cyclohexane and 150 ml anhydrous THF and 1.5 g sulphur were added. After stirring overnight at room temperature the polymer was filtered and washed with THF/6N HCl 2:1, then water. After extraction with THF in a Soxhlet extractor for 2 days to remove excess sulphur, the resin was dried then reduced by reaction with 2.5 g $LiAlH_4$ in 300 ml anhydrous THF for 4 h at reflux. After addition of 3N HCl to dissolve all aluminium salts, the polymer was collected by filtration and washed with water, THF, acetone, dichloromethane, and finally methanol. After drying, 14.6 g of polymer containing 1.4 mequiv sulphur/g was obtained. A similar reaction using 5 g resin, 7.5 ml n-BuLi and 0.72 g sulphur at 60°C gave a polymer with 1.98 mequiv sulphur/g.

With t-BuLi-TMEDA. A reaction carried out with 15 g polymer, 15 ml TMEDA, 80 ml t-BuLi (1.2N) and 125 ml cyclohexane for 4 h at 65°C, followed by addition of 1.5 g sulphur and reduction as above gave a polymer containing 0.98 mequiv sulphur/g.

Preparation of PSt–CH_2Cl

Chloromethylated polystyrene was prepared using a modification of the procedure of Pepper *et al.*[27]. Stannic chloride (20 ml) was added slowly to a mechanically stirred suspension of 103 g of crosslinked polystyrene in 600 ml chloroform and 150 ml of chloromethyl ethyl ether. The colour of the polymer changed to yellow-orange and an additional 50 ml chloromethyl ethyl ether were added. After stirring for 2 h at room temperature the resin was collected by filtration and washed with chloroform/methanol 1:1, dioxane/water 3:1, dioxane/3N HCl 2:1, dioxane, dioxane/water 3:1, water and methanol. After drying, the polymer weighed 129.5 g and contained 14.55% Cl (4.1 mequiv/g., D. F. = 0.53). Several polymers having a lower degree of functionalization were prepared by the same procedure using smaller amounts of stannic chloride and chloromethyl ethyl ether.

Preparation of PSt–CH_2SH

A suspension of 25 g of PSt–CH_2Cl (2.1 mequiv/g, D. F. = 0.244) and 17 g of thiourea in 350 ml of THF and 100 ml of ethanol was stirred and heated at reflux for two days. The resin was then washed with water followed by THF and benzene to remove all excess soluble reagents and byproducts. After this washing, the polymer was suspended in 300 ml benzene and a solution of 0.4 g tetrabutylammonium iodide and 15 g sodium hydroxide in 20 ml of boiled distilled water were added. The 3 phase mixture was then stirred at 80° under nitrogen for two days. After filtration the resin was washed with THF, water, THF/6N HCl 3:1, water, THF, acetone, methylene chloride, and finally methanol. After drying under vacuum 24.18 g of PSt–CH_2SH was obtained. The infrared spectrum of the polymer included an SH band centred at 2580 cm^{-1}. *Analysis:* Cl, none; S, 2.04 mequiv/g (D. F. = 0.234) for a functional yield of 96%.

When a similar reaction was attempted with 6.27 g of PSt–CH_2Cl (1.8 mmole/g, D. F. = 0.205) and 3.72 g of thiourea followed by reaction with 5 g sodium hydroxide and 0.18 g tetrabutylammonium iodide in 7 ml of distilled water (not deoxygenated) in the presence of air, 6.14 g of a polymer containing 5.8% (1.81 mequiv/g) was obtained. The polymer which showed no SH absorption in its i.r. spectrum was thought to be the disulphide PSt–CH_2–S–S–CH_2–PSt. This assumption is supported by the fact that following $LiAlH_4$ reduction the polymer exhibits an SH absorption in the i.r. spectrum. The functional yield in this reaction is essentially quantitative.

Reaction of PSt–CH_2SH with p-nitrophenethyl bromide

To 0.83 g of PSt–CH_2SH prepared above (2.04 mequiv/g) in 15 ml of *o*-dichlorobenzene were added 0.4g Adogen-464, 3g *p*-nitrophenethyl bromide and 2g of NaOH in 3 ml water. The mixture was stirred for 2 days at 75°C under nitrogen atmosphere. After filtration the polymer was collected on filter and washed repeatedly with acetone, water, THF, THF/6N HCl (2:1), water, THF, acetone, dichloromethane and finally methanol. The polymer obtained (1.07 g) contained 1.58 mequiv S/g and 1.58 mequiv N/g for an essentially quantitative conversion to the nitrophenyl derivative. The i.r. spectrum of the final product shows no –SH absorption band but rather NO_2 bands at 1345 and 1520 cm^{-1}.

Preparation of PSt–OH via bromination-lithiation

The reaction was carried out in one-pot using the reaction vessel shown in *Figure 1*. To 5.2 g of PSt–Br (3.14 mequiv/g) in 50 ml dry benzene was added 15 ml n-BuLi (2.6M) and the suspension was stirred under nitrogen atmosphere at 55° for 2.5 h. After filtration, the polymer was washed twice with dry benzene under nitrogen and after addition of 60 ml dry THF, oxygen was bubbled through the mixture for 20 h. The polymer was filtered and washed thoroughly with methanol, 5% $NaHSO_3$, water, THF, acetone, dichloromethane, and methanol. After drying, 4.3 g of a polymer containing 2.86 mequiv oxygen/g was obtained. The i.r. spectrum of the polymer included a large hydroxyl absorption at 3590 and 3500 cm^{-1}.

Preparation of PSt–OH via direction lithiation

With n-BuLi-TMEDA. To a suspension of 5.1 g 1% crosslinked polystyrene in 40 ml cyclohexane was added 7.6 ml TMEDA and 35 ml n-BuLi (1.6N). After stirring for 4 h at 65°C under nitrogen, the polymer was filtered and washed twice with cyclohexane. After addition of 60 ml cyclohexane, oxygen was bubbled through the reaction mixture for 20 h. After filtration and washing as above the polymer was dried to yield 5.3 g of a material containing 3.49% oxygen (2.18 mequiv/g).

With t-BuLi-TMEDA. A similar reaction carried out on 10 g of polymer in 100 ml cyclohexane with 10 ml TMEDA and 53 ml t-BuLi (1.2N) under nitrogen for 4 h at 65°C gave a product which after washing and drying contained 1.80 mequiv oxygen/g.

Hydroxymethylation of soluble polystyrene

To a solution of 1.5 g of chloromethylated polystyrene (soluble, M_n = 20 000, 4.4 mequiv/g) was added a mixture of 0.3 g40% aqueous tetrabutylammonium hydroxide, 3 g potassium acetate and 3 g sodium hydroxide in 6 ml H_2O The heterogeneous mixture was stirred rapidly at 85°C and a polymer gel was observed to form slowly. After two days of reaction the polymer was collected by filtration and was found to be insoluble in common organic solvents such as benzene, chloroform or dioxane. After washing with water, methanol, THF/water 3:1, THF, water, acetone, and dichloromethane, the polymer was dried (1.04 g). The dry polymer had a large hydroxyl absorption in its i.r. spectrum and still contained 0.3 mequiv. chlorine/g.

Preparation of PSt–CH_2OH

Phase transfer reaction with simultaneous addition of acetate and hydroxide ions. The reaction was carried out in a 3-phase system consisting of 1.1 g of PSt–CH_2Cl (1.8 mequiv/g) suspended in 10 ml 1,2-dichlorobenzene with 0.3 g of a 40% aqueous solution of tetrabutylammonium hydroxide, 3 g of potassium acetate and 2 g potassium hydroxide in 6 ml water. The mixture was stirred vigorously at 85°C for 2 days then filtered and washed thoroughly as above. After drying the polymer weighed 1.05 g. Its i.r. spectrum included a large hydroxyl and no carbonyl absorption. A small amount of chloride (0.1 mequiv/g) remained on the polymer. Similar results were obtained when the reaction period was extended to 5.5 days.

Phase transfer reaction with successive addition of acetate and hydroxide ions; The reaction was carried out as above except for the addition of potassium hydroxide which was made after 24 h of reaction of the polymer with aqueous potassium acetate. Adogen-464 was used as the phase transfer catalyst. The reaction proceeded smoothly to yield a hydroxymethyl polymer which contained no remaining chloride.

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