



Functionalised linear and cross-linked polystyrenes from chloromethylated polymers through their organolithium derivatives

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Abstract—The lithiation of soluble (linear) and insoluble (cross-linked) chloromethylated polystyrene (**1** and **15**, respectively) with lithium and a catalytic amount of 4,4'-di-*tert*-butylbiphenyl (DTBB, 10 mol%) followed by reaction with different electrophiles leads to the formation, after final hydrolysis, of the corresponding functionalised polymers **2–12** and **16–32**, respectively. © 2003 Published by Elsevier Science Ltd.

1. Introduction

The use of functionalised polymers in synthetic organic chemistry is mainly focused in the following processes: (a) liquid- and solid-phase synthesis; (b) support of several reagents; (c) use in chromatographic phases; and (d) supported catalysts.¹ In general, two different types of polymers can be used in order to be functionalised: insoluble (also called cross-linked) or soluble (also called linear) polymers. In the first case, the most important use of the resins is for the so-called solid-phase reactions, which have some advantages: (a) the isolation and purification of the reaction products is easy by simple filtration; (b) once the polymer is recovered, its regeneration and reuse is generally an easy operation; and (c) this technique is particularly interesting for unstable intermediates and toxic or bad-smelling molecules.² A drawback when using this cross-linked polymers is their characterisation, which is difficult by spectroscopic means due to their insolubility.³ In the case of linear polymers, their solubility favours their spectroscopic characterisation but makes difficult in some cases their recuperation and reuse.⁴ On the other hand, the chemical functionalisation of a polymer is of interest since this modification can change dramatically the physical properties of the macromolecule. For this purpose, it would be interesting to introduce carbon–metal bonds in the structure of the polymer in order to get its functionalisation by reaction with electrophiles. To the best of our knowledge this possibility has only been explored with cross-linked polymers such as chloromethylpolystyrene (Merrifield

resins⁵) and using activated magnesium⁶ or calcium.⁷ The lithiation of the same chlorinated material under a variety of conditions failed due to coupling processes, which increase the degree of cross-linking in the resin.⁸ The only way to generate such a lithiated polymer has been to use more sophisticated methodologies, such as sulfur–lithium exchange⁸ or a tin–lithium transmetallation,⁹ so the expected lithiomethyl resin could be prepared. Concerning halogen–lithium exchange, there is only one example of preparation of a lithiated resin using a bromine–lithium exchange with an excess of *n*-butyllithium starting from a resin in which the halogen is attached to the aromatic ring in the polymeric structure.^{1a} We report here the direct lithiation of both soluble and insoluble chloromethyl-containing polymers carrying out the corresponding chlorine–lithium exchange by using an arene-catalysed lithiation.^{10–13} This methodology has been extensively used in our group in the last decade mainly to generate organolithium compounds from non-halogenated materials,¹⁴ functionalised organolithium compounds,^{15,16} polyolithium synthons,¹⁷ as well as to activate other metals, especially nickel.^{18–20}

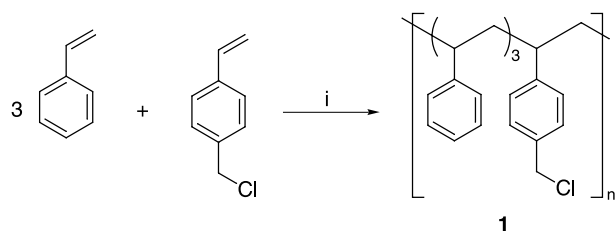
2. Results and discussion

2.1. Functionalised linear (soluble) polystyrene

The starting polymer was prepared according to the reported procedure²¹ by refluxing styrene and 4-chloromethylstyrene (3:1 molar ratio) in benzene and using 1,1'-azobis(isobutyronitrile) (AIBN) as the radical initiator. The obtained polymer is soluble in typical organic solvents such as chloroform, dichloromethane, ethyl acetate, benzene, THF or DMF, and insoluble in methanol or water (Scheme 1).

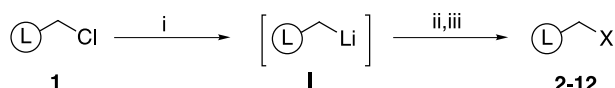
Keywords: lithiation; lithium and compounds; functionalised polymers; polymerisation.

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Scheme 1. Reagents and conditions: (i) AIBN (cat.), PhH reflux, 40 h.

Lithiation of dry polymer **1** with an excess of lithium (ca. 1:10 molar ratio) and a catalytic amount of 4,4'-di-*tert*-butylbiphenyl (DTBB, ca. 10% molar) in THF at -78°C for 2 h led to the corresponding lithiated polymer **I**. Further treatment of this polymeric intermediate with water or deuterium oxide gave the expected products **2** and **3**, respectively (Scheme 2, Chart 1 and Table 1, entries 1 and 2). However, with other electrophiles such as chlorosilanes, carbonyl compounds or chlorodiphenylphosphane [$\text{E} = \text{Me}_3\text{SiCl}$, Et_3SiCl , PhMe_2SiCl , $\text{Bu}'\text{CHO}$, PhCHO , Et_2CO , $(\text{CH}_2)_5\text{CO}$, Ph_2CO , Ph_2PCL] the best results were obtained working under Barbier-type reaction conditions,²² that is carrying out the lithiation in the presence of the electrophile at -78°C for 2 h and performing the final hydrolysis with methanol. Thus, functionalised polymers **4–12** were isolated (Scheme 2, Chart 1 and Table 1, entries 3–11). Either for the two-step (Grignard-type reaction) or the Barbier-type process, a chlorine–lithium exchange occurred prior to the reaction with the electrophile (second case), so the corresponding benzylic organolithium intermediate **I** is probably involved in the reaction. The solubility of functionalised polymers **2–12** allows their characterisation, not only by analytical methods,²³ but also by spectroscopic means, specially by NMR. Thus, yields were calculated by comparison of the integrals corresponding to the methylene benzylic signals for the products and



Scheme 2. Reagents and conditions: (i) Li, DTBB (10 mol%), THF, -78°C ; (ii) $\text{E} = \text{H}_2\text{O}$, D_2O or Me_3SiCl , Et_3SiCl , PhMe_2SiCl , $\text{Bu}'\text{CHO}$, PhCHO , Et_2CO , $(\text{CH}_2)_5\text{CO}$, Ph_2CO , Ph_2PCL under Barbier conditions (see text); (iii) MeOH.

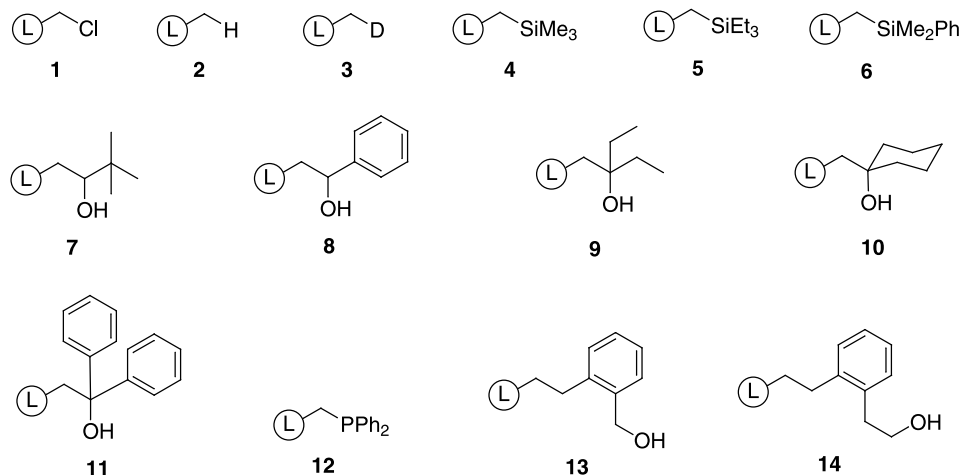


Chart 1. Starting linear polymer **1** and products **2–14** prepared.

Table 1. Preparation of functionalised linear polymers **2–12**

Entry	Electrophile	Product ^a		
		No.	X	Yield (%) ^b
1	H_2O	2	H	>99
2	D_2O	3	D	>99
3	Me_3SiCl	4	Me_3Si	>99
4	Et_3SiCl	5	Et_3Si	>99
5	PhMe_2SiCl	6	PhMe_2Si	>99
6	$\text{Bu}'\text{CHO}$	7	$\text{Bu}'\text{CHOH}$	75
7	PhCHO	8	PhCHOH	74
8	Et_2CO	9	Et_2COH	48
9	$(\text{CH}_2)_5\text{CO}$	10	$(\text{CH}_2)_5\text{COH}$	58
10	Ph_2CO	11	Ph_2COH	64
11	Ph_2PCL	12	Ph_2P	72

^a In all cases total conversion was observed (disappearance of the CH_2Cl band at 1266 cm^{-1} in the IR spectra, after hydrolysis).

^b Yields refer to the degree of functionality (also called 'functional yield') measured by ^1H NMR. The rest of the amount represents the % of methyl groups present in the final polymer product for a lithium–hydrogen interchange.

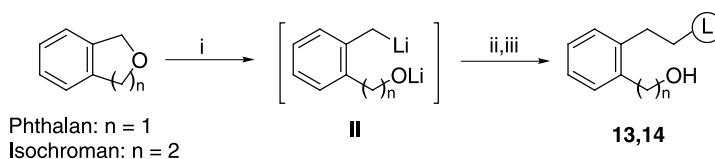
the methyl signal observed in some cases for the 'reduced' product (resulting from a lithium/hydrogen exchange).

A different approach to prepare functionalised linear polystyrene consists in using the polymer **1** as electrophile reacting with a functionalised organolithium compound.¹⁵ Thus, once phthalan²⁴ or isochroman²⁵ were opened using the arene-catalysed lithiation methodology, the corresponding functionalised organolithium compounds **II** were reacted with the polymer **1** giving, after hydrolysis with methanol, the corresponding functionalised polymers **13** and **14**, respectively in almost quantitative yields (Scheme 3 and Chart 1).

2.2. Functionalised cross-linked (insoluble) polystyrene

Among the types of Merrifield resins⁵ commercially available we chose resins **15a–c**, which show different properties [mainly the degree of functionalisation (DF) and cross-linking] (Table 2).

DTBB-catalysed lithiation of resins **15** was performed at different temperatures and reactions times, concluding that the best conditions were to work at room temperature and



Scheme 3. Reagents and conditions: (i) Li, DTBB (2.5 mol%), THF, 0°C; (ii) polymer **1**; (iii) MeOH.

for periods of 4–24 h. For resins **15a** and **15b**, longer reaction times were used (ca. 24 h) in order to ensure the total conversion of the starting polymer, whereas for resin **15c**, with higher DF, long reaction times should not be used

Table 2. Merrifield resins used

Entry	Resin (no.)	Cross-linking (% DVB)	Functionality (mequiv. Cl/g resin)	DF ^a (%)
1	15a	1	1	11
2	15b	1	1.7	19
3	15c	2	4.3	57

^a DF: degree of functionality (% of chloromethylated aromatic rings).

in order to avoid undesired cross-coupling side reactions during the lithiation step (see [Tables 2 and 3](#)).

The lithiation of polymers **15a–c** with an excess of lithium and a catalytic amount of DTBB (ca. 10% molar) at room temperature for 4–24 h (see above) gave the expected organolithium intermediates **III**, which by reaction with different electrophiles at different temperatures gave, after final hydrolysis with water, the expected products **16–32** ([Scheme 4](#), [Chart 2](#) and [Table 3](#)). In all cases, the conversion was total as checked by disappearance of the CH₂Cl band at 1266 cm⁻¹ in the IR spectra,²⁶ after hydrolysis with water of an aliquot. Different reaction conditions studied including

Table 3. Products **16–32** prepared

Entry	Starting resin (no.)	Electrophile	Reaction conditions ^a		Product	
			<i>T</i> (°C)	<i>t</i> (h)	No.	X
1	15a	H ₂ O	-40 to 25	2	16a	H
2	15a	Me ₃ SiCl	25	24	18a	Me ₃ Si
3	15a	Bu ^t CHO	-40	24	19a	Bu ^t CHOH
4	15a	PhCHO	-40	24	20a	PhCHOH
5	15a	Et ₂ CO	-40	24	21a	Et ₂ COH
6	15a	(CH ₂) ₅ CO	-40	24	22a	(CH ₂) ₅ COH
7	15a	Ph ₂ CO	-78	2	23a^b	Ph ₂ COH
8	15a	ClCO ₂ Et	25	24	24a	CO ₂ Et
9	15a	CO ₂	-40 to 25	2	26a^c	CO ₂ H
10	15a	PhCOCl	-78	2	27a^b	PhCO
11	15a	Bu ^t COCl	-78	2	28a^b	Bu ^t CO
12	15a	HCONMe ₂	-78	2	29a^b	HCO
13	15b	Me ₃ SiCl	-40	4	18b	Me ₃ Si
14	15b	ClCO ₂ Et	-45	3	24b	CO ₂ Et
15	15b	ClCO ₂ CH ₂ Ph	-45	2	25b	CO ₂ CH ₂ Ph
16	15c	H ₂ O	0	2	16c^d	H
17	15c	D ₂ O	-78	1	17c	D
18	15c	Me ₃ SiCl	-78	24	18c^e	Me ₃ Si
19	15c	Bu ^t CHO	-78	22	19c^f	Bu ^t CHOH
20	15c	PhCHO	-45	24	20c^{f,g}	PhCHOH
21	15c	Et ₂ CO	-78	24	21c^{f,g}	Et ₂ COH
22	15c	(CH ₂) ₅ CO	-78	24	22c	(CH ₂) ₅ COH
23	15c	ClCO ₂ Et	-30	2	24c^h	CO ₂ Et
24	15c	ClCO ₂ CH ₂ Ph	-40	2	25c	CO ₂ CH ₂ Ph
25	15c	CO ₂	-40	12	26c^e	CO ₂ H
26	15c	PhCOCl	-78 to 25	4	27cⁱ	PhCO
27	15c	Bu ^t COCl	-78 to 25	4	28cⁱ	Bu ^t CO
28	15c	PhCH=NPh	-78	4	30c	PhCHNPh
29	15c	CH ₂ =CHCH ₂ Br	-78 to 25	4	31cⁱ	CH ₂ =CHCH ₂
30	15c	CH ₂ =C(Me)CH ₂ Br	-78 to 25	4	32cⁱ	CH ₂ =C(Me)CH ₂

^a Reaction conditions for the reaction with the electrophile after lithiation at room temperature for ca. 24 h unless otherwise stated. Conversion was total (disappearance of the CH₂Cl band at 1266 cm⁻¹ in the IR spectra, after hydrolysis), so yields were in all cases almost quantitative.

^b Lithiation time at room temperature: 4 h.

^c Final hydrolysis was performed with 2 M HCl.

^d The same result was obtained after lithiation during ca. 4 h.

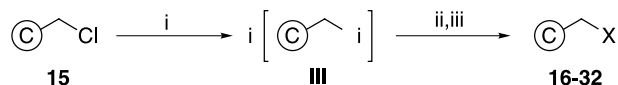
^e Alternatively, the reaction can be carried out at -40 to 25°C for 4 h (after lithiation at room temperature for ca. 4 h).

^f The same result was obtained using Barbier conditions, working at -60°C for 5 days.

^g The same result was obtained using BF₃ or ZnBr₂ (1 equiv.) to activate the carbonyl compound, working at -78 to 25°C for 4 h, after lithiation at room temperature for ca. 4 h.

^h This reaction was also performed using the following two reaction conditions: (a) -45 to 25°C for 4 h, after lithiation at room temperature for ca. 4 h; (b) lithiation step at 0°C for 16 h.

ⁱ The excess of lithium powder was separated from the lithiated polymer before the addition of the electrophile, the lithiation step being performed at room temperature for ca. 4 h.



Scheme 4. Reagents and conditions: (i) Li, DTBB (10 mol%), THF, rt; (ii) E=H₂O, D₂O, Me₃SiCl, Bu^tCHO, PhCHO, Et₂CO, (CH₂)₅CO, Ph₂CO, ClCO₂Et, ClCO₂CH₂Ph, CO₂, PhCOCl, Bu^tCOCl, HCONMe₂, PhCH=NPh, CH₂=CHCH₂Br, CH₂=C(Me)CH₂Br (for temperature, see Table 3); (iii) H₂O.

reaction time, temperature or Barbier-type reaction conditions are summarised in Table 3 (footnotes d–i). Characterisation of compounds 16–32 was made on the basis of their IR spectra and elemental analysis, since NMR spectra were not possible to be measured due to their insolubility in common NMR solvents.

From the results included in Table 3 the following remarks can be done: (a) almost in all cases, after the lithiation was complete the reaction with the electrophile was carried out at low temperature in order to avoid decomposition processes. (b) In the case of the carboxylation, the final hydrolysis was performed under acidic conditions to facilitate the isolation of the pure polymer (Table 3, entries 9 and 25, and footnote c). (c) In some cases different reaction conditions (temperature and time) were used, obtaining comparable results (i.e. Table 3, entries 16, 18 and 23, and footnotes d, e and h). (d) When the lithiation step was carried out in the presence of the electrophile (pivalaldehyde, benzaldehyde or 3-pentanone) (Barbier-type reaction conditions), the reaction time had to be

increases notably to get the same results (Table 3, entries 19–21, and footnote f). (e) In some cases, Lewis acids (BF₃ or ZnBr₂, 1 equiv.) could be used to accelerate the rate of reactions of the lithiated polymers with carbonyl compounds (Table 3, entries 20 and 21, and footnote g). (f) In the case of using allylic bromides (allyl and methallyl bromide) or acyl chlorides (benzoyl or pivaloyl chloride) it was necessary to remove the excess of lithium before adding the electrophile in order to avoid its decomposition (Table 3, entries 26, 27, 29 and 30, and footnote i).

3. Conclusions

From the results contained in this paper we conclude that the DTBB-catalysed lithiation methodology is a useful procedure to perform functionalisation of soluble (linear) or insoluble (cross-linked) chloromethylated polystyrene through the corresponding lithiated polymeric materials and by reaction with different electrophilic reagents.

4. Experimental

4.1. General

All reactions involving organometallic reagents were carried out under an atmosphere of nitrogen in oven-dried glassware. All reagents were commercially available and were used as received. THF was distilled from sodium

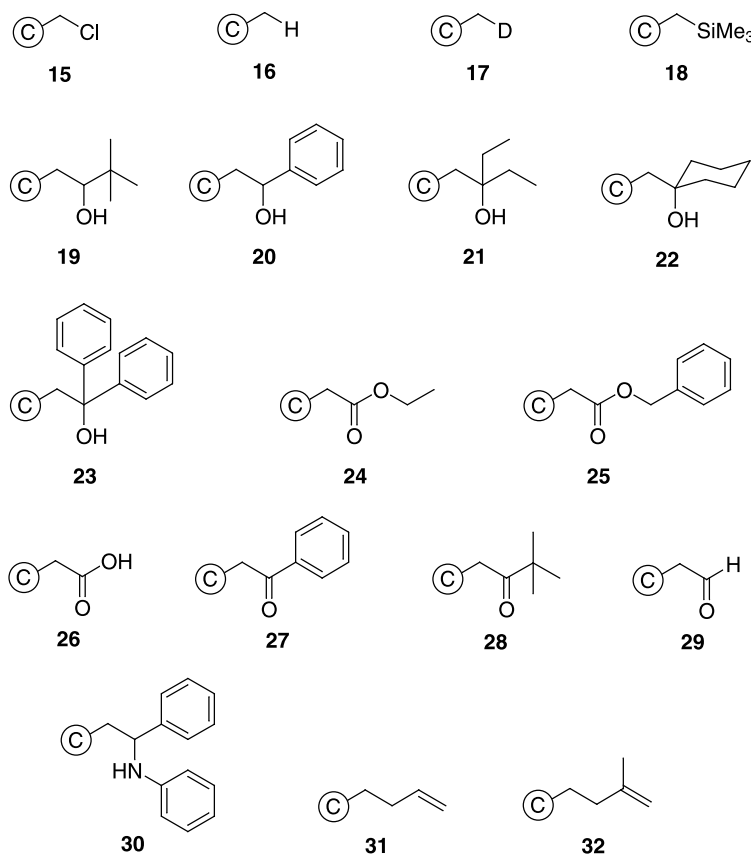


Chart 2. Starting cross-linked polymer **15** and products **16–32** prepared.

benzophenone ketyl. Lithium powder was prepared as it was previously reported by us.²⁷ IR spectra were measured (KBr) with a Nicolet Impact 400 D-FT Spectrometer. NMR spectra were recorded with a Bruker AC-300 (or a Bruker Advanced DRX-500 machine for the ²H NMR measurements) using CDCl₃ as the solvent. HRMS were measured with a Finnigan MAT95 S spectrometer. Elemental analyses were performed by the Microanalyses Service at the University of Alicante.

4.1.1. Preparation of soluble polymer 1. A solution of styrene (17.3 mL, 150 mmol), 4-chloromethylstyrene (7.8 mL, 50 mmol) and 1,1'-azobis(isobutyronitrile) (AIBN; 84 mg, 0.5 mmol) in benzene (50 mL) was degassed with argon for 20 min and then refluxed (85°C) for 40 h. The resulting solution was added over cold methanol (−40°C, 250 mL), the obtained precipitate was filtered, washed with methanol (3×25 mL) and dried under reduced pressure (0.1 Torr) to yield 5.60 g of a white solid (30% yield). The functionality of the polymer (DF=0.25, corresponding to 2.1 mequiv. Cl/g resin) was confirmed from ¹H NMR; ν (KBr) 3081, 3058, 3024, 1601, 1492, 1452 (C=CH), 1266 cm^{−1} (C–Cl); δ_{H} 1.41 (br s, CHCH₂), 1.78 (br s, CHCH₂), 4.50 (br s, CH₂Cl), 6.55, 7.05 (2 br s, ArH); δ_{C} 40.3 (CHCH₂), 40.5–46.0 (CHCH₂), 46.3 (CH₂Cl), 125.7, 127.5, 127.9 (ArCH), 145.0, 145.3 (ArC). HRMS (EI): calcd for C₈H₈⁺ 104.0626, found 104.0629 (47%); calcd for C₉H₉⁺ 117.0704, found 117.0706 (100%); calcd for C₉H₉Cl⁺ 152.0393, found 152.0400 (13%). Anal. found: C, 83.36; H, 7.01. (C₈H₈)₃(C₉H₉Cl) requires C, 85.22; H, 7.15.

4.2. Lithiation of polymer 1 and reaction with electrophiles. Two-step general procedure. Isolation of polymers 2 and 3

To a dark green suspension of lithium powder (75 mg, 10 mmol) and 4,4'-di-*tert*-butylbiphenyl (DTBB; 0.015 g, 0.05 mmol) in THF (5 mL) was slowly added (ca. 2 h) a solution of the polymer 1 (230 mg, 0.5 mmol) in THF (9 mL) at −78°C under argon. After stirring for 2 additional hours, water (1 mL) or deuterium oxide (0.5 mL) were added. Stirring was continued for 30 min and the resulting mixture was hydrolysed with cold methanol (−40°C, 10 mL). The resulting precipitate was filtered, washed with water (3×15 mL), methanol (3×15 mL) and dried under reduced pressure (0.1 Torr) to give compounds 2 and 3. Yields are given in Table 1; spectral and analytical data follow.

4.2.1. Polymer 2. ν (KBr) 3058, 3024, 1601, 1493, 1452 cm^{−1} (C=CH); δ_{H} 1.43 (br s, CHCH₂), 1.84 (br s, CHCH₂), 2.17 (br s, PhCH₃), 6.57, 7.05 (2 br s, ArH); δ_{C} 21.1 (PhCH₃), 40.3 (CHCH₂), 40.6–46.0 (CHCH₂), 125.7, 127.9 (ArCH), 145.3 (ArC). HRMS (EI): calcd for C₈H₈⁺ 104.0626, found 104.0608 (1%); calcd for C₉H₁₀⁺ 118.0782, found 118.0761 (3%). Anal. found: C, 90.31; H, 7.88. (C₈H₈)₃(C₉H₁₀) requires C, 92.04; H, 7.96.

4.2.2. Polymer 3. ν (KBr) 3082, 3058, 3024, 1601, 1493, 1452 cm^{−1} (C=CH); δ_{D} 2.97 (br s, CH₂D). HRMS (EI): calcd for C₇H₆D⁺ 92.0610, found 92.0615 (9%); calcd for C₈H₇D⁺ 105.0689, found 105.0708 (1%); calcd for C₉H₉⁺ 117.0704, found 117.0700 (63%). Anal. found C, 90.92; H, 7.82. (C₈H₈)₃(C₉H₉D) requires C, 91.83; H, 8.17.

4.3. Lithiation of polymer 1 and reaction with electrophiles: Barbier-type general procedure. Isolation of polymers 4–12

To a dark green suspension of lithium powder (75 mg, 10 mmol) and DTBB (0.015 g, 0.05 mmol) in THF (5 mL) was slowly added (ca. 2 h) a solution of the polymer 1 (230 mg, 0.5 mmol) and the electrophile (2.5 mmol) in THF (9 mL) at −78°C under argon. After stirring for 2 additional h, the resulting mixture was hydrolysed with methanol (10 mL) and the resulting precipitate was filtered, washed with water (3×15 mL), methanol (3×15 mL) and dried under reduced pressure (0.1 Torr) to give compounds 4–12. Yields are given in Table 1; spectral and analytical data follow.

4.3.1. Polymer 4. ν (KBr) 3060, 3025, 1601, 1509, 1452 (C=CH), 1247 (C–Si), 849 cm^{−1} (Si–Me); δ_{H} 0.01 (br s, 3×CH₃), 1.47 (br s, CHCH₂), 2.01 (br s, CHCH₂, PhCH₂), 6.64, 7.11 (2 br s, ArH); δ_{C} −1.73 (3×CH₃), 26.4 (CH₂Si), 40.5 (CHCH₂), 40.6–45.2 (CHCH₂), 125.6, 127.8 (ArCH), 137.2, 140.8, 145.2 (ArC). HRMS (EI): calcd for C₃H₉Si⁺ 73.0473, found 73.0461 (100%); calcd for C₉H₉⁺ 117.0704, found 117.0701 (23%); calcd for C₁₁H₁₅Si⁺ 175.0943, found 175.0950 (10%); calcd for C₁₁H₁₆Si⁺ 176.1021, found 176.1010 (2%); calcd for C₁₂H₁₈Si⁺ 190.1178, found 190.1177 (9%). Anal. found: C, 82.58; H, 8.62. (C₈H₈)₃(C₁₂H₁₈Si) requires C, 85.99; H, 8.42.

4.3.2. Polymer 5. ν (KBr) 3060, 3025, 1601, 1508, 1453 (C=CH), 1240, 1206 cm^{−1} (C–Si); δ_{H} 0.50 (br s, CH₂CH₃), 0.91 (br s, CH₂CH₃), 1.43 (br s, CHCH₂), 2.00 (br s, CHCH₂, PhCH₂), 6.60, 7.08 (2 br s, ArH); δ_{C} 3.1 (CH₂CH₃), 7.4 (CH₂CH₃), 21.0 (PhCH₂), 40.3 (CHCH₂), 41.0–46.6 (CHCH₂), 125.5, 127.8 (ArCH), 137.2, 145.4 (ArC). HRMS (EI): calcd for C₆H₁₅Si⁺ 115.0943, found 115.0955 (48%); calcd for C₈H₇Si⁺ 131.0317, found 131.0343 (11%); calcd for C₁₅H₂₄Si⁺ 232.1647, found 232.1667 (4%). Anal. found: C, 83.52; H, 9.18. (C₈H₈)₃(C₁₅H₂₄Si) requires C, 85.97; H, 8.88.

4.3.3. Polymer 6. ν (KBr) 3065, 3023, 1600, 1509, 1492, 1452 (C=CH), 1247, 1110 (C–Si), 832 cm^{−1} (Si–Me); δ_{H} 0.22 (br s, SiCH₃), 1.39 (br s, CHCH₂), 1.84 (br s, CHCH₂), 2.22 (br s, PhCH₂), 6.60, 7.07 (2 br s, ArH), 7.34 (br s, SiArH); δ_{C} −3.2, 0.0 (CH₃), 25.4 (CH₂Si), 40.4 (CHCH₂), 41.1–46.2 (CHCH₂), 125.6, 127.7, 128.9, 133.8 (ArCH), 145.2 (ArC). HRMS (EI): calcd for C₈H₁₁Si⁺ 135.0630, found 135.0657 (100%); calcd for C₁₀H₁₃Si⁺ 161.0786, found 161.0787 (2%); calcd for C₁₆H₁₈Si⁺ 238.1178, found 238.1152 (2%). Anal. found: C, 79.40; H, 8.00. (C₈H₈)₃(C₁₇H₂₀Si) requires C, 87.18; H, 7.85.

4.3.4. Polymer 7. ν (KBr) 3704–3140, 3588 (O–H), 3059, 3025, 1601, 1493 (C=CH), 1363 (CH₃), 1071, 1008 cm^{−1} (C–O); δ_{H} 1.00 (br s, 3×CH₃), 1.42 (br s, CHCH₂), 1.80 (br s, CHCH₂), 2.28, 2.80, 3.33 (3 br s, CH₂CHOH), 4.76 (br s, OH), 6.49, 7.05 (2 br s, ArH); δ_{C} 26.0 (3×CH₃), 34.7 [C(CH₃)₃], 37.9 (CH₂CHOH), 40.4 (CHCH₂), 40.7–45.6 (CHCH₂), 80.3 (CHOH), 125.6, 127.9 (ArCH), 136.7, 145.3 (ArC). HRMS (EI): calcd for C₅H₁₁O⁺ 87.0809, found 87.0785 (23%); calcd for C₈H₈⁺ 104.0626, found 104.0603 (26%); calcd for C₉H₉⁺ 117.0704, found 117.0712 (3%);

calcd for $C_{14}H_{20}O^+$ 204.1514, found 204.1481 (3%). Anal. found: C, 87.23; H, 8.51. $(C_8H_8)_3(C_{14}H_{20}O)$ requires C, 88.32; H, 8.58.

4.3.5. Polymer 8. ν (KBr) 3691–3134, 3561 (O–H), 3058, 3024, 1601, 1510, 1493 (C=CH), 1182, 1028 cm^{-1} (C–O); δ_H 1.41 (br s, CHCH₂), 1.84 (br s, CHCH₂), 2.88 (br s, CH₂CHOH), 4.75 (br s, CHOH), 6.54, 7.04, 7.27 (3 br s, ArH); δ_C 40.4 (CHCH₂), 41.0–47.2 (CHCH₂), 45.8 (CH₂CHOH), 75.1 (CHOH), 125.8, 128.0, 128.3, 129.0 (ArCH), 145.1, 145.2, 145.3, 145.5 (ArC). HRMS (EI): calcd for $C_8H_8^+$ 104.0626, found 104.0625 (38%); calcd for $C_9H_9^+$ 117.0704, found 117.0723 (5%); calcd for $C_8H_9O^+$ 121.0653, found 121.0659 (4%); calcd for $C_{16}H_{14}^+$ 206.1096, found 206.1096 (23%). Anal. found: C, 84.75; H, 7.06. $(C_8H_8)_3(C_{16}H_{16}O)$ requires C, 89.51; H, 7.51.

4.3.6. Polymer 9. ν (KBr) 3664–3127 (O–H), 3057, 3025, 1601, 1493 (C=CH), 1068, 1029 cm^{-1} (C–O); δ_H 0.92 (br s, 2×CH₃), 1.36 (br s, 2×CH₂CH₃, CHCH₂), 1.84 (br s, CHCH₂), 2.63 (br s, CH₂COH), 3.04 (br s, COH), 6.57, 7.05 (2 br s, ArH); δ_C 8.1 (2×CH₃), 30.4 (2×CH₂CH₃), 40.4 (CHCH₂), 40.6–46.2 (CHCH₂), 44.4 (PhCH₂), 74.4 (COH), 125.6, 126.6, 127.9 (ArCH), 138.2, 145.3, 149.9 (ArC). HRMS (EI): calcd for $C_5H_{11}O^+$ 87.0810, found 87.0807 (17%); calcd for $C_8H_8^+$ 104.0626, found 104.0624 (21%); calcd for $C_9H_9^+$ 117.0704, found 117.0725 (36%); calcd for $C_{12}H_{15}O^+$ 175.1123, found 175.1145 (13%). Anal. found: C, 87.71; H, 8.35. $(C_8H_8)_3(C_{14}H_{20}O)$ requires C, 88.33; H, 8.58.

4.3.7. Polymer 10. ν (KBr) 3686–3140, 3571 (O–H), 3082, 3058, 3024, 1601, 1511, 1493 (C=CH), 1059, 1029 cm^{-1} (C–O); δ_H 1.35 (br s, –CH₂-ring, CHCH₂), 1.84 (br s, CHCH₂), 2.63 (br s, PhCH₂), 3.03 (br s, COH), 6.56, 7.05 (2 br s, ArH); δ_C 22.2, 25.9, 37.3 (–CH₂-ring), 40.3 (CHCH₂), 41.2–46.5 (CHCH₂), 48.1 (PhCH₂), 71.0 (COH), 125.6, 127.9, 130.1, 133.9 (ArCH), 145.1, 145.4 (ArC). HRMS (EI): calcd for $C_6H_{11}^+$ 99.0810, found 99.0809 (49%); calcd for $C_8H_8^+$ 104.0626, found 104.0616 (45%); calcd for $C_9H_9^+$ 117.0704, found 117.0714 (15%); calcd for $C_{13}H_{11}O^+$ 216.1514, found 216.1543 (1%). Anal. found: C, 88.17; H, 8.31. $(C_8H_8)_3(C_{15}H_{20}O)$ requires C, 88.59; H, 8.39.

4.3.8. Polymer 11. ν (KBr) 3678–3140, 3551 (O–H), 3056, 3024, 1602, 1494, 1448 (C=CH), 1172, 1027 cm^{-1} (C–O); δ_H 1.42 (br s, CHCH₂), 1.73 (br s, CHCH₂), 3.53 (br s, CH₂COH), 3.95 (br s, COH) 6.54, 7.09, 7.26 (3 br s, ArH); δ_C 40.4 (CHCH₂), 40.4–45.8 (CHCH₂), 47.5 (CH₂COH), 77.7 (COH), 125.7, 126.2, 126.7, 127.8, 128.2, 128.8, 129.9, 130.4 (ArCH), 145.1, 146.6 (ArC). HRMS (EI): calcd for $C_{13}H_{11}O^+$ 183.0809, found 183.0817 (21%). Anal. found: C, 89.03; H, 7.07. $(C_8H_8)_3(C_{22}H_{20}O)$ requires C, 90.15; H, 7.24.

4.3.9. Polymer 12. ν (KBr) 3057, 3024, 1601, 1511, 1492 (C=CH), 739 cm^{-1} (P–C); δ_H 1.40 (br s, CHCH₂), 1.81 (br s, CHCH₂), 3.28 (br s, CH₂P), 6.55, 7.04 (2 br s, ArH), 7.25 (br s, P–ArH); δ_C 35.4 (CH₂P), 40.3 (CHCH₂), 41.2–46.3 (CHCH₂) 125.6, 127.9, 130.1, 133.9 (ArCH), 145.1, 145.4 (ArC). HRMS (EI): calcd for $C_6H_5P^+$ 108.1289, found 108.0169 (7%); calcd for $C_{12}H_{10}P^+$ 185.0520, found

185.0477 (6%). Anal. found: C, 87.86; H, 7.24. $(C_8H_8)_3(C_{21}H_{19}P)$ requires C, 87.91; H, 7.05.

4.4. Preparation of functionalised polymers 13, 14

To a dark green suspension of lithium powder (80 mg, 11 mmol) and DTBB (25 mg, 0.09 mmol) in dry THF (4 mL) at 0°C was added phthalan (230 μ L, 2 mmol) or isochroman (251 μ L, 2 mmol). After 45 min stirring at the same temperature, the organolithium intermediate was separated from the excess of lithium by filtration in argon atmosphere. To the resulting solution was added the soluble polymer **1** (230 mg, 0.5 mmol) at 0°C. After 30 min stirring at this temperature, the reaction was hydrolysed with methanol (10 mL) and the precipitated polymer was filtered, washed with water (3×15 mL) and methanol (3×15 mL) and dried under reduced pressure (0.1 Torr) to give compounds **13** and **14** in almost quantitative yield. Spectroscopic and analytical data follow.

4.4.1. Polymer 13. ν (KBr) 3704–3113, 3561 (O–H), 3058, 3023, 1601, 1492, 1451 (C=CH), 1181, 1018 cm^{-1} (C–O); δ_H 1.41 (br s, CHCH₂), 1.81 (br s, CHCH₂), 2.83 (br s, CH₂CH₂), 3.46 (br s, OH), 4.56 (br s, CH₂OH) 6.56, 7.07 (2 br s, ArH); δ_C 34.5, 37.5 (CH₂CH₂), 40.3 (CHCH₂), 41.2–46.0 (CHCH₂), 62.9 (CH₂OH), 125.6, 126.2, 127.9, 129.5 (ArCH), 138.4, 140.0, 145.2 (ArC). HRMS (EI): calcd for $C_7H_7O^+$ 107.0497, found 107.0527 (1%). Anal. found: C, 86.80; H, 7.46. $(C_8H_8)_3(C_{17}H_{18}O)$ requires C, 89.41; H, 7.69.

4.4.2. Polymer 14. ν (KBr) 3704–3113, 3561 (O–H), 3058, 3023, 1601, 1492, 1451 (C=CH), 1181, 1018 cm^{-1} (C–O); δ_H 1.48 (br s, CHCH₂), 1.82 (br s, CHCH₂), 2.86 (br s, CH₂CH₂), 3.78 (br s, PhCH₂), 4.54 (br s, PhCH₂CH₂O) 6.56, 7.07 (2 br s, ArH); δ_C 34.9, 35.7, 37.4 (CH₂CH₂, CH₂CH₂OH), 40.4 (CHCH₂), 40.5–46.0 (CHCH₂), 63.3 (CH₂OH), 125.7, 126.7, 128.0, 129.9 (ArCH), 145.5 (ArC). HRMS (EI): calcd for $C_8H_8^+$ 104.0626, found 104.0605 (15%); calcd for $C_9H_9^+$ 117.0704, found 117.0689 (11%); calcd for $C_8H_9O^+$ 121.0653, found 121.0674 (2%); calcd for $C_{18}H_{20}O^+$ 252.1514, found 252.1536 (2%). Anal. found: C, 84.70; H, 7.44. $(C_8H_8)_3(C_{18}H_{20}O)$ requires C, 89.31; H, 7.85.

4.5. Merrifield resin lithiation and reaction with electrophiles

Two-step reaction general procedure. To a dark green suspension of lithium powder (150 mg, 21 mmol) and DTBB (0.015 g, 0.05 mmol) in THF (5 mL) was added the corresponding Merrifield resin **15** (0.5 mmol) at room temperature. After stirring for several hours (see Table 3), the suspension colour changes to a pale pink colour, due to the formation of the benzylic organolithium intermediate. Then, the mixture was cooled and an excess of the electrophile (2.5 mmol) was added. After stirring for several hours (see Table 3), it was hydrolysed with water (10 mL), the resin was filtered, and successively washed with water (3×15 mL), methanol (3×15 mL) and ether (3×15 mL), and dried under reduced pressure (0.1 Torr) to give the expected functionalised polymer in essentially quantitative yield. In the case of compounds **27c–32c**, the precipitated (gel) lithiated polymer was separated from the remaining floating lithium powder via a syringe before adding the electrophile.

Barbier type reaction general procedure. To a dark green suspension of lithium powder (150 mg, 21 mmol) and DTBB (0.015 g, 0.05 mmol) in THF (5 mL) was added the corresponding Merrifield resin **15** (0.5 mmol) and an excess of the electrophile (2.5 mmol) at low temperature (see Table 3). After stirring for several days (see Table 3), it was hydrolysed with water (10 mL), the resin was filtered and washed with water (3×15 mL), methanol (3×15 mL) and ether (3×15 mL), and dried under reduced pressure (0.1 Torr) to give the expected functionalised polymer in essentially quantitative yield. The polymer was then dried (0.1 Torr) to remove solvents. Spectroscopic and analytical data for polymers **16–32** follow.

4.5.1. Polymer 16a. ν (KBr) No signal of C–Cl at 1266 cm^{-1} .

4.5.2. Polymer 18a. ν (KBr) 1247 (C–Si), 836 cm^{-1} (Si–Me). Anal. found: C, 89.35; H, 8.04. $(\text{C}_{10}\text{H}_{10})_{0.01}(\text{C}_8\text{H}_8)_{0.88}(\text{C}_{12}\text{H}_{18}\text{Si})_{0.11}$ requires C, 89.22; H, 8.07.

4.5.3. Polymer 19a. ν (KBr) 3578, 3439 (OH), 1182, 1066 cm^{-1} (C–O).

4.5.4. Polymer 20a. ν (KBr) 3561, 3433 (OH), 1180 cm^{-1} (C–O). Anal. found: C, 88.71; H, 7.52. $(\text{C}_{10}\text{H}_{10})_{0.01}(\text{C}_8\text{H}_8)_{0.88}(\text{C}_{16}\text{H}_{16}\text{O})_{0.11}$ requires C, 90.88; H, 7.63.

4.5.5. Polymer 21a. ν (KBr) 3572, 3463 (OH), 1115 cm^{-1} (C–O).

4.5.6. Polymer 22a. ν (KBr) 3571–3452 (OH), 1025 cm^{-1} (C–O). Anal. found: C, 90.56; H, 8.00. $(\text{C}_{10}\text{H}_{10})_{0.01}(\text{C}_8\text{H}_8)_{0.88}(\text{C}_{15}\text{H}_{20}\text{O})_{0.11}$ requires C, 90.43; H, 8.06.

4.5.7. Polymer 23a. ν (KBr) 3433 (OH), 1070 cm^{-1} (C–O).

4.5.8. Polymer 24a. ν (KBr) 1742 (C=O), 1254 cm^{-1} (C–O). Anal. found: C, 90.23; H, 7.88. $(\text{C}_{10}\text{H}_{10})_{0.01}(\text{C}_8\text{H}_8)_{0.88}(\text{C}_{12}\text{H}_{14}\text{O}_2)_{0.11}$ requires C, 89.23; H, 7.68.

4.5.9. Polymer 26a. ν (KBr) 3439 (OH), 1528 cm^{-1} (C=O).

4.5.10. Polymer 27a. ν (KBr) 1680 cm^{-1} (C=O).

4.5.11. Polymer 28a. ν (KBr) 1727 cm^{-1} (C=O).

4.5.12. Polymer 29a. ν (KBr) 1680 cm^{-1} (C=O).

4.5.13. Polymer 18b. ν (KBr) 1247 (C–Si), 846 cm^{-1} (Si–Me). Anal. found: C, 88.28; H, 7.73. $(\text{C}_{10}\text{H}_{10})_{0.01}(\text{C}_8\text{H}_8)_{0.80}(\text{C}_{12}\text{H}_{18}\text{Si})_{0.19}$ requires C, 87.30; H, 8.28.

4.5.14. Polymer 24b. ν (KBr) 1739 (C=O), 1258 cm^{-1} (C–O).

4.5.15. Polymer 25b. ν (KBr) 1747 (C=O), 1262 cm^{-1} (C–O).

4.5.16. Polymer 16c. ν (KBr) No signal of C–Cl at 1266 cm^{-1} (C–Cl).

4.5.17. Polymer 17c. ν (KBr) No signal of C–Cl at 1266 cm^{-1} (C–Cl).

4.5.18. Polymer 18c. ν (KBr) 1248 (C–Si), 847 cm^{-1} (Si–Me).

4.5.19. Polymer 19c. ν (KBr) 3584, 3457 (OH), 1363 (CH_3), 1183 cm^{-1} (C–O). Anal. found: C, 85.66; H, 7.80. $(\text{C}_{10}\text{H}_{10})_{0.02}(\text{C}_8\text{H}_8)_{0.41}(\text{C}_{14}\text{H}_{20}\text{O})_{0.57}$ requires C, 85.09; H, 9.27.

4.5.20. Polymer 20c. ν (KBr) 3568, 3448 (OH), 1183 cm^{-1} (C–O).

4.5.21. Polymer 21c. ν (KBr) 3570, 3449 (OH), 1019 cm^{-1} (C–O).

4.5.22. Polymer 22c. ν (KBr) 3569, 3457 (OH), 1186 cm^{-1} (C–O). Anal. found: C, 88.21; H, 8.03. $(\text{C}_{10}\text{H}_{10})_{0.02}(\text{C}_8\text{H}_8)_{0.41}(\text{C}_{15}\text{H}_{20}\text{O})_{0.57}$ requires C, 85.70; H, 8.90.

4.5.23. Polymer 24c. ν (KBr) 1740 (C=O), 1256 cm^{-1} (C–O). Anal. found: C, 83.72; H, 7.46. $(\text{C}_{10}\text{H}_{10})_{0.02}(\text{C}_8\text{H}_8)_{0.41}(\text{C}_{12}\text{H}_{14}\text{O}_2)_{0.57}$ requires C, 80.62; H, 7.51.

4.5.24. Polymer 25c. ν (KBr) 1746 (C=O), 1256 cm^{-1} (C–O).

4.5.25. Polymer 26c. ν (KBr) 3684–3134 (OH), 1716 cm^{-1} (C=O). Anal. found: C, 83.92; H, 7.28. $(\text{C}_{10}\text{H}_{10})_{0.02}(\text{C}_8\text{H}_8)_{0.41}(\text{C}_{10}\text{H}_{10}\text{O}_2)_{0.57}$ requires C, 80.04; H, 6.72.

4.5.26. Polymer 27c. ν (KBr) 1682 cm^{-1} (C=O). Anal. found: C, 88.77; H, 7.21. $(\text{C}_{10}\text{H}_{10})_{0.02}(\text{C}_8\text{H}_8)_{0.41}(\text{C}_{16}\text{H}_{14}\text{O})_{0.57}$ requires C, 87.98; H, 6.72.

4.5.27. Polymer 28c. ν (KBr) 1705 cm^{-1} (C=O).

4.5.28. Polymer 30c. ν (KBr) 3413 (NH), 826 cm^{-1} (C–N). Anal. found: C, 89.09; H, 7.61. $(\text{C}_{10}\text{H}_{10})_{0.02}(\text{C}_8\text{H}_8)_{0.41}(\text{C}_{22}\text{H}_{21}\text{N})_{0.57}$ requires C, 89.09; H, 7.21.²⁸

4.5.29. Polymer 31c. ν (KBr) 1638, 910 cm^{-1} (C=CH). Anal. found: C, 88.66; H, 7.69. $(\text{C}_{10}\text{H}_{10})_{0.02}(\text{C}_8\text{H}_8)_{0.41}(\text{C}_{12}\text{H}_{14})_{0.57}$ requires C, 91.48; H, 8.52.

4.5.30. Polymer 32c. ν (KBr) 1648, 887 cm^{-1} (C=CH).

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